



Getting started with the MARCHEMSPEC Marine Chemical Speciation Models

Supplement: Calculating the Inorganic Complexation
of Trace Metals

Version 1.01a

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The Marine Chemical Speciation Model (MARCHEMSPEC) was created by SCOR Working Group 145 (2015 – 2022), and it is being further developed under the auspices of the Joint Committee on the Properties of Seawater. The members of SCOR Working Group 145 were as follows:

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This document describes the use of the MARCHEMSPEC speciation model for natural waters containing the ions of seawater, trace metals, and acid-base equilibria involving minor species phosphate and silicate.

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It is available from marchemspec.org.

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Getting Started with the MARCHEMSPEC Marine Chemical Speciation Models

Supplement: Calculating the Inorganic Complexation of Trace Metals

version 1.01a (02/24)

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1. Preamble

This Supplement to the document of Clegg and Turner (2023) describes the use of the MARCHEMSPEC model that calculates the inorganic complexation of trace species in natural waters containing the ions of seawater. The additional species in this model are:

- Al^{3+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}
- PO_4^{3-} (and HPO_4^{2-} , H_2PO_4^- , and H_3PO_4), $\text{SiO}(\text{OH})_3^-$ (and $\text{Si}(\text{OH})_4$)

The complexation products with the major seawater anions that are included in the model can be found in the complete list of species in **Appendix 1**.

In general, there are far fewer data for the formation of metal complexes in aqueous solutions than there are for acid-base equilibria. Consequently, MARCHEMSPEC predictions of complexation are subject to much larger uncertainties, which we have not attempted to quantify. (There are no outputs of uncertainties for the calculated concentrations of the various complexes.)

This complexation model also calculates the values of the seawater state parameters, which are: pH (on three scales), $f\text{CO}_2$, $p\text{CO}_2$, total alkalinity, total dissolved inorganic carbon, the carbonate, borate, bisulphate, HF, and water dissociation constants K_1 , K_2 , K_B , K_S , K_F , and K_W . For definitions of these quantities, see Table 1 in Chapter 2 of Dickson et al. (2007). The calcium carbonate concentration product is also output. The names used for these parameters in the model output are given in Table 1 of this Supplement.

The values of the state parameters are output by this program in the same way as for the other MARCHEMSPEC models. The results will be the same, although we note that amounts of CO_3^{2-} and OH^- complexed by trace metals are not counted towards the totals used for the calculation of the state parameters for reasons of computational simplicity. However, given that in natural waters the concentrations of the metals are very low this limitation is unlikely to be significant.

The presence of the extra species in this model (up to 100 compared to 24 for the model of seawater) means that the calculation of chemical equilibrium is slow. We have therefore omitted the calculation of uncertainties of the seawater state parameters from this model. Users requiring values of these uncertainties should run the MARCHEMSPEC seawater model instead.

This version of the model differs from version 1.01 in these ways:

1. The equilibrium constants for the formation of Fe[III] hydrolysis products, and some of their activity coefficients, have been revised. The changes are summarised in a poster for the February 2024 Ocean Sciences meeting, and details are available on request from David Turner.
2. Some activity coefficient parameters (ZnOH^+ interactions with Cl^- , and some phosphate species with major seawater ions), and a few other errors have been corrected.
3. Formation of complexes of Mg^{2+} and Ca^{2+} with PO_4^{3-} has been enabled.

We have not yet implemented the ability to equilibrate input aqueous solutions to fixed values of seawater state parameters (which has recently been done for the standalone seawater model at version 1.1).

This document describes the setup and use of the program for trace species complexation. It works in the same way as the program the principal seawater model, and Clegg and Turner (2024) should be read in conjunction with this Supplement.

References

S. L. Clegg and D. R. Turner (2024) *Getting Started with the MARCHEMSPEC Marine Chemical Speciation Models*, SCOR/IAPSO WG 145. Available at marchemspec.org.

A.G. Dickson, C.L. Sabine, and J.R. Christian (Eds.) 2007. *Guide to Best Practices for Ocean CO₂ Measurements*. North Pacific Marine Science Organisation. PICES Special Publication 3, IOCCP Report No. 8, 176 pp.

2. This MARCHEMSPEC Program

It determines the inorganic complexation of trace metals by the anions of seawater, and includes the additional acid-base species phosphate and silicate. All concentrations and activity coefficients are calculated, and also the seawater state parameters, but no estimates of uncertainties are made.

The **inputs** are the temperature, and salinity or composition of a natural water (in terms of the concentrations of species in moles per kg of seawater, or alternatively moles per kg of pure water). If salinity is entered, rather than the concentrations of individual species, the trace metals will all be assigned arbitrary trace concentrations (typically about 1×10^{-8} moles per kg). This is *not* intended to be realistic for real seawater but is used to determine the fractions of each of the metals that are expected to be in the free form, or as complexes with Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , and F^- . Note that phosphate and silicate are not added in this case.

The **outputs** are:

- The equilibrium acid-base speciation and values of the seawater state parameters noted in the previous section, but *without* estimates of the total uncertainties of the state parameters. All outputs are presented on both an amount content (moles per kg of solution) and molality (moles per kg of pure water) basis.
- The fractional complexation of each trace metal (free, complexed by OH^- , complexed by CO_3^{2-} , etc.).

All inputs and outputs are from/to plain text files. Most outputs are also written to comma separated value (.csv) files, which can be read directly into spreadsheet applications.

An important note about **concentration scales**: The common practice in oceanography is to express compositions on a moles per kg of seawater basis (known as **amount content**). In solution chemistry and particularly solution thermodynamics – the calculation of activity coefficients and speciation – moles per kg of pure water solvent (**molality**) is used. The convenience of the latter scale becomes clear when considering changes of natural water composition from seawater stoichiometry. For example, in a seawater in which there is a more Mg^{2+} and less Na^+ than normal only the molalities of these two species are different from their values in standard seawater. However, when expressed on an amount content basis, *all* concentrations are changed.

The examples described in this document are generally presented and discussed in terms of molalities, although MARCHEMSPEC model results are given on both concentration scales. Also, all the example inputs in the MCS.dat input files are listed for both concentration scales (and either can be used by the model).

2.1 Availability

Separate versions of the programs are available to run on computers with the following operating systems:

- Windows (version 7 and higher), 64 bit
- Linux, and macOS (for “Apple Silicon”)

The programs and associated files and directories are provided as a zip file (Windows), and as zipped tar files (Linux and macOS).

