Impact of Organic Carbon Substrate Additions on Denitrification in Soils

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Groundwater Nitrate Bioremediation Simulation of In Situ Horizontal Well by Microbial Denitrification Using PHREEQC

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Background/Significance:

- Constraints on in situ experiments on nitrate leaching make collecting data difficult
- PHREEQC allowed for a numerical simulation model to be applied to simulate reactions and migration of nitrate under a wider variety of conditions
- Utilized 1_D Hydrogeochemical software to simulate an in situ horizontal well system
- Key data blocks in this paper include:
  - SOLUTION, COPY, RATES, KINETICS, TRANSPORT

Findings:

- Builds a conceptual model of geochemistry with PHREEQC software
  - Used to predict the NO3- -N Concentration law (Assumption: the flow rate continues to change)
- Theoretical data and related relationships obtained can provide references for actual nitrate restoration projects and provide practical guidance for subsequent work

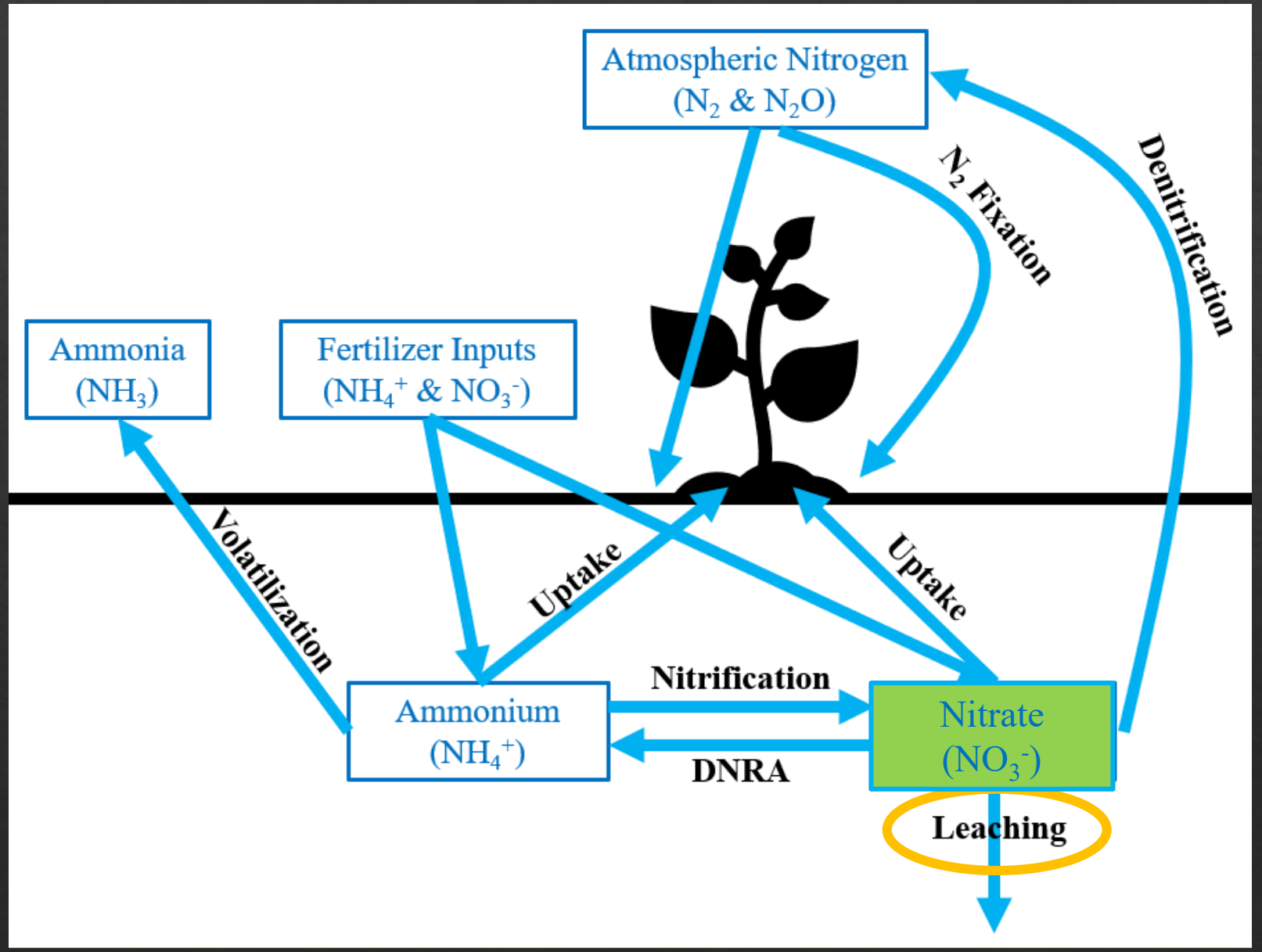
(Liu et al., 2021)

