

BRTSim v4.1



Bio-Reactive Transport Simulator
Version 4.1
Release a

A general-purpose multiphase and multispecies computational solver for
biogeochemical reaction-advection-dispersion processes in porous and
non-porous media

User Manual and Technical Guide 4.1a
First edition

Author
Federico Maggi
11 November 2020



Preface

This document describes the functioning principles and practical use of the BRTSim v4.1 computational solver.

BRTSim (BioReactive Transport Simulator) is a general-purpose multiphase and multicomponent computational solver for biogeochemical reaction-advection-dispersion processes in porous and non-porous media. BRTSim finds suitable applications to describe water flow in soils and geophysical media, to track transport and dispersion of aqueous and gaseous chemicals, as well as to assess their chemical equilibrium and their decomposition rates in both chemical and biochemical reactions. For these characteristics, BRTSim is an extraordinary computational tool in soil physics and biogeochemistry, soil and water quality assessment and prediction, soil bio- and phyto-remediation potential estimation, and in all environmental engineering contexts where physical, chemical and biological processes co-exist and affect each other with complex nonlinear feedbacks.

BRTSim allows defining a physical domain with an arbitrary number of grid elements that may be heterogeneous in their physical and hydraulic properties; BRTSim allows full control of initial and boundary conditions, and allows defining a biogeochemical system with an arbitrary number of primary aqueous species, secondary aqueous, mineral and gaseous species (in chemical equilibrium with primary species), and microbial functional groups with any specific metabolic requirement. Chemical and biochemical reactions can be defined for any kinetics framework and order including multiple Michaelis-Menten terms, multiple competitive substrate consumption effects, and multiple inhibition terms.

BRTSim bases on solvers that have been largely tested, but because of its potentiality, it is under continuing development and improvement in numerical accuracy, robustness, reliability, and computational performance. It is to be noted that, although all methods used to solve physical and chemical processes follow recommendations and methods largely accepted in the scientific literature, the integration of diverse processes, each one requiring time scales that may largely vary from any other, may have potential defects. BRTSim, as a consequence, is also a platform where newly developed algorithms are implemented and tested to improve older and less performing algorithms. Iteration number and tolerances can be set for the various processes but it is practically impossible to exhaustively cross-check mutual compatibility. The BRTSim framework is therefore designed to allow the user to correct potential instabilities, which depend on the specific problem to be solved, and set the numerical solvers to converge by criteria with an arbitrary level of accuracy.

BRTSim implements advanced computational algorithms that have given an enormous potentiality as compared to those used in its predecessors BRTSim v1, v2 and v3 releases. The performance has improved by more than 10 times in terms of computational time, while the numerical stability and solution accuracy have improved substantially, especially in the convergence of all solvers. The input file to BRTSim v4 has also largely been refurbished as compared to previous versions, making the control of all computational parameters more easily accessible and manageable also by third-party software. These newly implemented characteristics give BRTSim v4.1 a new level of flexibility and computability. In the remainder of this document, reference will be given to BRTSim instead of BRTSim v4.1 for simplicity, bearing in mind that all characteristics and properties described herein

are unique to BRTSim v4.1 only and do not generally apply to earlier versions. In particular, the input file has been changed in this version and is not compatible with earlier versions.

Contents

1	BRTSim package	1
1.1	Licensing	1
1.2	Access the BRTSim package	1
1.3	Contents of the package	2
1.4	Chronology of releases	3
1.5	Performance of earlier and current versions	4
1.6	Minimum requirements	4
1.7	Installation	4
1.8	Launching	5
2	BRTSim structure	7
2.1	File management	7
2.2	Input file	7
2.3	Compatibility of <code>Param.inp</code> file in earlier versions	8
2.4	BRTSim code	8
2.5	Output files	8
3	BRTSim computational principles	11
3.1	Flow chart of events	11
3.2	The solving domain and its phases	12
3.3	Phases and species	13
3.3.1	Primary aqueous species (PRI)	13
3.3.2	Primary biological species (BIO)	14
3.3.3	Secondary aqueous species (SEC)	14
3.3.4	Secondary mineral species (MIN)	15
3.3.5	Secondary gaseous species (GAS)	15
3.3.6	Composed species (COMP)	16
3.4	The solving domain and its hydraulic properties	16
3.5	Mass conservation and continuity laws of phases	17
3.6	Mass conservation and continuity laws of species	23
3.7	Mass conservation and continuity law of energy	25
3.8	Aqueous kinetic reactions	28
3.9	Equilibrium reactions	29
3.10	Phase dependence on temperature	30

4	Geometry, initial, and boundary conditions	31
4.1	0-, 1- and 1.5-dimensional domains	31
4.2	Initial conditions	32
4.3	Boundary flows	33
4.4	Boundary conditions	34
5	Solvers and feedback switches	37
5.1	Solvers switches	37
5.2	Synchronization across solvers	37
5.3	Feedback switches	37
5.3.1	L and G feedback	38
5.3.2	L and chemistry feedback	39
5.3.3	L and biology feedback	40
5.3.4	Chemistry and biology feedback	41
6	The Param.inp file	43
6.1	PARAM block	43
6.2	PARALLEL block	47
6.3	MATERIAL block	48
6.4	PHASE block	51
6.5	PRI block	53
6.6	BIO block	54
6.7	SEC block	56
6.8	GAS block	57
6.9	COMP block	58
6.10	KIN block	59
6.11	ICSTP block	63
6.12	ICPRI block	64
6.13	ICGAS block	65
6.14	ICFILE block	66
6.15	ELEM block	67
6.16	GEN block	68
6.17	PEST block	70
6.18	EXEC block	71
7	The output files	73
7.1	The Time.out file	73
7.2	The Flux.out file	73
7.3	The Grid.out file	73
7.4	The TimePST.out file	74
8	Samples	75
	Bibliography	79

Chapter 1

BRTSim package

1.1 Licensing

BRTSim is subject to authorship and therefore copyright. You can use BRTSim under the Attribution 4.0 International (CC BY 4.0), meaning that you can copy and redistribute BRTSim in any medium and format but we do not recommend you change, modify or adapt the distributed executables. In any of these instances, you must give appropriate credit, provide a link to the license, and indicate if changes were made and what they have affected. You may do so in any reasonable manner, but not in any way that suggests the licensor endorses you or your use.

Running BRTsim is subject to licensing. Depending on the license, you can run BRTSim with full capability for a limited time (full license) or with limited capability for an unlimited time (trial license). Currently, only full license is provided freeware but this may change in future releases of BRTSim. The License file is available at the repository link in Section 1.2.

1.2 Access the BRTSim package

The full package of the latest and earlier releases of BRTSim can be accessed at the QR link or at <https://sites.google.com/site/thebrtsimproject/home>.

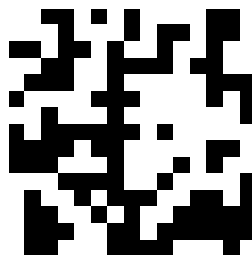


Figure 1.1: Link to BRTSim package.

1.3 Contents of the package

The package accessible via the QR code in Figure 1.1 contains all files required to run BRTSim and includes: a User Manual and Technical Guide describing the functioning principles and practical use of BRTSim; the BRTSim executable written for WINDOWS 64-bit operating systems, the shell and executable files for LINUX/UNIX/UBUNTU operating systems, the shell and executable files for OSX IMAC64 operating systems (see Table 1.1). The package also contains the Matlab Runtime for WINDOWS 64-bit, while other MCRs can be downloaded from the Mathworks ©webpage free of charge. The package includes examples with input files and post-processing scripts written in Matlab to represent the outputs. Finally, the package includes the BRTSim licencs file with the specific capabilities explained in Section 1.1.

OS	Content
Windows x64	BRTSim_v41a_WIN64_R2011b.exe BRTSim_v41a_WIN64_R2017a.exe BRTSim_v41a_WIN64_R2018b.exe license.txt MCR7.16 (for 2011b) MCR9.2 (for 2017a) User Manual and Technical Guide Samples
Linux Unix Ubuntu	BRTSim_v41a_GLNXA64_R2018b BRTSim_v41a_GLNXA64_R2019b run_BRTSim_v41a_GLNXA64_R2018b.sh run_BRTSim_v41a_GLNXA64_R2019b.sh license.txt User Manual and Technical Guide Samples
OSX	BRTSim_v41a_IMAC64_R2018a.app run_BRTSim_v41a_IMACA64_R2018b.sh license.txt User Manual and Technical Guide Samples

Table 1.1: Content of download package.

1.4 Chronology of releases

Table 1.2 lists the sequence of major implementations throughout the development of BRTSim.

Release	Date	Implementation	Support
v2.2a		- Improved stability - Improved performance - Bug fixes	Not supported
v2.2b		- Improved performance	Not supported
v2.2c		- Improved performance	Not supported
v2.2d		- Improved performance - Bug fixes	Not supported
v2.2e	15-Aug-17	- Improved performance - Bug fixes	Not supported
v2.2f	4-Oct-17	- Improved convergence in TR and KIN solvers - Improved performance - Improved error management - Bug fixes - Additional samples are added to package	Not supported
v2.2g	11-Oct-17	- Improved convergence in EQ solver - Improved performance	Not supported
v3.0a	18-Apr-18	- Revised Param.inp, Time.out, Flux.out files - Heat flow (not active) - Explicit primary BIO species, chemotaxis, L phase immobilization/remobilization - Minor bug fixes - improved performance - exe available only for Win64 platform with MCR 2011b	Not supported
v3.0b	6-Jun-18	- Revised Param.inp, Time.out, Flux.out files - Improved chemotaxis, and BIO response to environmental factors - Inclusion of G phase boundary conditions (see Sample 10 in distribution package) - Minor bug fixes	Not supported
v3.1a	15-Aug-18	- Minor bug fixes and improved stability - Improved manual - New samples	Not supported
v3.2a	23-Jul-19	- New features in Param.inp - Minor Bug fixes - Improved performance in MCR2017a - Improved manual	Not supported
v3.2b	3-Aug-19	- Improved performance - Minor bug fixes	Not supported
v3.2c	15-Aug-19	- Improved error management	Not supported
v3.2d	12-Sep-19	- Minor bug fix - Improved performance	Not supported
v4.0a	30-Oct-19	- Minor bug fix - Improved heat flow solver - New capabilities (TSAVE and ICFILE block)	Not supported
v4.0b	8-Dec-19	- Improved heat flow solver - Improved performance	Not supported
v4.0c	18-Dec-19	- Consolidated - Improved overall performance	Not supported
v4.0d	4-Apr-20	- Improved heat flow solver - Improved overall performance - New capabilities (EXEC block) - Improved manual	Not supported
v4.0e	2-May-20	- Improved transport solver - Improved overall performance - New capabilities (RELOOP in GEN block)	Not supported
v4.0f	3-Nov-20	- Improved "Early termination detection" - Support for OSX platform	Not supported
v4.1a	11-Nov-20	- Improved "Early termination detection" and new capability - Improved code for stability - Repurposed "ISAVE"	Supported

Table 1.2: BRTSim chronology.

1.5 Performance of earlier and current versions

Figure 1.2 compares the computational performance of the BRTSim releases against the samples provided in the download package.

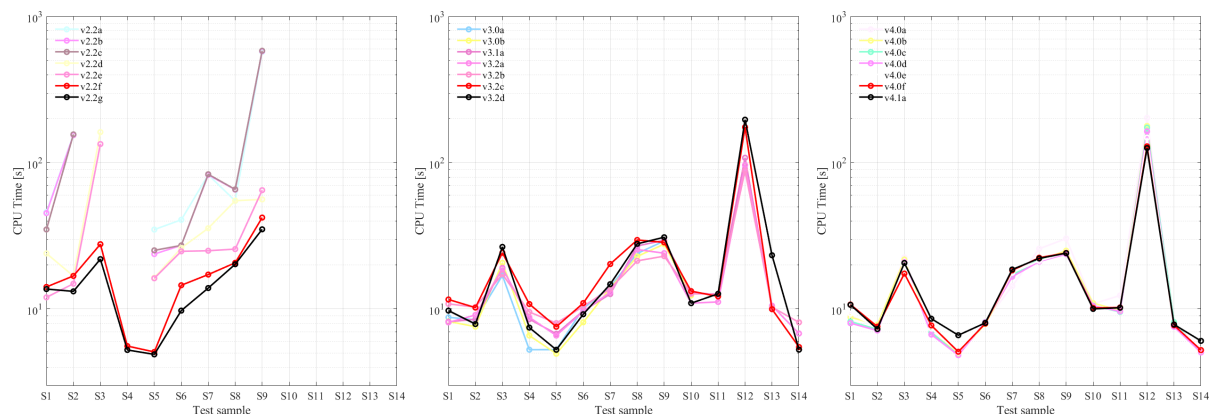


Figure 1.2: Summary of computational performance of earlier as compared to the current BRTSim version across the 14 samples distributed with the BRTSim package.

1.6 Minimum requirements

The minimum requirements for using BRTSim follow from the development environment and operating system; while earlier versions of BRTSim were distributed in both 32-bit and 64-bit versions, the 32-bit version has been discontinued because of limited memory management capability (about 2.5 GB) and a slightly lower computational performance. The 64-bit version allows computational problems with a large number of elements (say $> 10^3$) and chemical species (say $> 10^2$) on a single CPU, but on a CPU cluster it is practically limited only by the number of CPUs and memory. Note that the memory management has largely been redesigned since v2 so to accelerate performance while limiting memory use during a simulation run.

1.7 Installation

BRTSim does not require an installer or installation procedure. The files required to run BRTSim must be contained within a folder and include the executable (WINDOWS operating systems), the executable and shell files (UNIX and OSX operating systems), and the license file. Optional files that may be required are tables of the boundary conditions depending on the simulation setting.

1.8 Launching

The capability to run BRTSim is not subject to any third-party licensing or purchase of additional software.

In WINDOWS operating system, the executables can be launched from the command line of the operating system or by double-clicking the executable in the chosen folder. Note, however, that the executable can run only if the corresponding Matlab Runtime (MCR) has been pre-installed on that machine, or it will not run otherwise. The MCR can be accessed as described in Section 1.2. In UNIX and OSX operating systems, the folder must contain the shell file and the executable. The executable can be run by launching the corresponding shell file in the terminal.

It is possible to launch BRTSim with or without argument in any operating systems. In WINDOWS, you can launch BRTSim without arguments as

```
>> BRTSim_v41a_WIN64_R2011b
```

and BRTSim will search for the default input file `Param.inp`, and will generate the default output files `Time.out`, `Flux.out`, `Grid.out` and optionally also `TimePST.out`. If you want to read specific input files and give output files specific names, then you can use arguments as

```
>> BRTSim_v41a_WIN64_R2011b ParamARG.inp ...  
... TimeARG.out FluxARG.out GridARG.out
```

It is not possible, though, to specify a name to the optional output file `TimePST.out`.

In UNIX operating systems, you can launch BRTSim by using the shell file without arguments as

```
>> ./run_BRTSim_v41a_GLNXA64_R2018a.sh /usr/local/matlab/R2018a
```

or by using arguments as

```
>> ./run_BRTSim_v41a_GLNXA64_R2018a.sh /usr/local/matlab/R2018a ...  
... ParamARG.inp TimeARG.out FluxARG.out GridARG.out
```

In OSX operating systems, you can launch BRTSim in the same way as for UNIX.

Chapter 2

BRTSim structure

2.1 File management

The input file `Param.inp` contains all information needed to solve a computational problem and produce the output file `Grid.out`, `Time.out`, and `Flux.out` by default. The `Grid.out` file lists all material properties of the computational problem specified in the `Param.inp` file. `Time.out` contains the state variables calculated in each node and at each or selected time steps. `Flux.out` contains all cumulative fluxes of phases and species through the boundaries at each or selected time steps (Figure 1). An additional optional output called `TimePST.out` may be generated for selected compounds, nodes of the computational domain, and times.

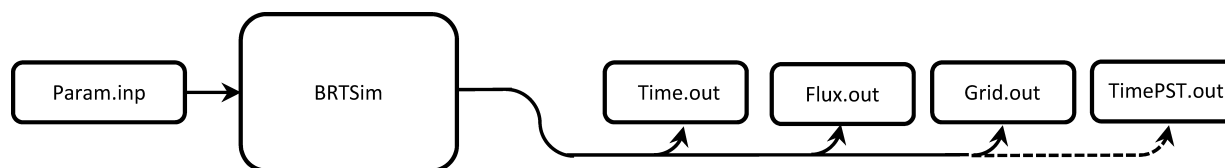


Figure 2.1: BRTSim file structure.

2.2 Input file

The `Param.inp` file contains various blocks that define the integration time, selected solvers, and convergence criteria (block `PARAM`). The definition and setting of the biogeochemical system is handled by specific blocks that define the materials types and their physical and hydraulic characteristics (block `MATERIAL`), the physical properties of the liquid and gaseous phases at given temperatures (block `PHASES`), the chemical and biological primary aqueous species (block `PRI` and `BIO`), the secondary aqueous species (`SEC` and `MIN`) and their chemical equilibrium with `PRI`, and the gaseous species and their chemical equilibrium with `PRI` (block `GAS`). In addition, any `PRI`, `BIO`, `SEC`, `MIN` and `GAS` species can be combined into composed species (block `COMP`) to perform additional computational tasks

such as mass balance verification. Any PRI and BIO species can be used to define the kinetic aqueous reactions and their parameters (block KIN), while the initial hydraulic conditions (block ICSTP), the initial and boundary qualities relative to the PRI species (block ICPRI), the initial conditions for the GAS species (block ICGAS), the domain geometry and boundary conditions (block ELEM), the boundary fluxes (block GEN), and selected species in arbitrary nodes and times for output (block PST) can be defined. These blocks are described in detail in Section 3.3, but it is important to mention here that each of these blocks allows to specify an arbitrary number of items. For example, it is possible to define several materials types in any generic order and only a few be attributed to the nodes in the solving domain. Similarly, it is possible to define an arbitrary number of PRI species including the solvent but, in this case, all will be solved for in the domain. Likewise, it is possible to set an arbitrary number of BIO, SEC, MIN and GAS species; each secondary species will be solved for in the domain as long as they exist in equilibrium with declared PRI species. In contrast, COMP specie cannot directly be used to define other processes in this release, but it is expected that future releases will implement this capability.

2.3 Compatibility of Param.inp file in earlier versions

The Param.inp file in BRTSim v4.0e is different from earlier BRTSim versions, and therefore it is not compatible with earlier versions. Earlier Param.inp files can be adapted with only minor changes, though, thus earlier computational problems may be reused in this new version of BRTSim. The user may therefore access earlier and this BRTSim versions from the repository and adapt his/her own Param.inp accordingly.

2.4 BRTSim code

BRTSim reads all needed information from the Param.inp file; if the problem is not stated correctly, BRTSim will send you a warning message and it will continue running, or will send an error message and it will stop running. When problem definition is correct, BRTSim will organize all information and will assemble the structured arrays of variables and computational structures that will be processed by various solvers to numerically calculate flows and reactions.

2.5 Output files

During computations, BRTSim saves a time table of all state variables in the Time.out file at a frequency specified by the user. The solved state variables include the hydraulic properties and the species concentrations in each element and each phase in [mol/L], [mg/L] and [kg/m³] depending on whether the species is a chemical, a microbial functional group, or a gas, respectively. If COMP species are used, BRTSim saves the mass of the COMP species defined in the COMP block with the unit defined by the user.

Likewise, BRTSim also produces the file `Flux.out`, which contains a table of cumulative boundary fluxes of the liquid phase in [kg] and species in the liquid phase in [mol] or [mg] depending on whether these are chemicals or microbial species, and in the user-defined unit for COMP species. Secondary species (aqueous, gaseous or mineral) do not cross the boundaries because are combinations of PRI, and will not appear in the `Flux.out` file. PRI species that are described as non-mobile will not cross the boundary; typical non-mobile species are MIN and microbial functional groups defined as PRI or explicitly defined in the BIO block. Yet, the user can select which species is mobile in full arbitrium. In particular, BIO species can undergo advection, diffusion, and chemotaxis, and can cross the boundary because they are primary species, but have other additional properties that PRI species do not have, which are described later.

