

The role of nitrogen as a driver of harmful algal blooms





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WRIGHT STATE

CHANGING LIVES

Ecosystem impacts from Nutrient loading

- Harmful Algal Blooms
- Toxin production
- Fish Kills
- Oxygen depletion
- Greenhouse gas production



Daniel Hoffman

Anthropogenic N ≥ Biological N fixation



Oct. 2008 Control (no nutrients) + N - NO3 + P-P04 3-+N+P **Courtesy of Hans Paerl**

Nutrient Addition experiments





Almost 6 per page of text

Cyanobacteria = 16 Microcystis = 5

ARTICLE INFO

ABSTRACT

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Relieving phosphorus loading is a key management tool for controlling Lake Erie eutrophication. During the 1960s and 1970s, increased phosphorus inputs degraded water quality and reduced central basin hypolimnetic oxygen levels which, in turn, eliminated thermal habitat vital to cold-water organisms and contributed to the extirpation of important benthic macroinvertebrate prey species for fishes. In response to load reductions initiated in 1972, Lake Erie responded quickly with reduced water-column phosphorus concentrations, phytoplankton biomass, and bottom-water hypoxia (dissolved oxygen <2 mg/l). Since the mid-1990s, cyanobacteria blooms increased and extensive hypoxia and benthic algae returned. We synthesize recent research leading to guidance for addressing this re-eutrophication, with particular emphasis on central basin hypoxia. We document recent trends in key eutrophication-related properties, assess their likely ecological impacts, and develop load response curves to guide revised hypoxia-based loading targets called for in the 2012 Great Lakes Water Quality Agreement, Reducing central basin hypoxic area to levels observed in the early 1990s (ca. 2000 km²) requires cutting total phosphorus loads by 46% from the 2003-2011 average or reducing dissolved reactive phosphorus loads by 78% from the 2005-2011 average. Reductions to these levels are also protective of fish habitat. We provide potential a pproaches for achieving those new loading targets, and suggest that recent load reduction recommendations focused on western basin cyanobacteria blooms may not be sufficient to reduce central basin hypoxia to 2000 km²

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Community Dominance: Lake Erie cyanobacterial Harmful Algals Blooms

1960s and 1970s

1990s to Present



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From http://cyanobacteria.myspecies.info

N Bioavailability



Triple bond -> difficult to break 18 ATP required for each N_2 molecule N_2 : limited bioavailability

More useful forms: NH_4^+ , Urea, NO_3^-

N and Cyanobacteria Toxicity



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Gobler et al. 2016

N and Cyanobacteria Toxicity

 Reduced N form additions to <u>non-N-</u> <u>fixing</u> cyanobacteria can increase toxicity.

(Davis et al. 2010, 2015; Chaffin et al. 2018)

- Low NH₄⁺ concentrations can inhibit toxin production (Kuniyoshi et al. 2010)
- NH₄⁺ and urea uptake may lead to both increased *Microcystis* biomass and toxin production (Harke et al. 2016)

Microcystins (µg/L)



Chaffin et al. 2018

Implications for Community Shift



Gobler et al. 2016

Nitrogen



Ammonium: the common currency

Pelagic diatoms



Diatoms use and store nitrate efficiently



Most phytos greatly prefer & *Microcystis* has a very strong affinity for NH₄⁺

N Assimilation in Phytoplankton





Beversdorf et al. 2015

Glibert et al. 2015

N in Fertilizer

Global shift toward urea and/or anhydrous ammonia.

Urea = >50% of worldwide applications (Glibert et al. 2006)

Nitrogen fertilizer demand – 5 key markets



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N Form and Community Structure

• NO₃⁻ : favors diatoms

• Reduced N (NH₄⁺ and urea): favors cyanobacteria



McCarthy et al. 2009

(Limited) Regulations on N Inputs

 U.S. EPA Bulletin 820-S-15-001 Advocates for <u>dual nutrient</u> control strategy

Separation United States Environmental Protection Agency

Protection Office of Water EPA - 820-S-15-001 MC 4304T February 2015

Preventing Eutrophication: Scientific Support for Dual Nutrient Criteria

Summary

Nutrient pollution resulting from excess nitrogen (N) and phosphorus (P) is a leading cause of degradation of U.S. water quality. The scientific literature provides many examples that illustrate the effects of both N and P on instream and water quality standards and are an effective tool for preventing nutrient pollution, for example, in helping to derive numeric limits in discharge permits. Development of numeric nutrient criteria is one aspect of a coordinated and comprehensive approach to nutrient management [⁷]. EPA has published several

No N reduction targets in Ohio
 Proposed 40% reduction in P loading
 Great Lakes Water Quality Agreement – Annex IV

Case study: Lake Erie



Maumee River

Increasing CyanoHABs in Western Lake Erie linked to increase in SRP



Fig. 4. Western basin (WB) median cyanobacteria wet-weight biomass (mg L⁻¹) (Cyano) as a function of Maumee River SRP load (metric tonnes) for water years 1996–2006.

Maumee N Loads to Western Lake Erie



Stow et al. 2015

N Inputs to Western Lake Erie



- Maumee River: largest Great Lakes watershed
- Kjeldahl N (NH4+ organic N) load from Maumee River to Lake Erie
 = 9000 metric tons/yr
 ¼ of total N load (Richards et al. 2010)

Reduced N % of Maumee Load increasing





*Most values outside of summer are <1; y-axis scale starts at 1

TKN/NO₃⁻ vs Chlorophyll concentrations



The proportion of reduced to oxidized N in the Maumee River load is significantly correlated to the increase in cyanobacterial bloom biomass in Western Lake Erie.