3. Installing MARCHEMSPEC

The executable program and its input and output files should present in one directory. The contents of the zip file (Windows), or other compressed archive, should be extracted into the directory you wish to work in, i.e., where the executable program and input and output text files will be. If you have any of the other MARCHEMSPEC programs, then you must choose a different directory (otherwise files will be overwritten). For example, if your chosen directory for this version of MARCHEMSPEC is `c:\marchemspec_trace`, then the resulting structure should be:

<code>c:\marchemspec_trace</code>	- contains program and input/output files
<code>c:\marchemspec_trace\docs</code>	- documentation, including this manual.

For this model there are no other subdirectories. See below for instructions specific to each operating system.

3.1 Windows

Copy the zip file to the directory you wish to work in (e.g., `c:\marchemspec_trace` in the above example), and extract the contents to the same directory by right-clicking on the file in Windows File Explorer, choosing 7-Zip, and then following the prompt. (This instruction works for Windows 10, and the procedure may differ slightly on other versions. There is also more than one program that can be used to zip/unzip files.)

3.2 Linux and macOS (“Apple Silicon”)

Copy the tar file to the directory you wish to work in, and extract the contents using the command

```
tar -xzf tar_file_name.
```

There is an extra action that *may* be needed for macOS and for Linux systems before you can run the model. The executable file `MCS_trace` in the top level directory must have ‘execute’ permission, and this can be added using the operating system command `chmod`. If you find that it is needed, navigate to the directory containing `MCS_trace`, and issue the command:

```
chmod +x ./MCS_trace
```

You should now be able to run the program, by typing `./MCS_trace`. If you are working on a macOS system, and a system error is returned (e.g., ‘permission denied’, ‘exec format error’), then check that execute permission was correctly updated in System Preferences. Open System Preferences and navigate to Privacy & Security > Developer Tools *or* Security & Privacy > General (depending on macOS version). Make sure that Terminal app has permission to execute programs downloaded from the internet.

Adding execute permission only needs to be done once, and then `MCS_trace` should run normally.

3.3 The MARCHEMSPEC files

After extracting the contents of the zip file or other archive, the directory that you will be running the program in should contain the files and other directories listed and described in the document [List_of_files_trace.pdf](#). Below we describe only the files of the model (executable, and input and output).

Executable:

MCS_trace.exe (Windows), or MCS_trace (Linux and macOS)

Data input:

MCS.dat – must contain input temperatures and compositions. The supplied file includes all the compositions used in the examples in this document, expressed on both a molality (moles per kg of pure water) and amount content (moles per kg of solution) basis.

Results output:

MCS.rs1 – contains verbose output of the chemical speciation and seawater state parameters.

MCS.rs2 – column output species amount contents, molalities, and activity coefficients.

MCS.rs4 – column output of calculated seawater parameters (molality-based).

MCS.rs5 – column output of calculated seawater parameters (amount content-based).

MCS_trace.res – this contains the fraction of each trace metal present in the solution that is free (uncomplexed), or complex by the inorganic anions present in the solution.

There are also three files with the extension .csv (for example, MCS.rs2.csv), which contain the same information as the files with normal column output, but as comma separated values. These .csv files can be read directly into spreadsheet programs.

Entries of 99.0 in the files of column output indicate property or uncertainty values that could not be calculated. This is likely to be either because the solution does not contain the species of interest (for example $K^*(BOH_3)$ will be assigned 99.0 for solutions that do not contain any borate species), or where there is no uncertainty because the quantity is defined exactly by the input composition. In the .rs1 files containing verbose results the equivalent entry is ‘n.a.’ (meaning ‘not applicable’).

Other files (these should *not* be altered):

MCS.sen, Pitzer.mst, Pitzer.par, Pitzer.rcn

Important: Successive runs of the model will overwrite the existing output files, so if you have results you want to save then move them to another directory.

4. Quick Start

In this section we demonstrate a simple MARCHEMSPEC calculation in which the inorganic complexation of the trace metals in the models is calculated for a seawater of specified salinity and temperature.

1. Open the text file **MCS.dat**, and go to the line that begins:

```
Enter the type of input composition (1, 2 or 3):
```

Type the number '3' (without quotes) after the semicolon. This means that the natural water compositions will be specified as salinities. Remember that, for this type of input, small amounts of the trace metals species will be automatically added to the solution as Cl^- salts.

2. All lines that begin with a '#' in **MCS.dat** will be treated as comments and ignored. On successive non-comment lines beneath that described above, enter values of the temperature (in Kelvin) followed by practical salinity, one pair of values per line. For example, enter the following for a calculation of the properties of a salinity 35 seawater at 298.15 K:

```
298.15 35.
```

You can enter as many lines of values as you wish. The program will only stop when it either reaches the end of the file, or encounters an error of some kind.

Suggestion: if you keep multiple sets of input data in **MCS.dat**, but only want to do calculations for a small group of values, then place a string of characters such as '===' (which cannot be read as numbers) on the line after the last of the compositions of interest. This will cause the program to stop.

3. Run the program by typing 'MCS_trace.exe' (without quotes) at the Windows prompt followed by <Enter>, (or './MCS_trace' followed by <Enter> on Linux or Apple systems). The text 'MCS working..' should then appear on the screen. This means that the program is running. When it has finished, there will be another message indicating completion. Error messages will also be written to screen.

How long do these calculations take? About 10-13 seconds for 1 composition on a typical PC.

4. Examine the results in the text files noted above. The contents are briefly summarised here. The quantities and symbols used are explained in more detail in **Appendix 2**.

MCS.rs1 – all the results, in an easy to read form. See **Table 1** for definitions of the symbols used for the seawater state parameters. The results are grouped under the following headings:

- Speciation and Activity Coefficients (note that 'molinity' is the amount content of the species, in moles per kg of solution).
- Seawater Related Quantities. This section contains the calculated thermodynamic pH (on the total, seawater and free scales), stoichiometric equilibrium constants of all acid-base equilibria,

and the concentration product of Ca^{2+} and CO_3^{2-} . Model estimates of uncertainties are also listed. All quantities are given on both an amount content and molality basis.

MCS.rs2 (and .csv) – contains all the results shown in the Speciation and Activity Coefficients section of the .rs1 file, but in column format. Species names are capitalised (hence ‘NA’ rather than ‘Na’ for sodium), and all parentheses are omitted (hence ‘BOH3’, not ‘B(OH)3’, for boric acid). Prefixes: m – molality; g – molality based activity coefficient; k – amount content (molinity).

Note: because of the large number of species, the **MCS.rs2** file has a width of over 4,500 columns. The corresponding .csv file is almost 4000 columns wide.

(MCS.rs3) – this filename is not used.