The number of items in the `Time.out` file, as well as in the `Flux.out` file depends on the list of declared species in the `Param.inp` file, such as the number of elements, the number of PRI, BIO, SEC, MIN, GAS and COMP species, the number of boundary fluxes, etc. Both `Time.out` and `Flux.out` are saved as a text file and allow post-processing by any software available to a user that can open `.TXT` files. `Time.out` and `Flux.out` are dynamic files because they are updated while BRTSim runs.

BRTSim produces also the static file `Grid.out`, which lists all parameters related to the grid elements, such as materials and related parameters, and it is used to inform the user on the actual values of hydraulic and thermodynamic parameters declared or estimated by BRTSim in building all needed information.

Finally, BRTSim allows to store the values of specific state variables at specific nodes and times in the static `TimePST.out` file. This file is particularly useful if the user is interested in selected species, or for parameters estimation through third-party softwares.

Chapter 3

BRTSim computational principles

3.1 Flow chart of events

Initialization of the biogeochemical system in BRTSim consists of assigning the initial saturation, pressure, and temperature to each element of the solving domain. Next, the concentration of all primary and secondary species (described in Section 3.3) are assigned to each element. The next step consists of balancing the concentration of all secondary species according to their declaration as per equilibrium with primary species. At the end of the initialization, the first output is saved for the system state variables at time $t = 0$. After initialization, BRTSim solves in a sequential manner for various processes over the solving domain. These processes are the liquid phase flow, gas phase flow, heat flow, advection-dispersion transport in the liquid and gas phases, chemotaxis of biological species, kinetic reactions, and equilibrium reactions. The flow chart in Figure 2 shows the sequence of events, which are called as:

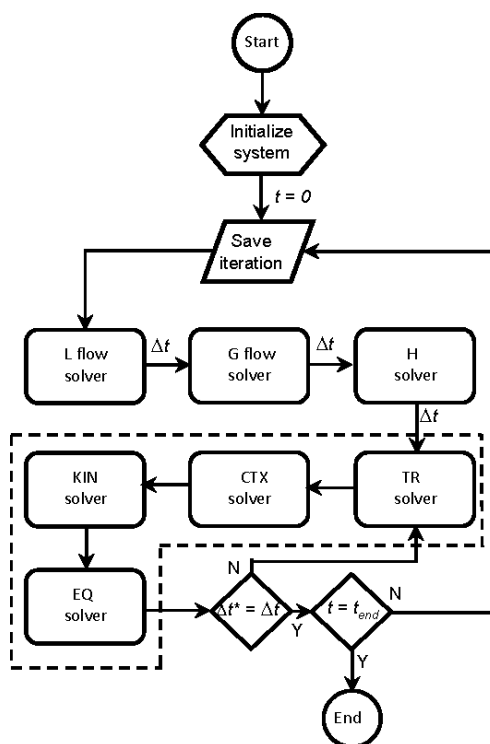


Figure 3.1: BRTSim sequence of calls to solvers.

1. hydraulics of the liquid phase flow (L Solver);
2. hydraulics of the gas phase flow (G Solver);
3. heat flow (H Solver);

4. transport in both liquid and gaseous phases (TR Solver);
5. chemotaxis (CTX Solver);
6. kinetic reactions in the liquid phase (KIN Solver);
7. equilibrium reactions (EQ Solver).

With the exception of the first solver for the liquid phase L, all solvers in the sequence of events can be switched on/off according to the complexity of the problem, and the user is given full control on which solver is to be used. All solvers are based on iterative algorithms to converge to a solution of the flow in a given time increment Δt , and must therefore receive instructions on the number of iterations and tolerance through the `Param.inp` file. The iterative schemes are described in greater detail later, but all allow the user to set the maximum iteration number and minimum tolerance as criteria to accept a solution. At the convergence of each individual solver, the state variables are updated and passed through the next solver, which calculates new, updated values of the same or other state variables.

In addition, an integrated cycle is used to re-iterate the TR, CTX, KIN, and EQ solvers depending on whether Δt has been completed in each Solver and matches the one of the L Solver or not. This integrated scheme assures that all processes are calculated to exhaustion of the corresponding rate and over a defined Δt in all phases and for all declared species.

At defined iterations, state variables are saved in the output files until when $t = t_{end}$.

3.2 The solving domain and its phases

BRTSim solves a multiphase flow problem over a defined domain with dimensionality that varies from 0 to 1.5 (Section 4.1). This domain is composed by a set of elements connected sequentially and defined by a position z , a volume V and the interface area A between two adjacent elements. The position z is that of the center of mass of the element and is accompanied by the distances Δz^+ and Δz^- to the above and below interfaces of that element, respectively. The position is relative to a system of reference centered in the lowest element and pointing upward in the vertical direction. The number of elements is arbitrary as well as any of the geometrical characteristics of each elements, which are individually assigned in the `ELEM` block of the `Param.inp` file. The physical properties of each element are determined by attributing a specific material defined in the `MATERIAL` block. A material defines the porosity ϕ , and other hydraulic and thermal properties detailed later in Section 3.4.

BRTSim uses three phases, namely a solid phase (M), a liquid phase (L) as the preferred phase, and a gas phase (G). However, it also allows to define primary biological species (BIO), which are cumulatively accounted for as an independent phase (the biological phase B) given its interactions with L and G phases. The two fluid phases can be any liquid or gas, each defined in their physical properties as a function of the temperature in the `PHASE` block of the `Param.inp` file. In that block, the L phase is characterized by a vector of density ρ_L , viscosity μ_L , surface tension γ_L , heat capacity c_{pL} and heat conductivity k_{hL} at

arbitrary temperatures, while the G phase is only defined by a vector of ρ_G , μ_G , c_{pG} and k_{hG} at arbitrary temperatures. The actual properties of the two phases at a given temperature are estimated as described later in Chapter 4, 5 and 6. The B phase can be made by an arbitrary number of BIO species defined in the BIO block of the `Param.inp`. If the L phase is water, BIO species can immobilize water according to the water volume fraction (WVF). In the most general case, the phases β and their volumes are defined following Maggi and Porporato (2007), and are represented in Figure 3.2. These definitions of the various volumes apply to each element of the solving domain.

3.3 Phases and species

In this version of BRTSim, every fluid phase and the biological phase can host an arbitrary number of species. These species determine the biogeochemical system within the solving domain. Because the liquid phase L is the preferred phase and must always be solved for, at least one PRI species must be declared to represent the solvent. All other primary and secondary species are optional, and the user can define as many as needed in a particular problem. The species are grouped into primary aqueous species (PRI), primary biological species (BIO), secondary aqueous species (SEC), secondary mineral species (MIN), secondary gaseous species (GAS), and composed species (COMP).

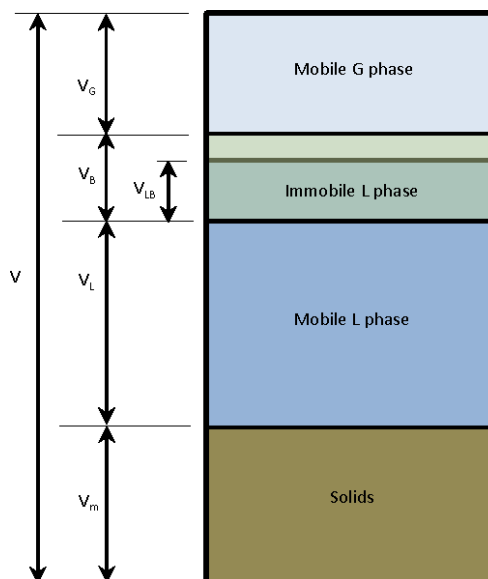


Figure 3.2: BRTSim volumes definition in each element of the solving domain.

3.3.1 Primary aqueous species (PRI)

These species can be any real or virtual ion, molecule or substance, or microbial functional group that will undergo the conservation and continuity laws of components described later in Section 3.6. All PRI are defined in the PRI block of the `Param.inp` file and are assumed to be in the aqueous phase and expressed in [mol/L]. Primary aqueous species can undergo an arbitrary number of equilibrium or kinetic reactions of chemical or biochemical nature. The attributes of any PRI species include the mobility (i.e., a PRI species undergoes diffusion and advection according to the flow conditions), whether it is the solvent in the biogeochemical system (only one PRI species must be defined as the solvent - typically water) or is a constant, the molar mass, and the diffusion coefficient.

Microbial functional groups such as bacteria, fungi, algae, etc., can be defined as PRI and are a particular case of PRI species accounted for by their concentration, which are expressed in BRTSim in [mg/L]. They are used in any of the ways PRI are normally used, hence, they can be part of any type of reactions (kinetic or equilibrium). However, microbial functional groups defined as PRI are not subject to peculiar mechanisms that characterize cells; therefore, depending on the specific problem the user is aiming, BIO species may be used to include specific processes related to living organisms (see Section 3.3.2). PRI species require declaration of initial condition and boundary conditions in the ICPRI block of the `Param.inp` file (see also Chapter 4).

3.3.2 Primary biological species (BIO)

Primary biological BIO species are defined in the BIO block of the `Param.inp` file and are a special case of PRI species. As such, they can be any real or virtual substance, even if their definition is particularly suited to describe living cells, microbial functional groups, or derived materials such as necromass or exopolymers. BIO species retain all properties of PRI, but have additional properties such as the capability to immobilize and remobilize the L phase (typically water). Because of this attribute, BIO species cumulatively constitute an additional phase in BRTSim, with related thermal properties and the capability to exert effects on the gas phase when BIO concentration increases or decreases. Depending on the conditions, BIO species can undergo space limitations as described later in Section 3.8, and chemotaxis against gradients in chemical repellents and toward chemical attractants with coefficients specified by the user in the BIO block. Additionally, BIO species can also be given specific responses to temperature and L phase saturation as described in Section 3.8. BIO species can be used in any other process like PRI except in equilibrium reactions with other secondary species. Because BIO species are of the primary type, they require declaration in the initial and boundary conditions in the ICPRI block of the `Param.inp` file (see also Chapter 4).

3.3.3 Secondary aqueous species (SEC)

An arbitrary number of secondary aqueous species (SEC) can be defined by means of equilibrium reactions between any PRI species and that secondary species. SEC species can be any real or virtual ion, molecule or substance. SEC species have similar attributes as PRI species, that is, mobility, molar mass and diffusion coefficient, and are described with the unit of [mol/L]. Additionally, SEC species include the equilibrium reaction that defines them. The chemical reaction includes negative stoichiometric coefficient indicating reactants and positive stoichiometric coefficients indicating products. No SEC species can be defined more than once even if it is the result of a different reaction. The equilibrium reaction is determined by an equilibrium constant K at eight different temperatures ranging from 0 to 300 °C. These definitions can be implemented by the user in the SEC block of the `Param.inp` file. The definition of the equilibrium constant K allows to determine the concentration of any component in an equilibrium reaction at any temperature within the

temperature range above by means of a generic polynomial interpolating function based on Maier and Kelley (1931) and defined as

$$\log K(T) = a \log T + b + cT + \frac{d}{T} + \frac{e}{T^2}, \quad (3.1)$$

where the coefficients a , b , c , d and e are calculated in BRTSim by least square fitting against experimental values with T in Kelvin. Experimental values are inputted by the user in the SEC block of the `Param.inp` file, while a comprehensive database of equilibrium reactions is available, for example, in the EQ3/6 V8.2b database (Wolery, 1992). Because the same SEC species may result from a different reactions, and because definition of a specific SEC species cannot be duplicated, a careful choice in selecting the PRI species in the first place is particularly important. Note that SEC species do not require declaration of initial conditions given that they are in equilibrium with PRI species.

3.3.4 Secondary mineral species (MIN)

Mineral species (MIN) are a particular case of SEC aqueous species and, as such, they can be any real or virtual molecule or substance. They are defined in the SEC block of the `Param.inp` file and can appear in an arbitrary number as any other SEC species. As mineral species are solid, they are typically defined as non-mobile (mobility = 0, or diffusion coefficient $D_s = 0$). No MIN species can be defined more than once even if it is the result of a different reaction. MIN species are determined by the equilibrium constant, which is available from chemistry handbooks or through thermodynamic databases such as the EQ3/6 V8.2b (Wolery, 1992). As for SEC, the equilibrium constant will be defined for temperatures ranging from 0 to 300 °C, and the equilibrium constant at any temperature will be calculated in BRTSim using Eq. (3.1). Note that MIN species do not require declaration of initial conditions given that they are in equilibrium with PRI species.

3.3.5 Secondary gaseous species (GAS)

In a similar way as for SEC and MIN, an arbitrary number of secondary gaseous species (GAS) can be defined by means of equilibrium reactions with PRI species. GAS species can be any virtual or real molecule or substance defined in the GAS block of the `Param.inp` file and include attributes of mobility, molar mass, and diffusion coefficient. GAS species are accounted for by their pressure, density, and mass within the solvers, but are saved in the `Time.out` file with the units of [kg/m³]. Also in this case, the temperature dependent equilibrium constant is estimated from experiments using Eq. (3.1). No GAS species can be defined more than once even if it is the result of a different reaction. Note, however, that because these species are in a different phase as compared to aqueous species, they require declaration of initial conditions in the ICGAS block of the `Param.inp` file (see also Chapter 4). No boundary GAS qualities are required in this version of BRTSim even if boundary fluxes using the G phase can be accounted for (see details in Chapter 4).

3.3.6 Composed species (COMP)

Composed (COMP) species are a linear combination of any other species declared in PRI, BIO, SEC, MIN, or GAS blocks, but cannot include PRI species that have been defined as constants. COMP can be defined in an arbitrary number and are not part of the biochemical system that is solved for, but are used for a number of controls and checks such as mass balances in the various phases, among specific species, or in a combination of phases and species. COMP are expressed in mass with the unit that is decided by the user and that depends on the coefficients of each term in the definition of COMP. COMP species are saved in the output files in the same way as any other species, and may appear in the `Flux.out` file if they include PRI or BIO aqueous species that cross the boundaries of the solving domain (see also Chapter 4).

3.4 The solving domain and its hydraulic properties

The physical properties of each element are determined by attributing a specific material defined in the MATERIAL block. A material defines the solid density ρ_m , porosity ϕ , absolute permeability k , hydraulic parameters, and residual saturation $S_{\beta r}$ for each fluid phase β . As mentioned earlier in Section 3.2, BRTSim uses two fluid phases, namely a liquid phase (L) and a gas phase (G). Hence, the residual saturations can be written as S_{Lr} and S_{Gr} for the two phases, respectively. In addition to the L and G phases, the biological phase B may exist depending on whether BIO species are defined, but no residual saturation is used. The B phase immobilizes the L phases and limits the L saturation in a similar way as any other phase. In practice the sum of saturations extended to all phases must respect $\sum S_{\beta} = 1$ as per Figure 3.2. The effective L and G saturations are written as Brooks and Corey (1962)

$$S_{Le} = \frac{S_L - S_{Lr}}{1 - S_{Gr} - S_{Lr}} \quad \text{with} \quad 0 \leq S_{Le} \leq 1, \quad (3.2a)$$

$$S_{Ge} = \frac{S_G - S_{Gr}}{1 - S_{Gr} - S_{Lr}} \quad \text{with} \quad 0 \leq S_{Ge} \leq 1, \quad (3.2b)$$

These relations are consistently used with the L and G phases regardless of whether also the B phase exists. The liquid saturation S_L is used as the preferred state variable in the hydraulic solver for the L phase, and is used to calculate the liquid capillary pressure P_c .

The relation between liquid saturation and potential (and its capillary pressure) can be selected in BRTSim between the Brooks and Corey (1962) and the van Genuchten (1990) models. The Brooks and Corey model describes the liquid capillary pressure $P_c = \rho_{Le} g \psi$ and relative permeability to the L phase k_{rL} and G phase k_{rG} as

$$P_c = \rho_{Le} g \psi_s (S_L)^{-b}, \quad (3.3a)$$

$$k_{rL} = \frac{k_L}{k} = (S_L)^{2b+3} \quad \text{with} \quad 0 \leq k_{rL} \leq 1, \quad (3.3b)$$

$$k_{rG} = \frac{k_G}{k} = (1 - S_L)^2 (1 - S_L^{2b+1}) \quad \text{with} \quad 0 \leq k_{rG} \leq 1, \quad (3.3c)$$

where ρ_{Le} is the effective liquid density accounting for temperature and dissolved species (see details in Chapter 5), $\psi_s < 0$ is the entry potential (suction), b is the pore volume distribution index, and k is the absolute permeability of that material. The van Genuchten model uses a similar approach and describes P_c , k_{rL} and k_{rG} as

$$P_c = \frac{\rho_{Le} g}{\alpha} \left(S_L^{-1/m} - 1 \right)^{m-1}, \quad (3.4a)$$

$$k_{rL} = \frac{k_L}{k} = (S_L)^{1/2} \left(1 - \left[1 - S_L^{1/m} \right]^m \right)^2 \quad \text{with} \quad 0 \leq k_{rL} \leq 1, \quad (3.4b)$$

$$k_{rG} = \frac{k_G}{k} = (1 - S_L^{1/2}) \left(1 - \left[1 - S_L^{1/m} \right]^m \right)^2 \quad \text{with} \quad 0 \leq k_{rG} \leq 1, \quad (3.4c)$$

where $1/\alpha$ is equivalent to the entry potential in the Brooks and Corey approach of Eq. (3.3), and m is an empirical parameter. The hydraulic conductivity K_β to either L or G phases is determined from the relative and absolute permeability as

$$K_\beta = k k_{r\beta} \frac{\rho_{\beta e} g}{\mu_\beta} = k_\beta \frac{\rho_{\beta e} g}{\mu_\beta}, \quad (3.5)$$

with $\rho_{\beta e}$ the effective phase density (accounting for the effect of dissolved species), μ_β the phase viscosity, and g the gravitational acceleration.

3.5 Mass conservation and continuity laws of phases

The mass M_β of phase β in an element of volume V of the solving domain is

$$M_\beta = \phi S_\beta \rho_{\beta e} V \quad \text{for} \quad \beta = L, G, B, \quad (3.6a)$$

$$M_\beta = (1 - \phi) \rho_\beta V \quad \text{for} \quad \beta = M. \quad (3.6b)$$

Because the M phase is not assumed to undergo dynamic changes within the solving domain, we treat only the fluid phases L and G, and the biological phase B here. In particular, the mass conservation law for these phases in an arbitrary volume V of the solving domain can be written in its general form as

$$\frac{\partial M_\beta}{\partial t} = \int_\Gamma \rho_{\beta e} v_\beta d\Gamma + \int_V \rho_{\beta e} u_\beta dV \pm \int_V f_\beta r_B \rho_{\beta e} dV, \quad \text{for} \quad \beta = L, G, B, \quad (3.7)$$

where v_β corresponds to the velocity of phase β through the surface Γ of a volume toward an adjacent volume, u_β is the rate of production and destruction of phase β in that volume, and r_β is the exchange rate between the L and B phases, with f_β the coefficient of conversion. The first integral on the RHS of Eq. (3.7) represents the internal fluxes, whether these be expressed by the Darcy's equation for $\beta = L, G$ or transport and chemotaxis for $\beta = B$. The second integral for the sources or sinks of mass is practically interpreted in BRTSim as the mass flux through the boundary of each element from outside the solving domain in contrast to the mass fluxes towards or from other

volumes of the solving domain. The rate u_β can be any positive or negative term for $\beta = L, B$, and G . The third integral in Eq. (3.7) is an internal mass exchange between phase and currently exists only for the L and B phases; hence, the conversion factor is $f_\beta = 0$ for the G phase, or when only the L phase exists, or it can assume values $0 \leq f_\beta \leq 1$ for the L and B phases if BIO species exist and undergo kinetic reactions. In specific, the current version of BRTSim accounts for immobilization and remobilization of the L phase into the B phase as a result of the dynamics of all BIO species declared in the BIO block of the `Param.inp` file, as described in detail later in Section 3.8 and is described by the net rate of change in the B phase after kinetic processes of growth or mortality.