Nitrogen Cycle



sediment

Newell Lab research objectives

- To use a paired molecular-biogeochemical approach to disentangle the intricacies of the nitrogen cycle
- To understand the impact of human activities (primarily climate change and increased nitrogen loading) on the nitrogen cycle

Ammonium: the common currency



NH₄⁺ half-saturation
constant (K_m) for
Microcystis is high:
0.5-37 μM
Nicklisch and Kohl 2007, Takeya et al. 2004



Ammonia-oxidizing bacteria can have a very high K_m (5-300 μ M) but ammonia-oxidizing archaea have a very, very low K_m 0.05-0.15 μ M

Internal N loading

Research Questions

- How quickly is NH₄⁺ recycled?
- To what extent can NH₄⁺ recycling support cyanobacterial bloom growth?
- When do phytoplankton become N-limited?

N Inputs to Western Lake Erie



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Ammonium cycling drives harmful algal blooms in Sandusky Bay, Lake Erie

Justyna J. Hampel, Mark J. McCarthy, George S. Bullerjahn, Robert M. McKay, Michelle Neudeck, and Silvia E. Newell

Sandusky Results: Potential Ammonium Uptake and Regeneration



Hampel et al. 2019

June 5th, 2017

40.7 metric tons NH₄⁺

 NH_4

Sandusky Bay 1.9x

21.1 metric tons N

Hampel et al., 2019 Harmf

Sandusk



62.5 metric tons NH₄⁺

 NH_4

Sandusky Bay



Hampel et al., 2019 Harmf

Sandusk

36x

August 14th, 2017

Sandusky Bay

123 metric tons NH₄⁺

NH₄



Hampel et al., 2019 Harmj

Sandusk

479x

August 28th, 2017

Sandusky Bay

199 metric tons NH₄+

 NH_4

1190x

0.167 metric tons N

Hampel et al., 2019 Harmf

Sandusk

Sandusky Bay: Ammonium Regeneration

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- Regeneration in the bay increases throughout the summer suggesting that toward the end of summer the bloom relies heavily on regenerated NH₄⁺.
 - With undetectable DIN in the water column, regeneration sustains the bloom
- When extrapolated to the whole bay volume, daily NH₄⁺ regeneration exceeded daily TN loadings at all sampling events.
 - Useful tool for N management practices and nutrient regulations.

Eutrophication in the Great Miami River: To What Extent Can Sediment Nitrogen Loss Compensate for Nutrient Over-enrichment? Lee Slone, M.Sc. student – WSU Slone et al. 2018 _{Slone et al., 2018}



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









Lee Slone





$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

- Requires anoxia
- Pathway ends at N₂O more often under low oxygen
- Removes excess N from ecosystem
- Critical ecosystem service in eutrophic systems!

Dissolved gas fluxes

- Dissolved gases (²⁸N₂, ²⁹N₂, ³⁰N₂, O₂, Ar)
- MIMS (Kana et al. 1994, An et al. 2001)





Excess ²⁸N₂ flux (Denitrification)



Impact on River Nutrient Load



LGMR Conclusions

- Denitrification removed nitrate at very high rates during high river flow, but N removal was still exceeded by external inputs (to a lesser extent during low flow).
- Sediments were a source of bioavailable ammonium, potentially contributing to local algal blooms, but were a strong nitrate sink and overall net N sink.
- River sediments were a P source, contributing an additional 2 - 6 % to the external P load from the agricultural and urban watershed.
- These results support calls for a dual nutrient (N & P) management approach to control eutrophication in inland waters and coastal marine systems.

Net Denitrification or Nitrogen Fixation Lower Great Miami River 2017-2018



Nutrient sample collection

• Megan Reed et al.

Journal article survey of nutrient sampling methods



Reed et al., L&O Methods, in review

Why does accurate nutrient data matter?

 Using data from Hampel et al 2018: Uptake: 0.759 μmol L⁻¹ h⁻¹ Regeneration: 0.337 μmol L⁻¹ h⁻¹ Ambient concentration of ammonium (NH₄⁺): 0.33 μM

An unfiltered water sample stored in the dark would have: $[NH_4^+]: 0.119 \mu M after 30 minutes$ $[NH_4^+]: 0 \mu M after only 47 minutes!$

Methods- Study site



Sample collection



Reed et al., L&O Methods, in review

Results- Phosphate concentrations



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Ammonium concentrations



Concentration (uM)

 \bigcirc

Percent change of phosphate concentrations



Percent change of ammonium concentrations



Concentration of P against percent change from 0.22 µM sample filtered in the field



Reed et al., L&O Methods, in review

Concentration of N against percent change from 0.22 µM sample filtered in the field



Reed et al., L&O Methods, in review

Sample Collection Conclusions

- Failing to filter samples in the field can lead to significant changes in the concentration compared to the ambient value
- Filtering in the field with 0.70 um filters has the most significant impact on nutrient concentration
- More specific filtering methods should be considered in order to ensure the accuracy of reporting nutrient monitoring data

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