MCS.rs4 (and .csv) – contains all the molality-based results shown in the Seawater Related Quantities section of the .rs1 file, but in column format. Acid-base equilibrium constants are expressed on the different pH bases indicated by the following suffixes: _T – total pH scale; _SW – seawater scale; _F – free scale. The prefix u indicates the estimated uncertainty of the calculated quantity.

MCS.rs5 (and .csv) – contains all the amount-content based results shown in the Seawater Related Quantities section of the .rs1 file, but in column format. Symbols have the same meanings as for the .rs4 file described above.

MCS_trace.res – contains a summary of the fractional trace metal speciation (free, and totals for each inorganic ligand). The results that correspond to each input solution can be distinguished by the value in column iCount.

5. Different Types of MARCHEMSPEC Calculation

In the Quick Start section we showed that calculations at specified temperatures and practical salinities can be done by entering pairs of T , S in the **MCS.dat** file. For example, to calculate the fractional trace metal complexation and seawater properties for practical salinities 35 and 5 at a temperature of 25 °C (298.15 K), the relevant lines of **MCS.dat** would look like this:

```
# END OF DESCRIPTION
#####
#
Enter the type of input composition (1, 2 or 3): 3
#
298.15  35.
298.15  5.
===
```

The lines beginning ‘#’ are all comment lines (ignored by the program). The entry of ‘3’ for the type of input composition means that practical salinities will be entered in the file. Next, after a blank comment line (which is optional) the temperatures and salinities are entered, with one pair per line. There is no limit to the numbers of lines.

The list of data can be terminated by starting a new line with *any* characters that cannot be read as a number. This will cause the program to stop. In the example above, ‘===’ has been used, so that the calculations will be for just these two solutions.

5.1 Input of composition in terms of individual species

To calculate complexation in a solution that does *not* have the composition of normal seawater it is necessary to input solute molalities or amount contents individually. These should be entered in **MCS.dat** on one line per solution (after the temperature), and in the order cations, anions, and then neutral (uncharged) solutes. The order of individual species is that shown in the tables in Appendix 1. The amounts of species that are involved in equilibria can be specified in **MCS.dat** whatever way is most convenient: for example, an amount content X of dissolved CO_2^* could be entered as this amount of CO_2^* , or alternatively as X of H^+ and X of HCO_3^- , or $2X$ of H^+ and X of CO_3^{2-} . The program will determine the equilibrium.

Any compositions that are entered must be charge balanced. If the fractional error in charge balance of the input solution exceeds a tolerance of $1/10^5$, the program will stop (and print an error message to the screen). For example, if we wanted to increase the molality of Mg^{2+} from the salinity 35 value of 0.0547421 by adding a further 0.01 mol kg^{-1} of Mg^{2+} then it is necessary either to increase the molalities of one or more anions to increase the negative charge by 2×0.01 , or reduce the molalities of one or more of the other cations to achieve the same effect (or some combination of the two).

There are a total of 100 concentration values that must be specified, and most convenient way of entering concentration values for the trace species and complexes will be to enter total amounts for the trace metals, and zero for all the complexes. First, in **MCS.dat**, enter a ‘1’ or ‘2’ for the desired concentration unit, and then on the following lines enter the temperature (K) followed by the species

concentrations. **Table A1.4** shows an example of such a line of input, and contains molalities for a salinity 35 seawater plus 1×10^{-8} mol kg⁻¹ of each trace metal (with the Cl⁻ molality increased so that the input is charge-balanced). The amount of PO₄³⁻ shown (1×10^{-7} molal) is charge balance by adding 3×10^{-6} of Na⁺ to the amount already present. The molality of Si(OH)₄ is 1×10^{-6} mol kg⁻¹. Note: the values have been split over many lines, for legibility, and the species names added. **Table A1.5** lists the species names in the same way, with integers for the numerical order in which the species must be entered in **MCS.dat**. Users should remember that these small added molalities of metal ions do not account for solubility in real seawater (that of Fe³⁺ is less than 1×10^{-8} mol kg⁻¹), and are for the purpose of calculating illustrative fractional complexation only. The model does not calculate solubilities.

See the supplied copy of **MCS.dat** for examples of input data that you can use.

The data can also be entered as comma separated values, which can be useful if the input data are prepared using a spreadsheet program. See **Appendix 3** for details.

Compositions of seawater used in the MARCHEMSPEC programs are those presented by Millero et al. (2008), and they entail an assumed alkalinity and equilibrium *p*CO₂, and a defined total inorganic carbon. In future versions of MARCHEMSPEC it will be possible to directly equilibrate the composition of the solutions to fixed values of pairs of the four quantities thermodynamic total pH (-log₁₀([H⁺] + [HSO₄⁻])), total alkalinity, dissolved organic carbon, and *p*CO₂ (partial pressure of CO₂). This has not been implemented yet. Alterations of these quantities therefore have to be made by altering the acidity of the solution directly and/or altering total carbonate or borate concentrations.

Examples of how the above can be done are given in the main document describing MARCHEMSPEC seawater model. We also recommend that you read the MARCHEMSPEC Supplement *Calculations for Natural Waters of Defined Alkalinity, Total Dissolved Inorganic Carbon, and Borate*, which shows how the input data for seawater can be recast so that values of total dissolved inorganic carbon, borate, and alkalinity can be input directly as elements of the solution composition (in place of values for species CO₂*, B(OH)₃, and OH⁻).

The results of some simple example calculations involving trace species are shown below.

5.2 Examples

Here we explain the results of two of the examples present in the supplied version of the **MCS.dat** file.

Example 1 (proportions of free and complexed trace species in seawater)

This is the simplest type of case to enter in **MCS.dat**, and is the same as shown in the Quick Start section above: a salinity 35 seawater, at 298.15 K. The trace metals are automatically assigned arbitrary concentrations of 1×10^{-8} mol per kg of seawater, but phosphate and silicate are zero.

In **MCS.dat**, '3' is entered for the type of composition, followed by '298.15 35.0' (without quotes) on the next non-comment line. On the following line (i.e., below the above entry) enter '=' so that the program will stop after the calculation and not read data that might be on other lines below.

Next, run the executable **MCS_trace.exe**.

The results files **MCS.rs1** and **MCS.rs2** show the same information as the MARCHEMSPEC program for seawater, but with all of the trace species included. The **MCS.rs2** file, which contains the calculated speciation in column form, is very wide because of all the extra species.

Note that the results for the seawater state parameters (in **MCS.rs1**, **MCS.rs4** and **MCS.rs5**) do *not* include estimates of uncertainties for this version of the model.

