

# Are anaerobic energy-generation pathways significant contributors to stream energy budgets?

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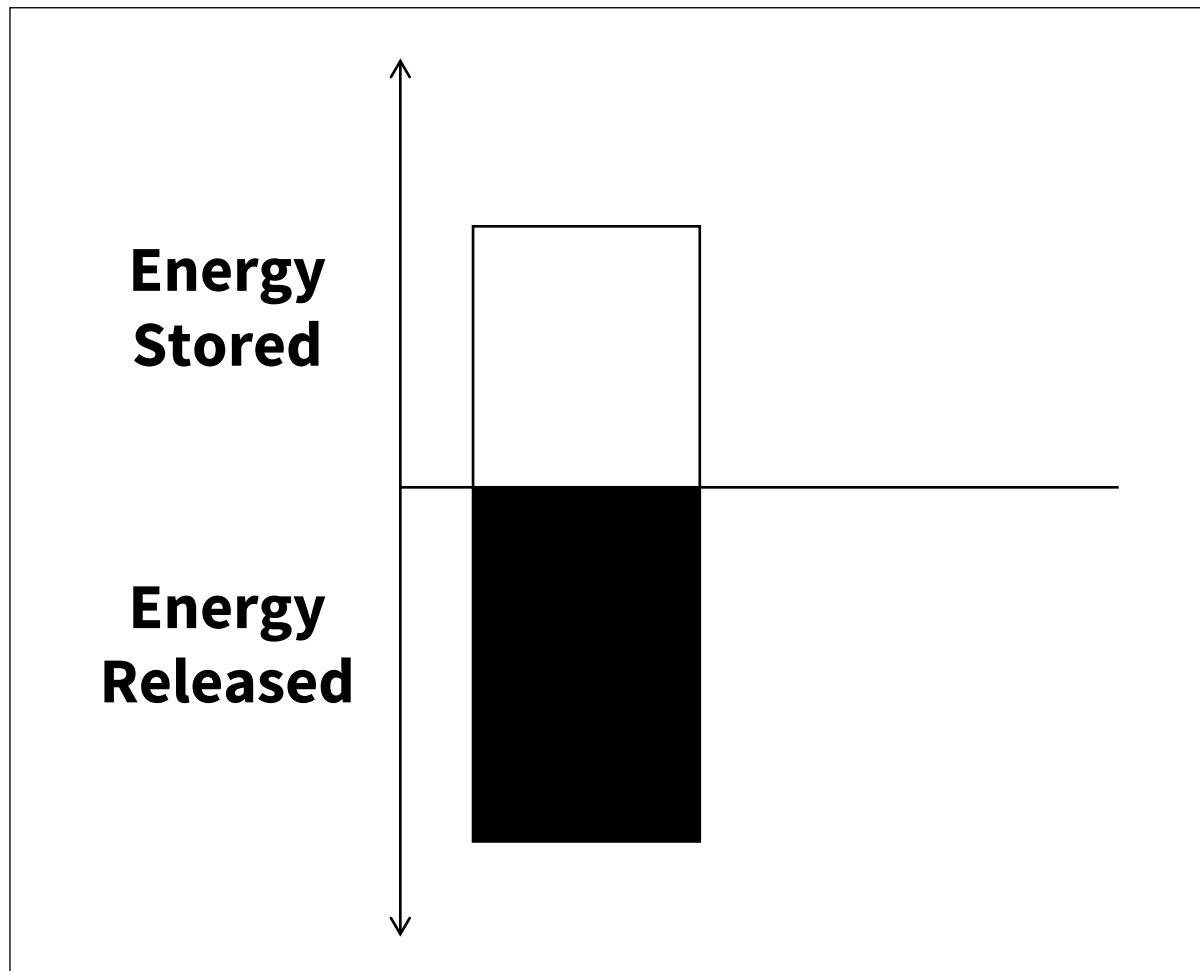
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Michigan Technological University, Houghton, MI, USA

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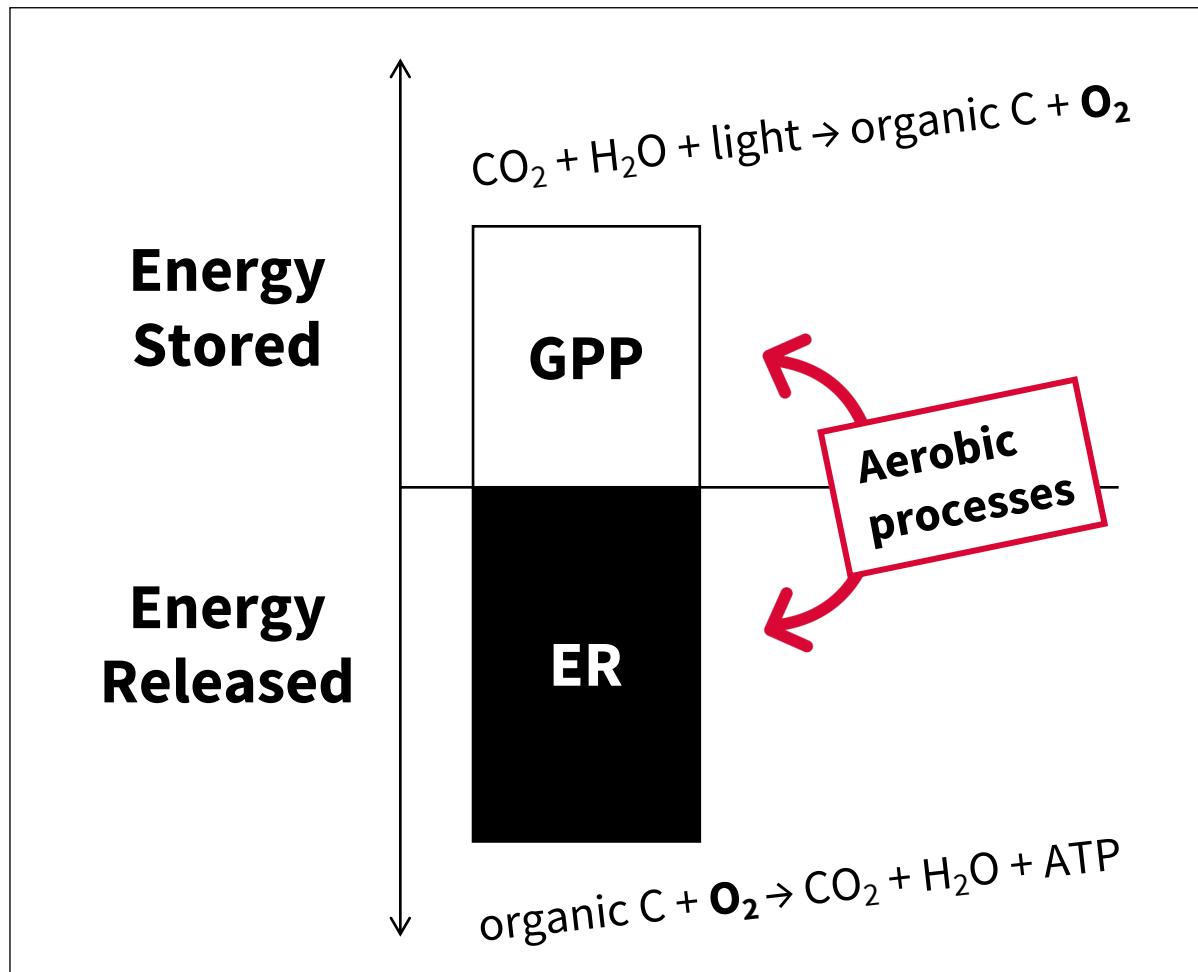


