Stoichiometric controls over nitrogen and phosphorus accumulation from soils to the sea

Philip Taylor and Alan Townsend, INSTAAR and EEB, Univ. of CO.
Unprecedented accumulation of bioavailable N and P

Population and Reactive N

Galloway et al. 2003

Reactive P

Global Phosphate Production (USGS 2007)
Impacts are concentration dependent, yet reactive N and P concentrations do not scale strongly with loading.
Denitrification across 230 streams and rivers
(conversion of $\text{NO}_3^-$ to $\text{N}_2$ gas)

And concentration is not a good predictor of key control processes
We need deeper insight.

Compelling pattern to work with
(seen in 6 other stream and groundwater systems, and many lakes and oceans)

reproduced from Goodale et al. 2003

\[ y = 380.5(x)^{-2.03} \]

\[ r^2 = 0.46 \]
Outline

1) Are inverse patterns everywhere?

2) If so, what biological processes could underlie these patterns?

And, what data exist to test a conceptual model?
We explored DOC-NO$_3$ relationships in all of earth’s major ecosystems.
Outline

1) Are inverse patterns everywhere? YES

2) If so, what biological processes could underlie these patterns?

And, what data exist to test a conceptual model?
Stoichiometry of microbial C-N coupling

DOC $+ \text{NO}_3^-$

- Nitrogen assimilation
- Nitrification
- Denitrification

[Diagram showing the relationship between DOC, [NO₃⁻], and nitrogen processes]
Stoichiometry of microbial C-N coupling

DOC + NO$_3^-$

Nitrogen assimilation  | Nitrification  | Denitrification

How may shifts in resource C:NO$_3^-$ stoichiometry govern these three processes?
Stoichiometry of microbial C-N coupling

DOC + NO$_3^-$

- **Nitrogen assimilation**
  - Anabolic
  - Biomass C:N ~5 (3 - 20)

- **Nitrification**

- **Denitrification**

Organic Nitrogen

High resource C:N ratios

Low resource C:N ratios

Low [DOC] High
Stoichiometry of microbial C-N coupling

DOC + NO$_3^-$

- Nitrogen assimilation
  - Anabolic Biomass C:N $\sim$5 (3 - 20)
- Nitrification
- Denitrification

Organic Nitrogen

[DOC] Low High

Low resource C:N ratios

High resource C:N ratios

Nitrogen Limitation
Stoichiometry of microbial C-N coupling

DOC + NO$_3^-$

- Nitrogen assimilation
  - Anabolic Biomass C:N ~5 (3 - 20)
- Nitrification
- Denitrification

Organic Nitrogen

Carbon Limitation

Low [NO$_3^-$] High

Low resource C:N ratios

Nitrogen Limitation

High resource C:N ratios

Low [DOC] High

Nitrogen Limitation

Carbon Limitation
Stoichiometry of microbial C-N coupling

- **DOC + NO$_3^-$**
  - **Nitrogen assimilation**
    - Anabolic Biomass C:N $\approx 5$ (3 - 20)
  - **Nitrification**
  - **Denitrification**

Organic Nitrogen

Carbon Limitation

- **Low resource C:N ratios**
- Threshold Point $\sim$ DOC:NO$_3^-$ of 3 - 20
- **High resource C:N ratios**

Low [DOC] High

Nitrogen Limitation
**Stoichiometry of microbial C-N coupling**

- **DOC + NO$_3^-$**
- **Nitrogen assimilation**
  - Anabolic Biomass C:N ~5 (3 - 20)
- **Nitrification**
  - Autotrophic Weak competitor for NH$_4^+$
- **Denitrification**
- **Organic Nitrogen**
- **NH$_4^+$ + CO$_2$**

**Carbon Limitation**
- Threshold Point ~ DOC:NO$_3^-$ of 3 - 20
- Low resource C:N ratios
- High resource C:N ratios

**Nitrogen Limitation**
- Low [NO$_3^-$] High
- Low [DOC] High
Stoichiometry of microbial C-N coupling

- **DOC + NO₃⁻**
  - **Nitrogen assimilation**
    - Anabolic Biomass C:N ~5 (3 - 20)
  - **Nitrification**
    - Autotrophic Weak competitor for NH₄⁺
  - **Denitrification**