Background

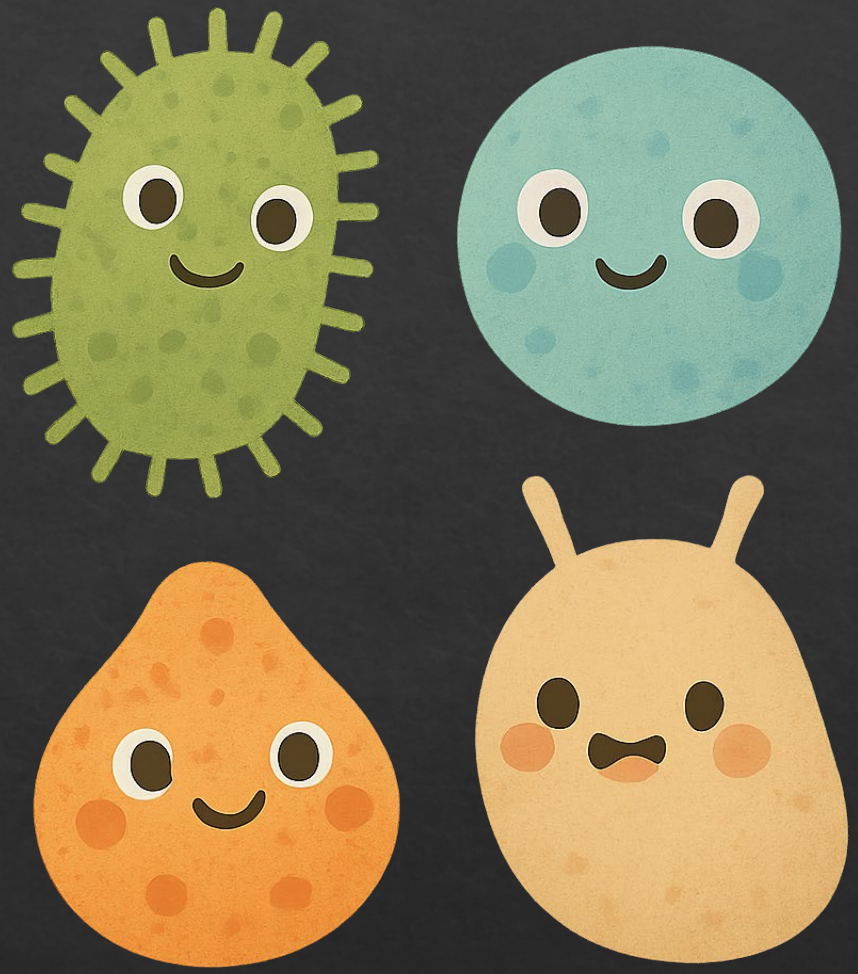
- AG expansion is currently the leading driver of habitat loss, contributing to the decline of animals, plant, and microbial diversity
- Soils are depleted/degraded to meet the increasing demand for food and chemical fertilizers applied to improve yields
  - Can lead to loss of biodiversity and pollution of surrounding ecosystems

(Akanmu et al., 2021)

