Model Formulation

Experimental Observations

Our batch experiments revealed two distinct denitrification patterns:

1. **Matrix-Driven Denitrification**: Constant nitrate reduction without DOC consumption
2. **DOC-Coupled Denitrification**: Concurrent reduction of nitrate and DOC

Evidence for Matrix-Driven Denitrification

Denitrification occurs at a seemly constant rate while DOC and sulfate concentration remains stable.
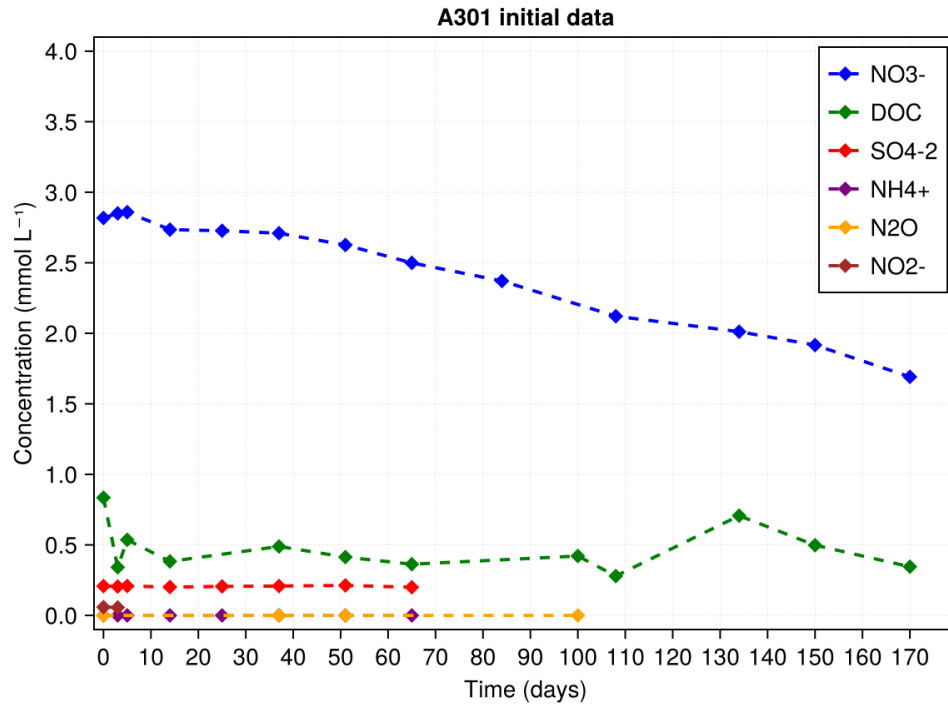

Figure 1: Denitrification occurs at constant rate while DOC remains static, indicating matrix-driven reduction

Evidence for DOC-Coupled Denitrification

Denitrification occurs with a nonlinear rate, analogous to the DOC compumption. The ratio between Nitrate consumption to DOC consumption is higher than 4/5 (the stoichiometric ratio). Our conclusion to this phenomena is that an extra pool of DOC is available, but sorbed to the solid-phase surface. At late times, one may note that denitrification continues, and DOC stabilizes, indicating that the matrix related denitrification is also involved. Moreover, the high stable DOC concentration signals that part of the initial DOC is not bioavailable, and thus remains in the system. The sulfate concentration seems to increase slighly, albeit at a much smaller magnitude than the nitrate reduction, indicating that sulfur related denitrification is likely a minor effect in the system.
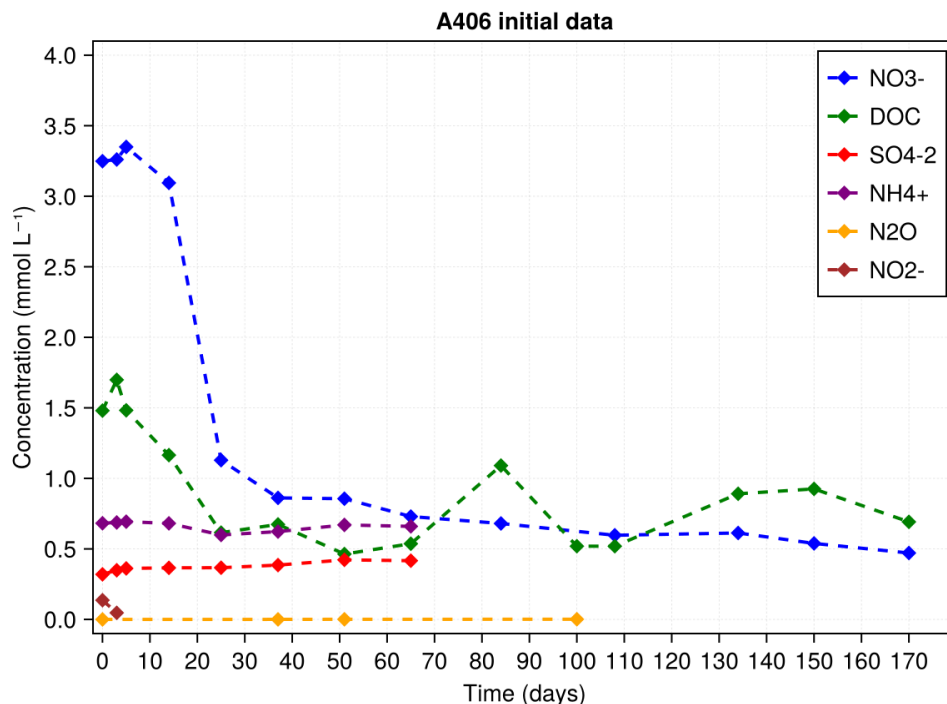

