

Denitrification example

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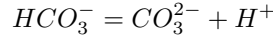
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1 Introduction

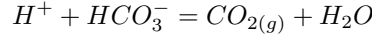
We consider a simplified denitrification process in a clean aquifer, where polluted water enters through the inflow. The aqueous species are H^+ , Cl^- , $N_{2(aq)}$, $CH_2O_{(aq)}$, HCO_3^- , $O_{2(aq)}$, NO_3^- , CO_3^{2-} , and the gases are $CO_{2(g)}$, $O_{2(g)}$ and $N_{2(g)}$.

We consider the following equilibrium reactions.

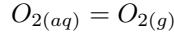
- Bicarbonate dissociation:



- Atmospheric CO_2 :

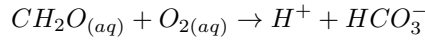


- Atmospheric O_2 :

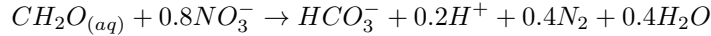


and kinetic reactions:

- Aerobic oxidation of DOC:



- Denitrification ($NO_3^- \rightarrow N_2$):



The kinetic reaction rates are governed by the Monod formula ([Monod \(2012\)](#)):

$$r_{K,1} = \mu_1 \frac{[CH_2O_{(aq)}]}{k_{DOC} + [CH_2O_{(aq)}]} \frac{[O_{2(aq)}]}{k_{O_2} + [O_{2(aq)}]}$$
$$r_{K,2} = \mu_2 \frac{I_{O_2}}{I_{O_2} + [O_{2(aq)}]} \frac{[CH_2O_{(aq)}]}{k_{DOC} + [CH_2O_{(aq)}]} \frac{[NO_3^-]}{k_{NO_3^-} + [NO_3^-]}$$

The boundary water is in equilibrium with atmospheric O_2 and CO_2 , therefore the stoichiometric matrix at the inflow is

$$\mathbf{S}_e^{inf} = \begin{pmatrix} H^+ & Cl^- & N_{2(aq)} & CH_2O_{(aq)} & HCO_3^- & O_{2(aq)} & NO_3^- & CO_3^{2-} & H_2O & CO_{2(g)} & O_{2(g)} \\ -1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & -1 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}$$

since there are no kinetic reactions. In the domain, there are only aqueous reactions, therefore the equilibrium stoichiometric matrix in the domain is

$$\mathbf{S}_e^{dom} = \begin{pmatrix} H^+ & Cl^- & N_{2(aq)} & CH_2O_{(aq)} & HCO_3^- & O_{2(aq)} & NO_3^- & CO_3^{2-} & H_2O \\ 1 & 0 & 0 & 0 & -1 & 0 & 0 & 1 & 0 \end{pmatrix}$$

18 and the kinetic stoichiometric matrix in the domain is

$$\mathbf{S}_K = \begin{pmatrix} H^+ & Cl^- & N_{2(aq)} & CH_2O_{(aq)} & HCO_3^- & O_{2(aq)} & NO_3^- & CO_3^{2-} & H_2O \\ 1 & 0 & 0 & -1 & 1 & -1 & 0 & 0 & 0 \\ 0.2 & 0 & 0.4 & -1 & 1 & 0 & -0.8 & 0 & 0.4 \end{pmatrix}.$$

19 There are 7 primary species; therefore, the component matrix is

$$\mathbf{U} = (\mathbf{I} \mid \mathbf{U}_2)$$

20 where

$$\mathbf{U}_2 = \begin{pmatrix} CO_3^{2-} \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}.$$

21 We choose a mesh made of 11 nodes with a separation of $0.1m$ between them. The time step (in days) is 10^{-1} . To solve
 22 transport, we consider $\phi = 0.5, q = 5m/d, D = 0.25m^2/d$. Regarding the boundary conditions, we prescribe the mass flux at
 23 the inflow and we assume no dispersive flux at the outflow. Moreover, we have considered 1 initial water ("clean" aquifer)
 24 and 1 inflow water ("polluted" water in equilibrium with atmospheric CO_2 and atmospheric O_2). The initial and boundary
 25 concentrations are in Table 1.

	initial	inflow
H^+	10^{-7}	10^{-8}
Cl^-	10^{-16}	10^{-3}
$N_{2(aq)}$	$5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
$CH_2O_{(aq)}$	10^{-5}	$2 \cdot 10^{-3}$
HCO_3^-	10^{-3}	$5.3761 \cdot 10^{-4}$
$O_{2(aq)}$	10^{-6}	$2.5295 \cdot 10^{-4}$
NO_3^-	10^{-5}	10^{-3}

Table 1: Primary species concentrations of initial and boundary waters (in molalities)