Simplified Nitrogen Cycle



Microbes

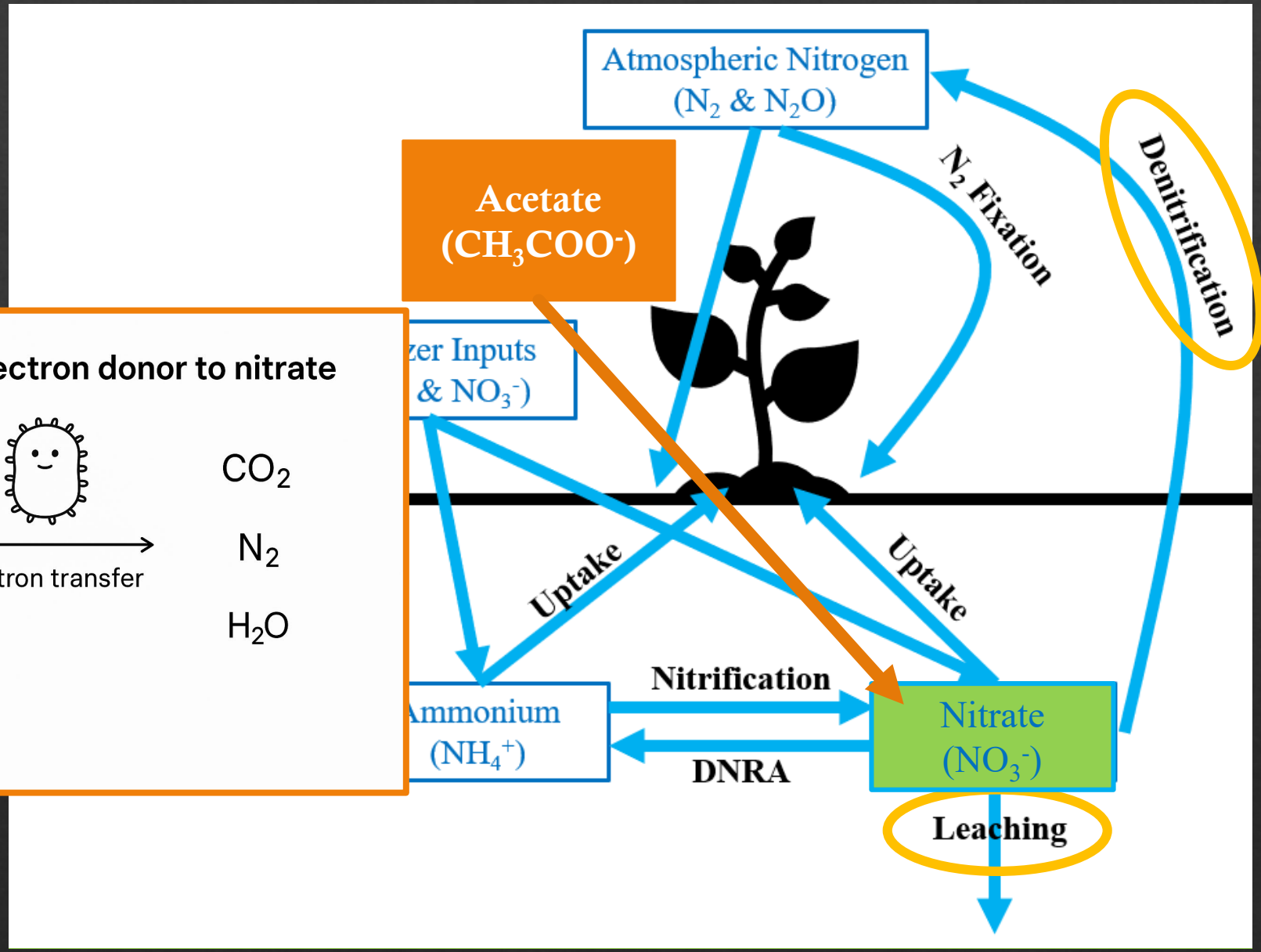


What is typically the limiting nutrient for soil microbes?

Carbon!

