Partitioning the contributions of minerogenic particles and bioseston to particulate phosphorus and turbidity

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Abstract

Protocols to partition the contributions of bioseston and minerogenic particles to turbidity ($T_n$) and particulate phosphorus (PP), as described by summations of the 2 components, are developed, tested, and applied. The analysis is based on coincident observations of $T_n$, PP, chlorophyll $a$ (Chl), and the summation of the projected areas of individual minerogenic particles per unit volume ($PA_Vm$) for the wide variations encountered in time and between near-shore and pelagic sites over an 8-year study of Cayuga Lake, New York. $PA_Vm$ was determined from an individual particle analysis technique, scanning electron microscopy interfaced with automated image, and X-ray analyses (SAX). The partitionings are based on a stoichiometric approach that adopts Chl and $PA_Vm$ as the metrics of bioseston and minerogenic particles, respectively, and estimates developed here for stoichiometric ratios that relate $T_n$ and PP to these 2 components. The systematically higher $T_n$ and PP levels at the near-shore site, particularly following runoff events, are demonstrated to be a result of elevated $PA_Vm$ associated with allochthonous inputs. A reasonably good match of the partitioned 2-component summations with bulk observations is reported. Application of the 2-component PP model establishes minerogenic particles made, on average, noteworthy (~10%) to substantial (≥20%) contributions to PP. The minerogenic particle component of PP was largely responsible for the greater summer average total phosphorus (TP) concentrations at the near-shore versus the pelagic site, the interannual variations in the differences between these sites, and exceedance of the TP water quality limit at the near-shore site. Minerogenic particles were the dominant component of $T_n$, a finding that is demonstrated to be consistent with optical theory, based on the much greater efficiency of side-scattering for minerogenic versus organic particles.

Key words: bioavailability, bioseston, minerogenic particles, particulate phosphorus, stoichiometry, turbidity

Introduction

Minerogenic (inorganic) particles play important ecologic and water quality roles in aquatic ecosystems by presenting reactive surfaces (O’Connor 1988, Hupfer et al. 1995), affecting the concentrations and stoichiometry of particulate constituents (Hecky et al. 1993, Effler et al. 2012), influencing metabolic activity (Phlips et al. 1995), contributing to net sedimentation (Bloesch 2004), and degrading optical water quality through the process of light scattering (Kirk 1985, Peng and Effler 2011). Sources of these particles to the water columns of lakes and reservoirs include allochthonous inputs from watersheds (Longabucco and Rafferty 1998), autochthonous production of oversaturated mineral phases (Yin and Johnson 1984, Homa and Chapra 2011), and sediment resuspended from bottom deposits (Bloesch 2004, Peng and Effler 2010). Water quality monitoring programs often do not include direct measurement of minerogenic particle assemblages, and those that do have primarily relied on gravimetric measurements: the mass remaining on a filter (per unit volume of sample) after exposure to a high temperature to burn off organic contributions. Such measurements have precision issues...
for the dilute conditions (Boss et al. 2009) that commonly prevail in lacustrine systems. Moreover, the projected (Peng et al. 2009a) and surface area (Chapra 1997) features of minerogenic particle populations are more mechanistically appropriate to represent their optical and surface chemistry implications, respectively.

Resolving the contributions of minerogenic versus organic particles in regulating bulk metrics is fundamental information for understanding patterns in time and space and identifying drivers of common water quality parameters. This partitioning is pursued here for 2 metrics, turbidity ($T_a$; in NTU) and particulate phosphorus (PP, in $\mu g$ L$^{-1}$), 2 parameters that are influenced by contributions from minerogenic particles (Reddy et al. 1999, Peng et al. 2009b, Kirk 2011). $T_a$ is a common optical metric of water quality (Davies-Colley and Smith 2001). As assessed with a nephelometer, it is a measure of light scattered from a beam within a rather wide angle centered on 90° (i.e., side-scattering; Davies-Colley and Smith 2001). $T_a$ has been used as a surrogate metric of the light-scattering coefficient (Kirk 2011). PP dominates total P (TP) in productive layers of the vast majority of lacustrine systems and, accordingly, is critical in common assessments of trophic state (Vollenweider 1982, Chapra 1997).