The fractions of the each trace metal that are ‘free’ (not complexed), and also complexed by each inorganic ligand, are displayed in file **MCS_trace.res**. Example output for salinity 35 seawater at 298.15 K is shown in **Table 2** (at the end of this document).

Example 2 (the effect of changes to seawater composition, and to pH and DIC)

The following 6 calculations were carried out:

1. Salinity 35 seawater at 298.15 K, without added trace metals, to provide ‘baseline’ values of total pH, $p\text{CO}_2$, and alkalinity.
2. The same salinity and temperature, with 1×10^{-8} mol kg⁻¹ (molality) of all trace metals, added as Cl⁻ salts (thus retaining charge balance).
3. The same as (2) above, but with a doubled Mg²⁺ molality (substituted for Na⁺ to retain charge balance).
4. The same as (2) above, but with 0.0001 mol kg⁻¹ (molality) of dissolved CO₂* added to the solution.
5. The same as (2) above, but with 0.0001 mol kg⁻¹ (molality) of Na₂CO₃ added to the solution.
6. The same as (2) above, but with 1×10^{-6} mol kg⁻¹ (molality) Si(OH)₄ and 1×10^{-7} mol kg⁻¹ Na₃PO₄ added to the solution.

The calculations are entered in the input file **MCS.dat** one after the other, and can be interspersed with comment lines (beginning with ‘#’).

Note: because the composition of the seawater is being altered, the input compositions in **MCS.dat** must be either molalities or amount contents of all species, and *not* salinities. The large number of species (100) makes this non-trivial.

The example input that we have provided in **MCS.dat** is in terms of molalities (this is composition input type 1).

For the input into the model used in this example – individual compositions – a summary statement of the fractional complexation of each metal is provided in **MCS_trace.res** in the same way as for solution compositions specified as salinities. These results are summarised, together with the calculated seawater state parameters on an amount content basis, in the table below.

Seawater state parameters and calculated free fractions of trace metals at 298.15 K in various solutions based upon salinity 35 seawater.

#	pH _T	pCO ₂ (10 ⁻⁴ atm)	DIC (10 ⁻³ mol kg ⁻¹)	Total Alkalinity (10 ⁻³ mol kg ⁻¹)	Al		Fe(III)		
1	8.1178	3.138	1.9663	2.3044	-		-		
2	8.1177	3.139	1.9663	2.3043	0.437×10 ⁻⁹		0.541×10 ⁻¹²		
3	7.9624	4.347	1.9686	2.3069	0.172×10 ⁻⁸		0.195×10 ⁻¹¹		
4	7.9497	5.032	2.0628	2.3043	0.188×10 ⁻⁸		0.171×10 ⁻¹¹		
5	8.2261	2.482	2.0628	2.4972	0.168×10 ⁻⁹		0.256×10 ⁻¹²		
6	8.1178	3.141	1.9663	2.3042	0.438×10 ⁻⁹		0.542×10 ⁻¹²		
#	pH _T	Cd	Co	Cu(II)	Fe(II)	Mn	Ni	Pb	Zn
1	8.1178	-	-	-	-	-	-	-	-
2	8.1177	0.996	0.858	0.00690	0.211	0.918	0.663	0.0369	0.801
3	7.9624	0.997	0.899	0.0220	0.285	0.940	0.744	0.0486	0.862
4	7.9497	0.997	0.892	0.0122	0.266	0.938	0.727	0.0469	0.861
5	8.2261	0.995	0.822	0.00415	0.170	0.896	0.601	0.0292	0.743
6	8.1178	0.996	0.858	0.00690	0.211	0.918	0.663	0.0369	0.802

The key points from the above calculations:

- (i) Comparisons of results (1,2, and 6) show that the values of the seawater state parameters are negligibly affected by the additions of the very small concentrations of trace metals and acid-base species Si(OH)₄ and Na₃PO₄.
- (ii) Only very small fractions of Al³⁺ and Fe³⁺ are calculated to be present as free ions. The free fractions of other species vary quite widely, but those of Cd²⁺, Co²⁺ and Mn²⁺ closest to unity.
- (iii) The increase in Mg²⁺ concentration (result 3), and addition of CO₂* to the solution (result #4) both cause a decrease in pH_T which *increases* the free fractions of Al³⁺ and Fe³⁺ in solution. They are very sensitive to pH because the metal ions mostly exist in solution as complexes with OH⁻ ions.
- (iv) The fractions of the free metal ions all vary with the changes made to the seawater medium (i.e., results 3-5, compared with 2). The changes are greatest for metals that are strongly complexed by OH⁻.

You should also try some examples based on the seawater composition in the table on Supplement *Calculations for Natural Waters of Defined Alkalinity, Total Dissolved Inorganic Carbon, and Borate*. This table shows, side by side, the amount content composition of salinity 35 reference seawater both as individual species concentrations, and as values corresponding to DIC, alkalinity and total borate. See what happens to trace metal complexation when you adjust these values (remembering to retain charge balance if you are adjusting alkalinity).

6. Help and Further Information

For news about the models, and downloads of the latest versions, go to marchemspec.org.

For questions about the models for solutions containing the species of artificial seawater, and standard seawater, contact Simon Clegg (s.clegg@uea.ac.uk). For questions about the model of complexation of trace species (described in one of the Supplements to this document), contact David Turner (david.turner@marine.gu.se).

Appendix 1. Species in the Trace Metal Model

Here we list the solute species that are included in the MARCHEMSPEC trace species complexation model. The order is important: it is the same as order in which species concentrations (as molalities or amount contents) must be entered in the data input file **MCS.dat**. It is also the order in which the species are listed on the various output files.

The model contains the same major and minor species present in the MARCHEMSPEC model of standard seawater of Millero et al. (2008), plus phosphate, silicate, and a number of trace metals and their complexes with seawater anions. This version of the model does not include the ability to estimate the total uncertainties of the equilibrium concentrations of the complexes or of other properties.

The species are listed below, in separate tables for cations, anions and uncharged species. The species numbering (down the left hand sides) is continuous. Table A1.4 contains input molalities for salinity 35 seawater plus small additions of trace species, and Table A1.5 identifies the seawater, trace metal, and additional acid-base species (phosphate and silicate) in the model, and their order.

Table A1.1. Cations of the seawater + trace species model.