(Polojarvi et al., 2020)

Simplified Nitrogen Cycle



Acetate as an electron donor to nitrate

(Chen et al., 2018; Dlamini et al., 2020; Ejack et al., 2021; Li et al., 2021; Song et al., 2023)

Objectives

- Develop a model in PHREEQCi to simulate an addition of organic carbon (acetate) to a soil profile and determine its impacts on denitrification.
- Determine the impacts of different levels of acetate additions on the amount of nitrate remaining in the soil profile.

Methods- Site Information

- Recently Converted Cropland from Forest
- Applied a bunch of Nitrate to the field to increase the productivity of their crops
- Groundwater nitrate levels came back elevated, so now actions are being taken to try to remediate this issue

```
SOLUTION 0
    temp 25
    pH 7
    pe 4
    redox pe
    units mmol/kgw
    density 1
    Ca 59
    Cl 36
    K 63
    Mg 37
    Na 11
    S(6) 62
    N(5) 12
    N(-3) 5
    water 1 # kg
```

(Soil Solution, n.d.)

Methods- PHREEQC

- Simplified 1D Transport Model
  - Creation of a 1D column model where solutes move, mix, and react chemically along a flow path
- Low (2 mmol), Ideal (13 mmol), and High (26 mmol) Acetate additions simulated

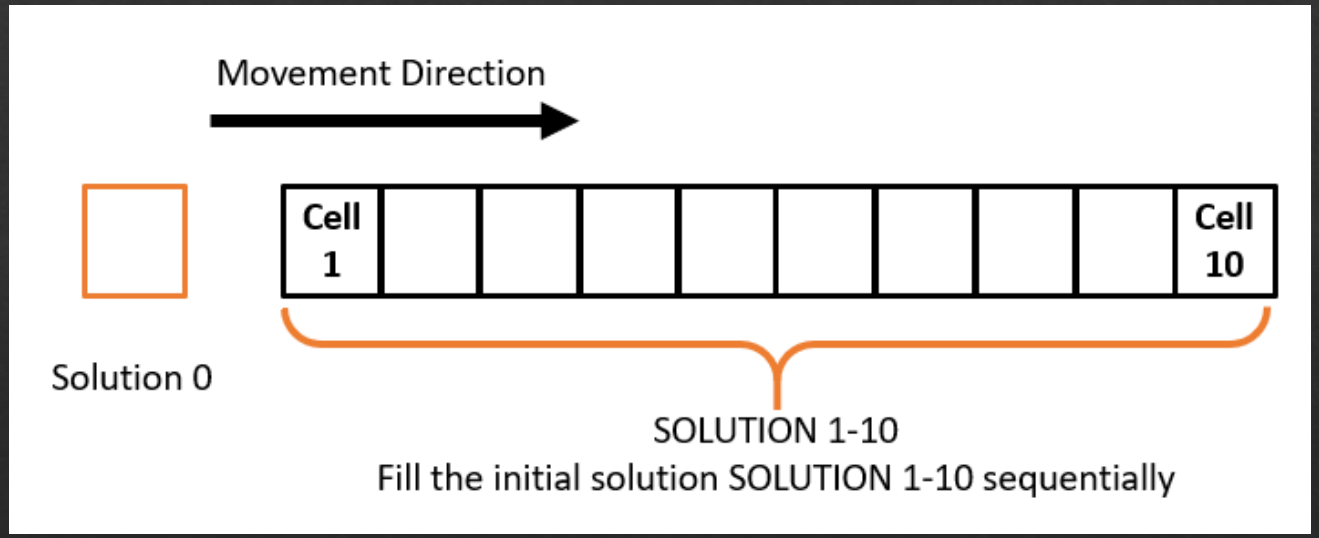


Figure 1: Input and calculation process of PHREEQCi model

(Liu et al., 2021)