# **Stream metabolism =**

## **Energy stored - energy released**



# Stream metabolism = Energy stored - energy released



# What about anaerobic processes?

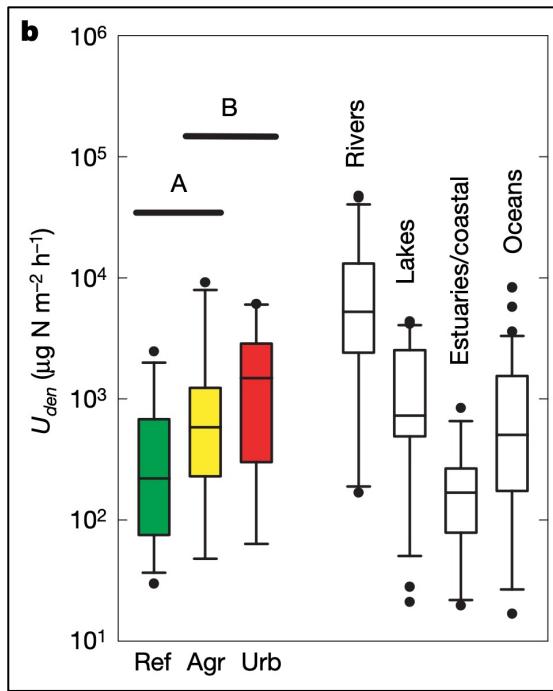
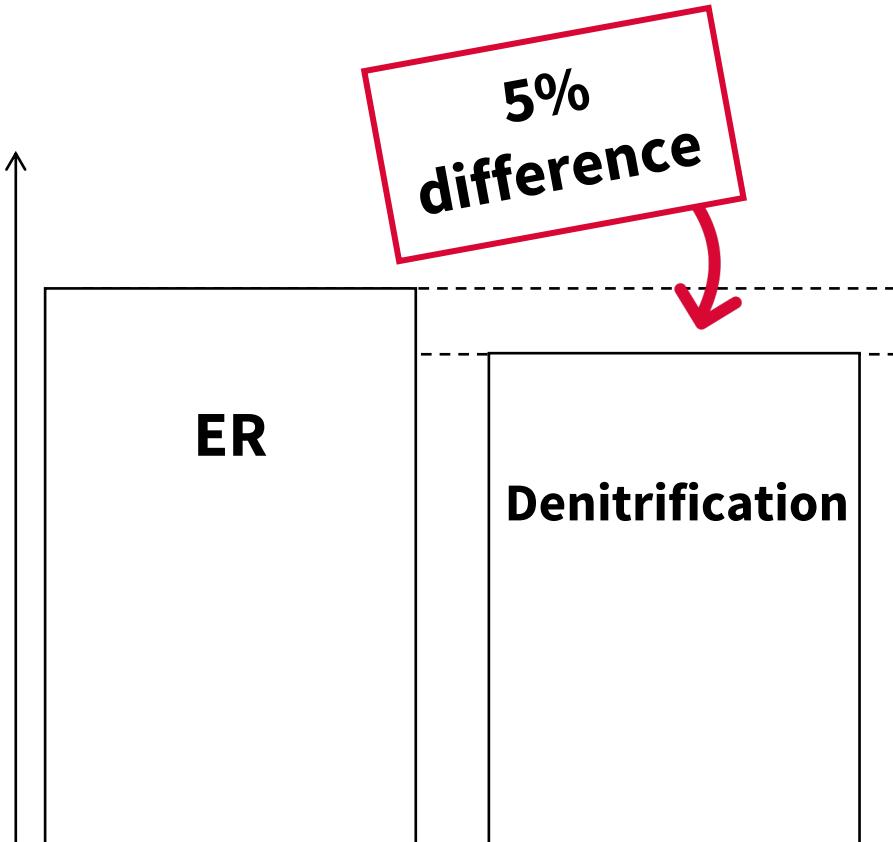


Figure from Mulholland et al. 2008

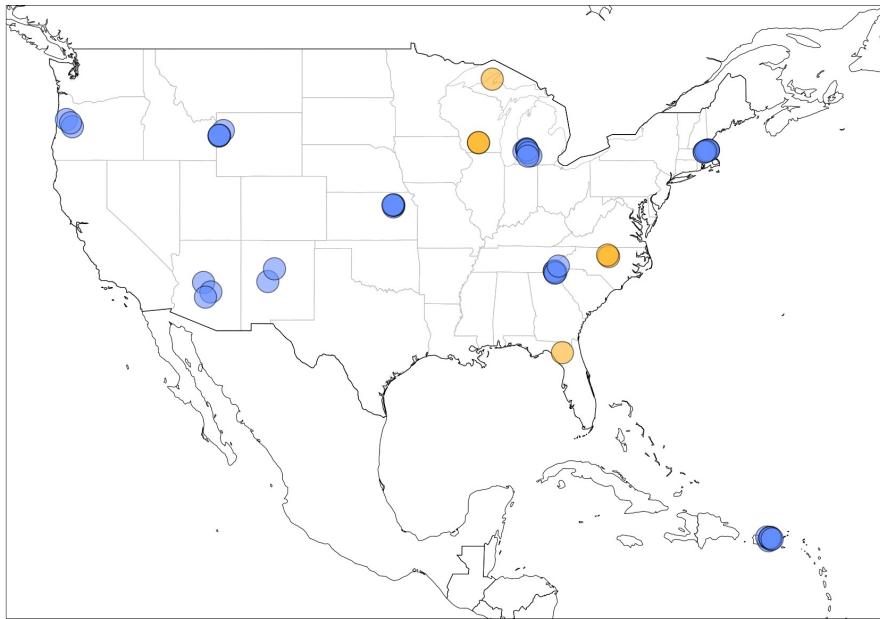
Gibbs free energy ( $\Delta G_0'$ )



Are anaerobic processes significant contributors to stream energy budgets?