- **Organic Nitrogen**
  - NH₄⁺ + CO₂

- **Carbon Limitation**
  - Low resource C:N ratios
  - Threshold Point ~ DOC:NO₃⁻ of 3 - 20
  - High resource C:N ratios

- **Nitrogen Limitation**
  - Low [DOC] High
Stoichiometry of microbial C-N coupling

DOC + NO₃⁻

- **Nitrogen assimilation**
  - Anabolic Biomass C:N ~5 (3 - 20)

- **Nitrification**
  - Autotrophic Weak competitor for NH₄⁺
  - Denitrification Catabolic DOC and NO₃⁻ 1:1 ratio

- **Organic Nitrogen**
- **NH₄⁺ + CO₂**
- **N₂ gas**

**Threshold Point**
~ DOC:NO₃⁻ of 3 - 20

**Carbon Limitation**
- Low resource C:N ratios
  - High [NO₃⁻] High

**Nitrogen Limitation**
- High resource C:N ratios
  - Low [DOC] High
Nitrogen assimilation
Anabolic Biomass C:N ~5 (3 - 20)

Nitrification
Autotrophic Weak competitor for NH$_4^+$

Denitrification
Catabolic DOC and NO$_3^-$ 1:1 ratio

Organic Nitrogen

NH$_4^+$ + CO$_2$

N$_2$ gas

Stoichiometry of microbial C-N coupling

DOC + NO$_3^-$

Low resource C:N ratios

Carbon Limitation

Threshold Point ~ DOC:NO$_3^-$ of 3 - 20

Nitrogen Limitation

High resource C:N ratios

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Stoichiometry of microbial C-N coupling

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NH$_4^+$ + CO$_2$

N$_2$ gas

Carbon Limitation

Threshold Point ~ DOC:NO$_3^-$ of 3 - 20

Nitrogen Limitation

[DOC] High

Low resource C:N ratios

High resource C:N ratios

NO$_3^-$ (mg/L)

DOC (mg/L)
Stoichiometry of microbial C-N coupling

DOC $+$ NO$_3^-$

Nitrogen assimilation
Anabolic Biomass C:N $\sim 5$ (3 - 20)

Nitrification
Autotrophic Weak competitor for NH$_4^+$

Denitrification
Catabolic DOC and NO$_3^-$ 1:1 ratio

Organic Nitrogen

NH$_4^+$ + CO$_2$

N$_2$ gas

Retention or DON loss?

Carbon Limitation

Low resource C:N ratios

Threshold Point
$\sim$ DOC:NO$_3^-$ of 3 - 20

Nitrogen Limitation

High resource C:N ratios

Low [NO$_3^-$] High

NO$_3^-$ assimilation

\[
\text{NO}_3^- \text{ (mg/L)}
\]

\[
\text{DOC (mg/L)}
\]

Unpolluted Lakes
Eutrophied Lakes
DOC:N-NO$_3^-$
Stoichiometry of microbial C-N coupling

DOC + NO$_3^-$

Nitrogen assimilation
- Anabolic Biomass C:N ~5 (3 - 20)
- Organic Nitrogen
- Retention or DON loss?

Nitrification
- Autotrophic Weak competitor for NH$_4^+$
- NH$_4^+$ + CO$_2$
- NO$_3^-$ accrual exacerbated

Denitrification
- Catabolic DOC and NO$_3^-$ 1:1 ratio
- N$_2$ gas

Thermal Limitation
- Low resource C:N ratios
- Threshold Point ~ DOC:NO$_3^-$ of 3 - 20
- Nitrogen Limitation
- High resource C:N ratios

Nitrification DOC (mg/L)

NO$_3^-$ (mg/L)

Unpolluted Lakes
Eutrophied Lakes
DOC:N-NO$_3^-$

Diurnal variation

Retention or DON loss?
Stoichiometry of microbial C-N coupling

- **Nitrogen assimilation**
  - Anabolic
  - Biomass C:N ~5 (3 - 20)

- **Nitrification**
  - Autotrophic
  - Weak competitor for NH$_4^+$

- **Denitrification**
  - Catabolic
  - DOC and NO$_3^-$ 1:1 ratio

- **Organic Nitrogen**
- **NH$_4^+$ + CO$_2$**
- **N$_2$ gas**

- **Threshold Point**
  - [DOC:NO$_3^-$] of 3 - 20

- **Low resource C:N ratios**
- **High resource C:N ratios**

- **Carbon Limitation**
- **Nitrogen Limitation**

- **Retention or DON loss?**
- **NO$_3^-$ accrual exacerbated**
- **Permanent NO$_3^-$ removal**