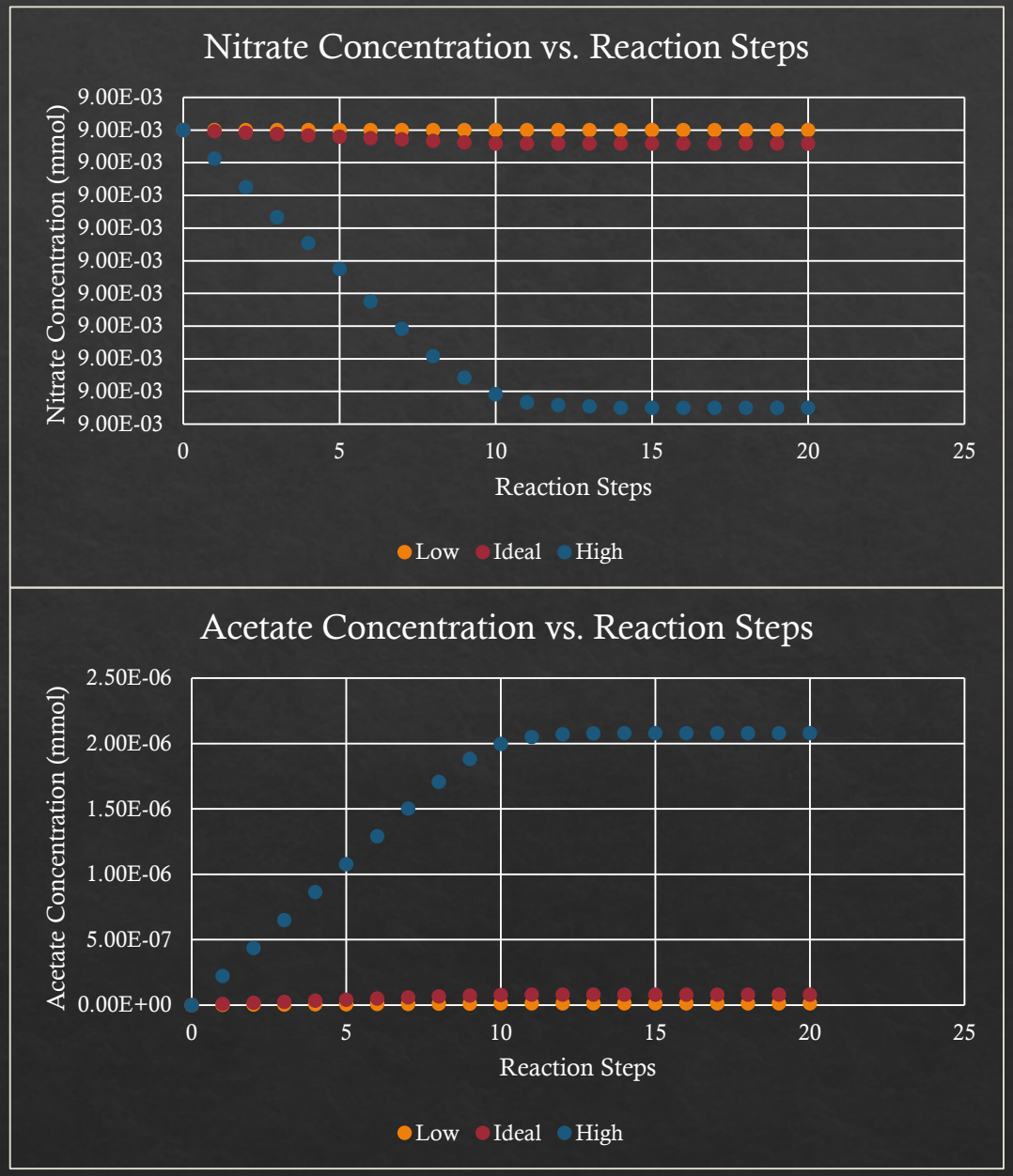
Methods- PHREEQC cont…

```
REACTION 1
    NaCH3COO 0.0026
    0.0026 moles in 5 steps

RATES
Denitrification
-start
10 REM Denitrification rate: First-order with respect to acetate and nitrate
20 rate = -0.01 * MOL("CH3COO-") * MOL("NO3-")
30 SAVE rate
-end

KINETICS 1
    Denitrification
        -formula CH3COO- 1 NO3- 1
        -m 1
        -steps 20 in 86400 seconds

TRANSPORT
    -cells 10
    -shifts 20
    -time_step 3600
    -lengths 0.1
    -flow_direction forward
    -boundary_conditions constant
    -dispersivities 0.01
    -diffusion_coefficient 1e-9
```

