

A GENERAL-PURPOSE MULTIPHASE AND
MULTICOMPONENT COMPUTATIONAL SOLVER
FOR BIOGEOCHEMICAL REACTION-ADVECTION-
DISPERSION-PROCESSES IN POROUS AND NON-
POROUS MEDIA

FEDERICO MAGGI

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THE UNIVERSITY OF
SYDNEY



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**BRTSIM
BIO-REACTIVE TRANSPORT SIMULATOR VER 1**

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Preface

This document describes the functioning principles and practical use of BRTSim framework at its version 1 stage of development.

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 geophysical domain with an arbitrary number of grid elements nodes 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 species, gaseous and mineral species (in chemical equilibrium with primary species), and biological microbial functional groups with any specific metabolic requirement. Chemical and biochemical reactions can be defined for any kinetics framework and order.

BRTSim version 1 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.

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1. BRTSim structure

BRTSim requires the input file Param.inp, which contains all information needed to solve a computational problem, and produces the output file Time.out, which contains the state variables calculated in each node and at each time, and Flux.out, which contains all cumulative fluxes of phases and compounds through the boundaries (Figure 1). BRTSim itself contains all routines to read Param.inp, assemble the working variables and computational structures, numerically solve flows and reactions by means of various solvers, and produce the output Time.out and Flux.out (Figure 1).

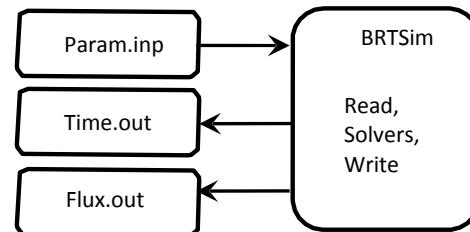


Figure 1. BRTSim overall structure.

1.1. Input file

The input file Param.inp contains various blocks that define the integration time, selected solvers, convergence criteria (block PARAM), and biogeochemical setting. The latter consists of specific blocks that define the materials (block MATERIAL) and their physical and hydraulic characteristics, the initial hydraulic conditions (block ICSTP), the chemical and biological primary aqueous species (block PRI), the secondary aqueous species and mineral species, and their chemical equilibrium with PRI species (block SEC), the gaseous aqueous species and their chemical equilibrium with PRI (block GAS), the kinetic aqueous reactions and their parameters (block KIN), the initial and boundary qualities for the liquid phase relative to PRI species (block ICPRI), the initial conditions for the GAS species (block ICGAS), the domain geometry (block ELEM), and the boundary conditions (block GEN).

These blocks are described in detail in Section 3, but it is important to mention here that each of these blocks allows specify an arbitrary number of items. For example, it is possible to set several materials types and only a few be attributed to the domain nodes in any generic order. Similarly, it is possible to define an arbitrary number of PRI species but, in this case, all will be solved for in the domain. Likewise, it is possible to set an arbitrary number of SEC and GAS species, each one being solved for in the domain as long as they exist in equilibrium with declared PRI species.

1.2. BRTSim solvers

BRTSim reads all needed information from the Param.inp file. If the biogeochemical problem is stated correctly, BRTSim organizes all information and structures arrays of variables that will be processed by various solvers. BRTSim includes 5 solvers: an hydraulic solver for the liquid phase, an hydraulic solver for the gas phase, an advection-dispersion solver for both aqueous (PRI and SEC) and gaseous (GAS) species, a solver for kinetic reactions in the liquid phase (KIN), and a chemical solver for the equilibrium chemical reactions of aqueous complexation (between PRI and SEC), gas dissolution (between PRI and GAS), and mineral dissolution (between PRI and MIN). Of the 5 solvers, 4 require an iterative numerical scheme and must receive instructions on the number of iterations and tolerance through the Param.inp file. With the exception of the solver for the liquid phase, all other solvers can be switched on/off depending on the problem to be solved and the required level of complexity.

1.3. Output files

During computations, BRTSim saves a time table of all state variables in the file Time.out at a specific frequency. The state variables include the element hydraulic properties and the chemical concentrations in each element. Likewise, it also produces a table of cumulative fluxes of boundary conditions according to the number of boundary flows and properties, including chemical components. 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.

2. BRTSim numerical structure and solvers

2.1. Numerical structure

BRTSims solves in a sequential manner for various processes over the solving domain. These processes are the liquid phase flow, gas phase flow, advection-dispersion transport in the liquid and gas phases, kinetic reactions, and equilibrium reactions. The flow chart in Figure 2 shows the sequence of events and the implicit exchange of state variables across each event.

Initialization of the biogeochemical system consists of assigning the initial condition for saturation, pressure and temperature to each element of the solving domain. Next, all primary aqueous species concentrations and gas species partial pressures are assigned to each element. The next step consists of calculating the concentration of all secondary species (SEC and MIN) and the partial pressure of all gaseous species (GAS) in each element. After initialization, dynamic solvers are called sequentially. Each solver takes the updated values of the state variables from the previous solver, and calculates new, updated values of the same or other state variables. With the exception of the first solver for the liquid phase flow, all other solvers in the sequence of events can be switched on or off according to the complexity of the problem, and the user is given full control on which solver is to be used.

Solvers for the liquid and gas phase flows as well as for the equilibrium reactions are based on iterative algorithms to converge to a solution of the flow in a given time increment Δt . 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. The iterative schemes assure mass conservation of both phases and all chemical species in any phase.

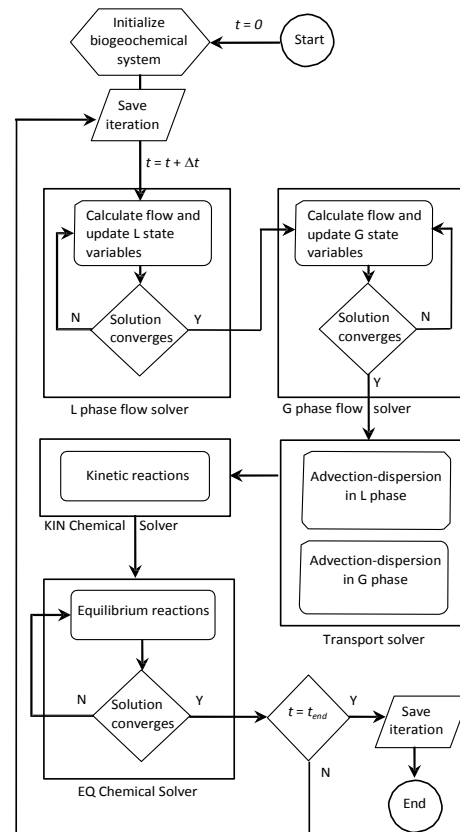


Figure 2. BRTSim sequence of calls to solvers.

