



Getting started with the MARCHEMSPEC Marine Chemical Speciation Models

Supplement: Calculations for Natural Waters of Defined Alkalinity, Total Dissolved Inorganic Carbon, pH, and Partial Pressure or Fugacity of CO₂

Version 1.1

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(See also the principal document for this version)



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 how to input natural water compositions into the models for defined values of pairs or single values of alkalinity, total dissolved inorganic carbon, pH (total or free), and $p\text{CO}_2$ or $f\text{CO}_2$.

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It is available from marchemspec.org.

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Alkalinity, Total Dissolved Inorganic Carbon, pH, and Partial
Pressure or Fugacity of CO₂

version 1.1 (02/2024)

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1. Introduction

This Supplement describes calculations for natural waters containing the ions of reference seawater, in which the input aqueous solutions (in file **MCS.dat**) are equilibrated to pairs or single values of the following quantities:

- TA (total alkalinity)
- DIC (dissolved inorganic carbon)
- pH (total or free)
- $p\text{CO}_2$ or $f\text{CO}_2$

Here we explain how to do these calculations with the seawater model, and the various options and limitations that apply. There are eleven different possibilities, which we refer to as *problem types*. These are as follows:

Table 1. The types of problem that MarChemSpec can solve.

Problem type	Equilibrate input solution to fixed values of these seawater state parameter(s)	Do the equilibration by varying the following quantity(ies)	Note
0	None (calculate properties of the input solution only)	--	
1	pH (total or free), and TA	DIC, and TA	
2	DIC, and TA	DIC, and TA	
3	($p\text{CO}_2$ or $f\text{CO}_2$), and TA	DIC, and TA	
4	DIC, and pH (total or free)	DIC, and TA	
5	($p\text{CO}_2$ or $f\text{CO}_2$), and pH (total or free)	DIC, and TA	
6	($p\text{CO}_2$ or $f\text{CO}_2$), and DIC	DIC, and TA	
7	TA	TA	
8	DIC	DIC	
9	pH (total or free)	TA	
10	($p\text{CO}_2$ or $f\text{CO}_2$)	DIC	
11	($p\text{CO}_2$ or $f\text{CO}_2$)	TA	

In all cases the variation of DIC in the aqueous solutions is carried out by adding/subtracting CO_2^* (which does not affect alkalinity). The variation of TA is done by adding and subtracting combinations of H^+ and either Na^+ or Ca^{2+} , and Cl^- and OH^- . The choice of ions is controlled by integer options in **MCS.dat**.

In the sections below we describe the parts of the **MCS.dat** in which are entered the problem type, and the options determining how calculation that will be done. These are additions to what was present in the file used by the previous version of the model.

This document should be read in conjunction with the principal document describing our seawater model Getting started with the *MARCHEMSPEC Marine Chemical Speciation Models, version 1.1*, which describes the output of the model and other aspects of the input.

2. Installation

The archive (Windows zip file, or Linux tar file) for this version 1.1 release contains the same files as the previous release, updated where necessary, plus individual example MCS.dat files for all the new problem types. These MCS.dat files can be found in named subdirectories \ProblemType_1, \ProblemType_2 etc. in the archive.

The updated main document for this version 1.1 release, *Getting Started with the MARCHEMSPEC Marine Chemical Speciation Models*, should be consulted for further details concerning installation, the directory structures, and what the different files are for.

3. The MCS.dat Input File

This plain text file contains the following information:

- The problem type (integer, with a value from 0 to 11)
- Up to four integer options that indicate choices related to each problem type;
- An integer option (values 1-3) indicating whether the input solution compositions will be entered as salinities, or molalities or amount contents (moles per kg of solution) of individual species.
- One or more lines each containing the temperature, any fixed values of property(ies) and uncertainties for the selected problem types, and then solution composition.