The velocity v_β in Eq. (3.7) is written as

$$v_\beta = -k \frac{k_{r\beta}(S_\beta)}{\mu_\beta} \nabla [P_\beta(S_\beta) + \rho_{\beta e} g z] \quad \text{for } \beta = L, G, \quad (3.8a)$$

$$v_\beta = \epsilon_\beta v_L X_\beta - D_{\beta,s} \nabla X_\beta + D_{\beta,c} X_\beta \nabla X_{L,c} - D_{\beta,r} X_\beta \nabla X_{L,r} \quad \text{for } \beta = B. \quad (3.8b)$$

Eq. (3.8)a is essentially the Darcy's velocity and includes the gravitational acceleration g , the total pressure P_β of phase β , and the vertical position z relative to the system of reference. If the pressure of the G phase is simply P_G , the total pressure for the L phase is $P_L = P_c + P_G + P_O$, with $P_c \leq 0$ calculated as either Eq. (3.3)a or Eq. (3.4)a, and P_O the osmotic pressure due to chemicals dissolved in the L phase (see Chapter 5). If P_O is excluded from the total liquid pressure, the expression of Brooks and Corey (1962) is found. Finally, the relative permeability of an element to each phase β is calculated as either Eqs. (3.3)b,c or Eqs. (3.4)b,c. Eq. (3.8)a can also be written using Eq. (3.5) for the L phase as $v_\beta = -K_\beta \nabla(\psi_\beta(S_\beta) - z)$.

In contrast to Eq. (3.8)a, Eq. (3.8)b only applies to the B phase, where X_β is the mass fraction of species X in phase β ; the first term on the RHS expresses the transport

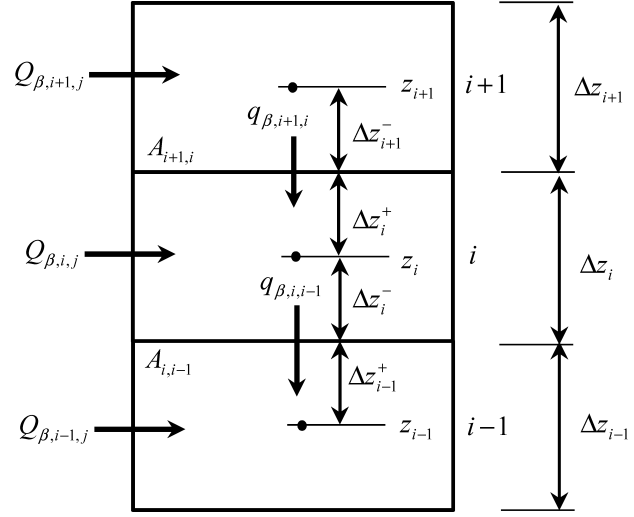


Figure 3.3: Discretization of mass conservation and continuity law for the L and G phases in BRTSim.

of phase B proportionally to an efficiency ϵ_B describing the detachment fraction of BIO species and the Darcy's velocity in the L phase, which product corresponds to a reduced advection. The second term expresses the diffusion of BIO species proportionally to the diffusion coefficient $D_{\beta,s}$. The third term expresses chemotaxis of BIO species against the concentration gradient of chemical attractant $X_{L,c}$ in the L phase with coefficient $D_{\beta,c}$, while the fourth term expresses chemotaxis away from the concentration gradient of chemical repellents $X_{L,r}$ in the L phase with coefficient $D_{\beta,r}$. Chemotaxis is therefore expressed here with a modified form of the Keller-Segel equation (Keller and Segel, 1971).

The solvers involved in the handling of the mass conservation laws for the phases are the L and G Solvers, and the TR and KIN Solvers if BIO species exists and if they have kinetic processes that result in mass exchanges with the L phase. The numerical scheme used to solve the mass conservation laws for phases $\beta = L, G, B$ in Eq. (3.7) follows the mass discretization in each grid element i of the 1-D domain along the z direction (Figure 3.3), so that Eq. (3.7) applied to each element becomes

$$M_{\beta,i}(t) = M_{\beta,i}(t - \Delta t) + \Delta t \left(\sum_j \rho_{\beta,i,j} q_{\beta,i,j} + \sum_j \rho_{\beta,i,j} Q_{\beta,i,j} \pm \sum_j f_{\beta} R_{B,j} \right), \quad (3.9)$$

where $q_{\beta,i,j} = v_{\beta,i,j} A_{i,j}$ is the internal volumetric flux of phase β through the interface $A_{i,j}$ between element i and the adjacent elements j , $Q_{\beta,i,j}$ is the j -th volumetric flow through the boundary of element i , and R_B is the mass rate of between-phase exchange. The net internal mass flux at element i in the vertical direction depicted in Figure 3.3 is therefore described as

$$\sum_j \rho_{\beta,i,j} q_{\beta,i,j} = \rho_{\beta e, i+1|i} q_{\beta, i+1, i} - \rho_{\beta e, i|i-1} q_{\beta, i, i-1}, \quad (3.10)$$

with the sign relative to the system of reference (here positive q is directed upward), and with $\rho_{\beta e, i+1|i}$ and $\rho_{\beta e, i|i-1}$ conditional to the densities in $(i+1)$ and i , and i and $(i-1)$ depending on the sign of q . This condition simply implies that if the internal mass flow is from $(i+1)$ to i then the fluid density is the one in $(i+1)$, or the one in i otherwise. The internal volume fluxes at element i are

$$q_{\beta, i+1, i} = v_{\beta, i+1, i} A_{i+1, i}, \quad (3.11a)$$

$$q_{\beta, i, i-1} = v_{\beta, i, i-1} A_{i, i-1}, \quad (3.11b)$$

with $A_{i+1, i} = \min\{A_{i+1}, A_i\}$ and $A_{i, i-1} = \min\{A_i, A_{i-1}\}$ the effective interface areas between elements $(i+1, i)$ and $(i, i-1)$. The Darcy's velocity between adjacent elements $(i+1)$ and i of the solving domain is discretized as

$$v_{\beta, i+1, i} = -\frac{k_{\beta, i+1, i}}{\mu_{\beta, i+1, i}} \left(\frac{\Delta(P_{\beta}(S_{\beta}) + \rho_{\beta e} g z)_{i+1, i}}{\Delta z_{i+1}^- + \Delta z_i^+} \right), \quad (3.12)$$

with the equivalent permeability $k_{\beta,i+1,i}$ and viscosity $\mu_{\beta,i+1,i}$ of phase β between two elements $(i+1, i)$ described by the weighted averages

$$k_{\beta,i+1,i} = \frac{\Delta z_{i+1}^- k_{\beta,i+1} + \Delta z_i^+ k_{\beta,i}}{\Delta z_{i+1}^- + \Delta z_i^+}, \quad (3.13a)$$

$$\mu_{\beta,i+1,i} = \frac{\Delta z_{i+1}^- \mu_{\beta,i+1} + \Delta z_i^+ \mu_{\beta,i}}{\Delta z_{i+1}^- + \Delta z_i^+}, \quad (3.13b)$$

where Δz_{i+1}^- and Δz_i^+ are the distances between the center of mass of the two elements and their interface (Figure 2). Note that the calculation of the gradient in the vertical direction z are carried out using these partial distances to the common interface of two elements so to allow the numerical management of flow conditions between elements through the definition of Δz^- and Δz^+ in the ELEM block. This is particularly useful to define specific boundary conditions.

Mass fluxes through the boundary and expressed by $\sum_j \rho_{\beta,i,j} Q_{\beta,i,j}$ with the volumetric flow rate Q_{β} assigned in the GENER block of the Param.inp file, and the density ρ_{β} at temperature T_{β} assigned for that specific phase in the PHASE block of the Param.inp file as described later in Section 3.10 and Section 4.

Sink and sources expressed by term $\sum_j f_{\beta} R_{B_j}$ in the mass conservation law for the L and B phase in Eq. (3.9) result from kinetic processes involved in BIO species and their discretization is described in better detail in Section 3.8.

As mentioned earlier, the L phase is the preferential phase in BRTSim. This means that the L phase flow is calculated first, and the result is next used to condition the G phase state. The numerical solution of the discretised mass conservation law of phases in Eq. (3.9) is carried out with an iterative technique. Currently, one of the mostly used schemes is the modified Picard algorithm (Celia and Couloutas, 1962); this algorithm foresees the iterative calculation of the new value of saturation using a Taylor expansion of the specific liquid capacity C to the first-order approximation. This algorithm provides stability of solution and mass conservation when there are no boundary fluxes, while it requires a substantial increase in iterations when boundary fluxes affect the saturation in any point of the solving domain, and mass conservation is not assured in those circumstances. In BRTSim, a different algorithm is developed, which does not imply iterative solution of a Taylor approximation function, but changes the Δt of integration according to a convergence criterion by reiterating the numerical solution at a given time only if needed for stability of solution. On the one hand, when this happens, time progression becomes slower while solution is assured to be stable and mass conservative. On the other hand, depending on the flow conditions, Δt of integration may become substantially greater, hence time progression becomes very fast. Overall, computational performance shows that this algorithm moves through time more rapidly than the modified Picard algorithm in many different situations of flows because it does not require inversion of a n_E -by- n_E matrix (with n_E the number of elements), and it conserves mass in full under any boundary fluxes. Additionally, the algorithm implemented in BRTSim allows handling variable saturated conditions, and can simulate exact full effective saturation $S_{Le} = 1$ instead of near

saturation approximation (e.g., $S_{Le} = 0.999\dots$) as in the existing algorithms.

For the liquid phase, this algorithm consists of four steps in the calculation of the new value of $M_L(t)$ and its corresponding saturation $S_L(t)$:

1. The first step is the calculation of the volumetric fluxes q_L as from Eq. (3.11).
2. The second step is to determine: (a) if $\Delta t \cdot q_L$ exceeds the available space in any receiving element of the solving domain and correct if necessary, and (2) if $\Delta t \cdot q_L$ exceeds the available supply from the releasing element and correct if necessary. This is noting but a mass balance within each node, and explicitly accounts for the cumulative boundary flux in that node and any other connected node. Corrections of these internal fluxes are carried out in one step throughout the domain and for a number of times equal to the number of exceedances. This step is the one that allows handling of full or null effective saturation, and mass conservation.
3. The third step is to update the fluxes q_L accordingly. This is done by calculating V_L in each element and determining if $\Delta t \cdot q_L$ exceeds the available space in the receiving element or the available supply of the releasing element depending of the sign of q_L . If necessary, excess mass is routed to the closest elements according to a partition function of the pressure and conductivity. Additionally, If the boundary flux $\Delta t \cdot Q_L$ is positive and exceeds the total available space in the domain, this flux is limited to the minimum allowed; if the boundary flux $\Delta t \cdot Q_L$ is negative and exceeds the available supply in a specific element, this flux is limited to the minimum allowed.
4. Finally, stability of the solution is determined by calculating the current tolerance TOL_{Lc} as

$$TOL_{Lc} = \max \left\{ \frac{\Delta t \sum_j \rho^{\beta e, i, j} Q_{L, i, j}}{M_{L, i}(t-1)} \right\}, \quad (3.14)$$

and comparing it to the tolerance TOL_L set by the user in the PARAM block of the `Param.inp` file. TOL_{Lc} is expected to be zero when the solution is stable, or be greater than zero when the flow solution shows instabilities (typically oscillatory). Note that instabilities may not necessary imply loss of mass conservation. If $TOL_{Lc} < TOL_L$, BRTSim will proceed to a new time step and a value of the integration time step Δt to be used in the next iteration is determined as

$$\Delta t \rightarrow \Delta t \frac{TOL_L}{TOL_{Lc}}, \quad (3.15)$$

so to increase or decrease Δt of the next time iteration according to the solution stability of the current time iteration. When $TOL_{Lc} < TOL_L$ is not satisfied, the time step is reiterated with the new Δt value, which is smaller than the one currently used. Iterations are continued until satisfaction of the condition, or when the maximum number of iterations $ITER_L$ is reached, parameter that is set by user in the PARAM block of the `Param.inp` file.

In contrast to the Picard iteration scheme, this algorithm typically converges in very few iterations given that the change in Δt is proportional to the reciprocal of the current tolerance. The result is that t is variable throughout the simulation. The user can decide if a variable Δt is to be used, in such case also the minimum and maximum Δt can be set in the block PARAM of the `Param.inp` file, or whether a constant Δt is to be used. Using a constant Δt excludes any control of convergence in the solver, hence numerical instabilities may arise depending on the internal and boundary fluxes.

Application of the discretization in Eq. (3.9) results in the calculation of the change in mass M_L of L phase in each grid element at time t from that at time $(t - \Delta t)$. Note that the L phase is considered to be incompressible while the G phase is described as compressible and is assumed to obey the ideal gas law

$$P_G V_G = \frac{M_G}{m_G} RT, \quad (3.16)$$

where V_G is the gas phase volume, M_G is the gas mass, m_G is the molar mass, $R = 8.314$ [Pa m³/K mol] is the gas constant, and T is the absolute temperature in Kelvin. After calculation of the L flow, an updated value of $P_{G,i}(t - \Delta t)$ at time $(t - \Delta t)$ is implicitly calculated in each element as

$$P_{G,i}(t - \Delta t) \rightarrow P_{G,i}(t - \Delta t) \frac{V_{L,i}(t - \Delta t)}{V_{L,i}(t)}. \quad (3.17)$$

This value of the G pressure is used to calculate the pressure gradient and Darcy's velocity for the G phase; the mass conservation law in Eq. (3.9) is next used to calculate the new values of $M_{G,i}(t)$ and $P_{G,i}(t) = M_{G,i}(t)RT/m_G V_{G,i}(t)$ in each element i of the solving domain at time t . The updated values of density $\rho_{G,i}(t) = M_{G,i}(t)/V_{G,i}(t)$ at time t are calculated as well. Note that the solution of the G phase uses the value of Δt that satisfies convergence within TOL_L in the L solver. This implies that Δt applied in the G solver may lead to instabilities such as negative values of $M_{G,i}$ in Eq. (3.9). For this reason, also the G solver uses two convergence criteria, that is, TOL_G and $ITER_G$ to check for negatives. If negatives are found for a given Δt , than Δt for the G flow is recalculated for the $\Delta M_{G,i} < 0$ as

$$\Delta t \rightarrow -TOL_G \frac{M_{G,i}(t - \Delta t)}{\Delta M_{G,i}} \quad (3.18)$$

and is used in iterations until when the cumulative time in the iterations for the G flow equals Δt of the L flow, or when the maximum number of iterations $ITER_G$ is reached. Additional adjustments to Δt may be needed during the iterations, and are calculated as above. The criteria TOL_G and $ITER_G$ are assigned by the user in the PARAM block of the `Param.inp` file.

3.6 Mass conservation and continuity laws of species

Excluding phase M (it does not host species in an explicit form) and phase B (details on conservation of B and the constituting BIO species are introduced in Section 3.5), the fluid phases $\beta = L, G$ can host any number of chemical species (PRI, SEC, MIN, and GAS). The total mass M^k of species k and phases $\beta = L, G$ in a volume V of the solving domain is

$$M_{\beta}^k = \phi S_{\beta} \rho_{\beta e} V X_{\beta}^k \quad \text{for} \quad \beta = L, G. \quad (3.19)$$

where $X_{\beta,i}^k$ is the mass fraction of component k in phase β of element i . The mass conservation law for M^k can be written similarly to Eq. (3.7) as

$$\frac{\partial M_{\beta}^k}{\partial t} = \int_{\Gamma} \rho_{\beta e} (v_{\beta} X_{\beta}^k - D_{\beta}^k \nabla X_{\beta}^k) d\Gamma + \int_V \rho_{\beta e} u_{\beta} X_{\beta}^k dV \pm \int_V r_{\beta}^k \rho_{\beta e} dV. \quad (3.20)$$

The first term on the RHS is the internal mass flux of species k in phase β through the surface Γ of a volume in the solving domain by Darcy's advection as in Eq. (3.8), and molecular diffusion, with D_{β}^k the diffusivity of species k in phase β . The second term is the integral of all mass sources or sinks of species k within phase β . The third term is the integral of all mass exchange rates of species k in the two phases $\beta = L$ and G , with r_{β}^k the rate of production or destruction of species k resulting from both kinetic and equilibrium reactions.

Discretization of Eq. (3.20) along the vertical direction z is carried out in a similar way as for Eq. (3.7), and its calculation is carried out in the transport solver for advection and diffusion (Figure 3.1). The mass $M_{\beta}^k(t)$ of species k in phase β is calculated for each element of the solving domain as

$$M_{\beta,i}^k(t) = M_{\beta,i}^k(t - \Delta t) + \Delta t \left(\sum_j \rho_{\beta,i,j} q_{\beta,i,j}^k + \sum_j \rho_{\beta,i,j} Q_{\beta,i,j} X_{\beta}^k \pm \sum_j R_{\beta,j}^k \right), \quad (3.21)$$

with

$$\sum_j \rho_{\beta,i,j} q_{\beta,i,j}^k = \rho_{\beta e, i+1|i} q_{\beta, i+1, i}^k - \rho_{\beta e, i|i-1} q_{\beta, i, i-1}^k, \quad (3.22)$$

where $\rho_{\beta e, i+1|i}$ and $\rho_{\beta e, i|i-1}$ the conditional densities in elements $(i+1)$ and i , and i and $(i-1)$ as described earlier in Section 3.5 for Eq. (3.10), and with the generic mass fraction flux q_{β}^k between element $(i+1)$ and i with effective interface area $A_{i+1,i}$ written as

$$q_{\beta, i+1, i}^k = \left[v_{\beta, i+1, i} X_{\beta, i+1|i}^k - D_{\beta, i+1, i}^k \left(\frac{X_{\beta, i+1}^k - X_{\beta, i}^k}{\Delta z_{i+1}^- - \Delta z_i^+} \right) \right] A_{i+1, i}, \quad (3.23)$$

where $X_{\beta, i+1|i}^k$ is the conditional mass fraction of species k in phase β that depends on the sign of the Darcy's velocity v_{β} between element $(i+1)$ and i . The diffusive contribution to the flux of component k relies on the diffusivity D_{β} in phase β between any two adjacent

elements $(i + 1)$ and i of the solving domain. This equivalent diffusivity is written in a similar way as the equivalent relative permeability of Eq. (3.13) according to a weighted average

$$D_{\beta,i+1,i}^k = D_{\beta}^k \frac{\Delta z_{i+1}^- \theta_{\beta,i+1} - \Delta z_i^+ \theta_{\beta,i}}{\Delta z_{i+1}^- - \Delta z_i^+}, \quad (3.24)$$

where Δz^+ and Δz^- were introduced earlier in Section 3.5, and where $\theta_{\beta} = S_{\beta} \phi$ is used as a reduction factor accounting for diffusion occurring in a porous medium with variable phase saturation. BRTSim does not explicitly implement or account for tortuosity, though approaches along the line delineated in Millington and Quirk (1961) can be used. Different ways to account for tortuosity in a practical way are described in the wider literature.

The second sum on the RHS of Eq. (3.21) is accounted for by the volumetric generation rate in either the L or G phases as described in the GENER block of the Param.inp file, with the density calculated at the temperature T_{β} using values provided in the PHASE block of the Param.inp file as described later in Section 3.10 and 4.

