



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
Using **MATLAB**

Version 1.1

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(See also the document *Using the Model Within MATLAB*, version 1.1)



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 MarChemSpec MATLAB function for defined values of pairs or single values of alkalinity, total dissolved inorganic carbon, pH (total or free), $p\text{CO}_2$ or $f\text{CO}_2$.

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It is available from marchemspec.org.

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version 1.1 (02/2024)

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1. Introduction

This document describes the use of MarChemSpec function arguments *iFix*, *ValuesFixed*, and *iUser* for calculations in which the input aqueous solutions (specified by arguments *S*, or *Species_in*) 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 $f\text{CO}_2$

We explain how to do these calculations with the seawater model (*iCalc* = 4 and 5 only), and the various options and limitations that apply. There are eleven different possibilities, which we refer to as *problem types*.

The problem type (an integer from 0 to 11) is input into the MarChemSpec function as argument *iFix*. The different problem types are as follows:

Table 1. The types of problem that MarChemSpec can solve (*iFix*)

Problem type (<i>iFix</i>)	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+} , or Cl^- and OH^- . The choice of ions, and some other aspects of the calculations, are controlled by integer options entered in array argument *iUser*.

This document should be read in conjunction with the principal document for the MATLAB function, which describes other requirements and the output of the model.

2. Installation

The archive (Windows zip file, or Linux tar file) for this version 1.1 release is complete and supersedes the previous version 1.01. The files in this archive should replace the ones from the previous release, which can be deleted. Please consult the main manual for instructions on installation and general use.

A number of the files in this archive have been updated from the previous version, and there are extra example scripts which demonstrate the new features of the model.

3. Options

All the calculations summarised in Table 1, except $iFix = 0$, require a number of integer options to be set. These must be entered in positions 1 to 4 of the new integer array argument *iUser*. The values and meanings are as follows:

Table 2. The options in array argument *iUser*

Options	Meaning	Possible Values	Meaning	Required for these <i>iFix</i> values
<i>iUser</i> (1)	Concentration scale for fixed values (DIC, TA, pH).	1	The values of the fixed seawater state parameters, entered in argument <i>ValuesFixed()</i> , 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)	
<i>iUser</i> (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	
<i>iUser</i> (3)	pH scale for the fixed value.	1	Total pH ($-\log_{10}(H^+ + HSO_4^-)$)	1, 4, 5, 9
		2	Free pH ($-\log_{10}(H^+)$)	
<i>iUser</i> (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) corresponding entries in *iUser()* are ignored by the program. The choice made by option *iUser*(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 (argument *iConc*).

The MarChemSpec function will test the values in *iUser()* to make sure they are valid for the input *iFix* value (except for $iFix = 0$, for which none of these options are required).

4. The Seawater State Parameters

Values of *iFix* from 1 to 11 require that either one or two fixed values of seawater state parameters, and their uncertainties, are entered in the 2x2 array argument *ValuesFixed()*. The entries must be as follows:

ValuesFixed(1,1) – value of the first fixed seawater state parameter.

ValuesFixed(1,2) – uncertainty of the first fixed seawater state parameter (set to zero if not known).

ValuesFixed(2,1) – value of the second fixed seawater state parameter (set to zero if there is only one fixed parameter).

ValuesFixed(2,2) – uncertainty of the second fixed seawater state parameter (set to zero if there is only one fixed parameter, or if the uncertainty is not known).

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. Contact the MarChemSpec author (s.clegg@uea.ac.uk) if you have difficulties. The current limits and ranges are shown in Table 3 below.

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	2
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). (2) The fixed values of gas phase CO_2 are in atmospheres.

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 $p\text{CO}_2$ coupled with a very high pH. Under these circumstances MARCHEMSPEC will fail, with an error message. Always think about the problem being solved, and whether your input makes sense. In the next section we describe and summarise the eleven different problem types shown in Table 1 and the information needed by MARCHEMSPEC to solve them.

