**A Future Tale of Two Winters? Sediment-water** interface nitrogen dynamics in Lake Võrtsjärv (Estonia) during the ice-free winter 2019/2020

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Rockstrom et al. 2009



#### **Slide Courtesy Bob Howarth**

Rockstrom et al. 2009

#### Global trends in nitrogen use per year



(Erisman et al. 2015)



Nutrient Balanced Growth Isn't Just For Bottles (or Lake 227)



(Paerl et al. 2016)

#### "Nutrient Balanced Growth" is the Rule, Not the Exception

(And N 'limitation' is just as likely as P 'limitation' in freshwaters)



(Elser et al. 2007)

### **N Form Matters, Too**



### Large spread at high NH4:NOx







Winter 2018/2019

Don't mess with my incubations!

11

Objectives:

1. Determine denitrification/anammox, N fixation, DNRA, SOD, and inorganic N and urea fluxes across the sediment-water interface under ice in Lake Võrtsjärv (Estonia).

2. Determine ammonium (NH<sub>4</sub><sup>+</sup>) cycling rates, including nitrification, regeneration, and potential uptake, under ice in Lakes Võrtsjärv and Peipsi (Estonia).







\*Collect intact sediment cores and near-bottom water for continuous-flow incubations to measure SWI N fluxes and transformations.



Intake water

**Collection Vessel** 







## **Incubation Design**



C = Control (no isotope addition) A =  ${}^{15}NH_4^+$  addition (ammonium) N =  ${}^{15}NO_3^-$  addition (nitrate)

### Methods: Intact sediment core incubations

- Sample inflow reservoirs and core outflows daily for:
- Nutrients (filtered 0.22  $\mu$ m) PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, urea
- Dissolved gases
  O<sub>2</sub>, <sup>28, 29, 30</sup>N<sub>2</sub>, N<sub>2</sub>O



### Methods: Lachat Quikchem 8500

- Nutrients measured by flow injection analysis
- PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, urea
  - Ambient concentrations
  - Sediment core fluxes



### Methods: Membrane Inlet Mass Spectrometry

- C cores
  - Net <sup>28</sup>N<sub>2</sub> flux, O<sub>2</sub>
- A cores
  - $^{15}NH_{4}^{+} + {}^{14}NO_{2}^{-} \rightarrow {}^{29}N_{2}$
  - Possible anammox
- N cores
  - $^{15}NO_{3}^{-} \rightarrow ^{29,30}N_{2}$
  - Denitrification
  - $^{15}NO_{3}^{-} \rightarrow ^{15}NH_{4}^{+}$
  - DNRA (OX-MIMS)





\*Consistent decrease in SOD from fall through winter; consistently higher SOD (28-70%) near river input (more OM/macrophyte biomass); SOD lower in LV than many other temperate, eutrophic lakes (e.g., Lake Erie, Lake Champlain).



\*Consistent in situ denitrification rates (net  ${}^{28}N_2$  flux) at LV-10, but higher potentials (DNF = potential denitrification) in winter. However, near river input at LV-PS, higher in situ denitrification in winter, but little or no change in potential (little or no measurable N fixation; 0 – 3% anammox contribution).



\*Opposite patterns at the two sites --- clear stimulation of  $N_2$  production with NO3 addition near inputs (LV-PS) in Sept (low in situ N), and in main basin in winter (high in situ N; 0 - 3% maybe via anammox; little or no measurable N fixation).



\*Note slight difference in y-axis scales --- internal P loading nil or minimal during these sampling events (no surprise, likely a different story in summer, and under ice?); possible stimulation of P release in Sept 2019 with NO3 addition near river input, perhaps worthy of additional investigation (see Smolders et al. 2010, Biogeochem. 98: 1-7). No results yet from Dec 2019.



\*Note slight difference in y-axis scale --- Lake Võrtsjärv sediments were releasing an appreciable amount of urea (highly bioavailable organic N form) at these times. Similar rates observed in summer in Lake Erie (see Boedecker et al. 2020, J Great Lakes Res 46: 920-932), but few, if any, other rates for comparison (who measures SWI N fluxes, much less urea?). No results yet from Dec 2019.



\*Lake Võrtsjärv sediments in the main basin, but not near the river input, were releasing an appreciable amount of NO2 in late winter. NO3 additions to water overlying main basin sediments stimulated NO2 release, likely due to incomplete denitrification, but cannot rule out incomplete nitrification (or DNRA, unlikely). No results yet from Sept or Dec 2019.



\*Lake Võrtsjärv sediments were a consistent NO3 sink (denitrified). No robust differences between sampling locations. Adding NO3 stimulated NO3 uptake in the main basin, and maybe near the river input. Net NO3 flux in main basin nearly identical to estimated denitrification rate, but NO3 influx ~50% of denitrification near river input (coupled NTR/DNF). No results yet from Sept or Dec 2019.



\*NH4 results not ready yet, but preliminary data indicate sediment NH4 releases ~150-300  $\mu$ mol N m<sup>-2</sup> h<sup>-1</sup> near river input and ~30-60  $\mu$ mol N m<sup>-2</sup> h<sup>-1</sup> in the main basin.

That's internal N loading, and it's important, too!!! Especially if cyanos are a problem!!! Don't forget about legacy N loads!!! (e.g., see Van Meter et al. 2017, Global BGC Cycles 31: 2-23).

### **Take Home Message**

Internal nutrient loads are not just a P story. Internal N cycling (fueled by external loads!) is often the main source of NH4 for sustaining biomass and toxin production in non-N-fixing cyanobacteria blooms.

At the same time, the N cycle provides the best defense against excessive N loading via denitrification. BUT, denitrification is less efficient as N loads increase (e.g., Mulholland et al. 2008; Gardner & McCarthy 2009).

### **Next Steps**

- Finish analyzing nutrient data for SWI fluxes
- Water column NH4 cycling results (regeneration, uptake, nitrification)
- Water column O<sub>2</sub> respiration results
- Incorporate mechanistic rate data into ongoing watershed/lake

models (Dr. Fabien Cremona, EMU)

• Do an ice dance in Nov 2021...stay tuned!

#### Finish analyzing

- Water column N
- Water column C
- Incorporate mea
  models (Dr. Fab
- Do an ice dance



#### take, nitrification)

#### ershed/lake

# "We can't solve 21<sup>st</sup> century problems with 20<sup>th</sup> century science" --- Dr. Bob Heath, IAGLR, 2014-05-28





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