Term $\sum_j R_{\beta,j}^k$ in the third sum of Eq. (3.21) represents the mass fluxes of species k in phase β from kinetic reactions with index j in the L phase, or between equilibrium reactions within the L phase or the L and G phases, and can be written as

$$R_{\beta,j}^k = V \phi S_{\beta} \rho_{\beta e} \left. \frac{dX_{\beta}^k}{dt} \right|_j. \quad (3.25)$$

For kinetic reactions, or for equilibrium reactions that must be solved by means of kinetic reactions, more details are given in Section 3.8 for the L phase. In contrast, changes due to equilibrium reactions that can be solved for as instantaneous adjustments of species concentration are accounted for by an implicit numerical scheme described in Section 3.9. Note that no kinetic reactions are implemented in the G phase in BRTSim, which are expected in later versions.

Solution of the discretized mass conservation law for species in the L and G phases in Eq. (3.21) may require an iterative solution if the newly calculated value is $M_{\beta,i}^k < 0$ (this depends on Δt). This may not be caused by advective flow given that q_{β} is already calculated to a satisfactory tolerance in the L and G phases solvers, but by diffusion, which can be particularly fast in the G phase. When iterative solutions are needed, the solver updates the value of Δt as

$$\Delta t \rightarrow -TOL_{TR} \frac{M_{\beta,i}^k(t - \Delta t)}{\Delta M_{\beta,i}^k}, \quad (3.26)$$

and uses this until when the cumulative time in the iterations for transport equals Δt of the L flow, or when the maximum number of iterations $ITER_{TR}$ is reached. Additional adjustments to Δt may be needed, and are calculated as in Eq. (3.26) above. The criteria TOL_{TR} and $ITER_{TR}$ are assigned by the user in the PARAM block of the Param.inp file.

3.7 Mass conservation and continuity law of energy

This version of BRTSim explicitly accounts for energy flows through the boundaries, across the phases within each elements of the solving domain, and across the phases and elements of the solving domain. Energy is assumed to be expressed in the form of heat, with the heat capacity and conductivity of each phase assumed to be invariant with the temperature, even if this version of BRTSim is already designed to implement heat capacity and conductivity adjustments that depend on the instantaneous temperature of each phase. Heat H_β in each phase β of an element can be written as

$$H_\beta = M_\beta c_{p,\beta} T_\beta \quad \text{for } \beta = M, L, G, \quad (3.27)$$

where M_β follows from Eqs. (3.6), and $c_{p,\beta}$ and T_β are the heat capacity and temperature of phase β . In this version of BRTSim, heat in the biological phase is neglected, but it is expected to be included in the energy conservation law in next developments. The heat conservation law within and across the phases B, L, and G is written in its general form as

$$\begin{aligned} \frac{\partial H_\beta}{\partial t} = & \int_{\Gamma} (v_\beta \rho_{\beta e} c_{p,\beta} T_\beta - K_{h,\beta} \nabla T_\beta) d\Gamma + \sum_{\gamma \neq \beta} \int_{\Gamma} -K_{h,\beta,\gamma} \nabla T_{\beta,\gamma} d\Gamma + \dots \\ & \dots + \int_V \rho_{\beta e} u_\beta c_{p,\beta} T_\beta dV + \int_V w dV + \int_V A^{-1} K_{h,\beta,\gamma} \Delta T_{\beta,\gamma} dV, \end{aligned} \quad (3.28)$$

The first integral on the RHS of Eq. (3.28) represents the internal heat fluxes expressed by advection through the Darcy's equation for $\beta = L$ and G , and conduction through phases $\beta = M, L$ and G , where v_β is defined in Eqs. (3.8) for the L and G phases, and $K_{h,\beta}$ is the heat conductivity in the β phase. The second integral on the RHS of Eq. (3.28) accounts for all combinatorial heat fluxes between phase β and any other phases $\gamma \neq \beta$, with $K_{h,\beta,\gamma}$ the equivalent heat conductivity between phases β and γ . The third integral describes the sources or sinks of heat carried by mass fluxes at temperature T_β in the L and G phases through the boundary of the volume V from outside the solving domain, where the rate u_β of heat production and destruction associated with phase β can be any positive or negative term for $\beta = L$ and G . The fourth integral in Eq. (3.28) describes sources or sinks of heat not associated to heat transported through mass fluxes, with w being the heat rate of production and destruction per unit volume and can be a positive or negative number. The fifth integral in Eq. (3.28) is an internal mass exchange between phases β and γ within volume V of the solving domain where $K_{h,\beta,\gamma}$ and A are the heat effective conductivity across phases β and γ accounted for after Whitman and Keats (1922), and the surface exchange area between the phases, respectively.

The H solver discretizes Eq. (3.28) in each phase of each ELEM i of the solving domain as

$$\begin{aligned}
H_{\beta,i}(t) &= H_{\beta,i}(t - \Delta t) + \Delta t \left(\sum_j \rho_{\beta,i,j} q_{\beta,i,j}^h + \sum_{j,\gamma \neq \beta} q_{\beta,\gamma,i,j}^k \right) + \dots \\
&\dots + \Delta t \left(\sum_j \rho_{\beta,i,j} Q_{\beta,i,j} c_{p,\beta} T_{\beta,i} + \sum_j f_{\beta,i} W_{i,j} + \sum_{\beta \neq \gamma} J_{i,\beta,\gamma} \right). \quad (3.29)
\end{aligned}$$

The advection-conduction term in phase β in the first sum on the RHS of Eq. (3.29) follows from Eq. (3.10) and Eq. (3.22) as

$$\sum_j \rho_{\beta,i,j} q_{\beta,i,j}^h = \rho_{\beta e, i+1|i} q_{\beta, i+1, i}^h - \rho_{\beta e, i|i-1} q_{\beta, i, i-1}^h, \quad (3.30)$$

where $\rho_{\beta e, i+1|i}$ and $\rho_{\beta e, i|i-1}$ are the conditional densities in elements $(i+1)$ and i , and i and $(i-1)$ that depend on the direction of q as described earlier in Eq. (3.10) of Section 3.5 relative to the phase density for the mass conservation and continuity of phases, and in Section 3.6 relative to the phase density and species mass fraction for the mass conservation and continuity of species. The generic internal heat flux q^h between element $(i+1)$ and i with effective interface area $A_{i+1,i}$ can be written as

$$q_{\beta, i+1, i}^h = c_{p,\beta} \left[v_{\beta, i+1, i} T_{\beta, i+1|i} - K_{h,\beta, i+1, i} \left(\frac{T_{\beta, i+1} - T_{\beta, i}}{\Delta z_{i+1}^- - \Delta z_i^+} \right) \right] A_{i+1, i}, \quad (3.31)$$

where $T_{\beta, i+1|i}$ is the conditional temperature in phase β that depends on the sign of the Darcy's velocity v_β between element $(i+1)$ and i , and $A_{i+1, i}$ is the effective interface area between elements $(i+1, i)$. The diffusive contribution to the heat flux is accounted for by $K_{h,\beta}$ in phase β between any two adjacent elements $(i+1)$ and i of the solving domain. Note that advective flow of the M phase is not described in BRTSim because the soil minerals in the MATERIAL of an element of the solving domain are assumed to be immobile, hence $v_L = 0$. The equivalent heat conductivity $K_{h,\beta, i+1, i}$ of phase β between two elements $(i+1, i)$ is written in a similar way as the equivalent relative permeability of Eq. (3.13) according to a weighted average

$$K_{h,\beta, i+1, i} = \frac{\Delta z_{i+1}^- K_{h,\beta, i+1} + \Delta z_i^+ K_{h,\beta, i}}{\Delta z_{i+1}^- + \Delta z_i^+}, \quad (3.32)$$

where Δz_{i+1}^- and Δz_i^+ are the distances between the center of mass of the two elements and their interface (Figure 2).

The second sum in Eq. (3.29) is expressed as

$$\sum_{j,\gamma \neq \beta} q_{\beta,\gamma,i,j}^k = q_{\beta,\gamma, i+1, i}^k - q_{\beta,\gamma, i, i-1}^k, \quad (3.33)$$

where the generic heat flux between phase β and $\gamma \neq \beta$ from element $i+1$ to i , respectively, is

$$q_{\beta,\gamma,i+1,i}^k = -K_{h,\beta,\gamma,i+1,i} \left(\frac{T_{\beta,i+1} - T_{\gamma,i}}{\Delta z_{i+1}^- - \Delta z_i^+} \right), \quad (3.34)$$

and where $K_{h,\beta,\gamma,i+1,i}$ is expressed in a similar way as in Eq. (3.32).

The third sum in Eq. (3.29) is accounted for by the generation of mass in either the L or G phases; the corresponding heat flows depends on the heat capacity c_β and temperature T_β of phase β as declared in the GENER block of the `Param.inp` file.

The fourth sum in Eq. (3.29) depends on the heat production or destruction rate W_i in element i of the solving domain. The way heat is partitioned across the phases in that element is given by factor $f_{\beta,i}$, which is calculated as

$$f_{\beta,i} = \frac{c_{p,\beta,i} M_{\beta,i}}{\sum_{\beta} c_{p,\beta,i} M_{\beta,i}}, \quad \text{for } \beta = M, L, G. \quad (3.35)$$

Finally, the fifth sum in Eq. (3.29) is described as

$$J_{i,\beta,\gamma} = \Delta z_i K_{h,\beta,\gamma,i} (T_\gamma - T_\beta), \quad \text{for } \beta \neq \gamma \quad \text{and} \quad \beta, \gamma \in M, L, G, \quad (3.36)$$

with the equivalent heat conductivity across phase β and γ described as

$$K_{h,\beta,\gamma,i} = \theta_\beta K_{h,\beta,i} + \theta_\gamma K_{h,\gamma,i}. \quad (3.37)$$

In a similar way as in the discretization of phase and species flows, also the solution of heat conservation and continuity requires iterations if the newly calculated heat value in Eq. (3.29) is $H_{\beta,i}(t) < 0$. This may not be caused by advective flow given that v_β is already calculated to a satisfactory tolerance in the L and G phase solvers, but by conduction within the same phases or by conduction across the phases. When iterative solutions are needed, the solver updates the value of Δt as

$$\Delta t \rightarrow -TOL_H \frac{H_{\beta,i}(t - \Delta t)}{\Delta H_{\beta,i}}, \quad (3.38)$$

and uses this until when the cumulative time in the iterations for transport equals Δt of the H flow, or when the maximum number of iterations $ITER_H$ is reached. Additional adjustments to Δt may be needed, and are calculated as in Eq. (3.38) above. The criteria TOL_H and $ITER_H$ are assigned by the user in the PARAM block of the `Param.inp` file.

Once heat $H_{\beta,i}(t)$ is calculated to the chosen level of tolerance as in Eq. (3.29), the phase temperature is updated in each element of the solving domain as

$$T_{\beta,i}(t) = \frac{H_{\beta,i}(t)}{c_{p,\beta,i} M_{\beta,i}}, \quad \text{for } \beta = M, L, G, \quad (3.39)$$

while the integral temperature throughout that element is calculated as

$$T_i(t) = \frac{\sum_{\beta} H_{\beta,i}(t)}{\sum_{\beta} c_{p,\beta,i} M_{\beta,i}}, \quad \text{for } \beta = M, L, G. \quad (3.40)$$

3.8 Aqueous kinetic reactions

Kinetic reactions in BRTSim are assumed to occur only in the L phase within each element of the solving domain, and exclude any secondary species, that is, they apply only to PRI and BIO species, and not to SEC, MIN, and GAS species. The rate of change in mass fraction in species X^k for a reaction in the L phase such as already introduced in Eq. (3.25) can be written as

$$\frac{dX^k}{dt} = x_k R \quad \text{for} \quad \beta = L, \quad (3.41)$$

where R is the reaction rate; the stoichiometric number x_k for component k is positive if X^k is a product or negative if X^k is a reactant. Kinetic reactions can be defined for any kinetic order and rate constant, and with an arbitrary number of n-th order product terms, Michaelis-Menten terms Michaelis and Menten (1913), competition terms, and inhibition terms in the KIN block of the `Param.inp` file. For a generic reaction with n_{BIO} BIO species, n_O n-order kinetic terms, n_{MM} Michaelis-Menten terms, n_{COM} competitive reactants, and n_{INB} inhibition terms, the reaction rate R is written as

$$R = r f_B \prod_{n_O} X^{x_{n_O}} \cdot \prod_{n_{MM}} \frac{X^{n_{MM}}}{X^{n_{MM}} + K_{n_{MM}}} \left(1 + \sum_{n_{COM}} \frac{X^{n_{COM}}}{K_{n_{COM}}} \right) \prod_{n_{INB}} \frac{K_{n_{INB}}}{X^{n_{INB}} + K_{n_{INB}}}, \quad (3.42)$$

where r is the rate constant of that reaction, and f_B is a function of the biomass saturation in V if BIO species are defined in that reaction or $f_B = 1$ otherwise (see more details in Section 5.3).

Kinetic reactions are classified as chemical or biological depending on whether BIO species do not appear in that reaction, or appear either as reactants or reaction products, or in a n-order kinetic terms, or in a Michaelis Menten term.

After BRTSim solves for the transport of species as in Eq. (3.6), it updates the value of X^k in each element of the domain according to the kinetic reaction rate of Eq. (3.41). Discretization of Eq. (3.41) is carried out by implicit finite difference for all kinetic reactions j that have an effect on X^k as

$$X^k(t) \rightarrow X^k(t) + \Delta t \sum_j x_j^k R_j, \quad (3.43)$$

where the value $X^k(t)$ at time t on the right-hand side of Eq. (3.43) is the result of advection-diffusion transport via Eq. (3.20) (see also the flow chart in Figure 3.1). If the mass (or concentration) of any reactants in any reactions becomes $M_\beta^k < 0$ when Δt from the L flow solver is used in the KIN solver, then iterations are launched to decrease Δt in a similar way as in the previous solvers as

$$\Delta t \rightarrow -TOL_{KIN} \frac{M_\beta^k(t)}{\Delta M_\beta^k}, \quad (3.44)$$

and this Δt is used until when the cumulative time in the iterations for the kinetic reactions equal Δt of the L flow, or when the maximum number of iterations $ITER_{KIN}$ is reached. If additional adjustments to Δt are needed, these are calculated as in Eq. (3.44). The criteria TOL_{KIN} and $ITER_{KIN}$ are assigned by the user in the PARAM block of the `Param.inp` file.

3.9 Equilibrium reactions

As the kinetic reactions, all equilibrium reactions are solved for in each element of the solving domain. They necessarily involve aqueous PRI species (with the exclusion of solvent and constants) and can involve either SEC, MIN, and GAS, but do not involve BIO species. Equilibrium reactions are defined by an equilibrium constant K at a given temperature T according to Eq. (3.1). For the number n_{PRI} of primary species, a generic equilibrium reaction between species for $\beta = L, M$ and G phases is written according to the mass-action law as

$$K(T) = X_{\beta}^k \prod_j X_j^{x_j}, \quad (3.45)$$

where X_{β} is the a secondary species in phase β that is to be solved for, while X_j and x_j are the list of PRI species and their stoichiometric numbers that are involved in the equilibrium reaction, respectively. The stoichiometric numbers can be either positive (if products) or negative (if reactants). When X_{β} is an aqueous species, the concentration in [mol/L] is used, while the pressure in [bar] is used if it is a gaseous species. Note that for equilibrium reactions, the mass fraction of the solvent (defined in the PRI block in BRTSim) is set to 1 always, so that it does not affect equilibrium. A PRI species that is used as a constant (i.e., 'mobility' is set to 2) cannot be used in equilibrium reactions. When BRTSim reads the equilibrium reactions, the solvent is excluded from the reaction if possible, thus generally leading to a faster calculation of equilibrium and a lower order algebraic equation. Use of constant PRI or BIO species in equilibrium reactions will cause BRTSim to send an error message and stop running.

The solution of Eq. (3.45) may be complicated by the stoichiometric coefficients, which may lead to a highly nonlinear equation that cannot always be solved algebraically. While BRTSim v1.0 only used an iterative solver, all versions from BRTSim v2.2 implement an analytical solver for reactions of order 1 and 2. This implementation has led to a substantial calculation speedup of the solver as most equilibrium reactions of practical use are either of order 1 or 2. Discretization uses a method similar to Maier and Kelley (1931) as

$$K(T) = (X_{\beta}^k + f x_k \Delta X)^{x_k} \prod_j (X_j^k + x_j \Delta X)^{x_j}, \quad (3.46)$$

and solves for ΔX . The calculated change ΔX is next applied in an implicit scheme as

$$X_{\beta}^k(t) \rightarrow X_{\beta}^k(t) + f x^k \Delta X, \quad (3.47)$$

where $f \neq 1$ is the factor to express the unit of species X_β^k if $\beta = \text{G}$, or $f = 1$ otherwise.

Reactions of order different than 1 or 2 are solved iteratively as kinetic reactions using the method in Sanderson and Chien (1973) and consists in solving equilibrium by means of two kinetic reactions, that is, the forward and backward pathways with rate constants $k_f = 10^{\log K}$ and $k_b = 1$, respectively. The two reactions are solved with the same discretization already introduced in Section 3.8 for the KIN solver. An iterative scheme is used to reiterate both forward and backward reactions until the relative difference between the current $\log K_c$ value of equilibrium between all species and the assigned equilibrium $\log K$ from Eq. (3.1) becomes smaller than a desired tolerance TOL_{EQ} . Iterations stop either when TOL_{EQ} is reached or a maximum number of iterations $ITER_{EQ}$ are reached. This assures that all components are always in equilibrium at least within a tolerance TOL_{EQ} chosen by the user. Stability of solution in BRTSim has largely improved with these newly implemented algorithms. Additionally, and regardless of the order of the reaction, equilibrium between all SEC, GAS, and MIN species with their PRI species is a particularly difficult problem; in fact, balancing the equilibrium of one reaction generally leads to disproportion in other equilibrium reactions. This disproportion may not be great at times, but depending on the geochemical system, convergence toward an aqueous solution that is in equilibrium with all components is a particularly difficult problem. To cope with this, a number of cycles through all the equilibrium reactions is used to assure that the aqueous solution is chemically equilibrated. Since BRTSim v2.2, the number of cycles can be decided by the user by setting the $CYCLE_{EQ}$ parameter in the PARAM block of the `Param.inp` file. Normally, 1 cycle is enough in most cases, however, 3 to 5 cycles assure that also complex and highly nonlinear geochemical systems converge to equilibrium solutes.

3.10 Phase dependence on temperature

The physical properties of the L and G phases are function of the temperature by default. This version of BRTSim allows the user to account for the effect of temperature on the density, viscosity, surface tension, heat capacity, and heat conductivity of the L phase, and density, viscosity, heat capacity and conductivity of the G phase as declared in the PHASE block of the `Param.inp` file. Here, an arbitrary number of values (not less than 6) of these physical properties at various temperatures can be declared. The actual T_β -dependent generic phase property $X_\beta(T_\beta)$ is calculated by using and interpolating polynomial function based on Maier and Kelley (1931) and written as

$$X_\beta(T_\beta) = a \log T_\beta + b + cT_\beta + dT_\beta^2 + \frac{e}{T_\beta} + \frac{f}{T_\beta^2}, \quad (3.48)$$

where the coefficients a , b , c , d , e and f are calculated in BRTSim by least square fitting against values provided by the user in the PHASE block.

Chapter 4

Geometry, initial, and boundary conditions

4.1 0-, 1- and 1.5-dimensional domains

BRTSim is essentially a 1-D solver, but it can be used also for 0-D and 1.5-D domains.

Specifically, 0-D domains can be constructed by defining only one element in the ELEM block of the Param.inp file. In this case, lack of neighbouring elements to exchange mass and energy makes the spatial scale be neglected. Additionally, one can design a 0-D domain made of an arbitrary number of disconnected individual elements disposed over a horizontal plain; this grid can be used to describe 2-D spacial domain such as watersheds or others, and solve for all mass conservations laws in each element, with no mass exchange through them. This is the typical configuration of grid management in Earth System Models (ESM) used for global scales simulations.