5. Required Values for Each Type of Calculation

The tabulation below summarises the required contents of *ValuesFixed()* and *iUser()* for each of the calculations listed in Table 1. Array elements of *ValuesFixed()* and *iUser()* that are used should be set to zero.

iFix: 0

Action	The equilibrium speciation and properties of the input solution are determined. There are no fixed values.	
Options to be set	<i>iUser</i> can be omitted from argument list.	
Seawater state parameters to be set: None	<i>ValuesFixed(1,1)</i>	<i>ValuesFixed(2,1)</i>
	None (set to zero)	None (enter zero)

iFix: 1

Action	The input solutions are equilibrated to fixed values of pH (total or free) and TA.	
Options to be set	<i>iUser(1)</i> , <i>iUser(2)</i> , and <i>iUser(3)</i>	
Seawater state parameters to be set: 2	<i>ValuesFixed(1,1)</i>	<i>ValuesFixed(2,1)</i>
	pH (total or free)	TA

iFix: 2

Action	The input solutions are equilibrated to fixed values of DIC and TA.	
Options to be set	<i>iUser(1)</i> and <i>iUser(2)</i>	
Seawater state parameters to be set: 2	<i>ValuesFixed(1,1)</i>	<i>ValuesFixed(2,1)</i>
	DIC	TA

iFix: 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	<i>iUser(1)</i> , <i>iUser(2)</i> , and <i>iUser(4)</i>	
Seawater state parameters to be set: 2	<i>ValuesFixed(1,1)</i>	<i>ValuesFixed(2,1)</i>
	$p\text{CO}_2$ or $f\text{CO}_2$	TA

iFix: 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	<i>iUser(1)</i> , <i>iUser(2)</i> , and <i>iUser(3)</i>	
Seawater state parameters to be set: 2	<i>ValuesFixed(1,1)</i>	Fixed value 2
	DIC	pH (total or free)

iFix: 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	$i\text{User}(1)$, $i\text{User}(2)$, $i\text{User}(3)$ and $i\text{User}(4)$	
Seawater state parameters to be set: 2	ValuesFixed(1,1)	ValuesFixed(2,1)
	$p\text{CO}_2$ or $f\text{CO}_2$	pH (total or free)

iFix: 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	$i\text{User}(1)$, $i\text{User}(2)$ and $i\text{User}(4)$	
Seawater state parameters to be set: 2	ValuesFixed(1,1)	ValuesFixed(2,1)
	$p\text{CO}_2$ or $f\text{CO}_2$	DIC

iFix: 7

Action	The input solutions are equilibrated to fixed values of TA only.	
Options to be set	$i\text{User}(1)$ and $i\text{User}(2)$	
Seawater state parameters to be set: 1	ValuesFixed(1,1)	ValuesFixed(2,1)
	TA	None (enter zero)

iFix: 8

Action	The input solutions are equilibrated to fixed values of DIC only	
Options to be set	$i\text{User}(1)$ only	
Seawater state parameters to be set:1	ValuesFixed(1,1)	ValuesFixed(2,1)
	DIC	None (enter zero)

iFix: 9

Action	The input solutions are equilibrated to fixed values of pH (total or free)	
Options to be set	$i\text{User}(1)$, $i\text{User}(2)$ and $i\text{User}(3)$	
Seawater state parameters to be set: 1	ValuesFixed(1,1)	ValuesFixed(2,1)
	pH (total or free)	None (enter zero)

iFix: 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	$i\text{User}(4)$ only	
Seawater state parameters to be set: 1	ValuesFixed(1,1)	ValuesFixed(2,1)
	$p\text{CO}_2$ or $f\text{CO}_2$	None (enter zero)

iFix: 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	<i>iUser(2)</i> and <i>iUser(4)</i>	
Seawater state parameters to be set: 1	<i>ValuesFixed(1,1)</i>	<i>ValuesFixed(2,1)</i>
	$p\text{CO}_2$ or $f\text{CO}_2$	None (enter zero)

6. Calling the MarChemSpec Function in MATLAB

The general use of the function for the seawater model is described in the Supplement document *Using the Models Within MATLAB*. The two types of calculation possible for this model correspond to input argument *iCalc* equal to 4 and 5. (Other values select the artificial seawater and trace metal models, for which the features described in this document have not yet been implemented.)

