Partitioning the Contributions of Minerogenic Particles and Bioseston to Particulate Phosphorus and Turbidity*

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* accepted *Inland Waters*
Background

1. Minerogenic particles play important roles in aquatic ecosystems:
   - Concentrations and stoichiometry of particulate constituents
   - Diminishes optical water quality
   - Reactive surfaces (nutrients, pollutants)
   - Influence on metabolic activity
   - Contribute to sedimentation

2. Allochthonous (watershed) sources usually dominate (e.g., clay)

3. Contributions of minerogenic particles to water quality metrics acknowledged qualitatively, but with little quantitative progress
   - Targeted metrics for this study: turbidity (Tn) and particulate phosphorus (PP)
Background

1) apportioning the contribution of minerogenic vs. organic particles (bioseston – phytoplankton and its retinue) for Tn and PP: 2-component models

- total Tn is the sum of its organic and minerogenic parts:
  \[ T_n = \text{organic } T_n + \text{minerogenic } T_n \]

- similarly, total PP is the sum of its organic and minerogenic parts:
  \[ PP = \text{organic } PP + \text{minerogenic } PP \]
Background

2) partitioning the organic and minerogenic fractions to total Tn and PP: a stoichiometric approach

\[ Tn = (Tn_o \cdot \text{Chl}) \cdot \text{Chl} + (Tn_m \cdot \text{PAVm}) \cdot \text{PAVm} \]

\[ PP = (PP_o \cdot \text{Chl}) \cdot \text{Chl} + (PP_m \cdot \text{PAVm}) \cdot \text{PAVm} \]

- Chl – chlorophyll a conc; proxy of bioseston
- PAVm – proj. area per unit vol. of water; proxy of minerogenic particles

ratios estimated from measurements and their relationships to each other
Objectives

- to develop, test, and apply protocols to partition Tn and PP according to contributions of minerogenic and organic particles
- elements of presentation include:
  - patterns of measurements in Cayuga Lake
  - development of stoichiometric ratios
  - evaluate extent of closure of 2-component models with observations
  - application of 2-component models to quantify the contributions of minerogenic vs. organic particles to Tn and PP
  - consider management implications (P)
Methods

- **Study system - Cayuga L.**
  - 2nd largest Finger Lake
  - mean and max. depths – 55 and 133m
  - localized tributary inputs, southern end (Fall Creek, others)

- **Sampling**
  - surface composites – 0,2,4m
  - sites:
    - pelagic, near-shore (on shelf)
  - timing:
    - biweekly, April – October, 1999-2006

- **Parameters**
  - Tn, PP, Chl (Cornell LSC monit.)
  - PAVm (UFI unfunded)
Methods:
PAVm measurements by SAX

- scanning electron microscopy interfaced with Automated image and X-ray analyses (SAX)
- detailed morphological and compositional characterizations

\[ PAV_m = \frac{1}{V} \cdot \sum_{n=i}^{N} PAV_{m,i} \]

- dominated by clay minerals
Methods: Development of Stoichiometric Ratios

- utilized measurements and their relationships (ratios)
- focus on ratio values when either Chl or PAVm were lowest
  - when Chl (organic proxy) is lowest, the minerogenic components for Tn and PP are approached
    - PP<sub>m</sub>:PAV<sub>m</sub>
    - Tn<sub>m</sub>:PAV<sub>m</sub>
  - when PAVm (minerogenic proxy) is lowest, organic components for Tn and PP are approached
    - Tn<sub>o</sub>:Chl
    - PP<sub>o</sub>:Chl
Methods:
Development of Stoichiometric Ratios

- Example: $T_n_{m}$ estimated from $Tn:PAVm$ when Chl is ~ 0
- step 1: bound ratio estimates
  - upper – median $Tn:PAVm$ at lowest 15 Chl
  - lower – average of 4 lowest $Tn:PAVm$ observations
- step 2: optimization calculations for closure of 2-component model with observations
  - generalized reduced gradient method
Methods: Theoretical Calculations of Side-Scattering Efficiency

- $T_n \propto$ side-scattering coefficient ($b_s$)
- nephelometer measures $b_s$ with acceptance angle of $\sim 85^\circ$ to $95^\circ$
- $b_s$ linearly depends on the side-scattering efficiency ($Q_{bs}$) and projected particle area ($PA$)
- relative effects of minerogenic vs. bioseston particles represented through Mie scattering theory calculations of $Q_{bs}$ for organic and minerogenic particles
- efficiencies for total scattering and back-scattering also calculated to provide context for other optical measures
Results: Distributions of Observations, Near-shore vs. Pelagic for 8 Years

