Characteristics and temporal trends of nutrient and sediment loads from the nontidal Chesapeake watershed

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Objectives

❖ Explore the **characteristics** of riverine loads:
   • **By species:** SS, TN, NOx, TP, PO4
     ❑ 9 major tributaries
     ❑ 4 seasons
     ❑ 4 discharge quantiles

❖ Explore the **temporal trends** of riverine loads:
   • **By species:** SS, TN, NOx, TP, PO4

* Focused on the RIM watersheds (nontidal) in 1985-2016
* Used USGS R workspaces by Moyer et al. (2017)
River Input Monitoring (RIM) Sites

 Susquehanna
- Area: 27,100 mi²
- Forest: 67%
- Agriculture: 29%
- Other: 4%

 Patuxent
- Area: 348 mi²
- Forest: 38%
- Agriculture: 41%
- Urban: 13%
- Other: 8%

 Mattaponi
- Area: 603 mi²
- Forest: 69%
- Agriculture: 19%
- Other: 12%

 James
- Area: 6,252 mi²
- Forest: 80%
- Agriculture: 16%
- Other: 4%

 Potomac
- Area: 11,600 mi²
- Forest: 61%
- Agriculture: 35%
- Other: 4%

 Rappahannock
- Area: 1,596 mi²
- Forest: 61%
- Agriculture: 36%
- Other: 3%

 Choptank
- Area: 113 mi²
- Forest: 29%
- Agriculture: 50%
- Other: 21%

 Appomattox
- Area: 1,342 mi²
- Forest: 72%
- Agriculture: 20%
- Other: 8%

 Pamunkey
- Area: 1,078 mi²
- Forest: 68%
- Agriculture: 24%
- Other: 8%

> 90% of NTCBW flow
~ 30-year daily flow
~ 20-30 samples/yr
WRTDS: Trend Analysis

**Daily** flow & discretely-sampled concentration data at a sampling site

**WRTDS**
(Hirsch et al. 2010)

**Daily** conc. and load estimates

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“For the latest load estimates, see Moyer et al. (2017); https://doi.org/10.5066/F7RR1X68."
Part I

❖ Explore the **characteristics** of riverine loads:

- **By species:** SS, TN, NOx, TP, PO4
  - 9 major tributaries
  - 4 seasons
  - 4 discharge quantiles

❖ Explore the **temporal trends** of riverine loads:

- **By species:** SS, TN, NOx, TP, PO4

  * Focused on the RIM watersheds (nontidal) in 1985-2016
  * Used USGS R workspaces by Moyer et al. (2017)
Distribution by Tributary

ordered by watershed size
Distribution by Tributary (% Load)

Q
- Top 3 = 92%
- Similar to Q fraction

SS
- Top 3 = 92%
- Smaller than Q fraction

TN
- Top 3 = 95%
- Similar to Q fraction

TP
- Top 3 = 91%
- Smaller than Q fraction

NOx
- Top 3 = 97%
- Similar to Q fraction

PO4
- Top 3 = 93%
- Smaller than Q fraction
Distribution by Tributary (FWC)

Range in average concentration:
SS: 14-160 mg/L (x11)
TN: 0.6-2.1 mg/L (x3.5)
TP: 0.056-0.2 mg/L (x3.6)
NOx: 0.15-1.33 mg/L (x8.8)
PO4: 0.011-0.038 mg/L (x3.5)
Distribution by Tributary (Ratio)

**NOx/TN**
- Ranges from 25% to 70% (contrast between MD and VA rivers)

**PO4/TP**
- Ranges from 9.6% to 29% (most rivers in the range of 15% to 21%)

**TN/TP**
- Ranges from 10 to 50 mol/mol (Susquehanna: the only river > mean) (James and Rap: two rivers <16:1)

**NOx/PO4**
- Ranges from 15 to 240 mol/mol (Susquehanna: the only river > mean) (James: the only river < 16:1)
Summary (Patterns by Tributaries)

• The three largest tributaries (SUS, POT, and JAM) represent > 90% of total flow and total load.

• Average concentration is more variable for SS (x11) and NOx (x8.8) than the other species (x3-x4).

• NOx is a major fraction of TN in MD rivers but a minor fraction in VA rivers; PO4 is consistently a minor fraction of TP in MD and VA rivers.