# Sites and Data



## LINX II Project

(n = 48)

Whole-stream **denitrification** measured using **15-N tracer**, data obtained from Mulholland et al. 2009 Supplemental,

<https://www.doi.org/10.4319/lo.2009.54.3.0666>

Modeled **metabolism** data obtained from Bernot et al. 2010 Supplemental,

<https://www.doi.org/10.1111/j.1365-2427.2010.02422.x>

## Marcarelli Nationwide Denitrification and N Fixation (here n = 7, 31 streams total in survey)

**Denitrification** measured on individual stream substrates using **acetylene inhibition** assays, see Amy Marcarelli's Wednesday AM talk

Modeled **metabolism** obtained from StreamPULSE repository,  
<https://data.streamPULSE.org>



# Energy Budget Calculation

**Aerobic respiration, reduction half-reaction:**  $O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$

**Energy released from ER, kCal per m<sup>2</sup> hr**

= ER rate × Gibbs free energy (at pH = 7) × e<sup>-</sup> in full reaction

= ER rate in g-O<sub>2</sub> per m<sup>2</sup> day × 29.9 kCal per e<sup>-</sup> × 4 e<sup>-</sup> per reaction

÷ 32 g-O<sub>2</sub> per mol O<sub>2</sub> × 2 mol-O per mol O<sub>2</sub> ÷ 1 mol-O<sub>2</sub> per reaction ÷ 24 hours per day

**Denitrification, reduction half-reaction:**  $2 NO_3^- + 12.5 H^+ + 10 e^- = N_2 + 6 H_2O$

**Energy released from denitrification, kCal per m<sup>2</sup> hr**

= Denitrification rate × Gibbs free energy (at pH = 7, kCal per e<sup>-</sup>) × e<sup>-</sup> in full reaction

= Denitrification rate in mg-N per m<sup>2</sup> hr × 28.4 kCal per e<sup>-</sup> × 10 e<sup>-</sup> per reaction

÷ 1000 mg-N per g-N ÷ 14 g-N per mol ÷ 2 mol-N per reaction



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# Energy Budget Calculation

**Total energy released, kCal per m<sup>2</sup> hr**

= Energy released from ER + Energy released from denitrification

**Energy released from denitrification as a proportion of total energy budget**

= Energy released from denitrification ÷ Total energy released × 100%

**Energy released from aerobic respiration as a proportion of total energy budget**

= Energy released from ER ÷ Total energy released × 100%



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# Predictive Modeling

## Pre-processing

- **Dummy variables** for categorical predictors
- Removed **near zero variance** predictors, cutoff ratio = 95/5
- **Centered, scaled**

## Splitting and resampling

- Data **randomly split** into training and testing sets, **80% training** and **20% testing**
- **10-fold cross-validation** for resampling, repeated **10 times**

## Evaluating model performance

- **Best fit model = Lowest** root mean squared error (**RMSE**) on testing set



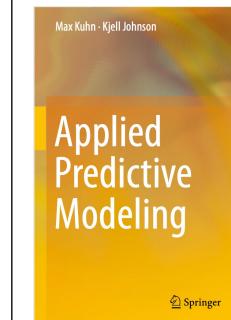
## Pre-processed **Marcarelli Nationwide dataset:**

- **17 observations, 24 predictors**

## Pre-processed **LINX II dataset:**

- **28 observations, 28 predictors**
  - 8 categorical (ex. state, land use, biome)
  - 20 continuous (ex. discharge, reach width, DOC, NO<sub>3</sub>, SRP, GPP, ER)
- **Response:** Energy released from denitrification as a proportion of total energy (%)

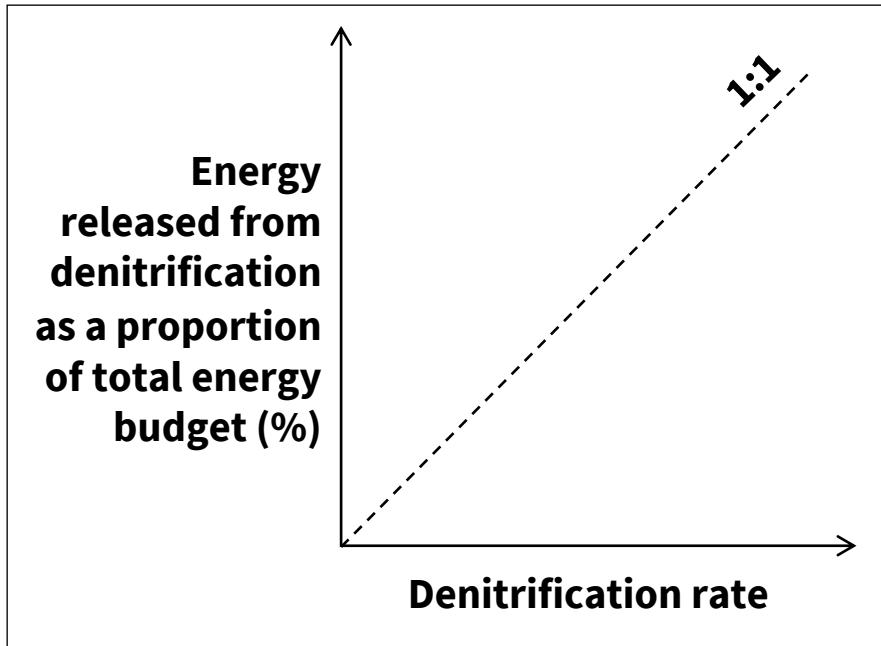
## Resources



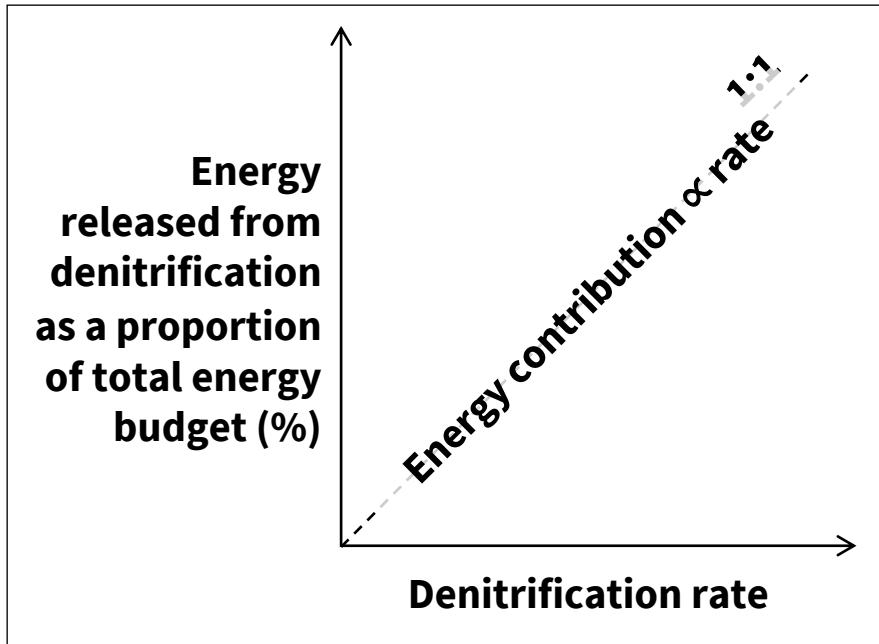
Kuhn et al. 2019. *caret: Classification and Regression Training* R package.  
<https://topepo.github.io/caret/>

