Model Formulation

Analysing the experiments and deriving the ODE models

From observing the concentration evolution in each sample, we can generatize two models of nitrate degradation.
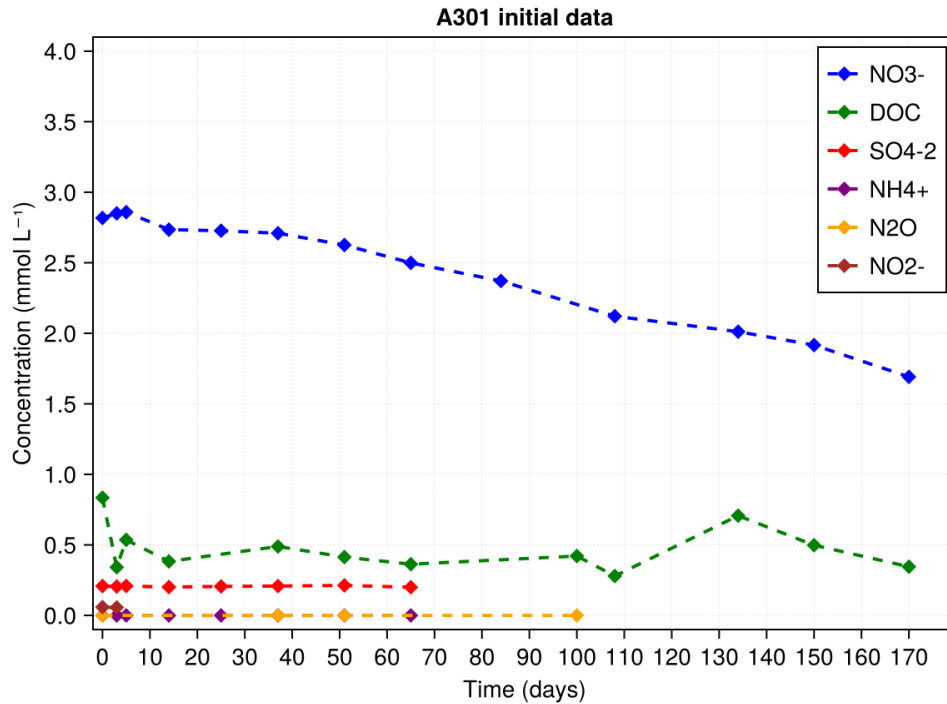
1. DOC independent denitrification

Figure 1: Example of denitrification independent of DOC concentration

In Figure 1, we see how denitrification happens, more or less at a constant rate, while DOC remains static. Moreover, SO4-2 also remains at a steady concentration, indicating that relative to the denitrification, sulfide, either soluble or in solid-phase constituents, is not a relevant electron donor. The conclusion, is that these samples do not contain enough soluble electron donors and the only denitrification comes from the matrix.

The proposed reaction rate is the 0th order rate model, and we do not observe the electron donor reaction product.

In other samples, it is visible the concurrent reduction between model nitrate and DOC (Figure
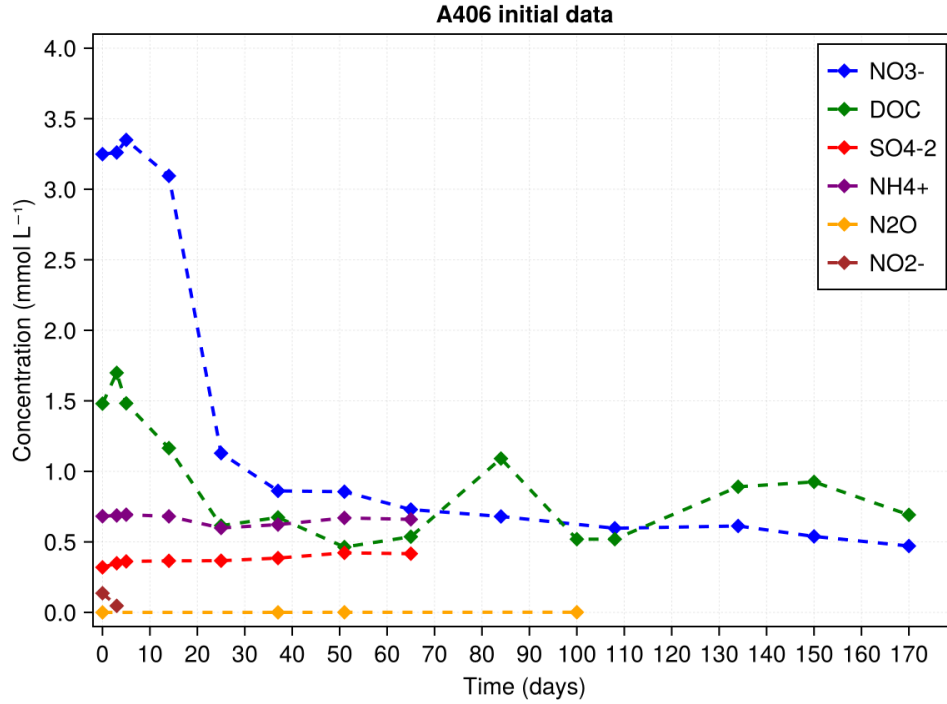
Figure 2: Example of data points where denitrification occurs alongside doc consumption, albeit not in the same stoichiometric ratios

2). However this reduction appear not to occur at the same electron equivalent stoichiometric rate (more DOC should have been consumed) and often, there is a plateau of DOC, from which the concentration does not reduce further.

The conclusion reached is that this happens because part of the DOC is still refractory (not bioavailable) and moreover, part is sorbed at the surface of the solid-phase material. As nitrate consumes the soluble DOC, the sorbed DOC is released and contributes to the reaction.

Therefore there are two alternative formulations envisaged for the observed behavior 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

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

- k_{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

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

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

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

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:

$$r_{transfer} = \alpha \cdot (c_{eq} - [DOC^s])\frac{m_s}{V_w}$$

- k_{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 $c_{eq} = K_d \cdot$ [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).

We also include N2O dynamics associated with solid-phase model and doc reduction as well

$$\frac{d[N2O_{water}]}{dt} = \frac{1}{2}\left(r_{NO3^-} + r_{DOC}\right) - k_{N2O} - r_{N_2O}^{DOC} + r_g(c_gH - c_w)$$

Where $r_{N_2O}^{DOC}$ is defined by the Michaelis-Mentem rate:

$$r_{N_2O}^{DOC} = k_{n2o}^{doc}\frac{[DOC]}{K_{DOC} + [DOC]}\frac{[N_2O]}{K_{N_2O} + [N_2O]}$$

with: - k_{n2o}^{doc} being the max rate of n2o reduction by DOC.

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

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)).

Differential Equations

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

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

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