- PP, PAVm significantly higher near-shore
  - Tn results similar to PAVm
  - distinctly right-skewed near-shore
    - importance of tributaries, runoff events on near-shore water quality
Results: Distributions of Observations, Near-shore vs. Pelagic for 8 Years

- Pelagic Chl slightly higher than near-shore
- No significant differences between near-shore and pelagic sites
## Results:
Observations, Near-shore vs. Pelagic

- median values

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Near-shore</th>
<th>Pelagic</th>
<th>p-value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP (µg/L)</td>
<td>10.2</td>
<td>7.70</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Tn (NTU)</td>
<td>1.17</td>
<td>0.91</td>
<td>0.001</td>
</tr>
<tr>
<td>PAVm (m⁻¹)</td>
<td>0.16</td>
<td>0.10</td>
<td>&lt;0.001</td>
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<tr>
<td>Chl (µg/L)</td>
<td>3.93</td>
<td>4.36</td>
<td>0.149</td>
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</tbody>
</table>

* Mann-Whitney U (medians)

- robust populations
  - 8 y of observations
  - (n~230)
- PP, Tn, PAVm were significantly higher near-shore vs. pelagic
  - near-shore proximity to tributary sources
- Chl – no significant differences
  - e.g. near-shore levels reflects lake-wide conditions
Results: Distributions of the PP:Chl Ratio, Near-shore vs. Pelagic for 8 Years

- significantly higher near-shore
- consistent with higher PP near-shore
- proximate to allochthonous sources
Results:

Highest Observed Tn Conditions and Ranking for Other Metrics

<table>
<thead>
<tr>
<th>Rank</th>
<th>Date</th>
<th>Tn (NTU)</th>
<th>PP (µg/L)</th>
<th>PAVm (1/m)</th>
<th>Chl (µg/L)</th>
<th>Flow (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6/06</td>
<td>42.4</td>
<td>48.5 (1)*</td>
<td>8.09 (1)</td>
<td>8.0 (16)</td>
<td>99</td>
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<tr>
<td>2</td>
<td>4/01</td>
<td>26.7</td>
<td>31.8 (2)</td>
<td>5.53 (2)</td>
<td>1.5 (215)</td>
<td>95</td>
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<tr>
<td>3</td>
<td>5/02</td>
<td>15.4</td>
<td>26.6 (4)</td>
<td>2.68 (3)</td>
<td>2.7 (183)</td>
<td>99</td>
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<tr>
<td>4</td>
<td>6/01</td>
<td>11.7</td>
<td>14.0 (39)</td>
<td>1.01 (10)</td>
<td>4.5 (101)</td>
<td>95</td>
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<td>5</td>
<td>6/02</td>
<td>10.3</td>
<td>28.9 (3)</td>
<td>2.02 (5)</td>
<td>8.5 (13)</td>
<td>95</td>
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*() indicates parameter ranking

- n = 230 observations
- highest Tn, PP, PAVm values on shelf after runoff events
- Chl not systematically coupled
Results: Near-shore PAVm Linkage to Hydrology

- near-shore PAVm vs. $Q_{F2}$ (day of and day prior to sampling) at Fall Creek
- quadratic fit
- $Q_{F2}$ explains 70% of variations in near-shore PAVm
- highly significant ($p<0.0001$)

$r^2=0.70$
$p<0.0001$
Results: Year-to-Year Near-shore vs. Pelagic

- No long-term trends
- Spatial differences
  - PP, Tn, PAVm higher near-shore
  - No differences in Chl
  - Interannual differences
- Smallest spatial difference
  - 1999 – dry year
- High Tn, PP, PAVm values most years near-shore – after runoff events
  - Supported by Fall Cr. Flow record

<table>
<thead>
<tr>
<th>Year</th>
<th>Tn (NTU)</th>
<th>PP (µg/L)</th>
<th>Chl (µg/L)</th>
<th>PAVm (m⁻¹)</th>
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Results:

2-Component Models, Including Stoichiometric Ratio Estimates

\[ Tn = (Tn_o \cdot Chl) \cdot Chl + (Tn_m \cdot PAVm) \cdot PAVm \]
\[ Tn = (0.081) \cdot Chl + (4.80) \cdot PAVm \]

\[ PP = (PP_o \cdot Chl) \cdot Chl + (PP_m \cdot PAVm) \cdot PAVm \]
\[ PP = (1.53) \cdot Chl + (7.10) \cdot PAVm \]

2-component models used to estimate the contribution of the organic and minerogenic components for Tn and PP
Results:
Performance of 2-Component Stoichiometric Models