2.1. The solving domain and its hydraulic properties

BRTSim solves for a multiphase flow problem over a defined domain. This domain is composed by a set of 1-dimensional 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 two interfaces of that element. The position is referenced to an arbitrary positioning frame. The number of elements is arbitrary as well as any of the geometrical characteristics, which are assigned to each element individually in the ELEM block of the Param.inp.

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_{br} for each phase. As detailed in Section 2.2, BRTSim uses two 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 liquid and gas phases, respectively. Under these circumstances, the effective liquid saturation is written as (Brooks and Corey, 1964)

$$S_L^e = \frac{S_L - S_{Lr}}{1 - S_{Gr} - S_{Lr}} \quad \text{with} \quad 0 \leq S_L^e \leq 1 \quad (1)$$

while the effective gas saturation is

$$S_G^e = 1 - S_L^e \quad (2)$$

These relations are consistently applied in BRTSim because only two phases are taken into account in version 1. The liquid saturation S_L is used as the preferred state variable in the hydraulic solver for the liquid phase, and is used to calculate the liquid capillary pressure P_c .

The relation between the saturation and the liquid potential (and its capillary pressure) can be selected in BRTSim between the Brooks and Corey (1964) and the van Genuchten (1981) models. The Brooks and Corey model describes the liquid capillary pressure $P_c = \rho_L g \psi$ and relative permeability to the liquid phase k_{rL} and gas phase k_{rG} as

$$P_c = \rho_L g \psi (S_L)^{-b} \quad (3)$$

$$k_{rL} = \frac{k_L}{k} = \left(\frac{S_L}{S_L^*} \right)^{2b+3} \quad \text{with} \quad 0 \leq k_{rL} \leq 1 \quad (4)$$

$$k_{rG} = (1 - S_L^*)^2 (1 - S_L^*)^{2b+1} \quad \text{with} \quad 0 \leq k_{rG} \leq 1 \quad (5)$$

where $\psi_s < 0$ is the air-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

$$P_c = - \frac{\rho_L g}{\alpha} (S_L^{-1/m} - 1)^{m-1} \quad (6)$$

$$k_{rL} = \frac{k_L}{k} = (S_L)^{1/2} \left(1 - [1 - (S_L)^{1/m}]^m \right)^2 \quad \text{with} \quad 0 \leq k_{rL} \leq 1 \quad (7)$$

$$k_{rG} = (1 - S_L^{1/2}) \left(1 - [1 - (1 - S_L)^{1/m}]^m \right)^2 \quad \text{with} \quad 0 \leq k_{rG} \leq 1 \quad (8)$$

where $1/\alpha$ is equivalent to the air-entry potential in the Brooks and Corey approach of Eq. (3), and m is an empirical parameter.

The hydraulic conductivity K_β for either phase can be determined from the permeability as

$$K_\beta = k k_{r\beta} \frac{\rho_\beta g}{\mu_\beta} \quad (9)$$

2.2. ss conservation law of phases

In BRTSim version 1, two phases β are described by the equations of state, namely a liquid phase (L) and a gas phase (G). These phases can be any liquid or gas, each defined in the PARAM block of the Param.inp file. The mass $M_{\beta,i}$ of phase β in the element i of volume V_i of the solving domain is

$$M_{i,\beta} = \phi_i S_{i,\beta} \rho_{i,\beta} V_i \quad (10)$$

The mass conservation law for the phase β in the volume V_i of any subset of the solving domain can be written as

$$\frac{\partial}{\partial t} M_{\beta} = -\rho_{\beta} \nabla q_{\beta} + \rho_{\beta} Q_{\beta} \quad (11)$$

where q_{β} is the internal volumetric flux of phase β through the connections of that element, and Q_{β} is the net volumetric flux (source or sink) of that phase through its boundary. The volumetric flux q_{β} corresponds to the product between the Darcy's velocity v_{β} through the interface A between two adjacent elements and is calculated as $q_{\beta} = v_{\beta} A$. The Darcy's velocity is written as

$$v_{\beta} = -k_{\beta} \frac{\nabla (P_{\beta} (S_{\beta}^e) - \rho_{\beta} g z)}{\mu_{\beta}} \quad (12)$$

with g the gravitational acceleration, P_{β} the total pressure of phase β , and z the position relative to a system of reference. If the total pressure of the gas phase is simply P_G , the total pressure for the liquid phase is $P_L = P_G + P_c$ (Brooks and Corey, 1962), with P_c calculated as either Eq. (3) or Eq. (6), and the relative permeability of each phase β calculated as either Eqs. (4-5) or Eqs. (7-8).

In BRTsim version 1, Q_L can be any positive or negative term, while Q_G is always 0, but new capabilities are expected to be included to allow for sources or sinks of the gas phase too.

The numerical scheme used to solve the mass conservation laws for each phase β in Eq. (11) follows the discretization of the mass in each grid element i of the 1-D domain along the z direction, so that the Eq. (11) applied to each element becomes

$$M_{\beta,i}(t + \Delta t) = M_{\beta,i}(t) + \Delta t \cdot \rho_{\beta} (\Delta q_{\beta,i} + Q_{\beta,i}) \quad (13)$$

with the volumetric flux difference at element i represented in Figure 3 and described as

$$\Delta q_{\beta,i} = v_{\beta,i-1,i} A_{i-1,i} - v_{\beta,i,i+1} A_{i,i+1}$$

with $A_{i-1,i}$ and $A_{i,i+1}$ the interface areas between element i and its adjacent elements $i-1$ and $i+1$. The flux between any couple of adjacent elements $i-1$ and i of the solving domain is written as

$$q_{\beta,i-1,i} = v_{\beta,i-1,i} A_{i-1,i} = -k_{\beta,i-1,i} \frac{\left[\Delta (P_{\beta} (S_{\beta}^e) - \rho_{\beta} g z) \right]}{\mu_{\beta} \Delta z} A_{i-1,i}$$

$$q_{\beta,i-1,i} = -k_{\beta,i-1,i} \left(\frac{P_{\beta,i} (S_{\beta,i}^e) - P_{\beta,i-1} (S_{\beta,i-1}^e)}{\Delta z} - \rho_{\beta} g \right) A_{i-1,i} \quad (14)$$