Uncertainties that are specified in *ValuesFixed* do not yet affect the uncertainties in the output quantities calculated by the model. This capability has not been coded, and for this reason we recommend that the uncertainties be set to zero (i.e., *ValuesFixed*(1,2) and *ValuesFixed*(2,2) = 0.0).

Because it is now possible to adjust the alkalinity of the seawater in the way described in this document, it is no longer necessary to use input argument *mH* for this purpose. Either method can still be used, however, but not both.

Here we summarise only the changes involving the arguments *iFix*, *ValuesFixed*() and new argument *iUser*(). The outputs of the function are the same as before.

6.1 Reference seawater (*iCalc* = 4)

For this calculation the MATLAB function call has the form:

[*Outputs*, *NamesOutputs*, *cSpecies_out*, *mSpecies_out*, *ActCoeffs*, *NamesSpecies*, *iFail*] = ...

MarChemSpec(*iCalc*, *tC*, *S*, *P*, *mH*, *nSpecies*, *iFix*, *ValuesFixed*, *nOut*, *strFilesDirectory*, *strCovmxDirectory*, *iUser*);

Input arguments

Argument	Value	Meaning
<i>iCalc</i>	4 (fixed)	
<i>tC</i>	-5 <= <i>tC</i> <= 45 ^a	Temperature (°C).
<i>S</i>	0 < <i>S</i> <= 45 ^a	Practical salinity.
<i>P</i>	1 (fixed)	Pressure (atm) (this version of MarChemSpec is coded only for 1 atmosphere pressure).
<i>mH</i>		The alkalinity (amount content) of the reference seawater is decreased by <i>mH</i> mol kg ⁻¹ (<i>mH</i> can be positive or negative).
<i>nSpecies</i>	9 (fixed)	The row lengths of <i>cSpecies_out</i> , <i>mSpecies_out</i> , <i>ActCoeffs</i> , and <i>NamesSpecies</i>
<i>iFix</i>	0 <= <i>iFix</i> <= 11	Integer, if >0 the input solution will be adjusted to values of the seawater state variables in array <i>ValuesFixed</i> .
<i>ValuesFixed</i>	2x2 array (fixed)	This array contains the desired values of the fixed seawater state parameter(s) and their

		uncertainties, as described in the previous section.
<i>nOut</i>	54 (fixed)	The number of calculated state variables and stoichiometric equilibrium constants to be returned in the array <i>Outputs</i> .
<i>strFilesDirectory</i>	c:\marchemspec_mb\ ^b	Folder containing the text files (Pitzer.par, Pitzer.rcn) read by the model.
<i>strCovmxDirectory</i>	c:\marchemspec_mb\ ^b	Folder containing directories seawater and ASWbuffer.
<i>iUser</i>	One dimensional array, of size at least 10. It is only needed for <i>iFix</i> > 0.	The first four elements of this array must contain the integer options required for the input value of <i>iFix</i> (see Table 2).

Notes :

^a If these ranges are exceeded, the calculation will fail, returning a value of *iFail* = 100 and an explanatory message.

^b These are the standard folder locations, but must be set to wherever the model files have been installed.

When using the MarChemSpec function for *iCalc* = 4 the essential points to remember are:

1. Adjusting the input aqueous solution – a seawater of salinity *S* for this value of *iCalc* – to fixed values of either one or two seawater state parameters involves using the two existing arguments *iFix* and *ValuesFixed()*, and new argument *iUser()*.
2. The function can still be called in the same way as described in the document *Using the Models Within MATLAB*.
3. The outputs arguments of the function are the same as before.