1-D domains can be defined by connecting in sequence any number of elements in the ELEM block of the Param.inp file. Connected elements can have any orientation depending on the value used for the direction and modulus of the gravitational acceleratio. By default, the system of reference in pointing upward in the vertical direction, hence $g_mod = 9.81 \text{ m/s}^2$ and $g_dir = -90$ can be used in the PARAM block. Using $g_dir = 0$ or $g_mod = 0 \text{ m/s}^2$ means that the 1D sequence of elements is horizontal; any preferred value of intensity in gravitational acceleration g_mod and direction g_dir can be used and will correspond to a particular orientation and intensity of the gravitational field relative to the vertical direction.

Finally, 1.5-D domains can be constructed by a sequence of disconnected sets of elements. For example, it is possible to build two or more 1-D vertical domains of elements, one next to each other likewise a 2-D domain, but with the mass conservation laws solving only for the vertical fluxes and neglecting the horizontal ones. This corresponds to a 2-D domain, with a partial solution of the governing equation, and from here it comes the definition of 1.5-D domain.

4.2 Initial conditions

The initial conditions for the state variables (L and G phases, total pressure, temperature, concentrations of primary aqueous species, and gas partial pressure fractions) are defined by the user in various blocks of the `Param.inp` file.

Assigning initial conditions to a specific problem first involves the declaration of the materials to be used in the solving domain. The user can declare an arbitrary number of materials in the MATERIAL block of the `Param.inp` file, and instruct BRTSim on all physical, hydraulic and thermal properties of each material. Materials are given a unique name, that is used as a tag to be called in each element of the ELEM block. Three MATERIAL columns are available in the ELEM block (i.e., (1)MAT, (2)MAT and (3)MAT); these allow the user to build up to three different material profiles and switch among them with ease. The one used for calculation in BRTSim is marked with a star “*”.

An arbitrary number of initial liquid saturation S_L , initial temperature T in degree Celsius, and initial total gas pressure P_G can be defined in the ICSTP block of the `Param.inp` file, each representing an initial condition for the above state variables. The initial liquid saturation will be limited within the range of saturation allowed for a particular material, as defined by S_{Lr} and S_{Gr} in the MATERIAL block. Next, S_L will be converted to its effective liquid saturation as in Eq. (3.2). Each initial condition is given a name, which serves to tag that specific ICSTP; the user can choose the initial condition to be used in each element of the solving domain defined in the ELEM block of the `Param.inp` file. Note that the choice is fully arbitrary and the user can define as many ICSTP for S_L , T and P_G as liked even if only some of them may eventually be used. To recall a flagged initial condition, the user will simply specify the name of that initial condition in one of the ICSTP column of the ELEM block. Note that three ICSTP columns are available in the ELEM block (i.e., (1)ICSTP, (2)ICSTP and (3)ICSTP); these allow the user to build up to three different initial condition profiles and switch among them with ease. The one used for calculation in BRTSim is marked with a star “*”.

The initial conditions relative to the species involve only the PRI and BIO species for the L phase, and the secondary GAS species for the G phase. In fact, SEC and MIN secondary species are functions of the PRI species in the liquid phase. Instead, the initial conditions for GAS species have to be specified because they belong to a different phase than the PRI species even if they are functions of the PRI species. The initial conditions for PRI and BIO are listed in the ICPRI block of the `Param.inp` file. The user can define as many initial conditions for PRI and BIO as liked; each initial condition is given a name and lists a sequence of concentrations for as many PRI and BIO as defined in the PRI and BIO blocks. The list of PRI and BIO in ICPRI can follow any order, and can include additional species not listed in PRI that will not be used for calculations. Naming each ICPRI serves also in this case to tag that specific ICPRI; the user can choose the initial condition to be used in each element of the ELEM block in a fully arbitrary way, and not all ICPRI must necessarily be used. To recall a flagged ICPRI condition, the user will simply specify the name of that initial condition in one of the three ICSTP columns of the GRID block (i.e., (1)ICPRI, (2)ICPRI and (3)ICPRI); this allows the user to build up to three different initial conditions profiles. The one used for calculation in BRTSim is the

one marked with a star “*”.

Since version v4.0b, BRTSim is equipped with a new capability that allows the user to read an existing `Time.out` file and use it for assigning initial conditions to any state variables including the L and G phase saturations, their temperature T (assigned homogeneously to all phases within an element of the grid), and any PRI, BIO, SEC, GAS, and MIN species concentration. To use this capability, the user can instruct BRTSim via the ICFILE block of the `Param.inp` file. If the selected pre-existing `Time.out` file includes multiple time steps, then the user can select the time step of interest to assign the initial conditions. To use this capability at the best, the grid and biogeochemical systems must be compatible. The reader can find more details in Section 6.

4.3 Boundary flows

The finite volume structure of BRTSim is such that any computational domain used in the solution of a problem is by default closed to mass and energy fluxes. However, BRTSim allows to account for sinks and sources of mass and energy in any arbitrary element at an arbitrary rate and temperature for the L and G phases, and at any rate for heat in the GENER block of the `Param.inp` file. For this reason, these sinks and sources are called GEN from this point on. GEN terms are given a user-defined name to tag that GEN; a GEN term must be defined for the element of the solving domain which is applied to, the phase that is used for generation (L or G) or whether it is heat (H), the rate of production or destruction, its temperature (for L and G) and its quality (only L). In this new release of BRTSim, both L and G phases can support a GEN term expressed by means of volumetric flow rate at a specific temperature, with the latter used to calculate the mass flow rate using the temperature-dependent density specific to that phase and declared in the PHASE block of the `Param.inp` file. While GENER of L phase in a node allows to specify also the quality by listing the concentration of all PRI species, GEN in the G phase disregards the quality - future developments of BRTSim are expected to implement qualities also for the G phase. GEN of heat does not require to specify a temperature and a quality.

The user can specify whether a GENER term is applied at a constant rate or variable rate. In the former case, the entry for that GEN term will include a volumetric rate and its temperature, and the initial time of application with the TABLE field specifying 'notable'. In the latter case, the user can specify a table identified by a file name in the TABLE field, which will be a .TXT file including at least three columns, for the time, the rate, and the temperature. Note that an arbitrary number of columns can be specified in the GEN table. The fields TIME, RATE and T in `Param.inp` will serve to indicate which column of the table in the .TXT file will be used for the time, rate, and temperature sequences. If two sequential GENER items are specified that use the same table, the user can call 'sametable' in the TABLE field, case in which BRTSim will use the memory to retrieve the columns of interest specified in the TIME, RATE and T fields.

Each GENER term in the L phase must include a definition of the phase quality, stating the concentration of PRI and BIO species if any. To declare the concentration on any arbitrary solute in that GEN term, the user can simply specify the name of any of the

ICPRI declared in the ICPRI block of the `Param.inp` file; this implies that ICPRI does not only serve to determine the initial conditions of PRI and BIO species, but also the quality of the L phase crossing the boundary of the solving domain. Also in this case, the user has a choice from three options ((1)QUAL, (2)QUAL, and (3)QUAL), but only the quality marked with a star “*” will be used for that phase. This allows the user to switch among different qualities with ease.

The rate of a GENER term can be either positive (source) or negative (sink). Since BRTSim v2, the user has the capability to control the quality of the L phase when GEN rate is a negative term. In practice, the user can choose which chemical species will be removed from an element of the solving domain. This capability only applies to PRI species in the L phase that are declared as mobile. As a consequence, the user will not be able to control the concentration of the L species that are removed. To mark the species that can be removed with a negative GEN term, it is sufficient to declare the PRI species concentration in the ICPRI used for the quality of that GEN with a negative sign, while the number will be disregarded because the removed mass of that PRI will be decided by the actual condition in that element. BIO species cannot be removed from the solving domain.

GENER terms can be included in the GENER block of the `Param.inp` file but only the GENER whose corresponding solver is switched on will be solved for. In specific, GENER in the L phase will always be solved for because the L phase is the preferred phase. Heat in the G phase of GEN will only be solved for if the G and H solvers are switched on.

Since BRTSim v4.0e, a new capability has been introduced to allow the user to reduce storage space for tables used as boundary flows. This applies in particular if boundary flows are re-cycled for the simulated time such as typically for weather and meteorological drivers. The user has now the choice to set the 'RELOOP' option in the GENER block and specify whether the time sequences in the .TXT file called for in TABLE field have to be relooped or not. This option does not apply if a boundary flow is declared as constant.

4.4 Boundary conditions

BRTSim is a finite volume solver and therefore one can define boundary flows such as in Section 4.3 but there are no true boundary conditions. One can emulate boundary conditions by introducing an additional element in a desired position and define its geometric or hydraulic properties to approximate a particular boundary condition without or in combination with boundary flows to or from that element. The geometry is declared in the ELEM block, while sink and source terms are declared in the GENER block of the `Param.inp` file. The geometry can be fully controlled in that the element position z , distance from above and below elements Δz^+ and Δz^- , interface surface area A , and volume V are assigned by the user to each node; these quantities are particularly important because they control the gradients that drive flows such as advection-diffusion and convection. For example, constant L saturation $S_L < 1$ in an element of the solving domain can be controlled by assigning V a large number; or, free water drainage from one element to another (typically at the bottom of the solving domain) can be set by assigning Δz^+ of the bottom element

and Δz^- of the upper element very large numbers. More combinations are possible by controlling the L and G saturation, or the MATERIAL properties such as porosity and capillary pressure. The reader is referred to the examples briefly described in Chapter 8, and accessible by downloading the package.

Chapter 5

Solvers and feedback switches

5.1 Solvers switches

As described in Chapter 3, BRTSim includes various solvers. With the exception of the solver for the L phase flow, all others can be switched on/off depending on the needs and the computation problem. Switching off solvers typically results in increased computational speed, and therefore the user may consider whether a specific solver is necessary or can be placed off line. Switching solvers on/off is very simple in BRTSim as compared to other computational solvers that use separate modules, and where simulations with or without specific solvers cannot be compared with ease. In particular, the G, H, TR/CTX, KIN, and EQ solvers switches are available to the user in the PARAM block of the `Param.inp` file.

5.2 Synchronization across solvers

The user can switch on/off any solvers in any combination. BRTSim is built to manage and synchronize the solvers without the need to control other conditions that make them running sequentially and smoothly. However, each solver has specific features and switching on/off one or more solvers has an effect on the computational results. The user can control the solvers through the PARAM block of the `Param.inp` file. Detailed in Figure 5.1 is a short summary of the effects of each solver on others.

5.3 Feedback switches

In addition to the switches that directly activate or deactivate a solver, BRTSim allows to account for interactions between processes dealt with by each individual solver. Accounting of these interactions is managed by means of higher level switches for the feedbacks. BRTSim currently includes 4 higher level switches for:

- the L and G phase interaction (LIQ_GAS_FEED);

	L Solver (on always)	G Solver (on)	H Solver (on)	TR Solver (on)	CTX Solver (on)	KIN Solver (on)	EQ Solver (on)
G Solver (off)	G pressure and density updated after solution of L flow but no mass advection due to G flow (only diffusion of species in the G phase). No G boundary flows.		No heat flow in the G phase by advection and conduction	No advection-diffusion of species in the G phase	No G flow induced by pressure changes due to BIO species taxis	No effect	GAS species undergo only diffusion in the G phase but no advection.
H Solver (off)	No H flow in the L phase by advection and conduction. No H boundary flows	No H flow in the G phase by advection and conduction. No H boundary flows		No effect	No effect	No H sinks and sources from kinetic reactions (not implemented yet)	No effect
TR Solver (off)	No advection-diffusion of mobile species in the L phase. Only dilution due to boundary flows	No advection-diffusion of species in the G phase. Only dilution due to boundary flows	No effect		No effect	No effect	TR limited only to PRI species even if SEC, GAS, MIN species exist
CTX Solver (off)	No mobility of BIO species in the L phase	No G flow induced by pressure changes due to BIO species taxis	No effect	No effect		No mobility of BIO species due to repellents or attractants	No effect
KIN Solver (off)	No reactions in the L phase, and no immobilization/remobilization of L phase with BIO species	No effects	No H sinks and sources from kinetic reactions (not implemented yet)	No effect	No mobility of BIO species due to repellents or attractants		No effect
EQ Solver (off)	No aqueous complexation reactions	No gas dissolution and exsolution reactions with species in the G phase	No H sinks and sources from equilibrium reactions (not implemented yet)	TR limited only to PRI species	No effect	No effect	

Figure 5.1: Map of synchronization between solvers and their relative interactions.

- the interaction between the L phase and its chemistry (LIQ_CHEM_FEED);
- the interaction between the L phase and its biology (LIQ_BIO_FEED);
- the interactions between the chemistry and biology (CHEM_BIO_FEED).

These switches are available in the PARAM block of the Param.inp file, and activate specific features that are described in greater detail in the following sections.

5.3.1 L and G feedback

While the solution of L phase flow is the preferred phase in BRTSim, that is, it is always solved for and must always be present, solution of the G phase flow is decided by the user. If the user needs the G phase flow to be calculated, it is possible to turn on the switch for the G solver. This enables compression of the G phase in concomitance with the movement of the L phase according to Eq. (3.17) in Section 3.5. Changes in P_G can be accounted for or neglected in the calculation of P_L via switch LIQ_GAS_FEED in the PARAM block of the Param.inp file. Recall that the total pressure of the L phase is (Section 3.4)

$$P_L = P_c + P_G + P_O, \quad (5.1)$$

with $P_c < 0$ the capillary pressure when $S_L < 1 - S_{Gr}$, P_G the G pressure, and P_O the osmotic pressure. If LIQ_GAS_FEED = 0, then $P_G = 0$ in Eq. (5.1) even if the G phase flow solver is switched on.

Activation of the LIQ_GAS_FEED is conditional to the G solver state. If the G solver is off, LIQ_GAS_FEED = 0 always, or it can be switched on/off if the G solver is on.

5.3.2 L and chemistry feedback

The presence of chemicals in the L and G phases leads to changes in the physical properties of density, viscosity, and surface tension of the phases themselves as a result of mixing and molecular interactions. These changes may depend linearly or nonlinearly on the concentration of chemicals depending on whether the liquid solvent and the gas phase dilute the chemicals only, or actively react with them. The dependency is not fully known and a generalized approach is not available to describe in detail how phase properties change for reacting mixtures. BRTSim uses a simplistic approach to account for changes in the liquid density only, thus it excludes effects of this type on the viscosity and surface tension. Likewise, BRTSim does not account for changes in properties in the G phase in this release, but is expected in later releases.

These types of interactions can be controlled by the LIQ_CHEM_FEED higher level switch. In particular, if LIQ_CHEM_FEED = 1, changes in L density in each element i of the solving domain are described by a linear scaling of the mass concentration of species in the L phase as

$$\rho_{Le,i} = \rho_{L,i} + \sum_k \rho_{X^k,i} X_i^k, \quad (5.2)$$

with ρ_L the density of the pure L solvent phase defined in the PHASE block of the `Param.inp`, ρ_{X^k} the density of the species k in liquid solution, and X^k the mass fraction of that species. The effective liquid density ρ_{Le} is updated in each iteration after all solvers; in this way, the next time iteration will account for changes in liquid density. For the G phase density, as already mentioned, no changes related to GAS species partial pressure are accounted for, thus implying that $\rho_{Ge} = \rho_G$. These expressions for ρ_{Le} and ρ_{Ge} are actually used in the mass conservation and continuity laws in Section 3.5 and 3.6. If LIQ_CHEM_FEED = 0, then the effective L density is simply $\rho_{Le} = \rho_L$.

In addition to effects in the L phase properties, chemicals in solution in the L phase provide an additional contribution to the L potential. This potential is called osmotic potential and is related to the osmotic pressure P_O in Eq. (5.1), which is defined by the Morse equation (Mansoor et al., 2002) and is calculated in each element i of the solving domain as

$$P_{O,i} = \epsilon_{O,i} RT \sum_k \frac{X_i^k \rho_{Le,i}}{m_i^k}, \quad (5.3)$$

where $\epsilon_{O,i}$ is the osmotic efficiency in element i , X^k is the mass fraction of species k , m^k is its molar mass, R the gas constant, and T the absolute temperature in Kelvin. Note that, because BRTSim can describe any chemical species in its molecular form as well as its dissolution products by means of secondary species, the van 't Hoff factor is not used explicitly. The osmotic efficiency ϵ_O is a measure of the degree of a particular

material to behave as an ideal semipermeable membrane, that is, permeable to L phase (e.g., water) but not to dissolved chemical species. In BRTSim, the osmotic efficiency ϵ_O depends therefore on the assigned MATERIAL in that element, and is defined using parameter eOSM in the MATERIAL block of the `Param.inp` file. While recent studies have highlighted that $\epsilon_O < 1$ (Barbour and Fredlund, 1989), the osmotic pressure is generally neglected in biogeochemical solvers under the hypothesis that some granular media such as soil do not have semipermeable functioning. However, even if $\epsilon_O^j < 1$, chemical osmosis is possible and corresponding effects are measurable (Barbour and Fredlund, 1989).

If `LIQ-CHEM-FEED` = 0, then $P_O = 0$ regardless of whether chemical species dissolved in the L phase exist, otherwise P_O is calculated as in Eq. (5.3). Note that only mobile PRI and SEC species in the L phase contribute to P_O , while BIO species are hypothesised to not have any effect on P_O .

5.3.3 L and biology feedback

This version of BRTSim includes the new capability introduced by BIO species. The BIO species declared in the BIO block of the `Param.inp` file can be microbial organisms. These can immobilize a chosen volume fraction (VWF) of the L phase (typically water) and they can also undergo KIN reactions because are a subgroup of the PRI species. As such, one can define BIO species that grow upon consumption of substrates, and die by aging. Any change in BIO concentration results therefore in immobilization or remobilization of a certain volume of L phase in such a way that the total L volume is

$$V_{L,t} = V_L + V_{B,L}, \quad (5.4)$$

with V_L the mobile water volume and $V_{B,L} = \sum_i f_{B_i} V_{B_i,t}$ the immobilized water volume. Here, $V_{B_i,t}$ is the total volume of BIO species i , and f_{B_i} the L volume fraction in BIO species i . Cumulatively, when multiple BIO species are declared, the L fraction of S_B is defined as

$$f_L = \frac{V_{B,L}}{V_B} = \frac{\sum_i f_{B_i} V_{B_i,t}}{V_B}, \quad (5.5)$$

with V_B the total BIO volume. This implies that a feedback can exist between the BIO species and the L phase. In specific, the `LIQ-BIO-FEED` allows to control this feedback; if `LIQ-BIO-FEED` = 1, then L immobilization and remobilization is explicitly accounted for as a mass flux of the L phase if BIO species have been defined. In this case, the mass conservation and continuity laws in Eq. (3.7)a,c of Section 3.5 will include the third terms expressing this mass exchange between the L and B phases - note in fact that BIO species cumulatively define a phase that communicates mass flows with the L phase, and is treated as intermediate between a phase and a collection of species for this reason. For this characteristic, the reaction rate of biochemical KIN reactions that include one or more BIO as reactants or reaction products, can be limited by physical constraints. For example, consumption of a substrate by a BIO species, and the consequent BIO growth, can continue as long as there is space available for BIO to grow. The overall limit in reaction rate and

consequent biomass growth is accounted for in BRTSim by factor $f(S_B)$ in Eq. (3.42) defined as

$$f(S_B) = \min \left\{ 1 - \frac{S_B}{1 - S_{Lr} - S_{Gr}}, 1 - \frac{f_L S_B}{S_L - S_{Lr}}, 1 - \frac{(1 - f_L) S_B}{S_G - S_{Gr}} \right\}, \quad (5.6)$$

meaning that BIO species in that biochemical reaction can grow as long as there is enough effective pore volume (i.e., excluding residual L and G volumes) to host the total BIO volume, or enough free L phase to immobilize, or G space available for the solid fraction of BIO species to occupy (see Figure 3.2). In addition, biochemical KIN reactions that include a BIO species as a n-order kinetic product, are affected by the BIO activity in response to the temperature T_L in the L phase and L saturation S_L as a consequence of metabolic processes. The effect of T_L on the reaction velocity is accounted for in BRTSim as

$$f(T) = \left(\frac{e^{TL}}{e^{TL} + e^{TL}} \right)^{aTL} \cdot \left(\frac{e^{TH}}{e^{TH} + e^{TL}} \right)^{aTH}, \quad (5.7)$$

where TL and TH are the lower and upper response temperatures expressed in Kelvin, and aTL and aTH are two empirical power scalings used to skew the response function to the specific microbial metabolic responses. A different approach to account for temperature effects on biological reaction will be used in future releases based on the thermodynamic approach developed in Maggi et al. (2018). The effect of S_L is described as

$$f(S_L) = \left(\frac{S_L}{S_{LL} + S_L} \right)^{aSLL} \cdot \left(\frac{S_{LH}}{S_{LH} + S_L} \right)^{aSLH}, \quad (5.8)$$

where S_{LL} and S_{LH} are the lower and upper response to L saturation, and $aSLL$ and $aSLH$ are two empirical power scalings similar to those in the temperature response. All response parameters in Eqs. (5.7) and (5.8) can be set by the user to each BIO in the BIO block of the `Param.inp` file. The overall response f_B introduced in Eq. (3.42) of Section 3.8 in biological reactions is expressed as

$$f_B = \min \{ f(S_B), f(T), f(S_L) / \max\{f(S_L)\} \}. \quad (5.9)$$

Note that a number of approaches are available to describe the living organisms and their activity under temperature and water stresses; for microbial species, we recall, for example, expressions summarized in Sierra et al. (2015). A full table of response characteristics is provided in Figure 5.1 for the case where the BIO species Bx and By are declared and interact with each other.