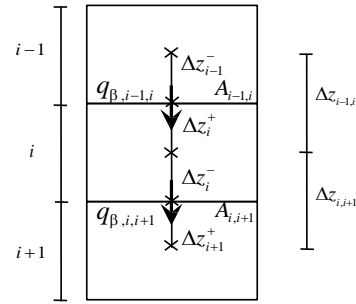


Figure 3. Discretization of mass conservation law in the solving domain.

with the equivalent relative permeability $k_{r\beta,i-1,i}$ of the two elements to phase β described by the weighted average

$$k_{r\beta,i-1,i} = \frac{\Delta z^- k_{i-1,\beta,i-1} + \Delta z^+ k_{i,\beta,i}}{\Delta z_{i-1,i}}$$

where Δz^+ and Δz^- are the distances between the center of mass of the two elements and their interface, while Δz is the distance between their centers of mass.

The discretization of Eq. (13) results in the calculation of the change in mass M_β of phase β in each grid element at time $(t+\Delta t)$ accordingly. Note that the liquid phase is considered to be incompressible, while the gas phase is described as compressible. To assign a pressure and density to the gas phase, the ideal gas law is used

$$P_G V_G = \frac{M_G}{m_G} RT$$

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_K is the absolute temperature in degree Kelvin. The gas mass $M_G(t)$ at time t is therefore determined as

$$M_G = \frac{P_G V_G m_G}{RT_K} \quad (15)$$

The numerical solver solves for the liquid phase first, and assigns the current values of liquid mass and volume to each element based on Eq. (13). Next an updated value of $P_G(t)$ at time t is implicitly calculated as

$$P_G(t) = P_G(t) \frac{V_L(t + \Delta t)}{V_L(t)}$$

and is used in Eq. (15) to determine the updated value of M_G at time t . These values of $M_G(t)$ and $P_G(t)$ are next used in Eq. (13) for the gas phase to determine their values at time $(t+\Delta t)$.

The numerical solution of the discretised mass conservation law of phases in Eq. (13) is carried out with an iterative technique. Currently, one of the mostly used scheme is the modified Picard algorithm (Celia and Bouloutas, 1990); 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 these 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, the Δt of integration may become substantially greater, hence time progression becomes very fast. Overall, computational performance shows that this algorithm moves through time much 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. Additionally, the algorithm implemented in BRTSim allows handling variable saturated conditions, and can simulate exact full saturation $S_\beta = 1$ instead of near saturation approximation (e.g., $S_\beta = 0.999\dots$) as in the existing algorithms.

For the liquid phase, this algorithm consists of four steps in the calculation of the new value of $M_L(t+\Delta t)$ and its corresponding saturation $S_L(t+\Delta t)$. The first step is the calculation of the volumetric fluxes q_L as in Eq. (14). The second step is to determine (1) if $\Delta t \cdot \Delta q_{L,i}$ exceeds the available space in any receiving element i of the solving domain and correct if necessary (for $q_{L,i} > 0$), and (2) if $\Delta t \cdot \Delta q_{L,i}$ exceeds the available supply from the releasing element $i-1$ and correct if necessary (for $q_{L,i} < 0$). 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 saturation, and mass conservation. The third step is to update the fluxes q_L according to the boundary fluxes Q_L . This is done by calculating V_L in each element and determining if $\Delta t Q_L$ exceeds the available space in the receiving 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 $\Delta t Q_L$ is positive and exceeds the total available space in the domain, this flux is limited to the minimum allowed; if the boundary flux $\Delta t Q_L$ is negative and exceeds the available supply in a specific element, this flux is limited to the minimum allowed. Finally, stability of the solution is determined by calculating the current tolerance TOL_c as

$$TOL_c = \sum_i |M_{\beta,i}(t + \Delta t) - M_{\beta,i}(t) - \Delta t \cdot \rho_\beta Q_{\beta,i}| \quad (16)$$

and comparing it to the tolerance TOL set by the user in the PARAM block of the Param.inp file. TOL_c , is expected to be zero when the solution is stable, or be greater than zero when the mass conservation law shows typical oscillatory instabilities. If $TOL_c < TOL$, BRTsim will proceed to a new time step. In any case, and regardless of whether the condition is satisfied, a new value of the integration time step is determined as

$$\Delta t = \Delta t \frac{TOL}{TOL_c}$$

so to increase or decrease the integration time step according to the solution stability. When $TOL_c < TOL$ 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 $ITER$ 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 distance from accepted tolerance. The result is that Δt is variable throughout the simulation time. 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 a constant Δt is to be used. Using a constant Δt excludes from the solver any control of convergence, hence numerical instabilities may arise depending on the internal and boundary fluxes.

The iterative solution of the gas phase follows from that of the liquid phase in that concerns with Δt therein calculated. Because Δt can become relatively great, and the gradient in gas pressure may be steep at times, the gas flow calculated as in Eq. (13) may not meet the Courant criterion. Hence, the ΔP_G calculated after the liquid phase flow is divided into a number of steps and solved for cumulatively over the corresponding Δt fraction. This allows for decreasing steep gradients and a solution accurate to a level of satisfaction determined by the current tolerance for the gas phase calculated as in Eq. (16), and by a maximum number of iterations $ITER$ set by the user in the PARAM block of the Param.inp file. Iterations stop in any case if the cumulative Δt fraction reaches the Δt for that time iteration.