• For both TN:TP and NOx:PO4 molar ratios, Susquehanna is the only river that exceeds the RIM average; James is the only river that is < 16:1.
Distribution by **Season (%) Load**

- **Q**: Similar to Q fraction
- **TN**: Similar to Q fraction
- **TP**: Similar to Q fraction
- **NOx**: Similar to Q fraction
- **PO4**: Similar to Q fraction
Distribution by Season (FWC)

Largest seasonal concentration:
SS: Sep-Nov
TN: Sep-Nov and Dec-Feb
TP: Sep-Nov
NOx: Dec-Feb
PO4: Sep-Nov
Distribution by Season (Ratio)

NOx is always the dominant fraction of TN

PO4 is always the less dominant fraction of TP

TN:TP ratio always > 16

NOx/PO4 ratio always > 16
Summary (Patterns by Seasons)

- Contributions of load by the four seasons are generally similar to their contributions of flow.
- Average seasonal concentration is at the highest in Sep-Nov (SS, TN, TP, PO4) and Dec-Feb (TN, NOx).
- NOx is a major fraction of TN in all four seasons, whereas PO4 is consistently a minor fraction of TP.
- For both TN:TP and NOx:PO4 molar ratios, all four seasons are > 16:1.
Distribution by Flow (% Load)

- **Q**: 5.3 (Q1), 13 (Q2), 24 (Q3), 58 (Q4)  
  Similar to Q fraction

- **SS**: 0.62 (Q1), 2.1 (Q2), 6.6 (Q3), 91 (Q4)  
  Larger than Q fraction

- **TN**: 4.1 (Q1), 11 (Q2), 22 (Q3), 63 (Q4)  
  Similar to Q fraction

- **TP**: 2.6 (Q1), 6.4 (Q2), 14 (Q3), 77 (Q4)  
  Larger than Q fraction

- **NOx**: 4.1 (Q1), 12 (Q2), 24 (Q3), 59 (Q4)  
  Similar to Q fraction

- **PO4**: 6 (Q1), 12 (Q2), 22 (Q3), 60 (Q4)  
  Similar to Q fraction
Distribution by **Flow (FWC)**

Flow-weighted concentration:
- **SS**: Q4 >> Q1, Q2, Q3
- **TN**: similar
- **TP**: Q4 > Q1, Q2, Q3
- **NOx**: similar
- **PO4**: similar
Distribution by **Flow (Ratio)**

**NOx/TN**
- Q1: 64
- Q2: 70
- Q3: 71
- Q4: 61

**PO4/TP**
- Q1: 39
- Q2: 33
- Q3: 27
- Q4: 13

**NOx is always the dominant fraction of TN**

**PO4 is is always the less dominant fraction of TP**

**TN/TP**
- Q1: 53
- Q2: 60
- Q3: 54
- Q4: 27

**NOx/PO4**
- Q1: 88
- Q2: 130
- Q3: 140
- Q4: 130

**TN:TP ratio always > 16**

**NOx/PO4 ratio always > 16**
Summary (Patterns by Flow Quantiles)

• Q4 represents 58% of flow among four quantiles. Q4 represents a similar % for TN, NOx, and PO4 but a much higher % for SS (91%) and TP (77%).

• Average flow-weighted concentration is similar among the four flow quantiles for TN, NOx, and PO4; it is much higher in Q4 than the other quantiles for SS and TP.

• NOx is a major fraction of TN in all four flow quantiles, whereas PO4 is a minor fraction of TP.

• For both TN:TP and NOx:PO4 molar ratios, all four flow quantiles are > 16:1.
Explore the characteristics of riverine loads:

- By species: SS, TN, NOx, TP, PO4
  - 9 major tributaries
  - 4 seasons
  - 4 discharge quantiles

Explore the temporal trends of riverine loads:

- By species: SS, TN, NOx, TP, PO4
  
  * Focused on the RIM watersheds (nontidal) in 1985-2016
  
  * Used USGS R workspaces by Moyer et al. (2017)
NTCBW Load = Sum of Loads at 9 RIM Stations

Rise due to Susquehanna
Trend - TP, PO4, TP-PO4

- **TP**
  - Rise due to Susquehanna
  - General decline vs. Susquehanna rise

- **PO4**
  - General decline vs. Susquehanna rise

- **TP - PO4**
  - Issue with particulate P
  - Rise due to Susquehanna
Trend - TN, NOx, TN-NOx

General decline in N

General decline

Issue with particulate N

Rise due to Susquehanna
Trend - Ratio

**NOx/TN**
- Ratio, %
- NTCBW, SUS, NTCBW-SUS
- 50%

**PO4/TP**
- Ratio, %
- NTCBW, SUS, NTCBW-SUS
- 50%

**TN/TP**
- Ratio, mol/mol
- NTCBW, SUS, NTCBW-SUS
- 16:1

**NOx/PO4**
- Ratio, mol/mol
- 16:1
Summary (Long-term Trends)

• Sediment and particulate nutrients loads from the NTCBW have risen since ~1995 – largely driven by Susquehanna trends.