6.2 User-defined compositions (*iCalc* = 5)

This calculation is essentially the same as for *iCalc* equal to 4, except that the composition of the natural water (the input solution) can be varied from that of reference seawater. The composition is therefore specified in terms of individual species molalities or amount contents in argument *Species_in*. The use of arguments *iFix*, *ValuesFixed* and *iUser* is the same as described for *iCalc* equal to 4 above, and below we only list the input arguments.

For this calculation the MATLAB function call has the form:

[*Outputs*, *NamesOutputs*, *cSpecies_out*, *mSpecies_out*, *ActCoeffs*, *NamesSpecies*, *iFail*] = ...

MarChemSpec(*iCalc*, *tC*, *P*, *iConc*, *Species_in*, *iFix*, *ValuesFixed*, *nOut*, *strFilesDirectory*, *strCovmxDirectory*, *iUser*);

Input Arguments

Argument	Value	Meaning
<i>iCalc</i>	5 (fixed)	

<i>tC</i>	-5 <= <i>tC</i> <= 45 ^a	Temperature (°C)
<i>P</i>	1 (fixed)	Pressure (atm) (this version of MarChemSpec is only for a pressure of 1 atmosphere).
<i>iConc</i>	1 or 2	1 - <i>Species_in</i> are molalities, 2 - <i>Species_in</i> are amount contents.
<i>Species_in</i>	3x9 array ^b	The molalities or amount contents of the solution components, see the following table for the species and their order.
<i>iFix</i>	0 <= <i>iFix</i> <= 11	Integer, if >0 the input solution will be adjusted to values of the seawater state variables in array <i>ValuesFixed</i> .
<i>ValuesFixed</i>	2x2 array (fixed)	This array contains the desired values of the fixed seawater state parameter(s) and their uncertainties, as described in the previous section.
<i>nOut</i>	54 (fixed)	The number of calculated state variables and stoichiometric equilibrium constants to be returned in the array <i>Outputs</i> .
<i>strFilesDirectory</i>	c:\marchemspec_mb\ ^c	Folder containing the text files (Pitzer.par, Pitzer.rcn) read by the model.
<i>strCovmxDirectory</i>	c:\marchemspec_mb\ ^c	Folder containing directories seawater and ASWbuffer.
<i>iUser</i>	One dimensional array, of size at least 10. It is only needed for <i>iFix</i> > 0.	The first four elements of this array must contain the integer options required for the input value of <i>iFix</i> (see Table 2).

^a If this range is exceeded, the calculation will fail, returning a value of *iFail* = 100 and an explanatory message.

^b The molalities or amount contents (according to the value of *iConc*) of the principal species are placed in this array. See section 4.2 of the document *Using the Models Within MATLAB* for the list of species, which is *not* the same as that for the output arrays.

^c These are the standard folder locations, but must be set to wherever the model has been installed.

7. Limitations

In the current version of the model the effect of uncertainties in one or both of the fixed seawater state parameters, for *iCalc* equal to 4 and 5, are not propagated to values of the other calculated quantities. In other words, uncertainties entered in argument *ValuesFixed()* do not affect the estimated uncertainties of output quantities. (This capability will be added in the future.)

8. Examples

MATLAB script files for $iCalc = 4$ calculations for $iFix$ values of 1 to 11 can be found in subdirectories of the distribution archive (names `\iFix_1`, `\iFix_2` etc.). Follow the instructions in the document *Using the Models Within MATLAB* to run the scripts. We do not include example scripts for $iCalc$ equal to 5 because the use of $iFix$, $ValuesFixed()$, and $iUser()$ is the same as for $iCalc$ equal to 4.

Many of the problem types involve extra iteration compared to the basic calculation of equilibrium of the input solution ($iFix = 0$). The program will therefore take longer to run. It may be helpful, if you intend to process large datasets, to assess first how long each input problem (i.e., for one aqueous solution) will take first.

9. 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).