Lines in **MCS.dat** that begin with a '#' are treated as comments and are ignored. The simplest possible type of input is one in which there is *no* equilibration to fixed values of seawater state parameters, and composition is entered as salinity. With most comment lines removed, the **MCS.dat** file for such a problem might contain this:

Panel 1. Contents of **MCS.dat** for a Problem Type = 0 case

```
#
Problem type (enter 0-11): 0
#
(1) Concentration scale for solution fixed values (1 or 2):
# (Problem types 1-9)
#
(2) Method of adjusting alkalinity (enter 1, 2, or 3):
# (Problem types 1-7, 9, and 11)
#
(3) Measure of pH (enter 1 or 2):
# (Problem types 1, 4, 5, and 9)
#
(4) Gas phase CO2 (enter 1 (for pCO2), or 2 (for fCO2)):
# (Problem types 3, 5, 6, 10, and 11)
#
Enter the type of input composition (1, 2 or 3): 3
#
#
298.15 35.0
298.15 25.0
298.15 15.0

{and further lines of temperature and composition, as needed}
```

Problem type

Type of composition (salinity, or species molalities or amount contents)

Temperatures and salinities (3 problems)

Entries in the data file for the simplest problem type, which is zero, are shown above in bold red. Not all of the four numbered options are needed for each problem type, as indicated in parentheses

beneath each option. Hence, for example, an entry for option (1) is only required for problem types 1-9. None of the numbered entries (1 to 4) are needed in the example above for problem type 0, and any values present will not be read by the program. From the input data above the program will calculate the equilibrium speciation, and seawater state parameters, for seawater of reference composition for three practical salinities (35, 25, and 15) all at 298.15 K (25 °C).

Next, Panel 2 shows an example of problem type 1 in which aqueous solutions are being adjusted to equilibrium with fixed values of total pH and alkalinity.

Panel 2. Contents of **MCS.dat** for a Problem Type = 1 case

```
#
Problem type (enter 0-11): 1
#
(1) Concentration scale for solution fixed values (1 or 2): 2
#   (Problem types 1-9)
#
(2) Method of adjusting alkalinity (enter 1, 2, or 3): 1
#   (Problem types 1-7, 9, and 11)
#
(3) Measure of pH (enter 1 or 2): 1
#   (Problem types 1, 4, 5, and 9)
#
(4) Gas phase CO2 (enter 1 (for pCO2), or 2 (for fCO2)):
#   (Problem types 3, 5, 6, 10, and 11)
#
Enter the type of input composition (1, 2 or 3): 3
#
#
8.10 0.005 2.30E-3 0.1E-3 298.15 35.0
8.10 0.005 1.65E-3 0.1E-3 298.15 25.0
8.10 0.005 1.00E-3 0.1E-3 298.15 15.0

{and further lines of input, as needed}
```

In this case there are a number of extra entries in the file. They will be explained in detail in the next section. The meanings of the non-blank entries above are:

- Problem type 1 (equilibrate to a specified total pH and alkalinity).
- The '2' here means that the values entered for total pH and alkalinity will be on the amount content scale (i.e., a per kg of seawater basis).
- The '1' here means that the alkalinity of the solution will be adjusted by: substituting H^+ for Na^+ to decrease alkalinity, or adding NaOH to increase alkalinity.
- The '1' here means that the total pH is being entered further below (and not free pH).
- The '3' here means that solution composition will be entered as practical salinity

f. For each of the three problems, the first two numbers on the line are the required value of total pH and its uncertainty (enter a zero if the uncertainty isn't known). The third and fourth numbers on the line are the required value of the total alkalinity followed by its uncertainty (again, enter a zero for the uncertainty if it isn't known). The last two numbers on each line are the temperature (K) followed by the salinity.

For problem types 7-11 only a single fixed value and its uncertainty are needed. These two numbers precede the solution temperature in the input, in the same way as for the case above. Panel 3 shows example input for problem type 10, in which the input solutions are being adjusted to a fixed $p\text{CO}_2$ of 400×10^{-6} atm by adding/removing DIC from the solution (as dissolved CO_2). The uncertainty in $p\text{CO}_2$ has been entered as zero.