#	Full Name	Column Name	#	Full Name	Column Name
1	H ⁺	H	21	AlF ₂ ⁺	ALF2
2	Na ⁺	NA	22	AlOH ²⁺	ALOH
3	Mg ²⁺	MG	23	Al(OH) ₂ ⁺	ALOH2
4	Ca ²⁺	CA	24	CdOH ²⁺	CDOH
5	K ⁺	K	25	CoOH ²⁺	COOH
6	MgOH ⁺	MGOH	26	Cu(II)HCO ₃ ⁺	CU[2]HCO3
7	Sr ²⁺	SR	27	Cu(II)OH ⁺	CU[2]OH
8	MgF ⁺	MGF	28	Fe(II)OH ⁺	FE[2]OH
9	CaF ⁺	CAF	29	Fe(III)F ²⁺	FE[3]F
10	Al ³⁺	AL	30	Fe(III)F ₂ ⁺	FE[3]F2
11	Cd ²⁺	CD	31	Fe(III)OH ²⁺	FE[3]OH
12	Co ²⁺	CO	32	Fe(III)(OH) ₂ ⁺	FE[3]OH2
13	Cu(II) ²⁺	CU[2]	33	MnOH ⁺	MNOH
14	Fe(II) ²⁺	FE[2]	34	NiOH ⁺	NIOH
15	Fe(III) ³⁺	FE[3]	35	PbCl ⁺	PBCL
16	Mn ²⁺	MN	36	PbHCO ₃ ⁺	PBHCO3
17	Ni ²⁺	NI	37	PbOH ⁺	PBOH
18	Pb ²⁺	PB	38	ZnHCO ₃ ⁺	ZNHCO3
19	Zn ²⁺	ZN	39	ZnOH ⁺	ZNOH
20	AlF ²⁺	ALF			

Notes: The species names listed in the “Speciation and Activity Coefficients” section of the .Rs1 file are the same as the full names listed above, but without charges, and with ‘[2]’ replacing ‘(II)’, and ‘[3]’ replacing ‘(III)’. The column names, which are all in capital letters, are used in the output in the .Rs2 file. These names do not include parentheses.

Table A1.2. Anions of the seawater + trace species model.

#	Full Name	Column Name	#	Full Name	Column Name
40	Cl ⁻	Cl	55	AlF ₆ ³⁻	ALF6
41	SO ₄ ²⁻	SO4	56	Al(OH) ₄ ⁻	ALOH4
42	HSO ₄ ⁻	HSO4	57	CaPO ₄ ⁻	CAPO4
43	OH ⁻	OH	58	Cd(CO ₃) ₂ ²⁻	CDCO32
44	Br ⁻	Br	59	Co(OH) ₃ ⁻	COOH3
45	HCO ₃ ⁻	HCO3	60	Cu(II)(CO ₃) ₂ ²⁻	CU[2]CO32
46	CO ₃ ²⁻	CO3	61	Fe(II)OH ₃ ⁻	FE[2]OH3
47	B(OH) ₄ ⁻	BOH4	62	Fe(III)(OH) ₄ ⁻	FE[3]OH4
48	F ⁻	F	63	MgPO ₄ ⁻	MGPO4
49	PO ₄ ³⁻	PO4	64	Ni(OH) ₃ ⁻	NIOH3
50	HPO ₄ ²⁻	HPO4	65	Pb(CO ₃) ₂ ²⁻	PBCO32
51	H ₂ PO ₄ ⁻	H2PO4	66	PbCl ₃ ⁻	PBCL3
52	SiO(OH) ₃ ⁻	SiOOH3	67	Pb(OH) ₃ ⁻	PBOH3
53	AlF ₄ ⁻	AlF4	68	Zn(OH) ₃ ⁻	ZNOH3
54	AlF ₅ ²⁻	AlF5	69	Zn(OH) ₄ ²⁻	ZNOH4

See also the Notes for the table for the cations in this model, above.

Table A1.3. Neutral species of the seawater + trace species model.

#	Full Name	Column Name	#	Full Name	Column Name
70	B(OH) ₃	BOH3	86	Cu(II)(OH) ₂	CU[2]OH2
71	CO ₂ [*]	CO2	87	Fe(II)CO ₃	FE[2]CO3
72	HF	HF	88	Fe(II)(OH) ₂	FE[2]OH2
73	MgCO ₃ ⁰	MGCO3	89	Fe(II)F ₃	FE[3]F3
74	CaCO ₃ ⁰	CACO3	90	Fe(III)(OH) ₃	FE[3]OH3
75	SrCO ₃ ⁰	SRCO3	91	MgHPO ₄	MGHPO4
76	H ₃ PO ₄	H3PO4	92	MnCO ₃	MNCO3
77	SiOH ₄	SIOH4	93	NiCO ₃	NICO3
78	AlF ₃	ALF3	94	Ni(OH) ₂	NIOH2
79	Al(OH) ₃	ALOH3	95	PbCO ₃	PBCO3
80	CaHPO ₄	CAHPO4	96	PbCl ₂	PBCL2
81	CdCO ₃	CDCO3	97	Pb(OH) ₂	PBOH2
82	Cd(OH) ₂	CDOH2	98	PbSO ₄	PBSO4
83	CoCO ₃	COCO3	99	ZnCO ₃	ZNCO3
84	Co(OH) ₂	COOH2	100	Zn(OH) ₂	ZNOH2
85	Cu(II)CO ₃	CU[2]CO3			

See also the Notes for the table for the cations in this model, above.

Table A1.4. Input species molalities (m) for an $S = 35$ seawater, with added $1 \times 10^{-8} m$ trace metals, $1 \times 10^{-7} m$ PO_4^{3-} , and $1 \times 10^{-6} m$ $\text{Si}(\text{OH})_4$. The species names are those used in the column output of results.

