Model Formulation

ODE Models

There were two alternative formulations envisaged for the observed behaviour of the experiments' concentrations.

1. A simple 0th order model (constant denitrification rate model), where denitrification occurs independently of the other variables, and thus is a function of matrix solid-phase electron donors.

2. A more complex model, that includes the previous model, but assumes that part of the DOC is bioavailable and reacts with nitrate via Michaelis-Mentem kinetics. This DOC, is also sorbed in the matrix, thus sorbing reactions occur.

1. Constant Denitrification Model

The constant denitrification model describes the rate of change of nitrate concentration (NO_3^-) over time.

Model Rates

- r_{NO3^-} is the zero-order rate of NO_3^- reduction (mol L ^{1} day ^{1}).

- r_{N2O} is the rate of N2O consumption (mol L ^{1} day ^{1}).

- r_g is the gas exchange rate (mol L ^{1} day ^{1}).

Differential Equations

$$\frac{d[NO_3^-]}{dt} = -r_{NO3^-}$$

$$\frac{d[N2O_{water}]}{dt} = \frac{1}{2}r_{NO3^-} - r_{N2O} + r_g(c_gH - c_w)$$

$$\frac{d[N2O_{gas}]}{dt} = -\frac{r_g(c_gH - c_w)}{H}$$

where:
- c_g is the gas concentration of N2O in ppmv.
- c_w is the concentration of N2O in water (mol/L).
- H is Henry's law constant for N2O (mol /(L atm)).

2. More complex model: DOC and NO3- Dynamics Model

The DOC and $NO3^-$ dynamics model describes the rates of change of nitrate (NO_3^-), bioavailable dissolved organic carbon (DOC^l), and sorbed DOC concentrations over time.

Model Rates

- r_{NO3^-} is the zero-order rate of NO_3^- reduction (mmol L ^{1} day ^{1}).
- r_{DOC} is the rate of DOC denitrification by Michaelis-Menten kinetics, given by:

$$r_{DOC} = r_{DOC^l}^{max} \frac{[DOC^l]}{K_{DOC} + [DOC^l]} \cdot \frac{[NO_3^-]}{K_{NO3^-} + [NO_3^-]}$$

- $r_{transfer}$ is the first-order rate of DOC transfer to the sorbed phase, given by:

$$r_{transfer} = \alpha \cdot (c_{eq} - [DOC^l]) \cdot \tanh([\text{sorbed DOC}])$$

- r_{DOC}^{max} is the maximum rate of DOC denitrification (mmol L ^{1} day ^{1}).
- α is the first-order rate constant for DOC transfer to the sorbed phase (day ^{1}).
- c_{eq} is the equilibrium concentration of labile DOC in water (mmol L ^{1}), given by $c_{eq} = K_d \cdot [\text{sorbed DOC}]$.
- K_{DOC} and K_{NO3} are the half-saturation constants for DOC and NO_3^- respectively (mmol L ^{1}).
- $[DOC^l]$ and $[NO_3^-]$ are the concentrations of DOC and NO_3^- respectively (mmol L ^{1}).
- [sorbed DOC] is the concentration of sorbed DOC (mmol L ^{1}).

Differential Equations

$$\frac{d[NO_3^-]}{dt} = -r_{NO3} - r_{DOC}$$

$$\frac{d[DOC^l]}{dt} = -\frac{5}{4} r_{DOC} + r_{transfer}$$

$$\frac{d[\text{sorbed DOC}]}{dt} = -r_{transfer}$$