- **Nitrification**
- **Denitrification**

- **NO$_3^-$ assimilation**

- **DOC (mg/L)**
  - 0
  - 25
  - 50
  - 75
  - 100
  - 125

- **NO$_3^-$ (mg/L)**
  - 0
  - 25
  - 50
  - 75
  - 100
  - 125
Examine critical threshold ratios at inflection point

\[ y = a + b \cdot k(x) \]
Examine critical threshold ratios at inflection point

\[ y = a + b \cdot k(x) \]

DOC or POC (mg/L)

Global mean inflection point ratio, \( \text{DOC:N-NO}_3 = 3.54 \)

<table>
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<tr>
<th></th>
<th>Soils</th>
<th>Streams/Rivers</th>
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Global inflection points for each of earth’s major ecosystems rests between the optimal resource stoichiometries for denitrification and heterotrophic \( \text{NO}_3^- \) assimilation.
System-specific scenarios for NO$_3^-$

Inflection Points range from 3 to 20, except Amazon
How about for phosphorus?

Inflection Points range from 3 to 20, except Amazon

Freshwater Rivers and Streams

Luquillo LTER

EPA EMAP

NSWS

Amazon

Lakes

NTL LTER

Open Ocean

CARIACO basin

Dissolved Phosphorus

OC:N-NO₃ atomic ratio

Low resource C:P ratios

High resource C:P ratios

Low

[DOC]

High

High resource C:P ratios
How about for phosphorus?

Inflection Points range from 3 to 20, except Amazon.
Emerges with C:P ratios too!

Inflection Points range from 20 to 300, except Amazon.
Why is C:P much more variable?
Greater bacteria C:P plasticity

Frost et al. 2004
Why is C:P much more variable?
Illustrative Model

Frost et al. 2004
Why is C:P much more variable?
Illustrative Model

Frost et al. 2004
System-specific scenarios
(eastern USA streams and rivers)

Bioavailable N and P accumulates only when resource conditions favor heterotrophic carbon limitation.
System-specific scenarios
(eastern USA streams and rivers)

Bioavailable N and P accumulates only when resource conditions of favor heterotrophic nutrient limitation
System-specific scenarios
(eastern USA streams and rivers)

Bioavailable N and P accumulates only when resource conditions of favor heterotrophic nutrient limitation

Assimilation of N and P in characteristic organismal C:N:P ratios
Stronger relative $\text{NO}_3^-$ accumulation shifts ecosystem N:P ratios across magic 16:1; role for nitrification?

*Freshwater Rivers and Streams*

- Luquillo LTER
- EPA EMAP
- National SW Survey
- Amazon (CAMREX)

*Lakes*

- Northern Lakes LTER

*Bays*

- Chesapeake + Delaware Bays and Rivers

*Coastal Margins*

- Atlantic Coastal Margins

*Open Ocean*

- CARIACO Basin

**OC:N-$\text{NO}_3^-$** atomic ratio
System-specific scenarios
(eastern USA streams and rivers)

Bioavailable P accumulates only when resource conditions of favor heterotrophic nutrient limitation
Simplified N Cycle

- NO$_3^-$
- Nitrogen assimilation
- Nitrification
- Denitrification
- Organic Nitrogen
- Ammonium
- N$_2$ gas

Resource
3) Denitrification

Heterotrophic C:N = 5

Microbial Community
Simplified N Cycle

Nitrogen assimilation
Nitrification
Denitrification

Organic Nitrogen
Ammonium
N₂ gas

Resource
3) Denitrification

Microbial Community

Catabolic C:N = 1

DOC

NO₃⁻
Simplified N Cycle

- **NO$_3^-$**
- **Nitrogen assimilation**
- **Nitrification**
- **Denitrification**