2.3. ss conservation law of components

Each phase β can host any number of chemical components. The total mass M^k of a component k in each element and phase of the solving domain is

$$M_i^k = \phi_i \sum_{\beta} S_{i,\beta} \rho_{i,\beta} V_{i,\beta} X_{i,\beta}^k \quad (17)$$

where X_{β}^k is the mass fraction of component k in phase β in element i . The mass conservation law for M^k can be written similarly to Eq. (11) as

$$\frac{\partial}{\partial t} M_{\beta}^k = -\rho_{\beta} \nabla q_{\beta}^k + \rho_{\beta} Q_{\beta} X_{\beta}^k + R_{\beta}^k \quad (18)$$

where the first term on the right-hand side is the total mass flux of component k in phase β , the second term is the net mass flux (source or sink) of component k through the boundaries, while R_{β}^k is the mass flux of component k in phase β from equilibrium and kinetic reactions. The flux q_{β}^k is in this case expressed as the sum of diffusive and advective flux in that phase through the interface A of two adjacent elements. The total flux is therefore written as

$$q_{\beta}^k = \left(-D_{\beta}^k \cdot \nabla X_{\beta}^k + v_{\beta} X_{\beta}^k \right) A \quad (19)$$

where v_{β} is the Darcy's velocity of phase β of Eq. (12), and D_{β}^k is the diffusivity of component k in phase β . Term R_{β}^k can be written as

$$R_{\beta}^k = V \phi S_{\beta} \rho_{\beta} \frac{dX_{\beta}^k}{dt} \quad (20)$$

where the rate of change in mass fraction X_{β}^k of component k in phase β is detailed later in Sections 2.7 for kinetic (liquid phase only) reactions, while changes due to equilibrium reactions are accounted for as an instantaneous adjustment of M^k by an implicit numerical scheme. Note that no kinetic reactions are implemented in the gas phase in BRTSim version 1.

Discretization of Eq. (18) along the vertical direction z is carried out in a similar way as Eq. (13); consider the phase β , the mass M_{β}^k of component k in phase β , is written for each element of the solving domain as

$$M_{\beta,i}^k(t + \Delta t) = M_{\beta,i}^k(t) + \Delta t \cdot \rho_{\beta} \left(\Delta q_{\beta,i}^k + Q_{\beta,i}^k \right) \quad (21)$$

with

$$\Delta q_{\beta,i}^k = q_{\beta,i-1,i}^k A_{i-1,i} - q_{\beta,i,i+1}^k A_{i,i+1}$$

and with the generic flux from element $i-1$ to element i written as

$$q_{\beta,i-1,i}^k = -\rho_{\beta} D_{\beta,i-1,i}^k \left(\frac{X_{\beta,i}^k - X_{\beta,i-1}^k}{\Delta z} \right) + v_{\beta,i-1,i} X_{\beta,i-1}^k \quad (22)$$

where 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 according to a weighted average

$$D_{\beta,i-1,i}^k = \frac{\Delta z^- \theta_{\beta,i-1} D_{\beta,i-1}^k + \Delta z^+ \theta_{\beta,i} D_{\beta,i}^k}{\Delta z_{i-1,i}} \quad (23)$$

where Δz^+ and Δz^- are the distances between the center of mass of the two elements and their interface, while Δz is the distance between their centers of mass, and where $\theta_\beta = S_\beta \phi$ is used as a reduction factor due to diffusion occurring in a porous medium.

Solution of the mass conservation law for chemicals does not require iterative solvers given that the flux q_β was already calculated in the liquid and gas solvers to a level of satisfaction TOL for stability, and are used in Eq. (21) directly.

2.4. Primary and Secondary aqueous species

The biogeochemical system integrated in BRTSim version 1 is based on the definition of an arbitrary number of chemical primary species (PRI). These can be any real or virtual ion, molecule or substance that will undergo the conservation law of components described in Section 2.3. All primary species are assumed to be in the aqueous phase and are defined in the PRI block of the Param.inp file. Primary aqueous species can undergo an arbitrary number of equilibrium or kinetic reactions of chemical or biochemical nature.

An arbitrary number of secondary aqueous species (SEC) can be defined by means of equilibrium reactions between any primary species and that secondary species. Secondary aqueous species can be any real or virtual ion, molecule or substance. The equilibrium reaction that defines a secondary aqueous species is described by a chemical reaction with negative stoichiometric coefficient indicating reactants and positive stoichiometric coefficients indicating products. The equilibrium reaction is defined also 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 defined as

$$\log K(T_K) = a \log T_K + b + c T_K + \frac{d}{T_K} + \frac{e}{T_K^2} \quad (24)$$

where the coefficients a , b , c , d and e are calculated in BRTSim by least square fitting of experimental values. A comprehensive database of equilibrium reactions is available, for example, in the EQ3/6 V8.2b database (Wolery, 1992). SEC species cannot undergo any other equilibrium or kinetic reactions.

2.5. Mineral and gaseous species

In a similar way as for the secondary aqueous species, an arbitrary number of solid minerals (MIN) and gaseous species (GAS) can be defined by means of equilibrium reactions with primary aqueous species. MIN and GAS species can be any virtual or real molecule or substance. MIN species are treated as SEC species, hence they can be defined in the SEC block of the Param.inp file. GAS species are defined in the GAS block of the Param.inp file. No MIN nor GAS species can be used in other equilibrium or kinetic reactions as these can be rewritten in terms of the corresponding equilibrium PRI species.

2.6. Kinetic aqueous reactions

Kinetic reactions in BRTSim version 1 are assumed to occur only in the liquid phase within each element of the solving domain, and can be written for any kinetic order and with an arbitrary number of Michaelis-

Menten terms, competition terms, and inhibition terms. For a generic reaction with n_O n-order compounds, n_{MM} Michaelis-Menten terms, n_{COM} competitive reactants, n_{INB} inhibition terms, the reaction rate is written as

$$R = r \prod_{n_O} X_{n_O}^{x_{n_O}} \cdot \prod_{n_{MM}} \frac{X_{n_{MM}}}{X_{n_{MM}} + K_{n_{MM}}} \left(1 + \prod_{n_{COM}} \frac{X_{n_{COM}}}{K_{n_{COM}}} \right) \prod_{n_{INB}} \frac{K_{n_{INB}}}{K_{n_{INB}} + X_{n_{INB}}} \quad (25)$$

where r is the reaction rate constant of that reaction. The rate of change in concentration of each component k in that reaction is written as

$$\frac{dX^k}{dt} = x^k R \quad (26)$$

where the stoichiometric coefficient x^k for component k is positive if X^k is a product or negative if X^k is a reactant. Eq. (26) also represents the sink or source of component k in the general conservation law of Eq. (20) for the liquid phase.