5.3.4 Chemistry and biology feedback

The feedback between chemistry and biology in the solving domain is controlled by the modes in which BIO species sense the surrounding environment. In particular, BRTSim identifies repellents and attractants for a BIO species, and allows for chemotaxis towards and against their concentration gradient, respectively. Chemotaxis is accounted for in

Reaction substrate	Reaction product	n-order term	Michaelis-Menten term	$f(S_B)$	$f(T)$	$f(S_L)$	f_B	Immobilization/ remobilization	CTX	Notes
	B_x			1	$\leq 1 (B_x)$	$\leq 1 (B_x)$	≤ 1	-	B_x	No growth of B_x
			B_x	1	1	1	1	-	-	Reaction limited by B_x
B_x		B_x		1	1	1	1	B_x	-	B_x mortality
	B_x			$\leq 1 (B_x)$	$\leq 1 (B_x)$	$\leq 1 (B_x)$	≤ 1	B_x	-	B_x growth
	B_x	B_x		$\leq 1 (B_x)$	$\leq 1 (B_x)$	$\leq 1 (B_x)$	≤ 1	B_x	B_x	B_x growth
B_x		B_y		1	$\leq 1 (B_y)$	$\leq 1 (B_y)$	≤ 1	B_x	B_y	B_y growth on B_x without growth
B_x	B_y			$\leq 1 (B_y)$	1	1	≤ 1	B_x, B_y	-	B_y growth on B_x with growth
B_x	B_y	B_y		$\leq 1 (B_y)$	$\leq 1 (B_y)$	$\leq 1 (B_y)$	≤ 1	B_x, B_y	B_y	B_y growth on B_x with grow

Table 5.1: Conditions for detection of BIO response and associated processes of growth limitation, immobilization and remobilization, and chemotaxis. Cases are exposed for B_x and B_y BIO species.

an explicit way for the B phase as in Eq. (3.7); however, various conditions have to be satisfied to have feedback between the chemical quality of the L phase and the BIO species. In specific, BIO species have to be declared in the BIO block, and must appear in aqueous kinetic reaction in the KIN block as a n-order kinetic product. If these conditions are satisfied, then any other reacting PRI in that reaction will be listed as 'attractant' for that BIO species, and any inhibiting PRI species will be listed as 'repellent' for that BIO species. The same BIO species may appear in additional KIN reactions and therefore multiple attractants and repellents may exist for one BIO species. If no other PRI species appear as reactants or inhibitors, no CTX solver is called.

Chapter 6

The Param.inp file

The `Param.inp` file controls all capabilities and settings of a simulation run of BRTSim. This file sets all physical, chemical, and biological parameters, the geometry of the problem, and the numerical solvers convergence criteria. This file is divided in blocks, each one having specific objectives. Below is given a brief description of each block.

6.1 PARAM block

The block PARAM reports the project title in the first line and it can be set by the user. This field cannot exceed 1 line but if no project title is present, than an empty line has to be used. Below the tag to the PARAM block there are sub-blocks (PARAM.1, PARAM.2 and PARAM.3), each containing various fields that are defined below.

PARAM.1	
tini, tend	Initial and end simulation time in [day].
dt	Integration time step in [day].
Vdt	Variable Δt . If $Vdt = 1$, variable Δt will be used and Δt will change at each time iteration. If $Vdt = 0$, the value $\Delta t = dt$ stated above will be used throughout the simulation. Values of Vdt different than 0 or 1 will result in an error message and BRTSim will not proceed further.
mindt, maxdt	Minimum and maximum Δt in [day]. Used only if $Vdt = 1$.
g_mod, g_dir	Modulus in $[m/s^2]$ and direction in [degree] of gravitational acceleration. The system of reference is directed upward in the vertical direction, hence $g_dir = -90$ degrees must be used for typical terrestrial applications
BEEP	With $BEEP = 1$ BRTSim plays a sound on 'ERROR' message and at the end of simulation. $BEEP = 0$ makes BRTSim silent.

PARAM.2	
GAS	Gas phase solver switch. Gas phase advection and diffusion, and boundary G flows are accounted for when GAS = 1, or disregarded if GAS = 0.
HEA	Heat flow solver switch. Heat flow by advection and conduction, and boundary H flows are accounted for when HEA = 1, or disregarded if HEA = 0.
TR	Chemicals dispersion solver switch. BRTSim solves for advection-dispersion in the G and L phases if TR = 1, or it disregards advection-dispersion if TR = 0.
EQ	Equilibrium reaction solver switch. BRTSim solves for equilibrium reactions if EQ = 1, and it disregards them if EQ = 0.
KIN	Kinetic reaction solver switch. BRTSim solves for kinetic reactions if KIN = 1, and it disregards them if KIN = 0.
LIQ_GAS_FEED	Feedback for liquid-gas phases interaction switch. If LIQ_GAS_FEED = 1 than the liquid pressure will include P_G .
LIQ_CHEM_FEED	Feedback for chemical-liquid interaction switch. If LIQ_CHEM_FEED = 1, BRTSim solves for chemical osmotic pressure in the liquid phase and the liquid pressure will include P_O . The liquid density will be updated at each iteration depending on the chemicals in aqueous solution that are declared as 'mobile'.
LIQ_BIO_FEED	Feedback for liquid-biological interaction switch. If LIQ_BIO_FEED = 1, BRTSim solves for immobilization and remobilization of the L phase into/from the B phase. Effects will appear only if primary BIO species are explicitly declared.
BIO_CHEM_FEED	Feedback for biological-chemical interaction switch. If BIO_CHEM_FEED = 1, BRTSim solves chemotaxis of BIO species due to repellents and attractants if primary BIO species are explicitly declared, and if chemical repellents and attractants can be identified in KIN reactions that include BIO species as a n-order kinetic product, and if reactants and inhibitors are identified in those KIN reactions. In that case, reactants will act as attractants, while inhibitors will act as repellents.
ISAVE	Time step for saving in [day]. 1 time iteration is saved in the Time.out and Flux.out files every ISAVE simulated days.
TSAVE	Saving time. This parameter controls the time since when BRTSim starts saving into Time.out and Flux.out files. Time $t = t_{ini}$ and $t = t_{end}$ are always saved.
PTER	Percent time for before testing "early termination" in [%]. If time $t > PTER (t_{fin} - t_{ini})$, BRTSim will test the hypothesis that the simulation is not preceeding at a linear time step dt . If the hypothesis is true, and "Early termination" signal is launched to the user.

PARAM.3	
RESID_C	Residual concentration in PRI, BIO, SEC and GAS species. This sets the minimum concentration for computability. It is an important parameter for the TR, KIN and EQ solvers. Note that a concentration equal to 0 is not allowed for EQ reactions.
ITER_L TOL_L	Maximum number of iterations and tolerance for convergence of the L phase flow.
ITER_G TOL_G	Maximum number of iterations and tolerance for convergence of the G phase flow.
ITER_TR TOL_TR	Maximum number of iterations and tolerance for convergence of transport in L and G phases, and chemotaxis of the B phase in the L phase.
ITER_KIN TOL_KIN	Maximum number of iterations and tolerance for convergence of KIN Solver.
CYCLE_EQ ITER_EQ TOL_EQ	Maximum number of cycles, iterations, and tolerance for convergence of EQ solver.
ITER_HEA TOL_HEA	Maximum number of iterations and tolerance for convergence of H Solver (not active yet).
ITER_V TOL_V	Maximum number of iterations and tolerance for convergence of V Solver (not active yet).

PARAM.4	
P_REF, T_REF, C_REF	Reference G pressure, temperature, and concentration. P_REF is used to calculate the mass flow rate of G boundary flow when the user declares the volumetric flow rate and temperature in the GENER block. T_REF is currently used to determine the physical properties of the L and G phases even if H solver is switched on. C_REF is not currently used.

- Note 1** Using variable Δt assures that the numerical solution will be stable and reliable during a run. Because the minimum and maximum Δt values can be arbitrary chosen, this capability allows a good control on the integration time steps in BRTSim. Note however, that use of variable Δt goes along with setting values for TOL_L and ITER_L that dictate how satisfactory convergence is. Typical values for purely hydraulic problems in soils may converge over relatively large Δt values (> 1 to 10 days) and for large tolerance TOL_L $> 10^{-2}$, while problems that show steep gradients and large and variable mass fluxes at the boundaries may require setting maxdt < 1 day and small tolerance TOL_L $< 10^{-2}$. Typical values for ITER_L can be up to 100 or more for complex flow problems. Examples are available in this package for consultation.
- Note 2** The gravitational acceleration can be set to any arbitrary values. However, the value g_mod = 0 [m/s²] cannot be handled in the mass conservation and continuity laws. When g_mod = 0 [m/s²] is used, BRTSim will correct it with a small number approaching zero (set to 10^{-20} m/s²).
- Note 3** g_mod $\rightarrow 0$ allows the user to simulate a horizontal instead of vertical solving domain (relative to the direction of gravitational acceleration), where the gravitational acceleration is energetically orthogonal to the system of reference. In this case, no advection will occur, and the only transport mechanism will be diffusion. Alternatively, it is possible to rotate the direction of the solving domain using g_dir. Values of g_dir intermediate between 0 and 90 degrees will define an inclined solving domain relative to the reference gravitational acceleration.
- Note 4** The TR switch activates or deactivates the solver for advection-diffusion (dispersion) of chemicals in both L and G phases. When TR = 1, BRTSim solves for the advection-diffusion of any mobile species in the L and G phases; when TR = 0, chemicals will not move from one element of the solving domain to another, condition that is equivalent to make them not mobile (mobility = 0). However, mobility also controls the capability for species to pass through the boundary in both L and G phases, and therefore careful choice of how one wants to manage transport is needed.
- Note 5** Values of GAS, HEA, TR, EQ, and KIN switches in PARAM.2 different than 0 or 1 will result in an error message and BRTSim will not proceed further.

6.2 PARALLEL block

This block is currently under development for future applications and is not used in this version of BRTSim.

6.3 MATERIAL block

This block defines the physical and hydraulic properties of any material that may be used in the elements of the solving domain. There is no limit to the number of materials that can be defined. Fields in this block are described in the following table.

MATERIAL.1	
NAM	Name of material. This is an user-defined tag to be called in the ELEM block, and will carry over to that element all properties listed below.
EQU	Model used for the saturation-potential relation. EQU = 1 uses the Brooks and Corey model, while EQU = 2 uses the van Genuchten model as described in Section 3.4.
SAND SILT CLAY	Sand, silt and clay (SSC) textural mass fractions percent.
rho_m	Mineral density in [kg/m ³]. If rho_m = -999, it is estimated from table in Figure 6.2.
phi	Porosity is a number between 0 and 1 [-]. If phi = -999, it is estimated by regression against the SSC fractions using Cosby et al. (1984).
k	Absolute permeability in [m ²]. If -999, it is estimated by regression against the SSCAY fractions using Cosby et al. (1984)) at conditions: 20°C, water, and 9.81 m/s ² gravitational acceleration.
b	Pore volume distribution index in the Brooks and Corey model [-]. If -999, it is estimated by regression against the SSC fractions using Cosby et al. (1984).
psi_s	Air-entry suction in the Brooks and Corey model in [m]. If -999, it is estimated by regression against the SSC fractions using Cosby et al. (1984) at conditions: 20°C, water, and 9.81 m/s ² gravitational acceleration.
alpha	van Genuchten empirical parameter in [1/m]. If alpha = -999, it is estimated from table in Figure 6.3.
m	van Genuchten empirical parameter [-]. If m = -999, it is estimated from table in Figure 6.3.
SLr	Liquid residual saturation [-]. If SLr = -999, it is estimated from table in Figure 6.2
SGr	Gas residual saturation [-]. If SGr = -999, it is assumed to be 0.2
eOSM	Osmotic efficiency; it must be a number between 0 and 1
cp	Heat capacity in [J/kg K]. If cp = -999, it is estimated from table in Figure 6.4 and the SSC fractions.
Kh	Heat conductivity in [J/m s K]. If Kh = -999, it is estimated from table in Figure 6.4 and the SSC fractions.

Note 6 Attention has to be paid when inputing values of hydraulic parameters either for the Brooks and Corey model (b and psi_s) or for the Van Genuchten model (alpha and m). If these are known for a liquid to be used in a simulation, values can be simply used directly in the MATERIAL block. Note that, however, parameters imputed after determination from experiments in some conditions may not apply universally. For example, if psi_s determined for water at experimental temperature T^* and a simulation in BRTSim is run at temperature $T \neq T^*$, then psi_s should be adjusted. BRTSim will adjust the value of psi_s assuming that the imputed value was derived at standard conditions, that is, $T^* = 20^\circ C$ or at the reference temperature declared in T_REF in the PARAM block. Next, it will calculate the capillary pressure Pcap_s and will adjust the density of the liquid phase rho_L at $T \neq T^*$. Finally, BRTSim will recalculate psi_s for the liquid density at temperature $T \neq T^*$. A similar sequence of adjustments will be taken if a simulation is run at a gravitational acceleration different than that in standard conditions $g^* = 9.81 \text{ m/s}^2$, and if the liquid properties change because of chemicals in solution (only if the switch LIQ_CHEM_FEED = 1 and for mobile PRI and SEC). BRTSim will undertake a similar adjustment also for the relative permeability and hydraulic conductivity to both L and G phases after changes in L and G phase properties as a consequence of temperature changes and chemicals in solution (only if the switch LIQ_CHEM_FEED = 1 and for mobile PRI and SEC).

	^(a) Textural fractions			^(b) Mineral density rho_m [kg/m ³]	^(c) Total porosity phi [-]	^(c) Permeability k m ²	^(a) Brooks and Corey parameters psi_s		^(d) van Genuchten parameters alpha		^(e) Residual L and G saturations SLr SGr	
	Sand %	Silt %	Clay %				b [-]	[m]	m [-]	[1/Pa]	SLr [-]	SGr [-]
Sand	92	5	3	2753	0.437	5.958E-12	3.39	-4.73E-02	0.580	2.75E-04	0.0458	0.2
Loamy Sand	82	12	6	2824	0.437	1.734E-12	3.86	-6.39E-02	0.430	3.45E-04	0.0801	0.2
Sandy Loam	58	32	10	2998	0.453	7.348E-13	4.50	-1.32E-01	0.345	3.15E-04	0.0905	0.2
Sandy Clay Loam	58	15	27	2674	0.398	1.220E-13	7.20	-1.32E-01	0.260	2.75E-04	0.1709	0.2
Sandy Clay	52	6	42	2632	0.430	3.405E-14	9.59	-1.58E-01	0.210	3.40E-04	0.2535	0.2
Loam	43	39	18	3017	0.463	3.745E-13	5.77	-2.07E-01	0.340	3.40E-04	0.0583	0.2
Silt	7	88	5	3231	0.480	1.205E-13	3.71	-6.14E-01	0.200	5.50E-04	0.3124	0.2
Silt Loam	17	70	13	3246	0.501	1.929E-13	4.98	-4.54E-01	0.160	5.65E-04	0.0299	0.2
Silty Clay Loam	10	56	34	2764	0.479	4.256E-14	8.32	-5.61E-01	0.210	5.00E-04	0.0835	0.2
Clay Loam	32	34	34	2817	0.464	6.526E-14	8.32	-2.89E-01	0.220	5.80E-04	0.1616	0.2
Silty Clay	6	47	47	2514	0.479	2.554E-14	10.4	-6.33E-01	0.085	6.00E-04	0.1169	0.2
Clay	22	20	58	2438	0.475	1.702E-14	12.1	-3.91E-01	0.340	9.00E-05	0.1895	0.2

^(a) Cosby et al. (1984)
^(b) Saxton and Rawls (2006) and Rawls et al (1982)
^(c) Rawls et al (1982)
^(d) Ghanbarian-Alavijeh et al. (2010)
^(e) Assumed

Table 6.2: Soil hydraulic parameters from various sources.

Texture class	Clay	C loam	Loam	L Sand	Sand	S Clay	S C L	S loam	Silt	Si Clay	Si C L	Si Loam
Sand [%]	20	33	40	82	92	55	62	62	6	10	8	25
Silt [%]	20	35	40	15	7	10	14	25	90	45	55	68
Clay [%]	60	32	20	3	1	35	24	13	4	45	37	7
theta_r [-]	0.098	0.079	0.061	0.049	0.053	0.117	0.063	0.039	0.05	0.111	0.09	0.065
phi [-]	0.459	0.442	0.399	0.39	0.375	0.385	0.384	0.387	0.489	0.481	0.482	0.439
log(alpha) log(1/cm)	-1.825	-1.801	-1.954	-1.459	-1.453	-1.476	-1.676	-1.574	-2.182	-1.79	-2.076	-2.296
alpha×10-4 [1/Pa]	1.643	1.683	1.445	2.370	2.384	2.330	1.907	2.112	1.150	1.702	1.279	1.026
log10(n) [-]	0.098	0.151	0.168	0.242	0.502	0.082	0.124	0.161	0.225	0.121	0.182	0.221
n [-]	1.253	1.416	1.472	1.746	3.177	1.208	1.330	1.449	1.679	1.321	1.521	1.663
m [-]	0.202	0.294	0.321	0.427	0.685	0.172	0.248	0.310	0.404	0.243	0.342	0.399

Table 6.3: Soil hydraulic parameters from the Rosetta database.

	rho_m ^(a)	Specific heat capacity	Specific heat capacity	Thermal conductivity	
	[-]	[kg/m ³]	[kJ/m ³ K]	[kJ/kg K]	[W/m K] = [J/m s K]
Sand	0.363	20	1400	0.5055	0.8
Silt	0.489	20	2800	0.9779	1.8
Clay	0.489	60	3300	1.1526	0.975

Table 6.4: Soil thermodynamic parameters from various sources database.

6.4 PHASE block

This block defines the physical properties of the L and G phases in the solving domain as a function of the temperature. Only two physical phases can be defined in this version of BRTSim, although an additional biological phase may exist and be defined as described in the BIO block.