Kuhn and Johnson. 2013. *Applied Predictive Modeling*.  
<https://appliedpredictivemodeling.com/>

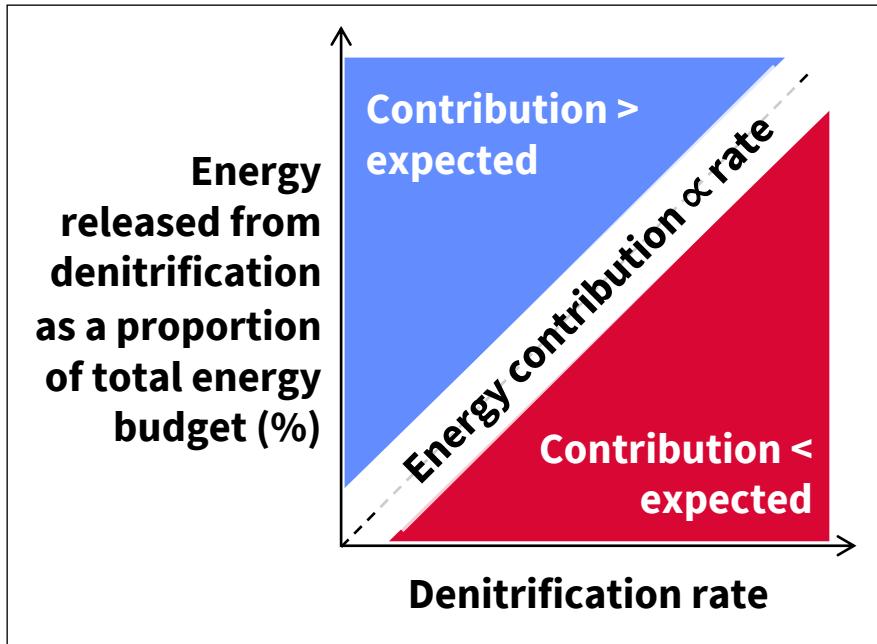
# Denitrification as a proportion of total energy