After BRTSim solves for the transport of components as in Eq. (21), it updates the value of X^k in each element of the domain according to the kinetic reaction rate of Eq. (25). Discretization of Eq. (25) is carried out through the implicit finite difference of Eq. (26) as

$$X^k(t + \Delta t) = X^k(t + \Delta t) + \Delta t \cdot x^k R \quad (27)$$

where the new value $X^k(t + \Delta t)$ at time $t + \Delta t$ on the right-hand side of Eq. (27) is the result of advection-diffusion transport at time t via Eq. (21) (see also the flow chart in Figure 2).

The reaction rate constant r in Eq. (25) is not described as an explicit function of the temperature in BRTSim version 1, though this capability is expected to be included in future developments. Note that the solver for kinetic reactions does not require an iterative scheme.

2.7. uilibrium reactions

As the kinetic reactions, all equilibrium reactions are solved for in each element of the solving domain, but can involve aqueous, gaseous or mineral species. Equilibrium reactions are defined by an equilibrium constant K at a given temperature according to Eq. (22). For the number n_{PRI} of primary chemical species, a generic equilibrium reaction between components in any phase is written according to the mass-action law as

$$K(T_K) = X_\beta \prod_{n_{PRI}} X_{n_{PRI}}^{x_{n_{PRI}}} \quad (24)$$

where $K(T_K)$ is the equilibrium constant of a temperature T_K , X_β is the secondary species in phase β that is to be solved for (either aqueous, gaseous or mineral), while $X_{n_{PRI}}$ and $x_{n_{PRI}}$ are the primary species and their stoichiometric coefficients, respectively. These can be either positive (if products) or negative (if reactants). When X_β is an aqueous species (SEC or MIN), the concentration is used, while the partial pressure fraction is used if it is a gaseous species.

The solution of Eq. (24) may be complicated by the stoichiometric coefficients, which may lead to a highly nonlinear equation that cannot always be solved algebraically. Hence, the equilibrium constant is written as the ratio between the rate constants $k_f = 10^{\log K}$ and $k_b = 1$ for the forward and backward reactions. Each one of the two reactions are solved as kinetic reactions and follow the same discretization

already introduced in Section 2.6. However, differently from kinetic reactions, an iterative scheme is used to reiterate both forward and backward reactions until the relative difference between the current $\log K_c$ value of the equilibrium between all species and the assigned equilibrium $\log K$ becomes smaller than a desired tolerance TOL . This assures that all components are always in equilibrium.

Note that for equilibrium reactions, the mass fraction of the solvent (water in BRTSim version 1) is set to 1 always, so that it does not affect equilibrium.

3. The Param.inp file

The Param.inp file controls all capabilities 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 block, each one having specific objectives. Below is given a brief description of each block.

3.1. PARAM block

The block PARAM (Figure 4) 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, which are defined below

```

Project title
%---- PARAM (PARAM)-----
tini[d]      tend[d]      dt[d]      Vdt      mindt[d]      maxdt[d]      g[m/s2]      rho_l[kg/m3]20      mmol_g[kg/mol]
0            30            0.001      1          0.001         0.5           9.81e-0      998                28.97e-3
GAS  TR  EQ  KIN  LIQ_GAS_FEED  LIQ_CHEM_FEED  ISAVE
0      1  0  0    0              0              10
MIN_Q_LIQ[m3/s]  ITER_LIQ  TOL_LIQ  ITER_GAS  TOL_GAS  ITER_TR  TOL_TR  ITER_EQ  TOL_EQ
1e-30      100    2e-3    100      1e-7     20      1e-6    10      5e-2
    
```

Figure 4. Example of PARAM block.

PARAM.1		
	tini, tend	Initial and end simulation time
	dt	Initial value for the integration time step
	Vdt	Variable Δt . If Vdt = 1, variable Δt will be used and Δt will change at each time iteration
	mindt, maxdt	Minimum and maximum Δt . Used only if Vdt = 1
	G	Gravitational acceleration
	rho_L	Specific density of liquid phase (solvent) at 20°C. In BRTSim version 1, the solvent is water. The specific density is recalculated as a function of temperature based on experimental data in Chin (2006). Although not explicit in the Param.inp, BRTSim also calculates the viscosity μ_L based on the same data.
	mmol_G	GAS molar mass at 20°C. In BRTSim version 1, the gas is air. Although not explicit in the Param.inp, BRTSim also calculates the viscosity μ_G as a function of temperature based on experimental data in Chin (2006).

PARAM.2		
	GAS	G as phase solver. Solves for the gas phase if GAS = 1
	TR	Aadvection-dispersion solver. Solves for advection-dispersion in the gas and liquid phase if TR = 1.
	EQ	Equilibrium reaction solver. Solves for equilibrium reactions if EQ = 1.
	KIN	Kinetic reaction solver. Solves for kinetic reactions if KIN = 1.
	LIQ_GAS_FEED	Feedback for liquid-gas phases interactions. If LIQ_GAS_FEED = 1 than the liquid pressure is calculated as $P_L = P_c + P_G$, otherwise it is $P_L = P_c$ only.
	LIQ_CHEM_FEED	Feedback for chemical-liquid interaction. If LIQ_CHEM_FEED = 1 solves for chemical osmotic pressure in the liquid phase and the liquid pressure is calculated as $P_L = P_c + P_G + P_o$.
	ISAVE	Saving frequency. 1 time iteration is saved in the Time.out file every ISAVE iterations.

PARAM.3		
	MIN_Q_LIQ	Minimum internal flow rate for calculation
	ITER_LIQ	Maximum number of iterations for convergence of the L phase flow
	TOL_LIQ	Minimum acceptable tolerance for convergence of the L phase flow
	ITER_GAS	Maximum number of iterations for convergence of the G phase flow
	TOL_GAS	Minimum acceptable tolerance for convergence of the G phase flow
	ITER_TR	Maximum number of iterations for convergence of transport in L and G phases
	TOL_TR	Minimum acceptable tolerance for convergence of transport in L and G phases
	ITER_EQ	Maximum number of iterations for convergence of equilibrium reactions
	TOL_EQ	Minimum acceptable tolerance for convergence of equilibrium reactions

3.2. PARALLEL block

This block (Figure 5) is currently under development for future applications and is not used in BRTSim version 1.

```
%---- PARALLEL (PAR) -----  
WORKERS  TR_PRI  TR_SEC  TR_GAS  
0         0       0       0
```

Figure 5. Example of PARALLEL block.