• Dissolved nutrients loads from the NTCBW have declined in general – suggesting effectiveness of management (e.g., WWTP upgrades, Clean Air Act).

• NOx is a major fraction of TN in all years, whereas PO4 is always a minor fraction of TP.

• TN:TP and NOx:PO4 molar ratios are > 16:1 in all years, but TN:TP ratios have declined in recent years due to opposite trends in TN and TP – potentials for changes in nutrient limitation in the downstream estuaries.
THANK YOU!
The largest estuary in North America;

64,000 mi$^2$ watershed -- Washington, D.C. and parts of six states (MD, VA, WV, DE, PA, NY);

14:1 land-to-water ratio, the largest of any coastal water body in the world;

N, P, SS reduction enforced by the 2010 Chesapeake Bay TMDL;

Many major and minor tributaries, with >90% of load from the 9 major rivers and ~60% of that from Susquehanna River;

River loads estimated and reported using a statistical tool called WRTDS.
WRTDS: Load Estimation

Daily flow & discretely-sampled concentration data at a sampling site

WRTDS (Hirsch et al., 2010)

[Weighted Regressions on Time, Discharge, and Season]

\[
\ln(C) = \beta_0 + \beta_1 t + \beta_2 \ln(Q) + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + \varepsilon
\]

• One single model (coefficient set) for each day of estimation;
• No assumption on fixed C-Q relations over time or season;
• Better model performance;
• Adopted in a range of studies, including Chesapeake, Great Lakes, Mississippi, Baltic Sea.

For the latest load estimates, see Moyer et al. (2017); https://doi.org/10.5066/F7RR1X68.
Method: WRTDS

Step 0: Sediment Record in Susquehanna River at Conowingo Dam

Concentration samples (~ 27/year)
Method: WRTDS

Step 2: WRTDS Regression Surface for Conowingo Sediment

Step 3: Daily Concentration for Conowingo Sediment
WRTDS Model Results

Zhang, Brady, Boynton, and Ball, JAWRA, 2015
NTCBW SS Load = Sum of Loads at 9 RIM Stations

(1.0 = long-term annual median load; color = season)

Zhang, Brady, Boynton, and Ball, JAWRA, 2015
TP: Total Phosphorus
DP: Dissolved Phosphorus
PP: Particulate Phosphorus

Steady decline in DP loading since 1985
Rising TP and PP in last decade

Zhang, Brady, Boynton, and Ball, JAWRA, 2015
NTCBW TN, PN, DN

TN: Total Nitrogen  
DN: Dissolved Nitrogen  
PN: Particulate Nitrogen

Steady but lessening decline in TN and DN loading since 1985

Rising PN in recent decades?? (small diff of large numbers)

Zhang, Brady, Boynton, and Ball, JAWRA, 2015
General pattern among tributaries:
- dissolved species (DN, TN, DP): down
- particulate species (SS, PP, TP): up
Tributary SS

Susquehanna

Potomac 1.0=4,100,000 Kg/day

James 1.0=2,300,000 Kg/day

Rappahannock 1.0=830,000 Kg/day

Appomattox 1.0=52,000 Kg/day

Pamunkey 1.0=140,000 Kg/day

Mattaponi 1.0=20,000 Kg/day

Patuxent 1.0=67,000 Kg/day

Choptank 1.0=7,100 Kg/day
Tributary TN

- Susquehanna: 1.0 = 160,000 Kg N/day
- Potomac: 1.0 = 64,000 Kg N/day
- James: 1.0 = 15,000 Kg N/day
- Rappahannock: 1.0 = 5,600 Kg N/day
- Appomattox: 1.0 = 1,900 Kg N/day
- Pamunkey: 1.0 = 1,900 Kg N/day
- Mattaponi: 1.0 = 800 Kg N/day
- Patuxent: 1.0 = 2,000 Kg N/day
- Choptank: 1.0 = 600 Kg N/day

Zhang, Brady, Boynton, and Ball, JAWRA, 2015
Tributary TN:TP Molar Ratio

Zhang, Brady, Boynton, and Ball, JAWRA, 2015