PHASE.1	
NAM	Name of liquid PHASE. This is an user-defined tag for a liquid substance associated with the PRI that has been tagged as solvent (solvent = 1 in the PRI block).
<i>T</i> list	List of temperatures in [°C] organized in a row used with a corresponding value of physical properties declared in the fields below.
rho_L	Liquid density in [kg/m ³] at any given temperature in the absence of dissolved chemicals.
mu_L	Liquid dynamic viscosity in [Pa s] at any given temperature in the absence of dissolved chemicals.
gamma_L	Liquid-gas surface tension in [mN/m] at any given temperature in the absence of dissolved chemicals.
cp_L	Heat capacity at any given temperature in [J/kg K].
Kh_L	Heat conductivity in [J/m s K]

PHASE.2	
NAM	Name of gas PHASE. This is an user-defined tag for a gas substance or mixture of substances.
<i>T</i> list	List of temperatures in [°C] organized in a row used with a corresponding value of physical properties declared in the fields below.
rho_G	Gas density in [kg/m ³] at any given temperature.
mu_G	Gas dynamic viscosity in [Pa s] at any given temperature
cp_G	Heat capacity in [J/kg K] at any given temperature.
Kh_G	Heat conductivity in [J/m s K]

Note 7 A minimum of 6 temperatures and corresponding properties must be used for both L and G phases.

Note 8 both L and G phases properties are defined at various temperatures in this block. An interpolation function of the type in Eq. 3.48 is used to write these properties as functions of the corresponding phase T_β . However, even if this version of BRT-Sim accounts for heat flow, the values of cp and Kh at the reference temperature T_REF will be used, while feedback between thermal properties and specific phase

temperatures will be incorporated in future releases. Composition dependence of fluid properties are updated at each time iteration according to Eq. 5.2. In BRTSim, an explicit accounting of the dependence of liquid density composition, and of the air-entry potential is included as explained in **Note 6**.

6.5 PRI block

This block defines the primary aqueous species (PRI) in the liquid phase of the biogeochemical system. An arbitrary number of PRI can be defined.

PRI.1	
NAM	Name of primary aqueous species. This is an user-defined tag for a substance in liquid solution
Mobility	Mobility = 0 implies that PRI is not subject to advection-diffusion or to GEN with negative volumetric flow rate, i.e., they cannot be removed from the solvingdomain. If Mobility = 1, PRI is subject to advection-diffusion and boundary flows. If Mobility = 2, the PRI species concentration will be constant and equal to the value assigned in ICPRI, and will not be subject to boundary flows.
Solvent	Flag to solvent substance. If Solvent = 1 then PRI is the substance making the liquid phase and carrying all other liquid species. If Solvent = 0 than PRI is a solute.
mmass	Molar mass of PRI in [g/mol].
Ds	Diffusion coefficient in the L phase in [m ² /s].

Note 9 A solvent is by definition mobile (Mobility = 1) because it is the substance that makes the liquid phase. In instances where the solvent is given Mobility = 0, this is automatically switched to Mobility = 1, and a warning signal is shown without interrupt.

Note 10 A solvent must be defined; therefore, at least 1 PRI species must be declared in the PRI block to be able to launch BRTSim.

Note 11 A PRI species given a Mobility = 2 is not allowed to be used in equilibrium reactions but can be used in kinetic reactions. However it cannot be used as a reactant or as a reaction product because it is against the nature of this type of PRI species. Hence it can be used to condition the reaction as in n-th order product terms, Michaelis-Menten terms, and inhibitions terms.

6.6 BIO block

This block defines the primary biological species (BIO). They are assumed to be in the liquid phase of the biogeochemical system, but they also constitute a phase itself that interacts with the liquid phase depending on the higher level switches described in Section 5.3. An arbitrary number of BIO species can be defined. These are lumped by BRTSim into the PRI species for faster computation and, therefore, undergo processes that are governed by the same rules that govern PRI species. However, additional solvers can apply to BIO species that do not strictly apply to PRI species, and are presented and discussed in Chapter 3.

BIO.1	
NAM	Name of primary biological species. This is an user-defined tag for a species in liquid phase
Size	Size of an individual cell in [m] if this is explicitly of biological nature, or size of molecule in [m] if this is a different substance.
rho.b	Mass density of the species in [g/mol].
WVF	Volume water fraction [-]. WVF is limited between 0 and 1. Exceeding this limit will produce an error message and BRTSim will interrupt.
cp	Heat capacity in [J/kg K]. This is not assumed to change with the temperature in this version of BRTSim.
Kh	Heat conductivity in [J/m s K]. This is not assumed to change with the temperature in this version of BRTSim.
eADV	Efficiency to transport by advection [-]. eADV is limited between 0 and 1; exceeding these limits will produce an error message and BRTSim will interrupt.
Ds	Diffusion coefficient in the L phase or at the interface between the solid and liquid interface in [m ² /s].
Dc	Chemotaxis coefficient to chemical attractants in [m ² /s].
Dr	Chemotaxis coefficient to chemical repellents in [m ² /s].
TL, TH,	Lower and upper temperature response parameters in [°C] .
aTL, aTH,	Lower and upper temperature response scaling powers [-] .
SLL, SLH	Lower and upper L saturation response parameters [-].
aSLL, aSLH,	Lower and upper L saturation response scaling powers [-] .

Note 12 BIO species are optional and do not necessarily have to be defined even if the user is aiming to solve problem that specifically involved biological species. However, BIO species have advantages in that they can be controlled in more details and are subject to limitations in the KIN solver such as explained earlier in Chapter 5. When BIO species are explicitly declared, the user can decide to account for all BIO-specific solvers such as CTX by setting the LIQ_BIO_FEED =1 or neglect specific

processes in BIO with LIQ_BIO_FEED = 0. In the latter case, all BIO species will not be neglected in the problem statement, but will be converted to PRI species with mobility = 0, WVF = 0, cp = 0, Kh = 0, eADV = 0, Dc = 0 and Dr = 0. Other quantities will be used to retrieve the mmass necessary to declare a PRI species.

Note 13 Typical mesophiles temperature response can be achieved using TL = 12°C , TH = 45°C, aTL = 0.1 and aTH = 0.5.

6.7 SEC block

This block defines the secondary species (SEC) of the biogeochemical system, which can be either liquid or mineral. An arbitrary number of SEC can be defined, but all have to be written as functions of PRI species.

SEC.1	
NAM	Name of secondary species. This is a user-defined tag for a substance in liquid solution SEC or a solid substance MIN.
Mobility	if Mobility = 1, SEC is subject to advection-diffusion. Mobility = 0 implies that SEC is not subject to advection-diffusion.
mmass	Molar mass of SEC in [g/mol].
Ds	Diffusion coefficient in the liquid phase in [m ² /s].
Reaction	Defines the equilibrium reaction as a sequence of stoichiometric coefficients and species. Stoichiometric coefficients are negative for reactants and positive for products. Stoichiometric coefficients can be numerical expressions that BRTSim evaluates as a number; the expression cannot contain unknowns or symbols, but only numerical values without space separations.
logK	Values of logK of equilibrium at eight different temperatures. logK values can be numerical expressions that BRTSim evaluates as a number; the expression cannot contain unknowns or symbols, but only numerical values without space separations.

Note 14 A minimum of 5 logK values must be used. However, it is not possible to define SEC species with a different number of logK values from each other, In practice, once decided the structure of logK values definition at given temperatures, this structure must be applied to all SEC declared in the SEC block. It is convenient to use consolidated thermodynamic databases such as the EQ3/6 V8.2b database (Wolery, 1992).

6.8 GAS block

This block defines the secondary gaseous species (GAS) of the biogeochemical system, which are in equilibrium with the primary liquid species. An arbitrary number of GAS can be defined, but all have to be written as a function of PRI species.

GAS.1	
NAM	Name of secondary gas species. This is an user-defined tag for a substance in the gas phase.
mobility	if Mobility = 1, GAS is subject to advection-diffusion. Mobility = 0 implies that GAS is not subject to advection-diffusion.
mmass	Molar mass of GAS in [g/mol].
Ds	Diffusion coefficient in the gas phase in [m ² /s].
Reaction	Defines the equilibrium reaction as a sequence of stoichiometric coefficients and species. Stoichiometric coefficients are negative for reactants and positive for products. Stoichiometric coefficients can be numerical expressions that BRTSim evaluates as a number; the expression cannot contain unknowns or symbols, but only numerical values without space separations.
logK	Values of logK of equilibrium at eight different temperatures. logK values can be numerical expressions that BRTSim evaluates as a number; the expression cannot contain unknowns or symbols, but only numerical values without space separations.

Note 15 A minimum of 5 logK values must be used. However, it is not possible to define GAS species from a different number of logK values with each other, In practice, once decided the structure of logK values definition at given temperatures, this structure must be applied to all GAS declared in the GAS block. It is convenient to use consolidated thermodynamic databases such as the EQ3/6 V8.2b database (Wolery, 1992).

6.9 COMP block

This block defines the composite species (COMP) of the biogeochemical system, which are any user-defined combination of species belonging to PRI, SEC, MIN, or GAS. COMP species cannot be used in any reactions (equilibrium or kinetic).

GAS.1	
NAM	Name of COMP species.
UNIT	User-defined unit of the COMP species. This depends on the stoichiometric coefficient used in the definition of 'Composition' field.
Composition	If different from an empty string, the composition is expressed as a sequence of stoichiometric coefficients and species. Stoichiometric coefficients can be negative, zero, or positive depending on the operation that the user wants to impose. Stoichiometric coefficients can be numerical expressions that BRTSim v2.2 evaluates as a number; the expression cannot contain unknowns or symbols, but only numerical values without space separations.

Note 16 COMP species are expressed in mass and not as concentrations, densities, or partial pressures. They are particularly useful if the user wants to check that mass is conserved not only in the L and G phases or energy is conserved in H, but also whether elements are conserved in the geochemical system. Currently, BRTSim is the only available software that allows for this capability in a complex multiphase and multi-species calculation environment.

6.10 KIN block

This block defines the kinetic reactions (KIN) occurring in the liquid phase of the biogeochemical system. An arbitrary number of KIN can be defined, but all have to be written as a function of PRI species only and can include BIO species if these are defined in the BIO block.

KIN.1	
NUM	Identification number for the KIN reaction. This can be a numeral of a string; in the latter case, the string cannot contain spaces.
Reaction	Defines the KIN reaction as a sequence of stoichiometric coefficients and declared PRI and BIO species. Stoichiometric coefficients are negative for reactants and positive for products. Stoichiometric coefficients can be numerical expressions that BRTSim evaluates as a number; the expression cannot contain unknowns or symbols, but only numerical values without space separations.

KIN.2	
Rate constant	Reaction rate constant in [1/s]. This can be a numerical expression that BRTSim evaluates as a number; the expression cannot contain unknowns or symbols, but only numerical values without space separations.
n-Order terms	This line requires entering the number of n-th order kinetic products. This is followed by the PRI and/or BIO species and their power. The powers can be numerical expressions that BRTSim evaluates as a number, but cannot contain unknowns or symbols, or space separations. The field can be empty.
MM terms	Number of Michaelis-Menten kinetic terms. This is followed by a sequence of PRI and/or BIO species and their Michaelis-Menten constant. MM constants can be numerical expressions that BRTSim evaluates as a number, but cannot contain unknowns or symbols, or space separations. The field can be empty.
Compet terms	Number of competition terms. This is followed by a sequence of PRI and/or BIO species and their competition constant, which typically corresponds to the Michaelis-Menten constant in the competing reaction for that PRI and/or BIO species. Competition constants can be numerical expressions that BRTSim evaluates as a number, but cannot contain unknowns or symbols, or space separations. The field can be empty.
Inhib terms	Number of inhibition terms. This is followed by a sequence of PRI and/or BIO species and their inhibition constants. The inhibition constants can be numerical expressions that BRTSim evaluates as a number, but cannot contain unknowns or symbols, or space separations. The field can be empty.

Note 17 The KIN block allows the user to define any type of kinetic reaction and set the kinetics to any order. For example, assume a first-order reaction is to be set as a function of PRI species X for that reaction. In this case, n-Order terms will be set to 1 followed by X and by a 1 as per the string

'n-Order 1 X 1'

If a second-order reaction for the same reaction must be used, then the string would be

'n-Order 1 X 2'

Multiple n-Order products can be used. Imagine the reaction depends linearly on X and Y, then the string will be

'n-Order 2 X 1 Y 1'

If no n-Order terms are present, then this field will simply be

'n-Order 0'

Note 18 If the reaction includes one Michaelis-Menten term in the PRI species X with Michaelis-Menten constant x, then the line for MM terms will write as

'MM 1 X x'

An arbitrary number of Michaelis-Menten terms can be included; suppose three PRI species X, Y and Z must be used to describe the kinetics of a reaction with Michaelis-Menten constants x, y and z, respectively, then the MM line would write as

'MM 3 X x Y y Z z'

Note also that Michaelis-Menten terms in this line do not necessarily have to be present in the reaction. This allows the user to use any number of Michaelis-Menten terms to impose inhibition at the lower end of the concentration of the PRI species expressing this Michaelis-Menten terms. For example, if a reaction is expressed by a Michaelis-Menten kinetics in substrate X and constant x, and is inhibited for a pH > 8, a MM line can be used as

'MM 2 X x H+ 1e-8'

even if H+ does not appear in the reaction.

Note 19 Note that any reactants in a reaction must explicitly appear either as a n-Order or Michaelis-Menten term. If a reaction is used with a reactant that does not have to

influence the reaction order, then a Michaelis-Menten term for that reactant should be used with a very low Michaelis-Menten term (1E-20 to 1E-10, or near but slightly greater than 'resid.C').

Note 20 Competitive inhibition of substrate consumption can be expressed for any Michaelis-Menten terms in a reaction. An arbitrary number of competitive terms can be included per each Michaelis-Menten term. To set competition, the user must first express as many Compet lines as the number of Michaelis-Menten terms, but at least one line of Compet must appear in that KIN field. For example, if 3 Michaelis-Menten terms are used, 3 Compet lines must appear. Yet, if no Michaelis-Menten terms are used (string 'MM 0'), at least one line (string 'Compet 0') must appear in that field. When these lines are set, the user can choose to include competition or not. If competition is included, the writing will be similar to that of MM terms. For example, a reaction with a Michaelis-Menten term expressed on PRI species X with constant x and a competing PRI species Y with constant y affects consumption of X, the writing will be

```
'MM 1 X x'
'Compet 1 Y y'
```

In algebraic terms, this means that term

$$\frac{X}{X + x(1 + Y/X)}$$

will be used to solve the differential equation in Eq. (3.42). Multiple competition terms on multiple Michaelis-Menten terms can be handled with ease. For example, the writing

```
'MM 3 X x Y y Z z'
'Compet 2 W w H h'
'Compet 0'
'Compet 1 K k'
```

means that the reaction kinetics is expressed by three Michaelis-Menten terms (X, Y and Z, with constants x, y and z, respectively). In addition, the first MM term will be affected by competitive consumption of w PRI species (W and H with constants w and h respectively), the second MM term will not be affected by any competition, while the third MM term will be affected by one PRI species (K with constant k). The corresponding algebraic is

$$\frac{X}{X + x(1 + W/w + H/h)} \cdot \frac{Y}{Y + y} \cdot \frac{Z}{Z + z(1 + K/k)}$$

Note 21 Reaction inhibition can be expressed for any arbitrary number of PRI species and not necessarily only for reactants appearing in the reaction. The writing is analogous to that of Michaelis-Menten terms, and is not described further here.

6.11 ICSTP block

This block defines the initial conditions for liquid saturation, temperature and total gas pressure. An arbitrary number of initial conditions can be defined, and only selected ones may be used and assigned to individual elements of the solving domain.

ICSTP.1	
NAM	Name of initial conditions. This is a user-defined tag to be called in the ELEM block, and will carry over to that element all properties listed below.
Sl	Initial liquid saturation. If $Sl < Slr$, then $Sl = Slr$. If $Sl > 1-Sgr$, then $Sl = 1-Sgr$ is used. Sl entry can be a numerical expression that BRTSim evaluates as a number; the expression cannot contain unknowns or symbols, but only numerical values without space separations.
T	Initial temperature in [°C]. T entry can be a numerical expression that BRTSim evaluates as a number; the expression cannot contain unknowns or symbols, but only numerical values without space separations.
P	Initial total gas pressure in [Pa]. P entry can be a numerical expression that BRTSim evaluates as a number; the expression cannot contain unknowns or symbols, but only numerical values without space separations.

Note 22 The entry value for T refers to the initial ELEM temperature, and is applied to all phases $T_\beta = T$ with $\beta = L, G$ and M . If the H solver is switched on, T_β will change across the phases because of heat flows regulated by T_β gradients and specific thermal properties of each phase declared in the PHASE block.

6.12 ICPRI block

This block defines the initial conditions for PRI in the solving domain and the quality of the liquid phase in the boundary fluxes defined in the GENER block. An arbitrary number of ICPRI can be defined, while a selected set of ICPRI may be used to assign initial conditions to each individual element of the solving domain.

ICPRI.1	
NAM	Name of ICPRI.
ICPRI list	Following NAM declaration, a list of PRI/BIO organized in columns is to be written and an initial concentration is to be given to each PRI/BIO. The list may not follow the same order by which species have been declared in PRI/BIO. Also, if more species are listed, BRTSim will provide a warning without interrupt. Concentrations of PRI/BIO can be numerical expressions that BRTSim evaluates as a number, but cannot contain unknowns or symbols, or space separations. They are expressed in [mol/L] for PRI or in [mg/L] for BIO and for some PRI (e.g., when PRI is intended as a biological species without all features available in BIO).

Note 23 When a declared ICPRI is used for an initial condition, all concentrations must be positive numbers. When a declared ICPRI is used for a positive boundary flux defined in the GENER block, all concentrations must be positive too. When a declared ICPRI is used for a negative boundary flux defined in the GENER block, the concentration of PRI species can be positive or negative. When positive, the corresponding PRI will not be removed by that boundary flux; when negative, PRI can be removed by that boundary flux, but the concentration itself will not be used because it will be determined internally by the dynamics in the solving domain. This allows the user to set and choose the PRI species actively removed by the solving domain when the liquid phase is abstracted from the control volume. If an ICPRI with negative concentrations (i.e., removable by negative boundary flows) is used with a positive boundary flow, the negative concentration is converted in positive, and that concentration will be used in that boundary flow.

6.13 ICGAS block

This block defines the initial conditions for GAS. An arbitrary number of ICGAS can be defined, while a selected set of ICGAS may be used to assign initial conditions to each individual element of the solving domain.

ICGAS.1	
NAM	Name of ICGAS.
ICGAS list	Following NAM declaration, a list of GAS organized in column is to be written and an initial partial pressure fraction is to be given to each GAS. The list may not follow the same order by which GAS species have been declared in GAS. Also, if more GAS are listed in ICGAS than used in the GAS block, only those used in the GAS block will be accounted for and BRTSim will provide a warning without interrupt. The partial pressure fraction of GAS can be numerical expressions that BRTSim evaluates as a number, but cannot contain unknowns or symbols, or space separations.

Note 24 Contrary to ICPRI, ICGAS are only used to initialize the G phase quality, but are not used to define the quality of any GEN boundary flow declared for the G phase in the GENER block. This capability is expected to become available in future releases of BRTSim.

6.14 ICFILE block

This block defines the initial conditions ICSTP, ICPRI and ICGAS using a pre-existing `Time.out`.

ICFILE.1	
NAM	Path, name and extension of the file used for ICFILE initial conditions.
time	Allows the user to specify the initial conditions from a specific time instant in the file listed under NAM. It is suggested not to use "Time.out" as a file for ICFILE; rather rename the file from which to extract the initial conditions. If 'time = end' is used, the last time in the file is used. BRTSim will check for consistency of the geometry between the provided file and the current Param.inp as well as all phases and species.
FWT	FWT = 1 forces the initial conditions to be extracted from within the available interval in file NAM. When FWT = 1 and 'time' is outside the available interval, then an error message is launched and BRTSim is interrupted. FWT = 0 allows to set 'time' to be outside the available interval in file 'NAM', the case in which BRTSim takes the closest available time.
UIM	Not used.