Panel 3. Contents of **MCS.dat** for a Problem Type = 10

```
#
Problem type (enter 0-11): 10
#
(1) Concentration scale for solution fixed values (1 or 2):
#   (Problem types 1-9)
#
(2) Method of adjusting alkalinity (enter 1, 2, or 3):
#   (Problem types 1-7, 9, and 11)
#
(3) Measure of pH (enter 1 or 2):
#   (Problem types 1, 4, 5, and 9)
#
(4) Gas phase CO2 (enter 1 (for pCO2), or 2 (for fCO2)): 1
#   (Problem types 3, 5, 6, 10, and 11)

#
Enter the type of input composition (1, 2 or 3): 3
#
#
400.E-6 0.0    298.15  35.0
400.E-6 0.0    298.15  25.0
400.E-6 0.0    298.15  15.0

{and further lines of input, as needed}
```

The meanings of the non-blank entries above are:

- Problem type 1 (equilibrate to a specified total pH and alkalinity).
- The '1' here means that the value of $p\text{CO}_2$ is being fixed, rather than the fugacity.
- The '3' here means that solution composition will be entered as practical salinity
- For each of the three problems, the first two numbers on the line are the required value of $p\text{CO}_2$ in atmospheres, and its uncertainty (enter a zero if the uncertainty isn't known). The last two numbers on each line are the temperature (K) followed by the salinity.

4. The Options and Values for Each Problem Type

The four numbered options that appear in **MCS.dat** are listed in the table below, together with their meanings and the problem types that they are required for.

Table 2. The numbered options in **MCS.dat**, and their meanings

Option Number	Meaning	Possible Values	Meaning	Required for these problem types
1	Concentration scale for fixed values (DIC, TA, pH).	1	The values of the fixed seawater state parameters, entered as item (f) on Panel 2, are on the molality scale (moles per kg of pure water).	1 – 9
		2	The values are on an amount content basis (moles per kg of solution)	
2	Method of alkalinity adjustment.	1	Add NaOH, or substitute H^+ for Na^+	1 – 7, 9, 11
		2	Add $Ca(OH)_2$, or substitute H^+ for $0.5Ca^{2+}$	
		3	Substitute OH^- for Cl^- , or add HCl	
3	pH scale for the fixed value.	1	Total pH ($-\log_{10}(H^+ + HSO_4^-)$)	1, 4, 5, 9
		2	Free pH ($-\log_{10}(H^+)$)	
4	Partial pressure or fugacity for fixed CO_2 .	1	Partial pressure (pCO_2 / atm) is input.	3, 5, 6, 10, 11
		2	Fugacity (fCO_2 / atm) is input.	

Notes: The alkalinity adjustments are carried out internally within MarChemSpec. For problem types where certain options are not relevant (i.e., omitted from the last column above) any entries in MCS.dat are ignored by the program. The choice made in option number 1 (concentration scale of the fixed DIC, TA, and pH) is independent of that made for the concentration scale for the species in the aqueous solutions input (item (f) in Panel 2).

4.1 Limits to the fixed values

The program has internal upper and lower limits to seawater state parameters that can be entered, and limits to the ranges within which DIC and TA can be adjusted. We have set these ranges to be quite broad but it is possible that problems might be encountered in some circumstances. Contact the MarChemSpec author (s.clegg@uea.ac.uk) if you have difficulties. The current limits and ranges are shown in Table 3 below.

Important: be aware that it is possible to input values of the fixed seawater state parameters that are not compatible with each other: for example a very high pCO_2 coupled with a very high pH. Under these circumstances MarChemSpec will fail, and write an error message. Always think about the problem being solved, and whether your input makes sense.

Table 3. Upper and lower limits to the fixed seawater state parameters, and adjusted quantities

Fixed seawater state parameter	Lower limit	Upper limit	Typical values (at salinity 35)	Note
DIC	0.015×10^{-3}	5.5×10^{-3}	2.0×10^{-3} (molality)	1
TA	-15.0×10^{-3}	$+20.0 \times 10^{-3}$	2.4×10^{-3} (molality)	1
pH (total or free)	3.0	11.0	~8	
$p\text{CO}_2$ or $f\text{CO}_2$	50×10^{-6} atm	2000×10^{-6} atm	400×10^{-6} atm	
Quantity being adjusted	Lower limit	Upper limit		Note
DIC	0.015×10^{-3}	5.5×10^{-3}	-	1
TA	-15.0×10^{-3}	$+20.0 \times 10^{-3}$	-	1

Notes: (1) The same numerical limits are applied irrespective of the chosen concentration scale (molality or amount content).

In the next section we summarise the different problem types listed in Table 1 and the information needed in the MCS.dat file to solve them.