3.3. MATERIAL block

This block (Figure 6) 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. The field in this block are described in the following.

```
%--- MATERIAL (MAT) -----
1: Cosby (psi_s b)
2: Van Genuchten (alpha m n = -1/(m-1) )
NAM EQU SAND SILT CLAY rho_m[kg/m3] phi[-] k[m2] (1)b[-] (1)psi_s[m] (2)alpha[1/Pa] (2)m[-] SLr[-] Sgr[-]
ATMOS 1 100 0 0 -999 0.9999 1e-7 1e-10 1e5 -999 -999 1e-5 0.9999
SOIL1 1 95 3 2 -999 -999 -999 -999 -999 -999 -999 -999 0.1
SOIL2 1 80 10 10 -999 -999 -999 -999 -999 -999 -999 -999 0.1
SOIL3 1 80 10 10 -999 -999 -999 -999 -999 -999 -999 -999 0.1
SOIL1vg 2 50 43 7 -999 -999 -999 -999 -999 -999 -999 -999 0.1
```

Figure 6. Example of MATERIAL block.

MATERIAL.1		
NAM,		Name of material. This is a user-defined tag.
EQU,		Model used for the saturation-potential relation. EQU = 1 uses the Brooks and Corey model, EQU = 2 uses the van Genuchten model.
SAND, SILT, CLAY		Sand, silt and clay textural mass fractions percent.
rho_m		Mineral density. If -999, it is estimated from Table 1.
phi,		Porosity. If -999, it is estimated porosity from regressions against the SSC fractions using Cosby et al, (1984).
k,		Absolute permeability. -999 estimated absolute permeability from regressions against the SSC fractions using Cosby et al, (1984) at conditions: 20°C, water, at 9.81 m/s ² gravitational acceleration.
b,		Pore volume distribution index in the Brooks and Corey model. If -999, it is estimated from regressions against the SSC fractions using Cosby et al, (1984).
psi_s		Air-entry suction in the Brooks and Corey model. If -999, it is estimated from regressions against the SSC fractions using Cosby et al, (1984).
alpha		van Genuscthem empirical parameter. If -999, it is estimated from Table 1
m		van Genucthem empirical parameter. If -999, it is estimated from Table 1
SLr		Liquid residual saturation. If -999, it is estimated from Table 1
SGr		Gas residual saturation. If -999, it is assumed to be 0.2

Table 1. Soil parameters.

	^(a) Textural fractions			^(b) Mineral density	^(c) Total porosity	^(c) Permeability	^(a) Brooks and Corey parameters		van Genuchten parameter		Residual ^(c) liquid and ^(e) gas saturation	
	Sand	Silt	Clay	rho_m	phi	k	b	psi_s	m	α	S _{lr}	S _{gr}
	%	%	%	[kg/m ³]	[-]	[m ²]	[-]	[m]	[-]	[1/Pa]	[-]	[-]
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) From Cosby et al., (1984)
^(b) From Saxton and Rawls (2006) and Rawls et al., (1982)
^(c) From Rawls et al., (1982)
^(d) From Ghanbarian-Alavijeh et al., (2010)
^(e) Assumed

3.4. ICSTP block

This block (Figure 7) defines the initial conditions for liquid saturation, temperature and 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.

```

%---- INITIAL SATURATION TEMPERATURE PRESSURE CONDITIONS (ICSTP) -----
NAM      S1      T [oC]      P [Pa]
STatm    0.1     20      101325
ST01     0.2     20      101325
ST02     0.65    20      101325
ST03     0.54    20      101325
ST04     0.5     20      150000
    
```

Figure 7. Example of ICSTP block.

ICSTP.1		
NAM,		Name of initial conditions. This is a user-defined tag to be called in the ELEM block.
S1,		Initial liquid saturation. If $S_l < S_{lr}$, then $S_l = S_{lr}$. If $S_l > 1 - S_{gr}$, then $S_l = 1 - S_{gr}$ is used.
T,		Initial temperature in [°C]
P,		Initial gas pressure in [Pa]

3.5. PRI block

This block (Figure 8) defines the primary aqueous species (PRI) of the biogeochemical system. An arbitrary number of PRI can be defined.

```

*----- PRIMARY ACQUEOUS SPECIES (PRIM) -----
NAM      Mobility  mmass[g/mol]  Ds[m2/s]
H2O(aq)   1           18            1e-9
X1        1           80            1e-9
X2        1          23.08          1.12e-9
X3        0           21.0          1e-9
    
```

Figure 8. Example of PRI block.

PRI.1		
	NAM,	Name of primary aqueous species.
	Mobility,	Mobility = 0 implies that PRI is not subject to advection-diffusion; if Mobility = 1, PRI is subject to advection-diffusion.
	mmass,	Molar mass of PRI
	Ds	Diffusion coefficient in the liquid phase

3.6. SEC block

This block (Figure 9) defines the secondary species (SEC) of the biogeochemical system, which can be both aqueous and mineral species. An arbitrary number of SEC can be defined, but all have to be written as a function of PRI species.

```

%--- SECONDARY AQUEOUS SPECIES (SEC) -----
NAM      Mobility  mmass[g/mol]  Ds[m2/s]  REACTION          logK[0  25  60  100  150  200  250  300]oC
OH-      1          17          1e-9      -1 H2O(aq)  1 H+  1 OH-    -14.9398 -13.9951 -13.0272 -12.2551 -11.6308 -11.2836 -11.1675 -11.3002
NO3-(ad) 0          62          1e-9      -1 NO3-  1 NO3-(ad)  2          2          2          2          2          2
NH4+(ad) 0          18          1e-9      -1 NH4+  1 NH4+(ad)  0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0
NH3(aq)  1          17          1e-9      -1 NH4+  1 H+  1 NH3(aq) -10.0691 -9.2410 -8.2847 -7.4010 -6.5156 -5.7992 -5.1995 -4.6767
    
```

Figure 9. Example of SEC block.