6.15 ELEM block

This block defines the solving domain, including assigning properties and initial conditions to each individual element of the solving domain. The number of element is arbitrary, but because BRTSim solves for a 1-dimensional problem, it is assumed that declared elements are connected sequentially to each other.

ELEM.1	
NAM	Name of element.
(1)MAT (2)MAT (3)MAT	Assign MATERIAL to ELEM by calling the NAM of that MATERIAL. Three columns are provided, one of which is starred. The starred column is the one that BRTSim will use to assign MATERIAL.
DZ	Thickness of ELEM in [m].
DZ+	Distance from center of mass of ELEM to upper interface in [m].
DZ-	Distance from center of mass of ELEM to lower interface in [m].
A+	Surface area of the upper ELEM interface in [m ²].
A-	Surface area of the lower ELEM interface in [m ²].
V	Volume of ELEM in [m ³].
(1)ICSTP (2)ICSTP (3)ICSTP	Assign ICSTP to ELEM by calling the NAM of an user-defined ICSTP. Three columns are provided, one of which is starred. The starred column is the one that BRTSim will use to assign ICSTP.
(1)ICPRI (2)ICPRI (3)ICPRI	Assign ICPRI to ELEM by calling the NAM of an user-defined ICPRI. Three columns are provided, one of which is starred. The starred column is the one that BRTSim will use to assign ICPRI.
(1)ICGAS (2)ICGAS (3)ICGAS	Assign ICGAS to ELEM by calling the NAM of an user-defined ICGAS. Three columns are provided, one of which is starred. The starred column is the one that BRTSim will use to assign ICGAS.

Note 24 The fields MAT, ICSTP, ICPRI, and ICGAS are structured in a particularly convenient way. The three options must be declared always but allow to switch from one setting to another very quickly by starring the preferred condition.

6.16 GEN block

This block defines the boundary fluxes GEN. In BRTSim version 1 only liquid boundary fluxes are implemented. The number of GEN is arbitrary, and can be defined for constant rates or variable rates according to a table in a separate file.

GEN.1	
NAM	Name of GEN.
ELEM	Call the user-defined name of the ELEM which GEN is applied to.
PHASE	PHASE = L signifies that the boundary flux is in the L phase; PHASE = G is for a boundary flux in the G phase. PHASE = H means that the boundary flux is heat.
RELOOP	RELOOP = R signifies that the boundary flux specified in TABLE is relooped in the simulated time; RELOOP = F does not reloop the boundary flux specified in TABLE. RELOOP will only affect fluxes that are declared via a table specified in TABLE.
TABLE	If TABLE = 'notable' then see next field for constant GEN rate; If TABLE = 'sametable', then the table from the line above is used; otherwise, specify the path, name and extension of the file where BRTSim finds a table of time and rates for GEN. This instance is used when variable GEN is used.
TIME	Initial time of application of a constant GEN rate in [s]. If TABLE is a file, TIME is the column in the specified file where a time vector is allocated.
RATE	Rate of application of a constant GEN in [m ³ /s] for L and G, and in [J/s] for H. If TABLE is a file, RATE is the column in the specified file where a rate vector is allocated.
T	Temperature in [°C] at which GEN flux is inputted in ELEM. If RATE is a negative flux, T is disregarded because the temperature in ELEM depends on the internal dynamics.
RFAC, TFAC	Multiplicative factor for RATE and T, regardless of whether RATE and T are constant or variable (from a table). These factors can be any positive or negative number, as well as 0. RFAC and TFAC can be also a numerical expression that BRTSim evaluates as a number; the expression cannot contain unknowns or symbols, but only numerical values without space separations.
(1)QUAL (2)QUAL (3)QUAL	Assign ICPRI to GEN by calling the NAM of an user-defined ICPRI. This allows specify the concentrations of PRI species in the boundary flow specified in GEN. Three columns are provided, one of which is starred. The starred column is the one that BRTSim will use to assign ICPRI. This capability allows switching from one setting to another by starring the preferred ICPRI column.

Note 25 Definition of GEN in any of the phases does not mean that GEN will be used. For example, if the G Solver is not activated, any GEN specified in the G phase will not be included in the calculation. Likewise, GEN of heat will not be accounted for if the H Solver is not activated. In contrast, any GEN in the L phase will be accounted for by default because the L Solver is always active.

6.17 PEST block

This block allows the user to save in the `TimePST.out` file any PRI, SEC, MIN and GAS species at any arbitrary element of the solving domain and time.

PEST.1	
NAM	Name of any PRI, BIO, SEC, MIN or GAS species.
ELEM	Element of the solving domain.
TIME	Time in [day] at which NAM at elem ELEM is saved in the TimePST.out file.
CFAC	Conversion factor if change in unit is needed; use CFAC = 1 otherwise.
UNIT	User-defined unit used to save NAM. This depends on CFAC.

6.18 EXEC block

This block allows the user to launch any command line either before or after BRTSim has completed a simulation.

EXEC.1	
NAM	Name of the instruction to be executed. This serves as a tag for the command.
<COMMAND>	This is a string contained between markers < and >. The string can contain any meaningful sequece of commands to be executed.
WHEN	WHEN = before means that BRTSim will execute COMMAND before running a simulation. WHEN = after means that BRTSim will execute COMMAND after a simulation has completed.
WHERE	Specifies the environment in which COMMAND is launched. In this version of BRTSim only the option "system" is allowed, meaning that COMMAND will be called in the OS in which BRTSim is running, be these WINDOWS or LINUX/UNIX/UBUNTU.

Note 26 COMMAND simply executes a command line. For example, the user may want to launch an executable after a simulation so to retrieve some specific data in a way the PEST block cannot do, then COMMAND will be the name of the executable without file extension.

Note 27 The user can also instruct the OS to open an interpreter environment and launch a script in that interpreter such as Matlab or Python. As for the example in the distribution package, the user may want to launch the "plotTime.m" script to plot some figures. The EXEC block will contain the following string

```
'MyScript <matlab -r "plotTime; quit"> after system'
```

meaning that a Matlab instance will be open and the script "plotTime.m" will be launched, and next Matlab will be closed.

Note 28 If COMMAND launches a script from an interpreter that produces a figure such as in **Note 27**, the figure may first have to be closed before the Matlab instance can quit and BRTSim complete a run.

Chapter 7

The output files

7.1 The Time.out file

This file collects all outputs as a set of instantaneous values of the time, element, position, material and state variables including: temperature, water and gas saturation, water potential, and concentrations of all primary, secondary and gaseous species. Not all iteration steps will be saved in the Time.out file; the frequency at which output data will be saved is decided by the user with the parameter ISAVE in the PARAM.2 field of the PARAM block. ISAVE = 10 means that 1 iteration output will be saved every 10 iterations. The Time.out file is in TXT format, thus allowing the user to further process the output with any software and environment with ease.

7.2 The Flux.out file

This file collects all cumulative mass fluxes through the boundary as per instructions in the GEN block, and therefore it is optional depending on whether a GEN block exists. The mass fluxes include the liquid phase and any component in it including the primary, secondary aqueous species as long as they are mobile components (parameter 'mobility' in the PRI and SEC block) as listed in the GEN block. Similarly to Time.out, this file adds outputs with the frequency chosen by the user with the parameter ISAVE in the filed PARAM.2 of the PARAM block.

7.3 The Grid.out file

This file collects all information of the grid used to describe the computational domain including material, geometry and hydraulic properties. It is particularly useful to have access to hydraulic parameters estimated by BRTSim when not known (see Chapter 6).

7.4 The TimePST.out file

This is an optional file depending on whether the PEST block is used in the Param.inp file. If used, this file collects the instantaneous values of selected state variables among PRI, BIO, SEC, GAS, MIN and COMP at arbitrary grid elements and times. Output can be converted using the CFAC parameter to change, for example, units. This file has TXT format, thus it allows a user to give it further purposes including coupling with third-party software such as for parameter estimation.

Chapter 8

Samples

This BRTSim package includes a number of examples that the user can access, run, and modify freely to test changes in any desired setting. The sections below provides a brief description of each example. A user who intends to describe a new problem is recommended to start modifying the an existing example and add individual contributions followed by simple tests and verifications.

Sample 1 - Close column

This is an example of gravitational flow of water in a vertical soil column with no boundary flow. Only one PRI species is declared in the PRI block, that is, the solvent. No other PRI, BIO, SEC and GAS species are used, neither EQ or KIN reactions are declared. This sample only solves for L flow, while all other solvers and high-level feedbacks are switched off.

Sample 2 - Close column with boundary fluxes

This example uses Sample 1 but adds two boundary L flows. Note that these are constant over time and therefore they can be declared without the additional use of an external table. Because these have different rate (inflow is greater than outflow), the soil column is filling up with water over time. However, the bottom element of the column is declared with a very large volume, hence its water saturation is remaining practically constant. As a consequence, the excess water incoming into the control volume travels downward to the bottom element and the saturation profile reaches an equilibrium profile. No other PRI, BIO, SEC, and GAS species are used, in any EQ or KIN reaction.

Sample 3 - Ponding

In this example, the control volume has been complicated by the combined presence of a soil column and a number of atmospheric elements. There are two constant boundary flows as in Sample 2, but these start at two different times: the first is an inflow of water close to the top soil, while the second has a greater rate and occurs at a lower depth in the

soil. This example shows that the soil saturates and the water level builds up to ponding above the soil surface. When the outflow starts, water is removed from the control volume at a faster rate than it is introduced in the top, and the ponding level decreases. No other PRI, BIO, SEC, and GAS species are used, in any EQ or KIN reaction.

Sample 4 - No g

In this example, a case is demonstrated where no gravitational acceleration exist (i.e., the system is horizontal). In addition, two isolated soil columns are declared sequentially in the ELEM block, and are separated by an interface surface area equal to 0. Hence the two subvolumes do not communicate mass and energy fluxes. The top subvolume includes a soil and some atmospheric nodes, while the bottom subvolume only includes soil. In addition, the upper subvolume is subject to a constant inflow of water, while the lower subvolume is subject to a constant water outflow. No other PRI, BIO, SEC, and GAS species are used, in any EQ or KIN reaction.

Sample 5 - Free drainage

Also in this example, no chemical or biological species are declared except water as the PRI solvent species. This example demonstrate a case of water flow through an homogeneous soil column in free drainage conditions. This condition is obtained by using a large volume of the bottom node and giving excess weight to Δz^- of the element above it and reduced weight to Δz^+ of the bottom element. This reduces the capillary pressure gradient and retain the hydraulic conductivity of the element above the bottom. No other PRI, BIO, SEC, and GAS species are used, in any EQ or KIN reaction.

Sample 6 - Free drainage and NaCl

This example uses the same geometry of Sample 5 but includes Na^+ and Cl^- as additional PRI species to water. In addition, it includes equilibrium salt dissociation in the L phase, and two equilibrium reactions for linear adsorption of Na^+ and Cl^- . Two boundary water flows are declared with constant rate different from each other, starting from time 0. In addition, the inflow water quality includes Na^+ and Cl^- , but these are not removed by the outflow water, hence their concentration increases over time. No KIN reactions are included in this example. This example includes COMP species that accumulates all Cl^- in the soil and all Cl^- injected with the inflow, and can used to calculate and verify mass balance using the outputs in the `Time.out` and `Flux.out`

Sample 7 - Free drainage, NaCl and HCl

This example extends Sample 6 by introducing a KIN reaction between H^+ and Cl^- to produce HCl at a given rate. Differently from Sample 6, dissolved Cl^- , Na^+ , H^+ and HCl are made removable with the outflow water, hence their concentration does not increases over time as in the previous examples. This is obtained by declaring the ICPRI conditions

with a negative number relative to all species that are allowed to be removed. The KIN reactions for HCl production is defined as a first-order kinetics in Cl^- and includes a Michaelis-Menten term in H^+ .

Sample 8 - Urine decomposition in soil

This example reports the complete `Param.inp` file and boundary tables that describe human urine decomposition used in agriculture to provide nutrients to plants and soil microorganisms. The reaction network, agricultural setting, and ecohydrological conditions, as well as soil heterogeneity and microbial metabolic characteristics are not detailed here, but can be found in Tang and Maggi (2015).

Sample 9 - Atrazine biodegradation in soil

Similarly to Sample 8, this case reports the `Param.inp` file and boundary tables that describe atrazine biodegradation in a soil agricultural field. The reaction network, agricultural setting, and ecohydrological conditions, as well as soil heterogeneity and microbial metabolic characteristics are not detailed here, but can be found in la Cecilia and Maggi (2017).

Sample 10 - Gas bubble

This example show a case of interaction between the L and G phases in an unsaturated soil column. In particular, G phase is injected at relatively high rate; this builds up the pressure in the gas phase, which propagates throughout to control volume. However, water received excess pressure locally, and is pushed away, i.e., upward in this case. This forms a gas bubble in the lower part of the soil column.

Sample 11 - Solar radiation

To show application of heat flow, this example includes a boundary flow of variable solar radiation reaching the top of a soil column. Heat causes an increased temperature of all phases, which propagates across the phases in the each element, and downward the soil column by advection and conduction.

Sample 12 - Glyphosate dispersion, contamination and degradation in soil

This sample provide the `Param.inp` file and boundary tables that describe glyphosate mobility and degradation in a soil agricultural field. The reaction network, agricultural setting, and ecohydrological conditions, as well as soil heterogeneity and microbial metabolic characteristics are not detailed here, but can be found in la Cecilia et al. (2018).

Sample 13 - Microbial chemotaxis

In this example, PRI species X and Y are substrates to two BIO species B_X and B_Y . Consumption of Y by B_Y is inhibited by the presence of X, hence B_Y is repelled by X and attracted by Y, while B_X is only attracted by X. The substrate X and Y are not uniformly distributed but have a concentration gradient over space that is maintained constant after a transient by two large elements at the ends of the control volume. The concentration gradients have opposite direction. The BIO species dynamics is controlled also by diffusion. The resulting profile in BIO concentration is highly nonlinear and results in an expected chemotaxis effect of B_Y from X and toward Y. Other combinations can be constructed with ease for predator-prey like systems that include also nutrients and other conditions.

Sample 14 - Isotope kinetic fractionation

This example shows how labeling of species such as in isotopic techniques can be implemented in BRTSim with simple definitions of the primary species and chemical kinetic reactions. We used experimental data from Mariotti *et al.* (1981) and we modeled the combinatorial reactions involved in denitrification as described in Maggi and Riley (2009) and Maggi and Riley (2010), and we compared the modeling results with experiments. For a full description of the experiments and modeling in BRTSim, you can refer to Maggi (2019).

Bibliography

- Barbour SL and DG Fredlund, (1989), Mechanisms of osmotic flow and volume change in clay soils, *Can. Geotech. J.* 26, 551 – 562.
- Brooks RH and Corey AT, (1962), Hydraulic properties of porous media, Hydrology Papers, A14407-599281, Colorado State University, Fort Collins, CO, USA.
- Celia MA and Bouloutas ET, (1990), A General Mass-Conservative Numerical Solution for the Unsaturated Flow Equation, *Water Resources Research* 26(7), 1483-1496.
- Chin DA, *Water-Resources Engineering*, 2nd ed., Pearson Education International, Upper Saddle River, New Jersey, 2006, pp. 962.
- Cosby BJ ,Hornberger GM, Clapp RB Ginn TR, (1984), A Statistical Exploration of the Relationships of Soil Moisture Characteristics to the Physical Properties of Soils, *Water Resources Research* 20(6) 682–690.
- Ghanbarian-Alavijeh B, Liaghat A, Guan-Hua H and van Genuchten MT, (2010), Estimation of the van Genuchten Soil Water Retention Properties from Soil Textural Data, *Pedosphere* 20(4): 456–465,
- Keller EF, and Segel LA (1971) Traveling bands of chemotactic bacteria: a theoretical analysis, *J. Theor. Biol.* 30:235.
- la Cecilia D., and Maggi F., (2017), In-situ atrazine biodegradation dynamics in wheat (*Triticum*) crops under variable hydrologic regime. *Journal of contaminant hydrology*, 203, 104-121.
- la Cecilia D., Tang F.H., Coleman N.V., Conoley C., Vervoort R.W., and Maggi F., (2018), Glyphosate dispersion, degradation, and aquifer contamination in vineyards and wheat fields in the Po Valley, Italy. *Water research*, 146, 37-54.
- Maggi F. and Porporato A., (2007), Coupled moisture and microbial dynamics in unsaturated soils. *Water resources research*, 43(7).
- Maggi F., Tang FHM, and WJ Riley, (2018), The Thermodynamic Links between Substrate, Enzyme, and Microbial Dynamics in Michaelis–Menten–Monod Kinetics, *International Journal of Chemical Kinetics*, DOI 10.1002/kin.21163.
- Maggi F., (2019), BRTSim, a general-purpose computational solver for hydrological, biogeochemical, and ecosystem dynamics, arXiv:1903.07015 [cs.CE].

- Maggi, F., and Riley, W.J. (2009) Transient competitive complexation in biological kinetic isotope fractionation explains non-steady isotopic effects: Theory and application to denitrification in soils. *J. Geophys. Res.- Bio.* 2009, 114, G04012. DOI: 10.1029/2008JG000878.
- Maggi F., and Riley, W.J. (2010) Mathematical treatment of isotopologue and isotopomer speciation and fractionation in biochemical kinetics. *Geochim. Cosmochim. Acta* 2010, 74, 1823.
- Maier CG and Kelley K, (1932), An equation for the representation of high-temperature heat content data. *J. Am. Chem. Soc.*, 54(8), 3243-3246.
- Mansoor M. Amiji, Beverly J. Sandmann (2002). *Applied Physical Pharmacy*. McGraw-Hill Professional. pp. 54–57. ISBN 0-07-135076-4.
- Mariotti A., J.C. Germon, P. Hubert, P. Kaiser, R. Letolle, A. Tardieux, P. Tardieux, (1981), Experimental determination of nitrogen kinetic isotope fractionation - Some principles - Illustration for the denitrification and nitrification processes, *Plant and Soil* 62(3), 413-430.
- Millington RJ and JP Quirk, (1961), Permeability of porous media, *Faraday Soc.* 57, 1200-1207.
- Michaelis L. and Menten M., (1913), The Kinetics of Invertase Action, *Biochem. Z.* 49, 333, English translation by R.S. Goody and K.H. Johnson.
- Rawls WJ, Brakensiek DL, and Saxton KE. (1982). Estimation of soil water properties. *Trans. ASAE* 25, 1316–1320.
- Sanderson RV and HY Chien, (1973), Simultaneous chemical and phase equilibrium calculation, *Ind. Eng. Chem. Process. Des. Develop.* 12(1), 81-85.
- Saxton KE and Rawls WJ, (2006), Soil Water Characteristic Estimates by Texture and Organic Matter for Hydrologic Solutions, *Soil Sci. Soc. Am. J.* 70, 1569–1578.
- Sierra C.A., Trumbore S.E., Davidson E.A., Vicca S., and Janssens I., (2015), Sensitivity of decomposition rates of soil organic matter with respect to simultaneous changes in temperature and moisture. *Journal of Advances in Modeling Earth Systems*, 7(1), 335-356.
- Tang F.H., and Maggi F., (2016), Breakdown, uptake and losses of human urine chemical compounds in barley (*Hordeum vulgare*) and soybean (*Glycine max*) agricultural plots. *Nutrient cycling in agroecosystems*, 104(2), 221-245.
- Whitman W.G., and Keats J.L., (1922), Rates of absorption and heat transfer between gases and liquids. *Industrial & Engineering Chemistry*, 14(3), 186-191.
- Wolery TJ, (1992), EQ3/6: Software package for geochemical modeling of aqueous systems: Package overview and installation guide (version 8.0), Lawrence Livermore National Laboratory Report UCRL-MA-110662 PT I, Livermore, California.
- Van Genuchten MT, (1980), A Closed-form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils, *Soil Sci. Soc. Am. J.* 44, 892-898.