T 298.15	H 0.0	Na 0.486060	Mg 0.054742102	Ca 0.0106568	K 0.0105797	MgOH 0.0	Sr 9.400E-05	MgF 0.0	CaF 0.0
Al 1.0E-08	Cd 1.0E-08	Co 1.0E-08	Cu[2] 1.0E-08	Fe[2] 1.0E-08	Fe[3] 1.0E-08	Mn 1.0E-08	Ni 1.0E-08	Pb 1.0E-08	Zn 1.0E-08
AlF 0.0	AlF2 0.0	AlOH 0.0	AlOH2 0.0	CdOH 0.0	CoOH 0.0	Cu[2]HCO3 0.0	Cu[2]OH 0.0	Fe[2]OH 0.0	Fe[3]F 0.0
Fe[3]F2 0.0	Fe[3]OH 0.0	Fe[3]OH2 0.0	MnOH 0.0	NiOH 0.0	PbCl 0.0	PbHCO3 0.0	PbOH 0.0	ZnHCO3 0.0	ZnOH 0.0
Cl 0.56576516	SO4 0.0292643	HSO4 0.0	OH 8.2E-06	Br 0.0008728	HCO3 0.0017800	CO3 0.00024770	BOH4 0.0001045	F 7.080E-5	PO4 1.00E-7
HPO4 0.0	H2PO4 0.0	SiOOH3 0.0	AlF4 0.0	AlF5 0.0	AlF6 0.0	AlOH4 0.0	CaPO4 0.0	CdCO32 0.0	CoOH3 0.0
Cu[2]CO32 0.0	Fe[2]OH3 0.0	Fe[3]OH4 0.0	MgPO4 0.0	NiOH3 0.0	PbCO32 0.0	PbCl3 0.0	PbOH3 0.0	ZnOH3 0.0	ZnOH4 0.0
BOH3 0.00032580	CO2 1.0E-5	HF 0.0	MgCO3 0.0	CaCO3 0.0	SrCO3 0.0	H3PO4 0.0	SiOH4 1.0E-6	AlF3 0.0	AlOH3 0.0
CaHPO4 0.0	CdCO3 0.0	CdOH2 0.0	CoCO3 0.0	CoOH2 0.0	Cu[2]CO3 0.0	Cu[2]OH2 0.0	Fe[2]CO3 0.0	Fe[2]OH2 0.0	Fe[3]F3 0.0
Fe[3]OH3 0.0	MgHPO4 0.0	MnCO3 0.0	NiCO3 0.0	NiOH2 0.0	PbCO3 0.0	PbCl2 0.0	PbOH2 0.0	PbSO4 0.0	ZnCO3 0.0
ZnOH2 0.0									

Notes: In order to retain charge balance, the PO_4^{3-} was added to the solution as Na_3PO_4 , and all the trace metals as Cl^- salts. Hence, for example, the Na^+ molality is increased by $3 \times (1 \times 10^{-7})$ above that present in standard seawater.

Table A1.5. The order of input of the seawater and trace species in file **MCS.dat** (temperature, H⁺, Na⁺, Mg²⁺... etc.). The species names are those used in the column output of results.

T	H	Na	Mg	Ca	K	MgOH	Sr	MgF	CaF
10	11	12	13	14	15	16	17	18	19
AlF	AlF2	AlOH	AlOH2	CdOH	CoOH	Cu[2]HCO3	Cu[2]OH	Fe[2]OH	Fe[3]F
20	21	22	23	24	25	26	27	28	29
Fe[3]F2	Fe[3]OH	Fe[3]OH2	MnOH	NiOH	PbCl	PbHCO3	PbOH	ZnHCO3	ZnOH
30	31	32	33	34	35	36	37	38	39
Cl	SO4	HSO4	OH	Br	HCO3	CO3	BOH4	F	PO4
40	41	42	43	44	45	46	47	48	49
HPO4	H2PO4	SiOOH3	AlF4	AlF5	AlF6	AlOH4	CaPO4	CdCO32	CoOH3
50	51	52	53	54	55	56	57	58	59
Cu[2]CO32	Fe[2]OH3	Fe[3]OH4	MgPO4	NiOH3	PbCO32	PbCl3	PbOH3	ZnOH3	ZnOH4
60	61	62	63	64	65	66	67	68	69
BOH3	CO2	HF	MgCO3	CaCO3	SrCO3	H3PO4	SiOH4	AlF3	AlOH3
70	71	72	73	74	75	76	77	78	79
CaHPO4	CdCO3	CdOH2	CoCO3	CoOH2	Cu[2]CO3	Cu[2]OH2	Fe[2]CO3	Fe[2]OH2	Fe[3]F3
80	81	82	83	84	85	86	87	88	89
Fe[3]OH3	MgHPO4	MnCO3	NiCO3	NiOH2	PbCO3	PbCl2	PbOH2	PbSO4	ZnCO3
90	91	92	93	94	95	96	97	98	99
ZnOH2									
100									

Notes: The species of the seawater model are in **blue** text, the uncomplexed ‘free’ trace metals in **red**, and the added minor acids in **green**.

Appendix 2. Description of Model Output

This appendix contains detailed descriptions of the model output in the various results text files.

A2.1 Results in file MCS.rs1

Here we explain the output in this file, starting from the top.

1. The problem number is listed, and the temperature (Kelvin). The pressure, in the current version of the model, is always 1 atm.

2. Speciation and Activity Coefficients

This is the calculated composition of the solution, involving the usual acid-base equilibria and also the formation of a number of ion pairs (e.g., CaCO_3° , MgF^+ , MgOH^+). Values are listed for the molality-based activity coefficients (Act. Coeff.) the species molalities (Molality, moles per kg of pure water), and amount content or molinity (Molinity, moles per kg of solution).

At the bottom of this section are listed the water activity, the molality-based osmotic coefficient, and ionic strength.

3. Seawater Related Quantities

This section contains values of the various measures of pH, the stoichiometric equilibrium constants for the carbonate system and other acid-base reactions, and the concentration product of calcium carbonate. The symbols used in this section are defined in **Table 1**, which also lists the corresponding symbols used by Dickson et al. (2007), and defined in their Chapter 2, Table 1. An entry of 'n.a.' for a quantity means 'not applicable'.

Note that this section of the .rs1 output file is divided into two parts: in the first part all values are molality based (moles per kg of pure water), and in the second part they are amount content based (i.e., moles per kg of solution). In the second part the equilibrium constants are listed as pK values ($-\log_{10}(K)$), to correspond to common usage elsewhere.

4. Tests of the Calculation of Solution Equilibria, and Solver Details

These sections display results that are only useful for checking that the program works correctly. The percentage errors in the calculation of each chemical equilibrium in the computation are first listed. The calculation of equilibrium is carried out in two parts: a simple first estimate, and then a complete calculation. Values of the integer flag 'iFail' of zero indicate success.

Reference: Dickson, A.G., Sabine, C.L., Christian, J.R. (Eds.), 2007. *Guide to Best Practices for Ocean CO₂ Measurements*. North Pacific Marine Science Organisation. PICES Special Publication 3, IOCCP Report No. 8, 176 pp.

A2.2 Results in file MCS.rs2, and .csv

These files contains the same results as in section 'Speciation and Activity Coefficients' of the .rs1

file, but in column format (separated by spaces, not tabs). The comma separated value (.csv) file contains the same information, and can be read directly into spreadsheet programs such as Excel. The column headers have the following meanings:

iCount – the problem number.

iFail – the status flag for the calculation of equilibrium. A zero indicates success.

Err – if errors are detected there will be character codes in this column.

T – temperature (Kelvin)

P – pressure (atmospheres). This value is fixed at unity.

aW – water activity.

