Model Formulation

ODE Models

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

1. A simple 0th order model, where denitrification occurs independently of the other variables, and thus was a function of matrix borne 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.

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

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

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

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

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)).

Examples

DOC and NO3- Dynamics Model

The DOC and $NO3^-$ dynamics model describes the rates of change of nitrate (NO_3^-), labile 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

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

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

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