26 2 Data Input

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'TITLE OF THE PROBLEM: Denitrification with 2 reactions'
'-----'
'DEFINITION OF THE GEOCHEMICAL SYSTEM'
'PRIMARY AQUEOUS SPECIES'
'h2o(p) '
'h+'
'cl-'
'n2(aq) (p) '
'ch2o(aq) '
'hco3-'
'o2(aq) '
'no3-'
'*'
'AQUEOUS COMPLEXES'
'co3-2'
'*'
'MINERALS'
'*' .true. .true.
'GASES'
'co2(g) ' .true. .true.           ! name of gas, flag equilibrium, flag constant activity
'o2(g) ' .true. .true.
'n2(g) ' .true. .true.
'*' .false. .false.
'REDOX REACTIONS'
'aerobic oxidation of DOC' .false.      ! name of redox reaction, flag equilibrium
'denitrification' .false.
'*' .false.
'-----'
'end'

```

Figure 1: Chemical system file

3 Pseudocode

1. Define path to databases
2. Define path to input files for denitrification problem
3. Choose option for transport: either compute or read lambdas.
 - If option is to compute lambdas:
 - Read transport data: call subroutine *initialise_transport_1D_transient_RT*
 - Allocate transport arrays: call subroutines *allocate_arrays_PDE_1D* and *allocate_conc*
 - Compute lambdas: call *compute_mixing_ratios_Delta_t_homog*
 - Set transport attribute in reactive transport object: call *set_transport_trans*
 - If option is to read lambdas:
 - Set transport attribute in reactive transport object: call *set_transport_trans*
 - Read time discretisation: call *read_time_discretisation*
 - Read transport data to apply WMA: call *read_transport_data_WMA*
4. Read chemistry: call *read_chemistry*
5. Call reactive mixing solver: there will be different solvers depending on the model for activity coefficients (ideal or not) and the WMA method (lumped or consistent):
 - If lumped and ideal: call *solve_reactive_mixing_ideal_lump*
 - If consistent and ideal: call *solve_reactive_mixing_ideal_cons*
 - If lumped and non-ideal: call *solve_reactive_mixing_lump*
 - If consistent and non-ideal: call *solve_reactive_mixing_cons*
6. Set chemistry attribute in reactive transport object: call *set_chemistry*
7. Write data and results: call *write_RT_1D*

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'TITLE OF THE PROBLEM: Denitrification with 2 reactions'
'-----'
'INITIAL AND BOUNDARY WATER TYPES'
0                                ! activity coefficients model
2                                ! n° water types
1      25.0                      ! iwtype initial, temp (C)
'entrada'                       ! name
'      icon          guess      ctot      constrain'
'h+'          1      1d-8      1d-8      ''
'cl-'         1      1d-3      1d-3      ''
'hco3-'       4      1d-6      3.5d-4      'co2(g) '
'o2(aq) '     4      1d-4      2d-1      'o2(g) '
'ch2o(aq) '   1      2d-3      2d-3      ''
'h2o(p) '     1      1d-9      1d-9      ''
'no3-'        1      1d-3      1d-3      ''
'n2(aq) (p) ' 1      5d-4      5d-4      ''
'*'           0      0.0      0.0      ''
2      25.0                      !iwtype initial, temp (C)
'dominio'                       ! name
'      icon          guess      ctot      constrain'
'h+'          1      1d-7      1d-7      ''
'cl-'         1      1d-16     1d-16     ''
'hco3-'       1      1d-3      1d-3      ''
'o2(aq) '     1      1d-6      1d-6      ''
'ch2o(aq) '   1      1d-5      1d-5      ''
'h2o(p) '     1      1d-9      1d-9      ''
'no3-'        1      1d-5      1d-5      ''
'n2(aq) (p) ' 1      5d-4      5d-4      ''
'*'           0      0.0      0.0      ''
'-----'
'INITIAL AND BOUNDARY GAS ZONES'
1                                !ngtype= number of gas zones
1      25      1d9              !igtype, temp (°C), volume
'atmosphere'                   ! name of gas zone
'gas          partial pressure' ! pressure in atm
'co2(g) '     3.5d-4
'o2(g) '      2d-1
'n2(g) '      7.99965d-1
'*'           0.00
'-----'
'end'

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Figure 2: Local chemistry file

References

Monod, J. (2012). The growth of bacterial cultures. *Selected Papers in Molecular Biology by Jacques Monod*, 139:606.

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'TITLE OF THE PROBLEM: Denitrification with 2 reactions'
'-----'
'CHEMICAL OPTIONS'
1      ! Chemical input data option (1: CHEPROO-based, 2: PHREEQC, 3:PFLOTRAN)
1      ! Option to compute Jacobians (0:incremental coefficients, 1:analytically)
.true.  ! Lumping flag
2      ! Consistent WMA option (1: explicit, 2: upstream to downstream)
2      ! Estimation of downstream waters reaction amounts
2      ! Average of reaction rates option (1: concentrations, 2: reaction rates)
'-----'
'end'

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Figure 3: Chemical options