- REACTION
  - Define any solutions used in simulation not defined in the database and how much to add
- RATES
  - Defines a custom rate law and the math behind the kinetic reaction
- KINETICS
  - Applies the RATES expression to specific cells
  - Specifies how much reactant present and the time steps to run it
- TRANSPORT
  - Defines how many cells, how fast things move (advection) and how they spread (Dispersion)

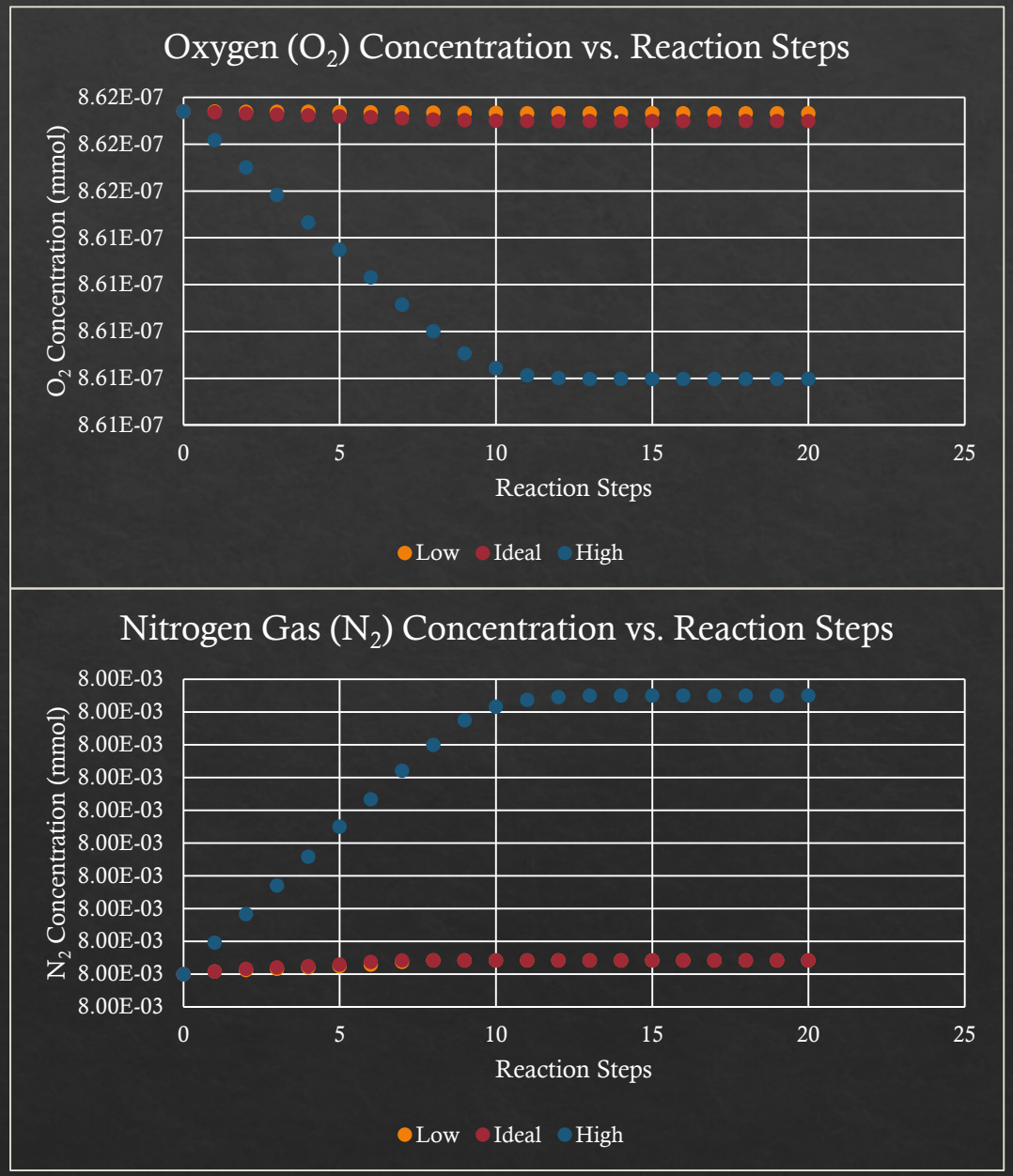
(Liu et al., 2021)