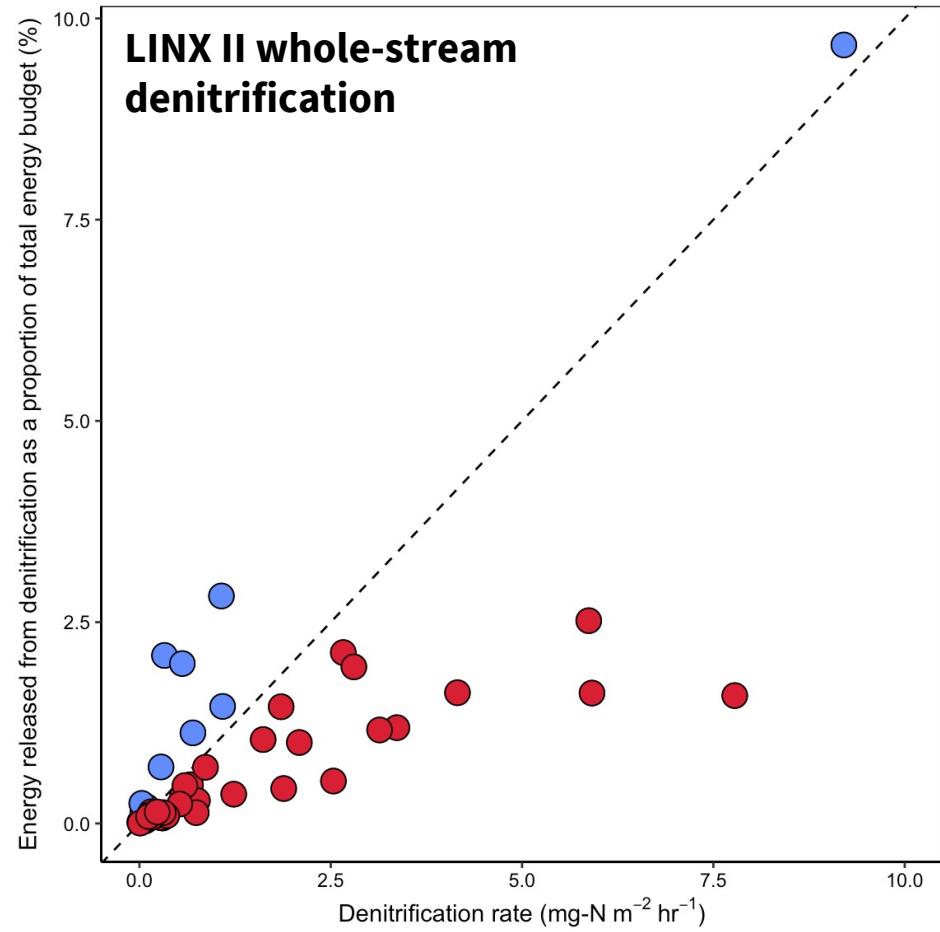
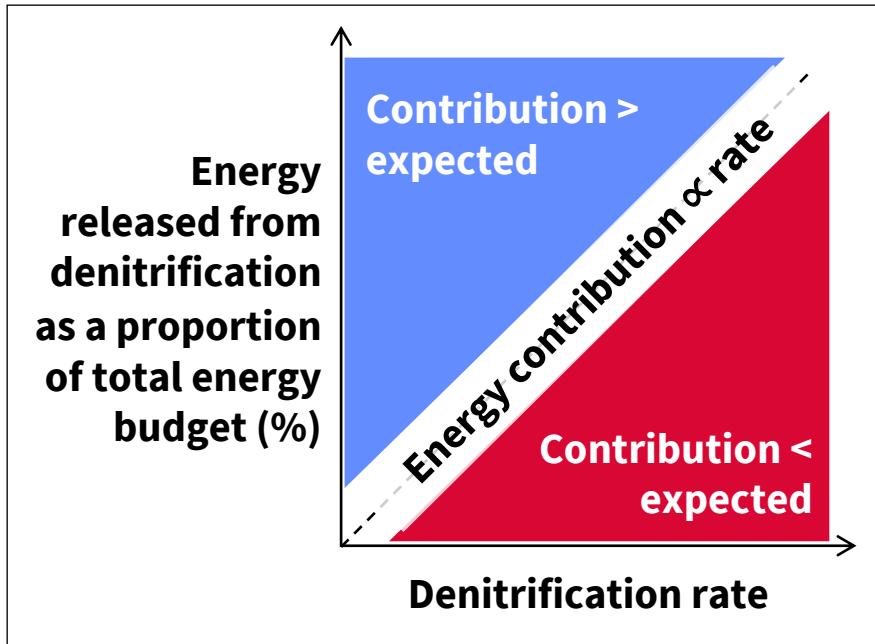
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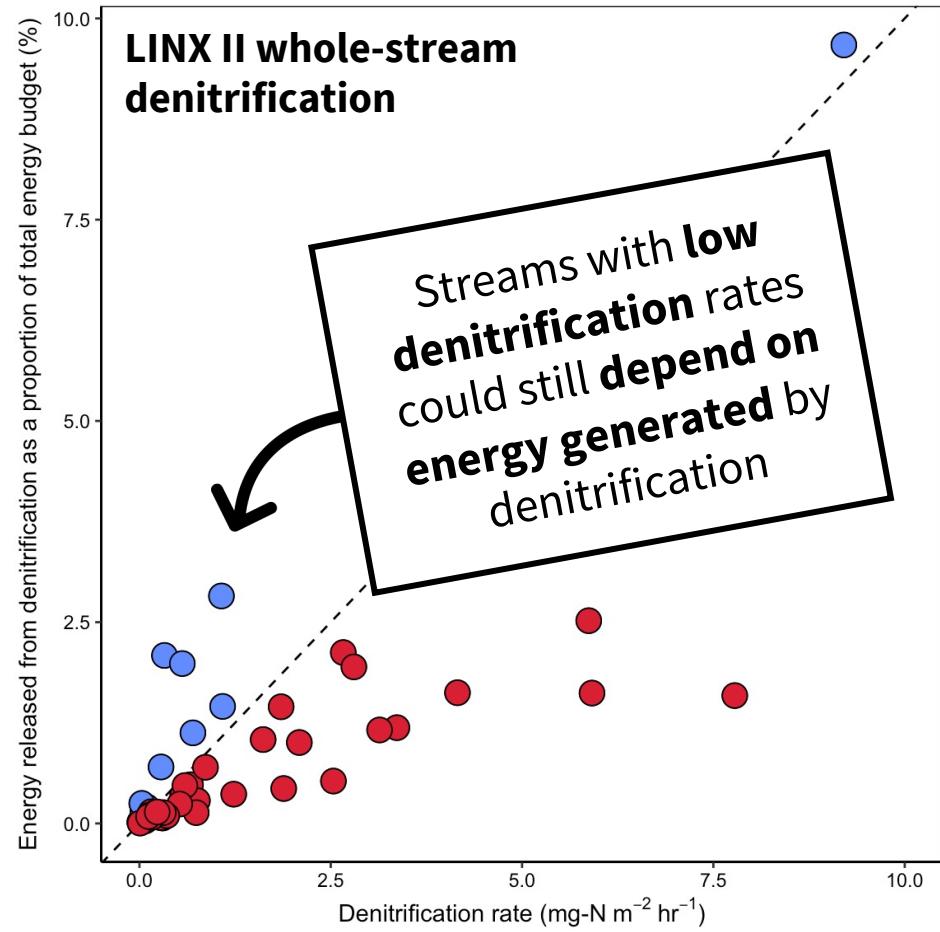
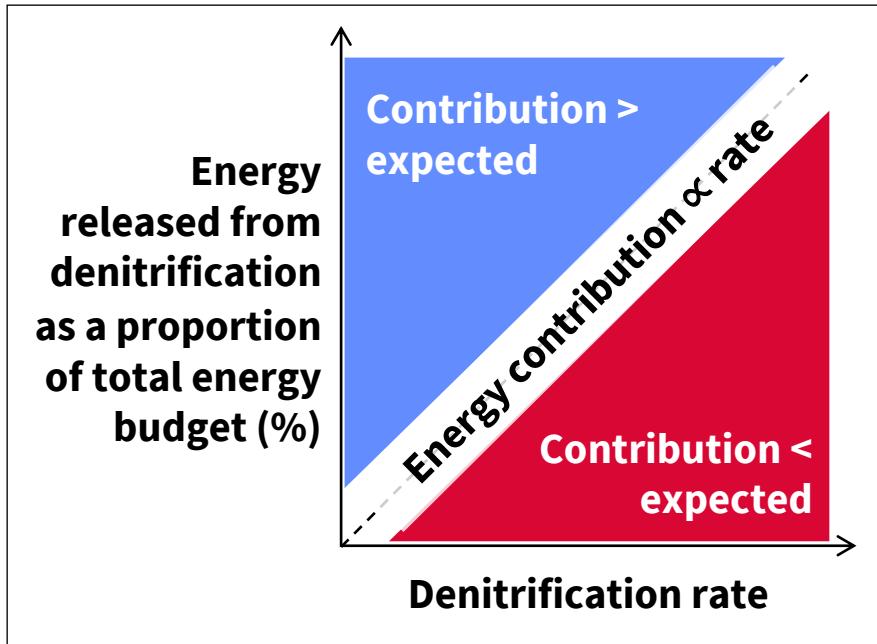
# Denitrification as a proportion of total energy



# Denitrification as a proportion of total energy



# Denitrification as a proportion of total energy

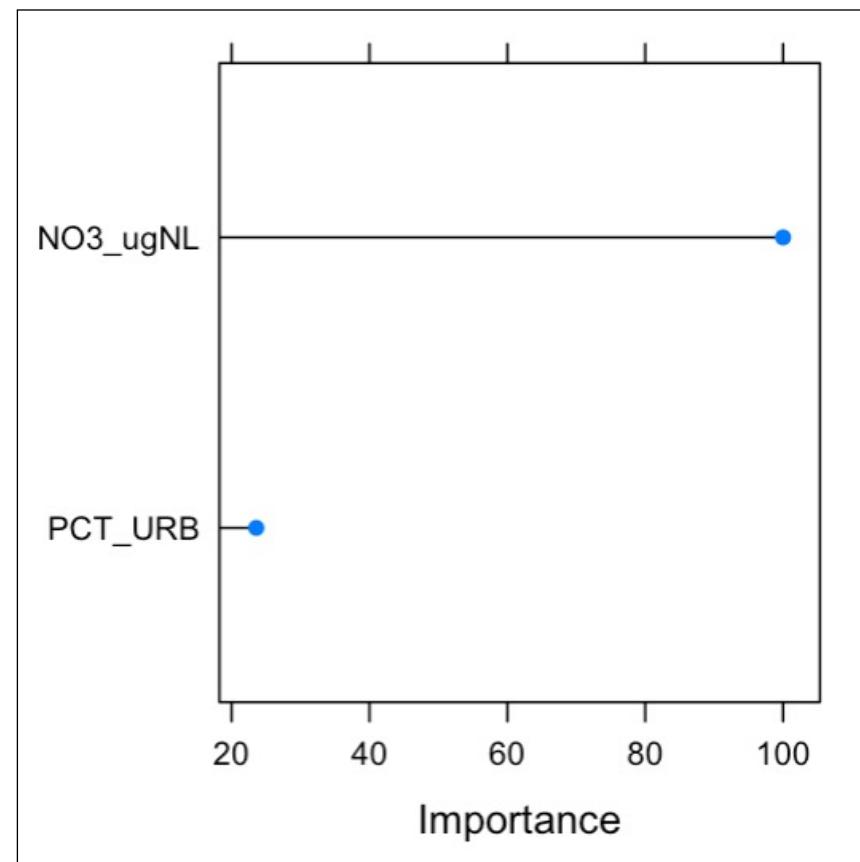


# Predictive modeling results

## LINX II dataset

**Response: energy released from denitrification as a proportion of total energy (%)**

Model	RMSE on testing set
Partial least squares (PLS)	0.548
Elastic net	0.423
Neural net	0.526
<b>MARS</b>	<b>0.394</b>
SVM	0.5347
KNN	0.5304
Random forest	0.4799
Boosted tree	0.54749