Osm – molality-based osmotic coefficient.

prefix ‘k’ – the amount content (also called ‘molinity’) of the solute species. For example, **kH** is the amount content (moles per kg of solution) of the H^+ ion.

prefix ‘m’ – the molality (moles per kg of pure water) of the solute species.

prefix ‘g’ – the molality-based activity coefficient of the species.

The order of the dissolved species (cations, then anions, then uncharged species, left to right) is given in the tables in Appendix 1. There is a total of 100 values.

This is the same order as it used for input compositions in the **MCS.dat** file. Note the omission of charges in the names of ions in the output file, the use of all capital letters in the chemical symbols, and the omission of parentheses (e.g., **BOH3** instead of **B(OH)3**) because these can cause problems when read into other applications and used as column names.

A2.3 Results in file **MCS.rs4**, and **.csv**

These files contains the molality-based results from section ‘Seawater Related Quantities’ of the **.rs1** file, but in column format. The comma separated value (.csv) file can be read directly into spreadsheet programs such as Excel.

Entries of 99.0 indicate property or uncertainty values that could not be calculated, most likely because the solution does not contain the species of interest (for example $K^*(BOH3)$ will be assigned 99.0 for solutions that do not contain any borate species). Column headers have the following meanings:

iCount – the problem number.

T – temperature (Kelvin)

P – pressure (atmospheres). This value is fixed at unity.

pH_{T, SW, F} – pH on the total (T), seawater (SW) or free (F) scales

upH_{T, SW, F} – the model-estimated uncertainties of the three different forms of pH.

pCO₂, and **upCO₂** – the calculated equilibrium partial pressure of CO₂ (atm.), and its estimated uncertainty.

fCO₂, and **ufCO₂** – the calculated equilibrium fugacity of CO₂ (atm.), and its estimated uncertainty.

DIC, and **uDIC** – the total dissolved inorganic carbon content of the solution (moles per kg of pure water), and its estimated uncertainty.

TotAlk, and **uTotAlk** – the alkalinity of the solution (moles per kg of pure water), and its estimated uncertainty.

Ca_CO3, **uCa_CO3** – the molality product of total Ca²⁺ and total CO₃²⁻, and its uncertainty.

Acid – base equilibrium constants – these stoichiometric constants are listed in the form **K{dissociating species}_{pH scale}**. Thus the dissociation constant of HCO₃⁻ on the total pH scale is given as **KHCO3_T**, and on the seawater scale by **KHCO3_SW**, and on the free pH scale by **KHCO3_F**. A prefix of ‘u’ denotes the corresponding uncertainty (hence **uKHCO3_F** for the estimated uncertainty in **pKHCO3_F**).

A2.4 Results in file MCS.rs5, and .csv

These files contain the amount content based results from section ‘Seawater Related Quantities’ of the .rs1 file, but in column format. The comma separated value (.csv) file can be read directly into spreadsheet programs such as Excel.

Column headers have the same meanings as for the .rs4 files described above, apart from the change in concentration units to amount contents. However, equilibrium constants and amount content concentration product of Ca²⁺ and CO₃²⁻ are presented on a log₁₀ basis, as follows.

Equilibrium constants

These values, and their estimated uncertainties, are expressed as **pK** (-log₁₀(K)), to conform to general usage elsewhere and for ease of comparability. The headers of the columns of results are named as follows:

pK{dissociating species}_{pH scale}. Thus the **pK** of the dissociation constant of HCO₃⁻ on the total pH scale is given as **pKHCO3_T**, on the seawater scale by **pKHCO3_SW**, and on the free pH scale by **pKHCO3_F**. A prefix of ‘u’ denotes the corresponding uncertainty (hence, for example, **upKHCO3_T** for the estimated uncertainty in **pKHCO3_T**).

The column headers for the **pK** value of the amount content product of total Ca²⁺ and total CO₃²⁻, and its uncertainty, are enclosed in [] hence: **p[Ca_CO3]** and **up[Ca_CO3]**.

A2.5 Results in file MCS_trace.res

This file contains a summary of the complexation for all the trace metals present in each input solution. The first column, **iCount**, contains the problem number (the same the order of the input

data in the **MCS.dat** file. Note that, if there are no trace metals present in an input solution, then there will be no output for that solution in **MCS_trace.res**.

The second column, **Species**, indicates the trace metal and the free or complexed fraction for which the value is given in the third column, **Fraction**. Each complexed fraction, e.g. 'AL (as OH)' is the total for all complexes of the trace metal with the indicated anion. For example, for Al^{3+} there are four complexes with OH^- . Concentrations of individual complexes can be found in files **MCS.rs1** and **MCS.rs2**.

Appendix 3. Input Data as Comma Separated Values

The normal layout of the **MCS.dat** file, as supplied is as follows:

1. Information about how to enter data, with each line of this information beginning with a comment character '#' (without quotes).
2. The line: Enter the type of input composition (1, 2 or 3): 1
The number after the semi-colon indicates whether solution compositions will be entered as molalities (1), amount contents (2) or salinities (3).
3. Lines of temperatures and compositions, consisting of numbers separated by spaces.
4. The data can be interspersed with comment lines, which begin with a '#'.

The essential elements of the data file are items 2 and 3 only. So, a valid **MCS.dat** file could begin like this:

```
Enter the type of input composition (1, 2 or 3): 1
298.15 0.00000E+00 6.699568E-05 7.545337E-06 1.468872E-06 (+ further values)
298.15 0.00000E+00 6.699871E-04 7.545678E-05 1.468939E-05 (+ further values)
```

where the values above are temperature followed by the molalities of H^+ , Na^+ , Mg^{2+} and Ca^{2+} .

It is also possible to read data as comma separated values, which is useful if the input compositions are prepared using a spreadsheet program such as Excel. If seawater species molalities or amount contents were created using a spreadsheet and written to a file as comma separated values (.csv) then the file will look something like this:

```
T, mH, mNa, mMg, mCa, (+ further names)
298.15, 0.00000E+00, 6.699568E-05, 7.545337E-06, 1.468872E-06, (+ further values)
298.15, 0.00000E+00, 6.699871E-04, 7.545678E-05, 1.468939E-05, (+ further values)
```

The first row contains whatever column names you used in the spreadsheet. To edit this comma separated value file into a form that can be read by the MARCHEMSPEC program, just comment out the line of column names (with a '#'), and add the line that specifies the type of input composition, like this:

```
Enter the type of input composition (1, 2 or 3): 1
# T, mH, mNa, mMg, mCa, (+ further names)
298.15, 0.00000E+00, 6.699568E-05, 7.545337E-06, 1.468872E-06, (+ further values)
298.15, 0.00000E+00, 6.699871E-04, 7.545678E-05, 1.468939E-05, (+ further values)
```

The additions are in **bold**.