- comparison of individual observations and predictions

\[
Tn = (0.081) \cdot Chl + (4.80) \cdot PAVm
\]
\[
PP = (1.53) \cdot Chl + (7.10) \cdot PAVm
\]

- coarse degree of closure
  - significant, slopes approach 1.0
  - better performance for Tn
- consistent with variability in stoichiometric ratios reported at short-term time steps in literature

\[\text{int.}=0.07, \quad \text{slope}=1.02, \quad r^2=0.93, \quad p<0.001\]

\[\text{int.}=4.40, \quad \text{slope}=0.62, \quad r^2=0.56, \quad p<0.001\]
Results:
Performance of 2-Component Stoichiometric Models

- comparison of observations and predictions on an annual average basis

\[ Tn = (0.081) \cdot Chl + (4.80) \cdot PAVm \]
\[ PP = (1.53) \cdot Chl + (7.10) \cdot PAVm \]

- stronger relationships at this longer time-step
- more appropriate time scale for application
- good closure

\[ \text{int} = -0.12 \quad \text{slope} = 1.14 \quad r^2 = 0.95 \quad p < 0.001 \]
\[ \text{int} = 0.93 \quad \text{slope} = 1.01 \quad r^2 = 0.62 \quad p < 0.001 \]
Application of the 2-Component Models: Contributions to Minerogenic Particles, Tn and PP

- predictions of contributions of minerogenic particles to Tn and PP
- as distributions for the entire populations of observations for the 2 sites; consistency with performance features

- minerogenic particles:
  - dominate component of Tn
  - noteworthy component of PP (usually 10-30%)
  - greater contribution in the near-shore (proximity to allochthonous inputs)
Results: Predicted Scattering Efficiencies for Minerogenic and Organic Particles

- 660 nm common reference wavelength
- Minerogenic particles have a much greater effect than bioseston on Tn
- Similar greater sensitivity of backscattering
  - Reflectance (e.g., remote sensing) implications
- Differences between minerogenic particle and bioseston less for total scattering
  - Implications for beam transmissometer and Secchi depth measurements
Application of the 2-Component Models: Implications for the TP Guidance Value

- apportion contributions of PP\textsubscript{m} and PP\textsubscript{o} to observed PP for near-shore and pelagic sites for each of 8 study years
- total P (TP) guidance value (June-September average) – 20 µg/L

- interannual differences in PP\textsubscript{m} explained much of the site-to-site (48%) and most of the yr-to-yr differences in TP (71%)
- approach to, and exceedance of, TP guidance values in years of the highest PP\textsubscript{m}

- TDP < 20%
- TDP higher near-shore
  - ~0.5 µg/L
  - proximity to tribs.
Implications for Water Quality Model Structure

- PP needs to be partitioned according to $PP_o$ and $PP_m$
- PAVm or a proxy is a potentially valuable state variable to represent minerogenic particles
- external loads of PAVm or a proxy would be necessary
- longitudinal segmentation needed to differentiate near-shore versus pelagic waters conditions
Implications: Ecosystems-specific Shortcomings of TP as a Trophic State Metric Near-Shore

- TP guidance value intended to protect against eutrophication-based degradations in water quality
- only forms of P that can support phytoplankton growth (bioavailable) should be included
- bioavailability of P forms:
  - soluble reactive P (SRP) - completely
  - dissolved organic P (DOP=TDP-SRP) - mostly
  - \( PP_o \) – completely (bioseston)
  - \( PP_m \) – limited (quantified by bioavailability assays)
- exceedances near-shore during summers of high \( PP_m \)
  - if low bioavailability, is this a trophic state issue?

Total P: false-high metric of trophic state on shelf
Summary

- protocols to partition contributions of bioseston and minerogenic particles to Tn and PP, as 2-component summations were developed, tested, and applied.
- basis: coincident observations of Tn, PP, Chl, and PAVm, 8 years, 2 sites (near-shore and pelagic) for Cayuga Lake – robust variations.
- stoichiometric approach – 4 ratio values developed:
  1. $\text{Tn}_o$ : Chl
  2. $\text{Tn}_m$ : PAVm
  3. $\text{PP}_o$ : Chl
  4. $\text{PP}_m$ : PAVm
- Tn, PP, PAVm – higher near-shore than for pelagic.
Summary

- reasonably good match of 2-component summations with observations for Tn and PP
  - good performance at an annual time step
- minerogenic particles
  - noteworthy to substantial contributions to PP
  - exceedances of TP guidance values near-shore in certain years due to high PPₘ (allochthonous inputs);
    TP likely a “false-high” representation of trophic state for shelf
- dominant component of Tn, supported by optical theory
Questions