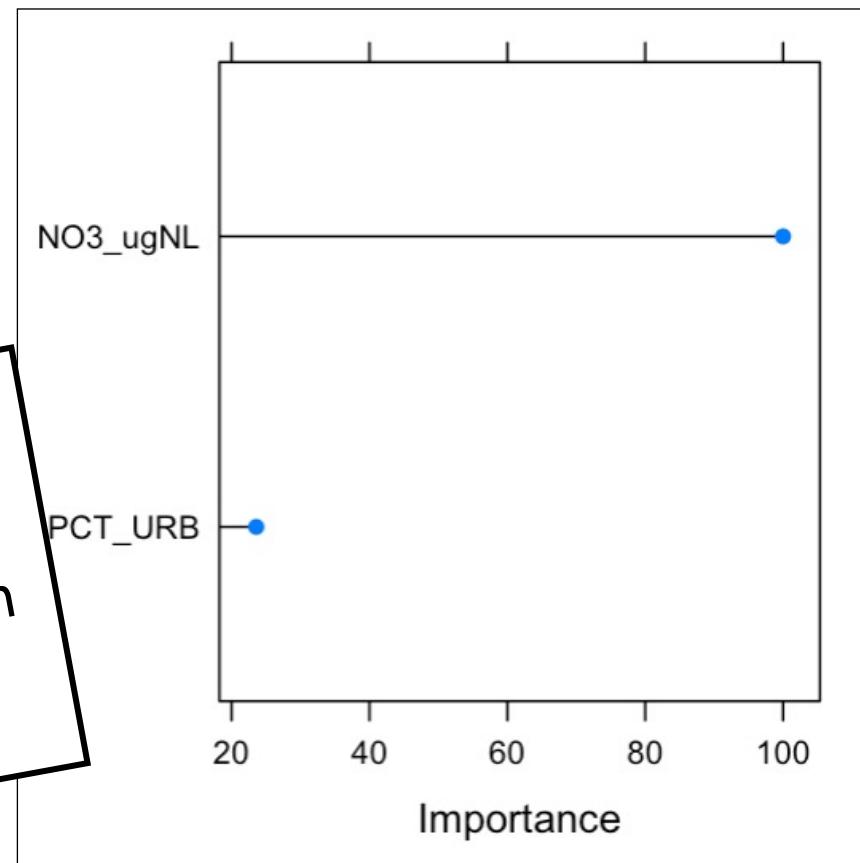
# Predictive modeling results

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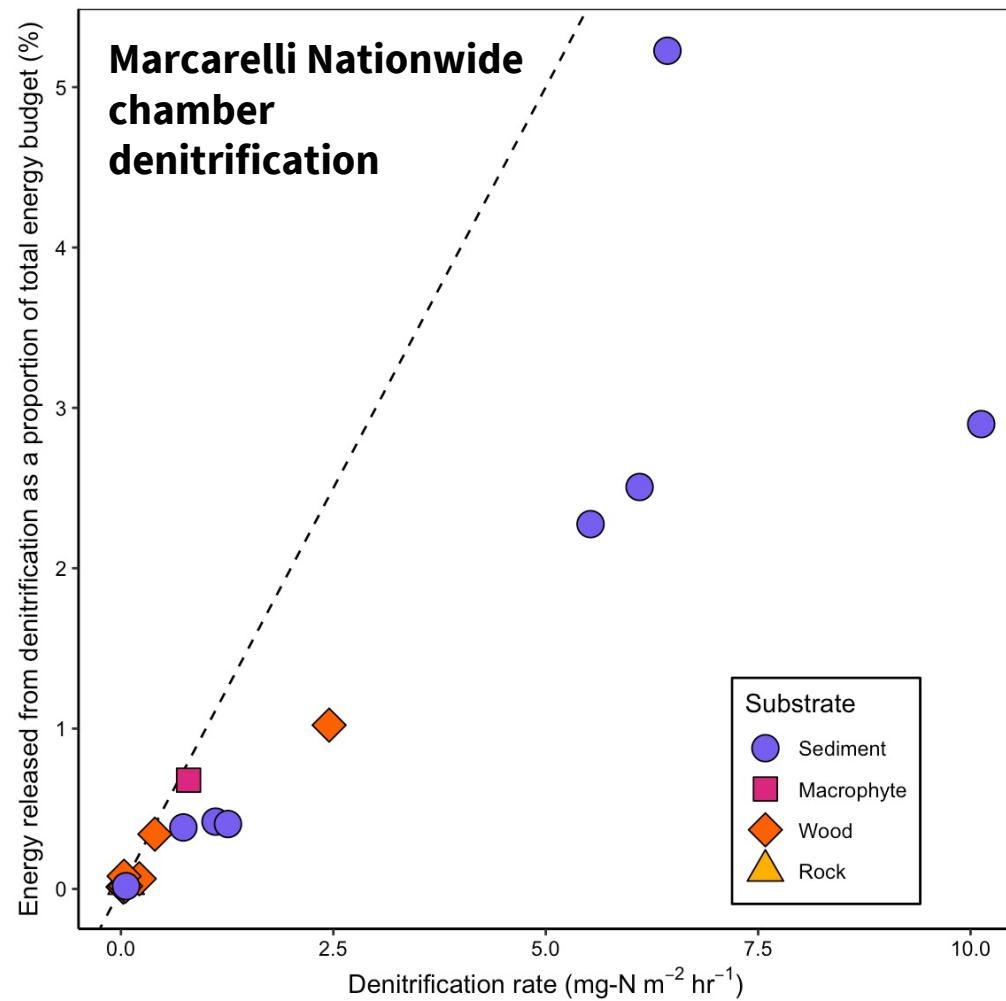
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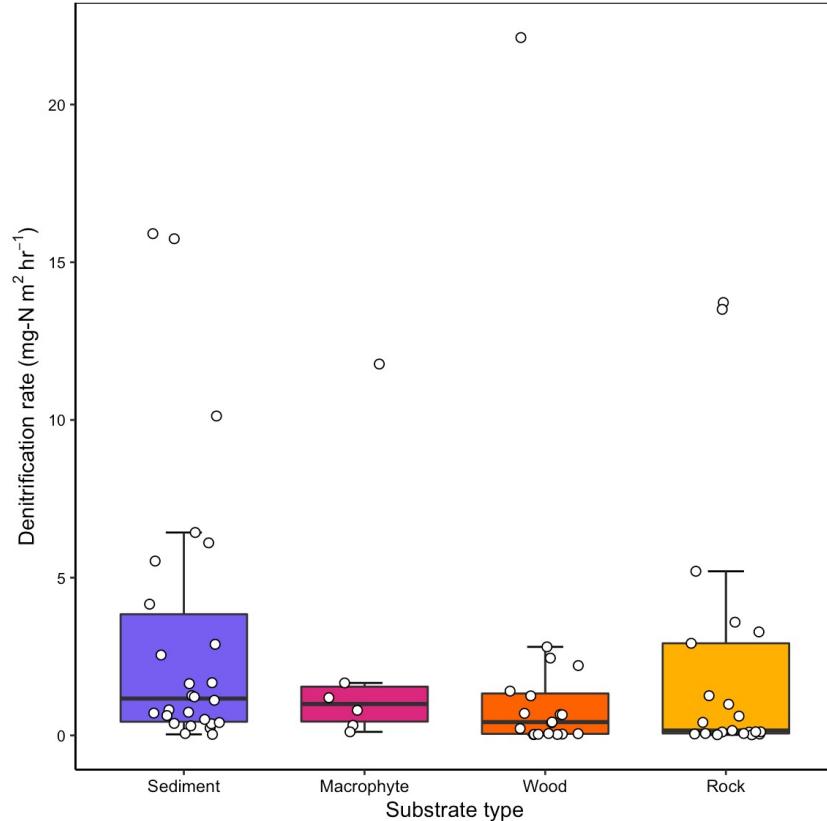
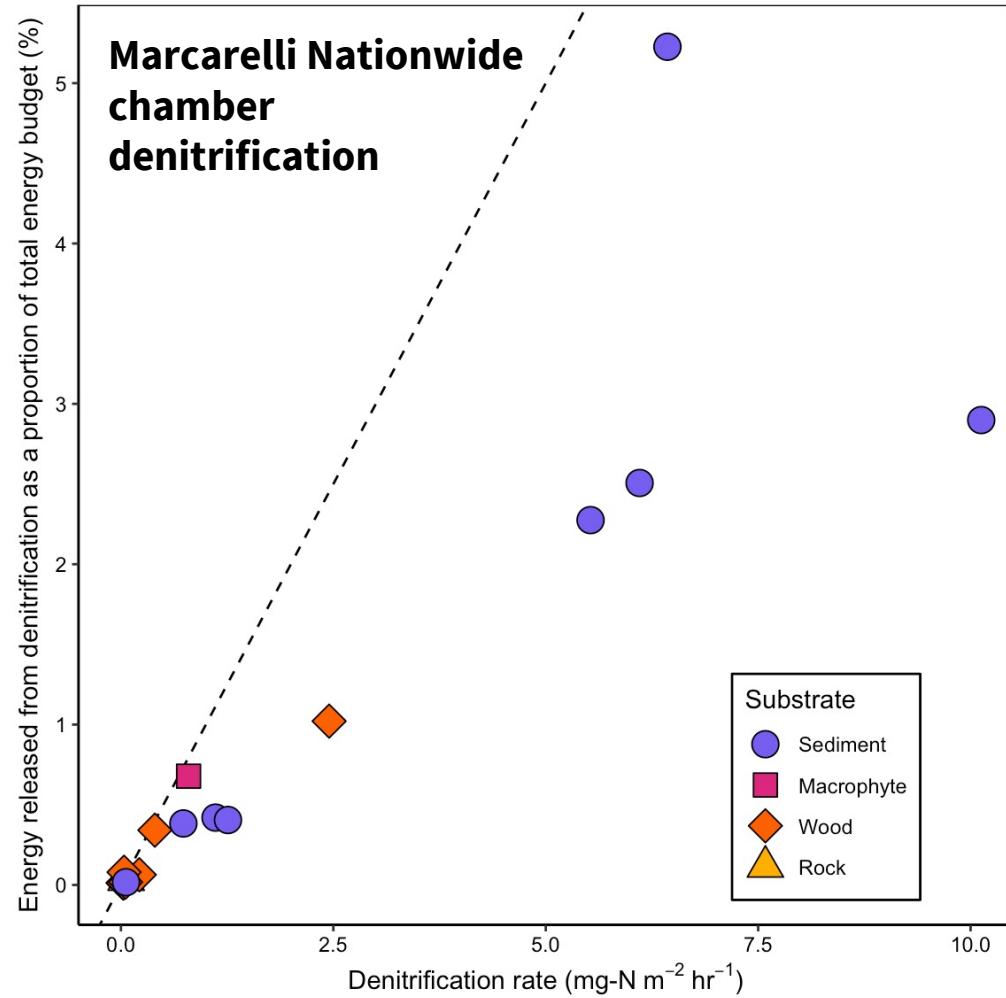
[Nitrate] important  
factor in **controlling**  
energy production from  
denitrification