5. The Required Inputs in MCS.dat for Each Problem Type

Below we have listed the options and fixed values required in **MCS.dat** for each problem type. This information should be entered following the examples shown in Panels 1-3 earlier.

Problem type: 0

Action	The equilibrium speciation and properties of the input solution are determined. There are no fixed values.	
Options to be set	None	
Fixed values to be set: None	Fixed value 1	Fixed value 2
	None (omit)	None (omit)

Problem type: 1

Action	The input solutions are equilibrated to fixed values of pH (total or free) and TA.	
Options to be set	1, 2, and 3	
Fixed values to be set: 2	Fixed value 1	Fixed value 2
	pH (total or free)	TA

Problem type: 2

Action	The input solutions are equilibrated to fixed values of DIC and TA.	
Options to be set	1 and 2	
Fixed values to be set: 2	Fixed value 1	Fixed value 2
	DIC	TA

Problem type: 3

Action	The input solutions are equilibrated to fixed values of ($p\text{CO}_2$ or $f\text{CO}_2$) and TA.	
Options to be set	1, 2, and 4	
Fixed values to be set: 2	Fixed value 1	Fixed value 2
	$p\text{CO}_2$ or $f\text{CO}_2$	TA

Problem type: 4

Action	The input solutions are equilibrated to fixed values of ($p\text{CO}_2$ or $f\text{CO}_2$) and TA.	
Options to be set	1, 2, and 3	
Fixed values to be set: 2	Fixed value 1	Fixed value 2
	DIC	pH (total or free)

Problem type: 5

Action	The input solutions are equilibrated to fixed values of ($p\text{CO}_2$ or $f\text{CO}_2$) and pH (total or free).	
Options to be set	1, 2, 3 and 4	
Fixed values to be set: 2	Fixed value 1	Fixed value 2
	$p\text{CO}_2$ or $f\text{CO}_2$	pH (total or free)

Problem type: 6

Action	The input solutions are equilibrated to fixed values of ($p\text{CO}_2$ or $f\text{CO}_2$) and DIC.	
Options to be set	1, 2 and 4	
Fixed values to be set: 2	Fixed value 1	Fixed value 2
	$p\text{CO}_2$ or $f\text{CO}_2$	DIC

Problem type: 7

Action	The input solutions are equilibrated to fixed values of TA only.	
Options to be set	1 and 2	
Fixed values to be set: 1	Fixed value 1	Fixed value 2
	TA	None (omit)

Problem type: 8

Action	The input solutions are equilibrated to fixed values of DIC only	
Options to be set	1 only	
Fixed values to be set:1	Fixed value 1	Fixed value 2
	DIC	None (omit)

Problem type: 9

Action	The input solutions are equilibrated to fixed values of pH (total or free)	
Options to be set	1, 2 and 3	
Fixed values to be set: 1	Fixed value 1	Fixed value 2
	pH (total or free)	None (omit)

Problem type: 10

Action	The input solutions are equilibrated to fixed values of $p\text{CO}_2$ or $f\text{CO}_2$, by adjusting DIC	
Options to be set	4 only	
Fixed values to be set: 1	Fixed value 1	Fixed value 2
	$p\text{CO}_2$ or $f\text{CO}_2$	None (omit)

Problem type: 11

Action	The input solutions are equilibrated to fixed values of $p\text{CO}_2$ or $f\text{CO}_2$, by adjusting TA	
Options to be set	2 and 4	
Fixed values to be set: 1	Fixed value 1	Fixed value 2
	$p\text{CO}_2$ or $f\text{CO}_2$	None (omit)

6. Limitations

In the current version of the model the effect of uncertainties in one or both of the fixed seawater state parameters are not propagated to values of the other calculated quantities. In other words, uncertainties entered in **MCS.dat** do not affect the estimated uncertainties of output quantities. (This capability will be added in the future.)

7. Examples

Examples of all problem types can be found in the MCS.dat files in the subdirectories “..\ProblemType_0” to “..\ProblemType_11”. Just copy the required example into the directory containing the executable MarChemSpec program, and then run it.

Many of the problem types involve an extra level of iteration, compared to the basic calculation of equilibrium of the input solutions (problem type zero). The program will therefore take longer to run. It may be helpful, if you intend to process large datasets, to assess how long each single input problem (i.e., one aqueous solution) will take.

8. 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).