SEC.1		
NAM,		Name of secondary species.
Mobility,		Mobility = 0 implies that SEC is not subject to advection-diffusion; if Mobility = 1, SEC is subject to advection-diffusion.
mmass,		Molar mass of SEC
Ds,		Diffusion coefficient in the liquid phase
Reaction,		Defines the equilibrium reaction as a sequence of stoichiometric coefficients and components. Stoichiometric coefficients are negative for reactants and positive for products. Stoichiometric coefficients 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.
logK,		Values of logK of equilibrium at eight different temperatures.

3.7. GAS block

This block (Figure 10) defines the secondary gaseous species (GAS) of the biogeochemical system, which are in equilibrium with the primary aqueous species. An arbitrary number of GAS can be defined, but all have to be written as a function of PRI species.

```

%--- GAS SPECIES (GAS) -----
NAM      Mobility  mmass[g/mol]  Ds[m2/s]  REACTION      logK[0  25  60  100  150  200  250  300]oC
O2(g)    1         32                1e-6       -1 O2(aq)     1 O2(g)    2.6570  2.8980  3.0630  3.1080  3.0350  2.8740  2.6490  2.3540
CO2(g)   1         31.999           1e-6       -1 X2        1 CO2(g)   2.6567  2.8      3.0633  3.1076  3.0354  2.8742  2.6488  2.3537
    
```

Figure 10. Example of GAS block.

GAS.1		
	NAM,	Name of gaseous species.
	Mobility,	Mobility = 0 implies that GAS is not subject to advection-diffusion; if Mobility = 1, GAS is subject to advection-diffusion.
	mmass,	Molar mass of GAS
	Ds,	Diffusion coefficient in the gas phase
	Reaction,	Defines the equilibrium reaction as a sequence of stoichiometric coefficient and components. Stoichiometric coefficients are negative for reactants and positive for products. Stoichiometric coefficients 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.
	logK,	Values of logK of equilibrium at eight different temperatures.

3.8. KIN block

This block (Figure 11) defines the aqueous kinetic reactions (KIN) in the biogeochemical system. An arbitrary number of KIN can be defined, but all have to be written as a function of PRI species.

```

%---- KINETIC AQUEOUS REACTIONS (KIN) -----
NUM      RATE CONSTANT      REACTION
1         1e-6                -0.6 O2(aq) -0.8 X2  1.25 X4
  n-Order  0
  MM       2   O2(aq) 2e-3  X2 3e-3
  Compet  1   X2 1e-2
  Inhib    0
2         1e-6                -1 X4    0.3 X2
  n-Order  1   X4 1
  MM       0
  Compet  0
  Inhib    0
    
```

Figure 11. Example of KIN block.

KIN.1		
NUM,		Identification number for the KIN reaction.
Rate Constant		Reaction rate constant
Reaction		Defines the KIN reaction as a sequence of stoichiometric coefficients and components. Stoichiometric coefficients are negative for reactants and positive for products. Stoichiometric coefficients 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.

KIN.2		
n-Order,		Number of n-th order kinetic products. This is followed by the primary species (if any) and its power (see example in Figure 11)
MM,		Number of Michaelis-Menten kinetic terms. This is followed by a sequence of PRI and its Michaelis-Menten constant (see example in Figure 11)
Compet,		Number of competition terms. This is followed by a sequence of PRI and its competition constant, which corresponds to the Michaelis-Menten constant in the competing reaction for that PRI
Inhib,		Number of inhibition terms. This is followed by a sequence of PRI and its inhibition constant

3.9. ICPRI block

This block (Figure 12) defines the initial conditions for PRI. 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.

```

%---- INITIAL and BOUNDARY PRIMARY SPECIES CONDITIONS (ICPRI) [mol/L] -----
NAM      O2 (aq)  H2O(aq)  H+      X2      X3      X4      xxx7      H2O(vv)
ATMqua   1e-10   1        1e-7    1e-10   1e-10   1e-10   1e-10     55.56
ICPR00   1e-10   1        1e-7    1e-10   1e-10   1e-10   1e-10     55.56
ICPR01   1e-10   1        1e-7    1.6e-3  4.3e-3  2.5e-3   1e-3      55.56
ICPR02   1e-3     1        1e-7    1e-10   1e-10   1e-10   1e-10     55.56
ICPR03   3.4e-3   1        1e-7    1.2e-3  3e-3    1e-10   1e-10     55.56
ICPR04   1.6e-3   1        1e-7    1.2e-3  1e-10   1e-10   1e-10     55.56
BC00     1e-10   1        1e-7    1e-10   1e-10   1e-10   1e-10     55.56
BC01     1.4e-3   1        1e-7    1e-10   1e-10   1e-10   1e-10     55.56
BC04     1e-3     1        1e-7    3e-03   1e-10   1e-10   1e-10     55.56
    
```

Figure 12. Example of ICPRI block.

ICPRI.1		
	NAM,	Name of ICPRI.
	ICPRI list	Following NAM declaration, a list of PRI organized in column is to be written and an initial concentration is to be given to each PRI. The list may not follow the same order by which PRI have been declared in PRI. Also, if more PRI are listed, only a number of columns equal to the actual number of declared PRI will be read. BRTSim will provide a warning in this case.

3.10. ICGAS block

This block (Figure 13) 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.

```

$---- INITIAL GAS SPECIES (ICGAS)  [-] partial pressure fraction -----
NAM          O2 (g)      H2O (g)      CO2 (g)
ICGAS00      1e-10      1e-10      1e-10
ICGAS01      0.21       3e-2       1e-5
    
```

Figure 13. Example of ICGAS block.

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, only a number of columns equal to the actual number of declared GAS will be read. BRTSim will provide a warning in this case.