Results/Data



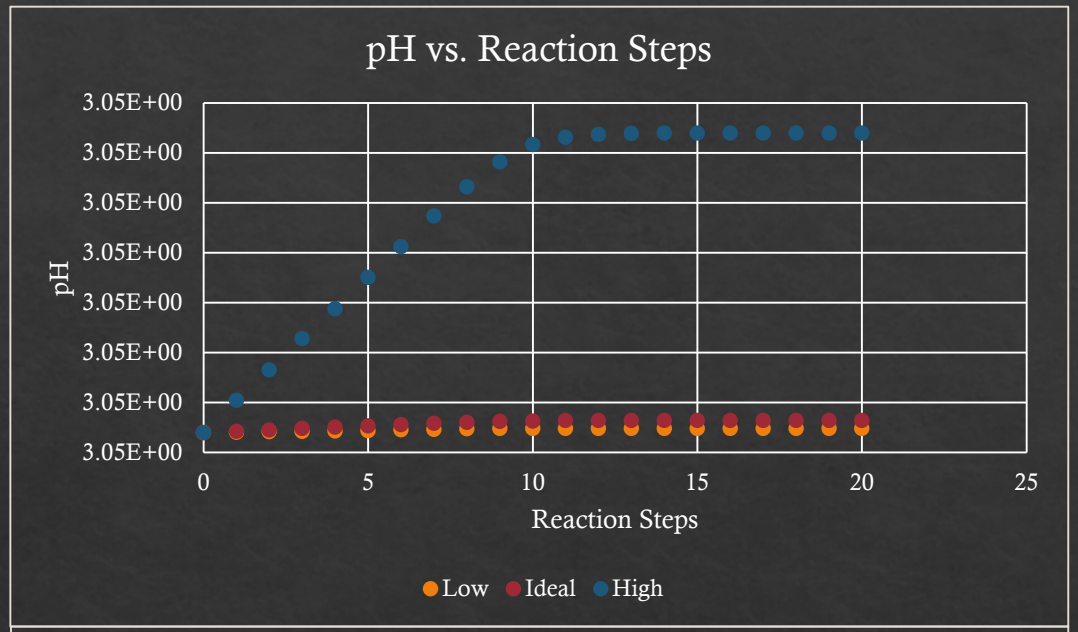
- Low and ideal acetate additions did little to decrease the nitrate content in the soil
- High acetate drastically decreased the nitrate concentration in the soil
- Plateau at which nitrate is no longer being denitrified and thus acetate is no longer being used.