Organic Nitrogen

Ammonium

$N_2$ gas

Resource

3) **Denitrification**

Microbial Community

- **Catabolic C:N = 1**
- **DOC**
- **NO$_3^-$**
- **DOC**
- **NO$_3^-$**

**Nitrification**

**Denitrification**
Microbial Community

**Resource**

3) Denitrification

C:N = 1 - 3

**Catabolic C:N = 1**

- DOC
- NO$_3^-$
- N$_2$ gas

**Simplified N Cycle**

- Nitrogen assimilation
- Nitrification
- Denitrification

- Organic Nitrogen
- Ammonium
- N$_2$ gas

- NO$_3^-$

60% N$_2$ gas
Microbial Community

Catabolic C:N = 1

DOC

Nitrification

Denitrification

NO$_3^-$

Organic Nitrogen

Ammonium

N$_2$ gas

Simplified N Cycle

3) Denitrification

C:N = 1 - 3

Nitrogen assimilation

Nitrification

Denitrification

Low resource C:N ratios

High resource C:N ratios

DOC

[DOC]

High

Low

NO$_3^-$

N$_2$ gas

CO$_2$

Low resource C:N ratios

High resource C:N ratios

DOC:N-NO$_3$ ratio

Conceptual Model

N$_2$ gas

N assimilation

Nitrification

1

5 +
**Simplified N Cycle**

- **NO₃⁻**
- **Nitrogen assimilation**
- **Nitrification**
- **Denitrification**

**Resource**

3) **Denitrification**

C:N = 1 - 3

**Microbial Community**

- **Catabolic C:N = 1**
- **DOC**
- **NO₃⁻**

**Conceptual Model**

- **Low resource C:N ratios**
- **High resource C:N ratios**

**NO₃⁻ assimilation**

- **Natrification**
- **Denitrification**

**DOC:N-NO₃ ratio**

- 1
- 5 +
Simplified N Cycle

- $\text{NO}_3^-$
-\text{Nitrogen assimilation}
- Nitrification
- Denitrification

Organic Nitrogen
Ammonium
$\text{N}_2$ gas

Resource

3) Denitrification
C:N = 1 - 3

Microbial Community

Catabolic C:N = 1

Conceptual Model

- $\text{NO}_3^-$ assimilation
- Nitrification
- Denitrification

$\text{r}^2 = .68$

- $\text{DOC}:\text{N-NO}_3^-$ ratio

$\text{DOC} 
\rightarrow \text{NO}_3^-
\rightarrow \text{DOC}$

60%

$\text{N}_2$ gas
CO$_2$
Implications

1. Ecological stoichiometry is a fundamental control over bioavailable nitrogen and phosphorus accumulation among earth’s major ecosystems (not simply kinetic or thermodynamic).
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2. Major role for heterotrophic microbes in N and P retention, accrual and loss.
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![Graph showing retention and loss of NO₃⁻ and DOC](image)
Implications

1. Ecological stoichiometry is a fundamental control over bioavailable nitrogen and phosphorus accumulation among earth’s major ecosystems (not simply kinetic or thermodynamic).
2. Major role for heterotrophic microbes in N and P retention, accrual and loss.
3. Argues for explicit stoichiometric considerations in both diagnostic and prognostic modeling.
Implications

1. Ecological stoichiometry is a fundamental control over bioavailable nitrogen and phosphorus accumulation among earth’s major ecosystems (not simply kinetic or thermodynamic).
2. Major role for heterotrophic microbes in N and P retention, accrual and loss.
3. Argues for explicit stoichiometric considerations in both diagnostic and prognostic modeling.
4. Offers a unique theoretical framework to explore similarities and differences in patterns (strength, breakpoints, etc.) between systems.
Thanks to…

Noah Fierer and Peter Vitousek for excellent insights.

providers of online data repositories, like the LTER, without which this meta-analysis would be impossible.
Threshold behavior reveals role for C quality

\[ y = a + b \cdot k(x) \]

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**DOC or POC (mg/L)**

**High**
- Forests and shrublands
- Mangroves
- Grasslands
- Marshes
- Seagrass meadows
- Freshwater macrophyte meadows
- Macroalgal beds
- Benthic microalgal beds
- Phytoplanktonic communities

**Low**
- Soils
- Impacted Rivers/Streams
- Rivers/Streams
- Lakes/Wetlands
- Ocean Margins
- Oceans

**Increase in C quality**

\( k \) (day\(^{-1}\))
Same idea for phosphorus!

Inflection Points range from 3 to 30, except Amazon