3.11. ELEM block

This block (Figure 14) defines the solving domain, including assigning properties and initial conditions to each individual element. The number of element is arbitrary, but because BRTSim version 1 solves for a 1-dimensional problem, it is assumed that declared elements are connected sequentially to each other.

```

-----
!---- GRID (ELEM) -----
ELEM *NAM1 MAT1 MAT2 DZ[Z] Z[m] DZ+[m] DZ-[m] A[m2] V[m3] ICSTP1 *ICSTP2 ICSTP3 *ICPRI1 ICPRI2 ICPRI3 ICGAS1 ICGAS2 *ICGAS3
F01 SOILL SOILL SOILL 5.000e-2 0.525 2.5000e-2 2.5000e-2 1 5.000e-2 ST01 ST01 ST01 ICFR01 ICFR02 ICFR03 ICGAS0 ICGAS0 ICGAS0
F02 SOILL SOILL SOILL 5.000e-2 0.575 2.5000e-2 2.5000e-2 1 5.000e-2 ST01 ST01 ST01 ICFR01 ICFR03 ICFR04 ICGAS0 ICGAS0 ICGAS0
F03 SOILL SOILL SOILL 5.000e-2 0.625 2.5000e-2 2.5000e-2 1 5.000e-2 ST01 ST01 ST01 ICFR01 ICFR03 ICFR04 ICGAS0 ICGAS0 ICGAS0
F04 SOILL SOILL SOILL 5.000e-2 0.675 2.5000e-2 2.5000e-2 1 5.000e-2 ST01 ST01 ST01 ICFR01 ICFR03 ICFR04 ICGAS0 ICGAS0 ICGAS0
F05 SOILL SOILL SOILL 5.000e-2 0.725 2.5000e-2 2.5000e-2 1 5.000e-2 ST01 ST01 ST01 ICFR01 ICFR03 ICFR04 ICGAS0 ICGAS0 ICGAS0
F06 SOILL SOILL SOILL 5.000e-2 0.775 2.5000e-2 2.5000e-2 1 5.000e-2 ST01 ST01 ST01 ICFR01 ICFR03 ICFR04 ICGAS0 ICGAS0 ICGAS0
F07 SOILL SOILL SOILL 5.000e-2 0.825 2.5000e-2 2.5000e-2 1 5.000e-2 ST01 ST01 ST01 ICFR01 ICFR03 ICFR04 ICGAS0 ICGAS0 ICGAS0
F08 SOILL SOILL SOILL 5.000e-2 0.875 2.5000e-2 2.5000e-2 1 5.000e-2 ST01 ST01 ST01 ICFR01 ICFR03 ICFR04 ICGAS0 ICGAS0 ICGAS0
F09 SOILL SOILL SOILL 5.000e-2 0.925 2.5000e-2 2.5000e-2 1 5.000e-2 ST01 ST01 ST01 ICFR01 ICFR03 ICFR04 ICGAS0 ICGAS0 ICGAS0
F10 SOILL SOILL SOILL 5.000e-2 0.975 2.5000e-2 2.5000e-2 1 5.000e-2 ST01 ST01 ST01 ICFR01 ICFR03 ICFR04 ICGAS0 ICGAS0 ICGAS0

```

Figure 14. Example of ELEM block.

ELEM.1		
	NAM,	Name of element
	MAT1, MAT2, MAT3	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. This capability allows switching from one setting to another by starring the chosen MAT column.
	DZ,	Thickness of ELEM
	Z,	Position of the center of mass of ELEM
	DZ+,	Distance from center of mass of ELEM to upper interface
	DZ-,	Distance from center of mass of ELEM to lower interface
	A,	Surface area of ELEM interfaces
	V,	Volume of ELEM
	ICSTP1, ICSTP2, ICSTP3	Assign ICSTP to ELEM by calling the NAM of a 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. This capability allows switching from one setting to another by starring the chosen ICSTP column.
	ICPRI1, ICPRI2, ICPRI3	Assign ICPRI to ELEM by calling the NAM of a 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. This capability allows switching from one setting to another by starring the chosen ICPRI column.
	ICGAS1, ICGAS2, ICGAS3	Assign ICGAS to ELEM by calling the NAM of a 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. This capability allows switching from one setting to another by starring the chosen ICGAS column.

3.12. GEN block

This block (Figure 15) 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.

```

%---- GENER (GEN) -----
NAM      ELEM  PHASE  TABLE      TIME[s]  RATE[m3/s]  FAC  *QUAL1  QUAL2  QUAL3
GEN08    F40   L      -            0        -5.58E-8    1    ICPR01  ICPR01  ICPR01
Precip   F01   L      Table_Precip.txt  3         4          0.6  BC04    ICPR01  ICPR01
    
```

Figure 15. Example of GEN block.

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 relative to L phase. BRTSim version 1 does not allow GEN of G phase yet.
TABLE	If TABLE = '-' then see next field for constant GEN rate, otherwise, specify the file name and extension where BRTSim finds a table of time and rates for GEN. This instance is used when variable GEN is or needs to be used. See Figure 16 for an example of TABLE. TABLE is a .TXT file with 2 lines as a header, the first defining the vectors and the second defining the units.
TIME	Initial time of application of a constant GEN rate. 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. If TABLE is a file, RATE is the column in the specified file where a rate vector is allocated.
FAC	Multiplicative factor for RATE, regardless of whether RATE is constant or variable (from a table). This can be any positive or negative number, as well as 0. FAC 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.
QUAL1, QUAL2, QUAL3	Assign ICPRI to GEN by calling the NAM of a 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 chosen ICPRI column.

Time	Precip	Time	Precip	Evap
[d]	[mm]	[s]	[m3/s]	[m3/s]
0	0	0	0	0
1	0	86400	0	0
2	0	172800	0	0
3	27.7	259200	3.20602E-07	0.000566217
4	0	345600	0	0
5	0	432000	0	0
6	79.5	518400	9.20139E-07	0.000959239
7	6.6	604800	7.63889E-08	0.000276385
8	9.7	691200	1.12269E-07	0.000335065
9	0	777600	0	0
10	0	864000	0	0
11	0	950400	0	0
12	0	1036800	0	0
13	0	1123200	0	0
14	0	1209600	0	0

Figure 16. Example of TABLE used in the GEN block.

4. 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.

5. The Flux.out file

This file collects all cumulative mass fluxes from the boundary as per instructions in the GEN block. 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 add outputs with the frequency chosen by the used with the parameter ISAVE in the filed PARAM.2 of the PARAM block.

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7. References

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