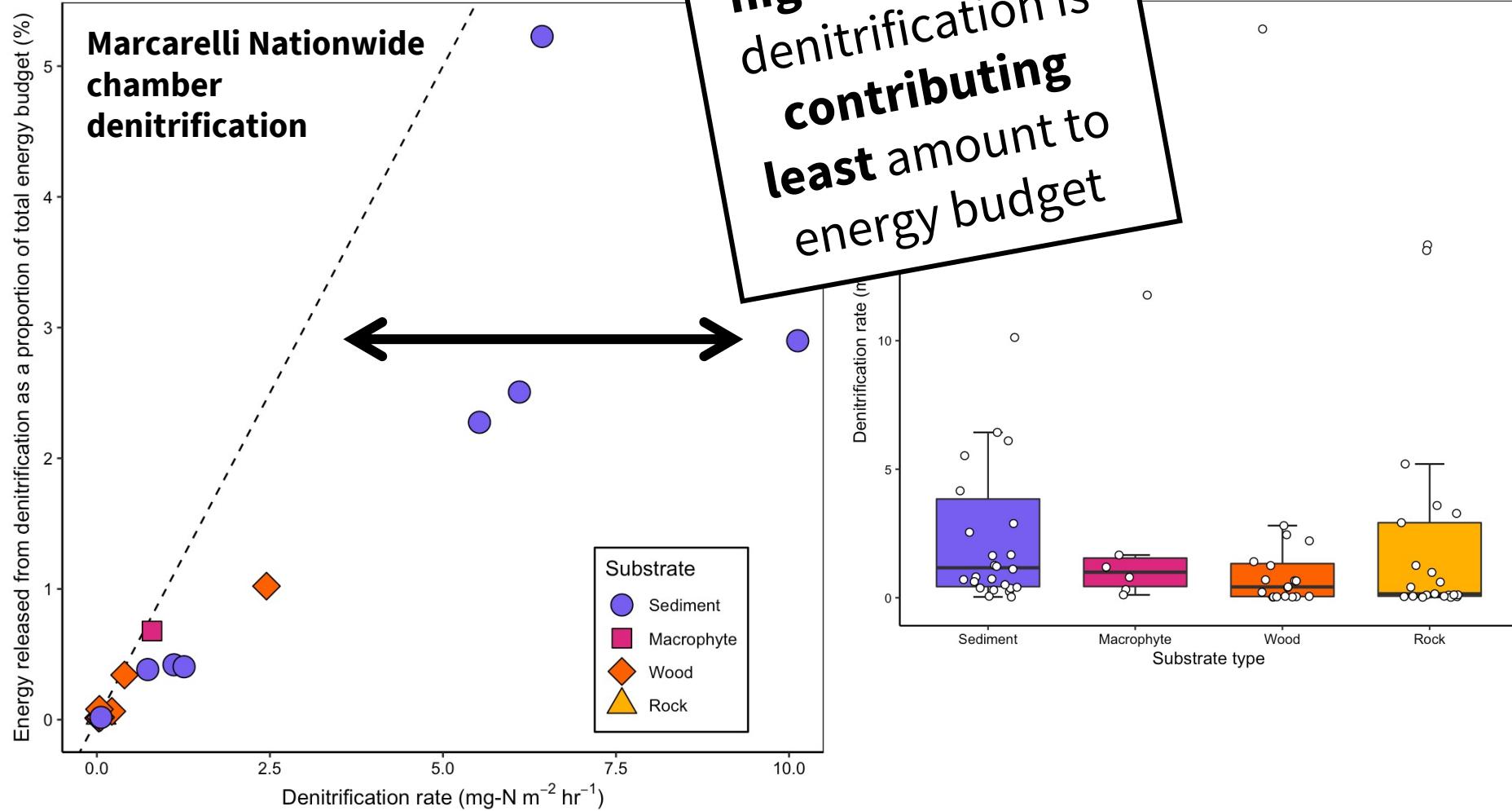
# Denitrification as a proportion of total energy: Substrate breakdown



# Denitrification as a proportion of total energy: Substrate breakdown

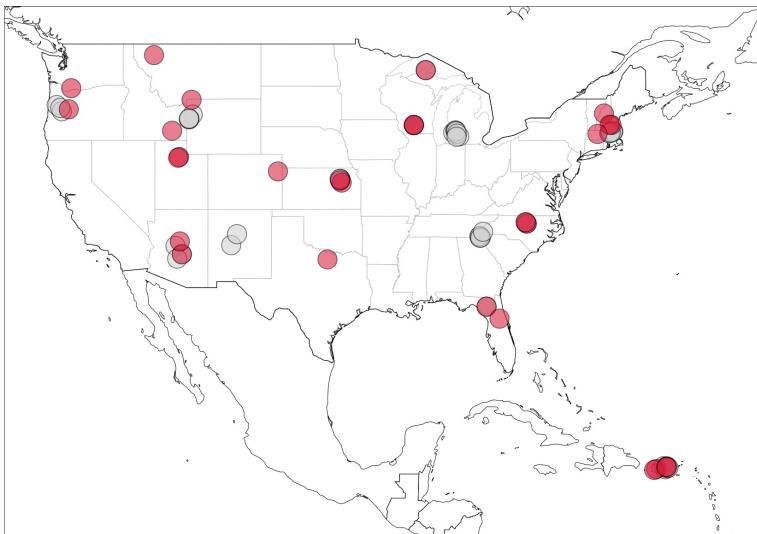


# Denitrification as a proportion of total energy: Substrate breakdown

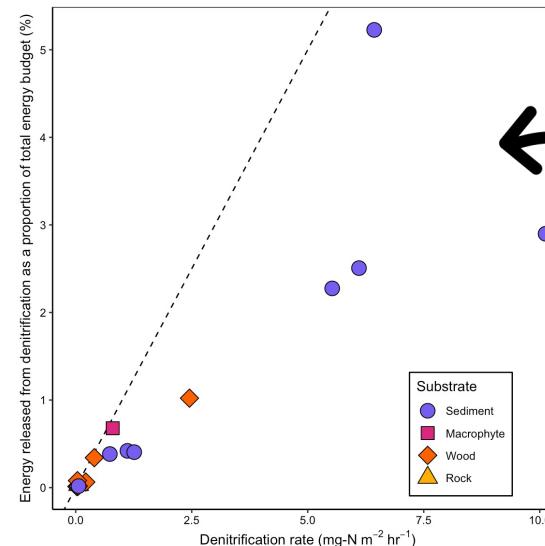


# Further directions

1. Remaining metabolism modeling for Marcarelli Nationwide Survey ( $n = 24$ )



2. Scaling chamber rates to whole-stream estimates at NEON sites ( $n = 14$ ) using NEON stream morphology data products
3. Exploring factors that impact the energy production from denitrification in each substrate



What's happening here?

# Acknowledgements



Michigan  
Technological  
University



## Marcarelli Nationwide Denitrification and N<sub>2</sub> Fixation Survey

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## StreamPULSE Network

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## National Ecological Observatory Network (NEON)

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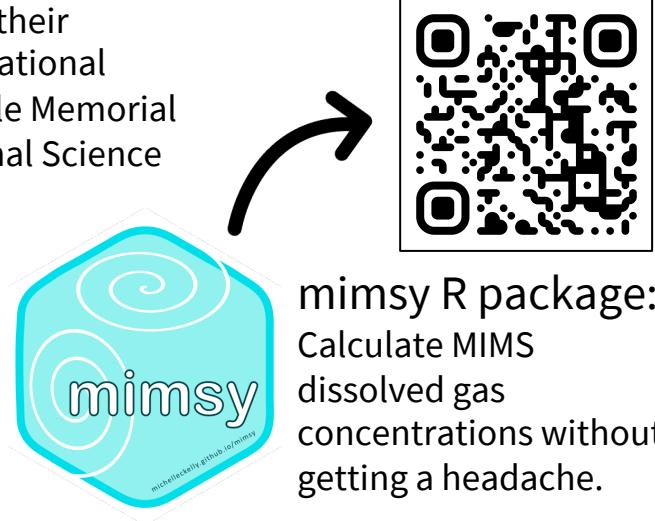
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<https://github.com/michelleckelly>



mimsy R package:  
Calculate MIMS  
dissolved gas  
concentrations without  
getting a headache.