Don't forget: the input file must still be called **MCS.dat**. The program always reads this file for its input data.

Tables

This section contains the tables referred to earlier in the document.

Table 1. Definitions of the seawater-related quantities ('seawater state parameters') tabulated in the MCS.rs1 results file (and presented in column form in files MCS.rs4 and MCS.rs5)

Quantity	Definition	Quantity	Definition
pH (T)	pH _T , pH on the total scale	pH (SW)	pH _{SW} , pH on the seawater scale
pH (F)	pH _F , pH on the free scale	pCO ₂	<i>p</i> CO ₂ , the equilibrium partial pressure of CO ₂ (atm).
fCO ₂	<i>f</i> CO ₂ , the equilibrium fugacity of CO ₂ (atm.)	DIC	<i>C</i> _T , total dissolved inorganic carbon
Tot .Alk .	A _T , total alkalinity		
Total pH basis (indicated by suffix ‘_T’, in the files of column output)			
K* (CO ₂)	<i>K</i> ₁ , the stoichiometric dissoc. constant of CO ₂ *.	K* (HCO ₃)	<i>K</i> ₂ , the stoichiometric dissoc. constant of HCO ₃ ⁻ .
K* (B (OH) 3)	<i>K</i> _B , the stoichiometric dissoc. constant of B(OH) ₃ .	K* (H ₂ O)	<i>K</i> _W , the ion product of water.
K* (HF)	<i>K</i> _F , the stoichiometric dissoc. constant of HF.		
SW pH basis (seawater scale) (indicated by suffix ‘_SW’, in the files of column output)			
K* (CO ₂)	These definitions are the same as those above, but with the concentration of H ⁺ expressed on the seawater scale.	K* (HCO ₃)	These definitions are the same as those above, but with the concentration of H ⁺ expressed on the seawater scale.
K* (B (OH) 3)		K* (H ₂ O)	
Free pH basis (indicated by suffix ‘_F’, in the files of column output)			
K* (CO ₂)	These definitions are the same as those above, but with the concentration of H ⁺ expressed on the free scale.	K* (HCO ₃)	These definitions are the same as above, but on the free pH scale.
K* (B (OH) 3)		K* (H ₂ O)	
K* (HF)		K* (HSO ₄)	<i>K</i> _S , the stoichiometric dissoc. constant of bisulphate ion.
Other properties			
Ca . CO ₃	The product of the concentrations (on a molality or amount content basis) of total dissolved Ca ²⁺ and total dissolved CO ₃ ²⁻ .		

Table 2. Example output (from **MCS_trace.res**) for salinity 35 and 298.15 K

Fractions of trace metals that are free and complexed by seawater anions

The results printed in this file are, for each trace metal present in the solution, the fraction in the free (uncomplexed form) and then the fractions complexed by each of the seawater anions that are also present. If a trace metal and/or anion is not present in a particular solution then there will be no entry for it in the list.

iCount	Species	Fraction
1	AL (free)	4.365970511E-10
1	AL (as OH)	9.999999236E-01
1	AL (as F)	7.600358503E-08
1	CD (free)	9.961343613E-01
1	CD (as CO3)	3.472520685E-03
1	CD (as OH)	3.931179838E-04
1	CO (free)	8.576609130E-01
1	CO (as CO3)	1.272474214E-01
1	CO (as OH)	1.509166563E-02
1	CU[2] (free)	6.902635386E-03
1	CU[2] (as HCO3)	6.967076438E-05
1	CU[2] (as CO3)	9.849426259E-01
1	CU[2] (as OH)	8.085067964E-03
1	FE[2] (free)	2.111858533E-01
1	FE[2] (as CO3)	7.838489477E-01
1	FE[2] (as OH)	4.965198988E-03
1	FE[3] (free)	5.410124002E-13
1	FE[3] (as OH)	9.999999999E-01
1	FE[3] (as F)	1.284570169E-10
1	MN (free)	9.182883029E-01
1	MN (as CO3)	8.004914701E-02
1	MN (as OH)	1.662550070E-03
1	NI (free)	6.628483235E-01
1	NI (as CO3)	3.287978437E-01
1	NI (as OH)	8.353832722E-03
1	PB (free)	3.688741602E-02
1	PB (as CL)	2.589565872E-01
1	PB (as SO4)	9.576048797E-03
1	PB (as HCO3)	8.128812303E-04
1	PB (as CO3)	6.087160648E-01
1	PB (as OH)	8.505100198E-02
1	ZN (free)	8.014280440E-01
1	ZN (as HCO3)	1.041629336E-02
1	ZN (as CO3)	7.419213134E-02
1	ZN (as OH)	1.139635313E-01

Notes: iCount is the problem number (the order in which data appear in **MCS.dat**). All species names are given in the same form – upper case, and without parentheses – as in file **MCS.rs2**. The fractions are given to large numbers of digits because some complexed fractions, such as Fe(III) by OH⁻, can be extremely close to unity.

Version History

1.00 – The initial release, prepared for the Launch and Tutorial sessions at Woods Hole Oceanographic Institution (15-16 June, 2023).

1.01 (July, 2023) – Revisions to the underlying MarChemSpec code to correct the treatment of Cu^{2+} interactions with Cl^- ions, which previously gave erroneous activity coefficients and complexation of this metal ion at temperatures other than 25 °C. Revisions to the underlying MarChemSpec code to correct the reading of a directory path from file Uncert.mst (this does not affect the use of the currently released versions of the code, because this path entry is left blank).

1.01a (February, 2024) – This version of the model differs from version 1.01 in the following ways:

- The equilibrium constants for the formation of Fe[III] hydrolysis products, and some of their activity coefficients, have been revised. The changes are summarised in a poster for the February 2024 Ocean Sciences meeting, and details are available on request from author David Turner.
- Activity coefficient parameters for $\text{ZnOH}^+ - \text{Cl}^-$, and some phosphate species have been corrected and revised, $\text{Fe}^{2+} - \text{Cl}^-$ parameters have been corrected, and the formation of Mg^{2+} and Ca^{2+} complexes with PO_4^{3-} enabled. A small error (fraction of 1%) in the calculation of the fugacity coefficient of CO_2 has been corrected.

In this document, the table in section 5.2, and Table 2 have been revised to reflect the corrected values noted above, all of which have only very small effects on the calculated fractions of free and complexed species in Table 2. We have not yet implemented the ability to equilibrate input aqueous solutions to fixed values of seawater state parameters (which has recently been done for the standalone seawater model at version 1.1).

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