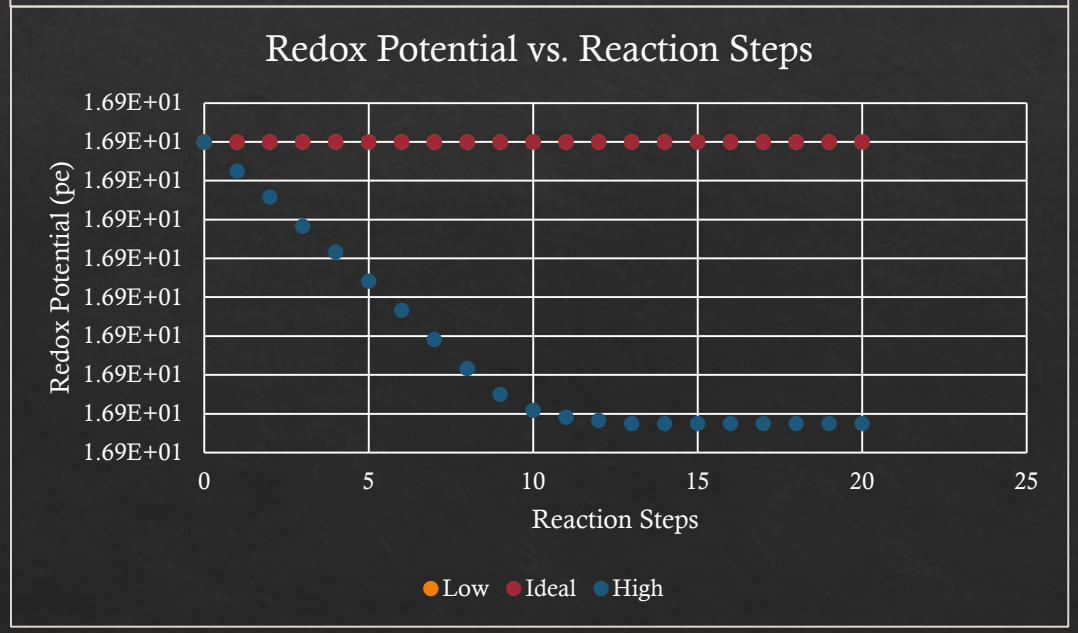
Results/Data



- Similar trends to nitrate and acetate, ideal and low have minimal impact and high has drastic impacts
- O2 decreased with high acetate
- N2 increased with high acetate
  - Indicating denitrification

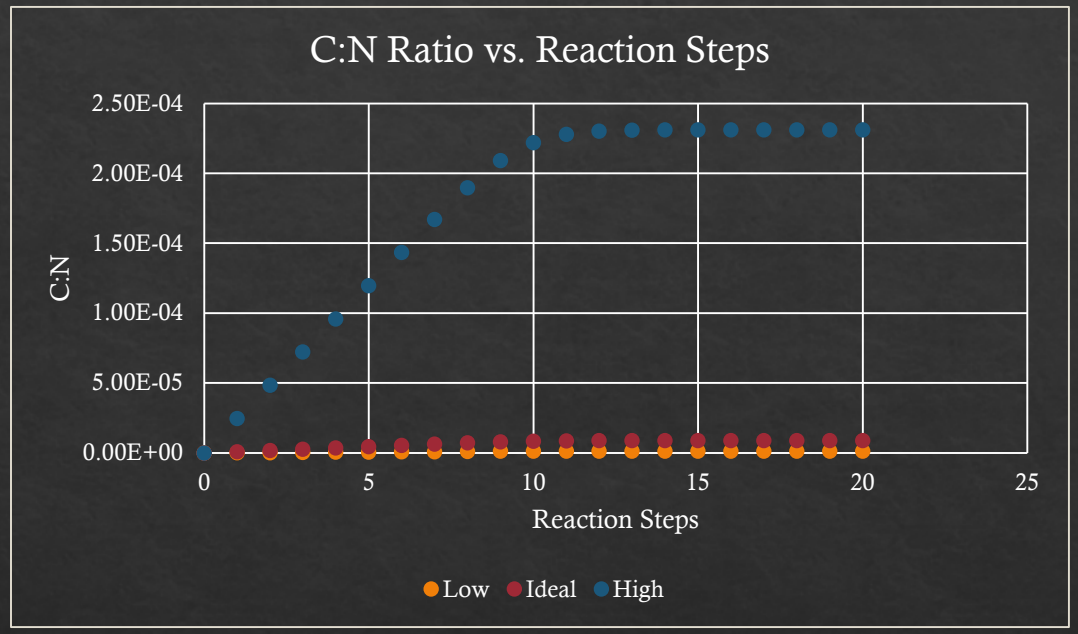
Results/Data





- Similar trends to nitrate and acetate, ideal and low have minimal impact and high has drastic impacts
- pH increases slightly with high acetate
- Pe decreases slightly with high acetate

Results/Data



- C:N ratio increased as acetate was added
  - Adding more carbon into the solution and removing nitrogen through denitrification

Conclusions

- At higher rates of acetate additions, nitrate did decrease along with O2 and redox potential of the system
- An improved knowledge of PHREEQC could lead to some better, more accurate models of what actually occurs in the soil
  - External water transport models and microbial activity models to pair with PHREEQC

References

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Questions?