Figure 2: Concurrent reduction of nitrate and DOC with apparent sorption effects

Model Formulations

We model the measured nitrogen and carbon species as they signal the relevant processes occurring in the system. For nitrogen these are nitrate and nitrous gas, while for carbon it is the bioavailable DOC.

For the gas-phase measurements of nitrous gas (N_2O), we include a gas transfer rate to the model. The gas-phase concentrations is sensible to sample collections during the experiment, that either take a water sample or a gas sample. Both dilute the gas phase with the anoxic atmosphere of the experiment. The sampling dilution is handled with callbacks that modify the underlying ode model during the solution.

1. Matrix Denitrification Model

A zero-order kinetic model representing matrix-driven denitrification.

State Variables

Variable	Description	Units
$[NO_3^-]$	Nitrate concentration	mmol L^{-1}
$[N_2O_{water}]$	Dissolved N O	mmol L^{-1}
$[N_2O_{gas}]$	Gaseous N O	atm

Governing Equations

$$\frac{d[NO_3^-]}{dt} = -k_{NO3^-} \tag{1}$$

$$\frac{d[N_2O_{water}]}{dt} = \frac{1}{2}k_{NO3^-} - k_{N2O} + r_g(c_gH - c_w) \tag{2}$$

$$\frac{d[N_2O_{gas}]}{dt} = -\frac{r_g(c_gH - c_w)}{H} \tag{3}$$

2. DOC-Coupled Denitrification Model

An extended model incorporating DOC dynamics and sorption processes.

Additional State Variables

Variable	Description	Units
$[DOC]$	Dissolved organic carbon	mmol L^{-1}
$[DOC_{sorbed}]$	Sorbed organic carbon	mmol L^{-1}

Rate Equations

$$r_{DOC} = k_{DOC}^{max}\frac{[DOC]}{K_{DOC} + [DOC]} \cdot \frac{[NO_3^-]}{K_{NO3^-} + [NO_3^-]} \tag{4}$$

$$r_{transfer} = \alpha \cdot (K_d[DOC_{sorbed}] - [DOC])\frac{m_s}{V_w} \tag{5}$$

$$r_{N_2O}^{DOC} = k_{n2o}^{doc}\frac{[DOC]}{K_{DOC} + [DOC]}\frac{[N_2O]}{K_{N_2O} + [N_2O]} \tag{6}$$

Governing Equations

$$\frac{d[NO_3^-]}{dt} = -k_{NO3^-} - r_{DOC} \tag{7}$$

$$\frac{d[DOC]}{dt} = -\frac{5}{4}r_{DOC} + r_{transfer}\frac{m_g}{V_w} - \frac{1}{2}r_{N_2O}^{DOC} \tag{8}$$

$$\frac{d[DOC_{sorbed}]}{dt} = -r_{transfer} \tag{9}$$

$$\frac{d[N2O_{water}]}{dt} = \frac{1}{2}(k_{NO3^-} + r_{DOC}) - k_{N2O} - r_{N_2O}^{DOC} + r_g(c_gH - c_w) \tag{10}$$

$$\frac{d[N2O_{gas}]}{dt} = -\frac{r_g(c_gH - c_w)}{H} \tag{11}$$