The partitioning of $T_a$ is described by a 2-component summation:

$$T_a = T_{a,o} + T_{a,m}, \quad (1)$$

where $T_{a,o}$ and $T_{a,m}$ are the organic (i.e., bioseston) and minerogenic components of $T_a$. Similarly, the partitioning for PP is described as:

$$PP = PP_o + PP_m, \quad (2)$$

where $PP_o$ and $PP_m$ are the bioseston and minerogenic components of PP. The partitioning for $T_a$ and PP are pursued here based on a stoichiometry-type approach that adopts estimates of bioseston and minerogenic particle contributions developed from stoichiometric ratios of bulk metrics. The expression for $T_a$ is:

$$T_a = (T_{a,o}:Chl) \cdot Chl + (T_{a,m}:PAV_m) \cdot PAV_m, \quad (3)$$

where Chl is the concentration of chlorophyll $a$ and PAV$_m$ is the projected area of minerogenic particles per unit volume of water (associated with the light-scattering effect; Peng and Effler 2007), and $T_{a,o}:Chl$ and $T_{a,m}:PAV_m$ are the stoichiometric ratios used to estimate the bioseston and minerogenic components of $T_a$, respectively. Similarly, the relationship for PP is:

$$PP = (PP_o:Chl) \cdot Chl + (PP_m:PAV_m) \cdot PAV_m. \quad (4)$$

where $PP_o:Chl$ and $PP_m:PAV_m$ are the stoichiometric ratios used to estimate the bioseston and minerogenic components of PP, respectively.

Chl is the accepted contemporary surrogate of phytoplankton biomass, despite widely recognized limitations (Reynolds 2006). Other organic particle types (e.g., bacterioplankton, detritus, viruses; the retinue) may covary with phytoplankton (e.g., Wetzel 2001, Huot et al. 2008), and these together with phytoplankton constitute bioseston. PAV$_m$ is the summation of the projected areas of individual minerogenic particles per unit volume, as determined from an individual particle analysis technique (SAX), scanning electron microscopy interfaced with automated image and X-ray analyses (Peng et al. 2009a). PAV$_m$ is a valuable summary statistic from SAX characterizations that is linearly related to the minerogenic component of metrics of the magnitude of light scattering for various angular ranges of the volume scattering function, including the total scattering ($b_o$, 0–180°), the backscattering ($b_s$, 90–180°; Peng et al. 2009a, Peng and Effler 2010, 2011), and the side-scattering ($b_t$; i.e., $T_a$, ~85–95°; Peng and Effler 2007, Peng et al. 2009b) coefficients.

The scattering process is central in regulating optical metrics of water quality including clarity (Secchi depth); $T_a$, the light attenuation coefficient; and the remote sensing signal (Kirk 2011). Moreover, PAV$_m$ does not have the precision issues of gravimetric measurements in dilute waters (Effler et al. 2013). The appropriateness of PAV$_m$ as an indicator of the content of PP$_m$ instead of a particle volume metric, depends on the extent to which surface processes (e.g., adsorption; Froelich 1988, Reddy et al. 1999) versus the P content throughout the particle (Reynolds and Davies 2001) is responsible for PP$_m$.

The overarching goals of this study were to develop, test, and apply protocols to partition $T_a$ and PP according to the contributions of bioseston and minerogenic particles, as described by the above 2-component models. The analysis is based on coincident observations of $T_a$, PP, Chl, and PAV$_m$ for robust variations encountered in time and space during an 8-year study of Cayuga Lake, New York. Elements of the presentation include: (1) description of the patterns of these bulk measurements; (2) development of values of the stoichiometric ratios; (3) evaluation of the extent of match, or closure, of the 2-component estimates with the bulk measurements; (4) estimates of the bioseston and minerogenic particle components of $T_a$ and PP; and (5) consideration of the implications of such findings in a phosphorus management context.
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Methods

System description

Cayuga Lake (42°41′30″N; 76°41′20″W) is the fourth easternmost of the 11 New York Finger Lakes (Fig. 1). It has the second largest surface area (172 km$^2$) and volume (9.4 × 109 m$^3$) of the Finger Lakes, with maximum and mean depths of 133 and 55 m, respectively. This alkaline hardwater lake has a warm monomictic stratification regime (Oglesby 1978). Its average retention time is about 10 years (Shaffner and Oglesby 1978). Approximately 40% of the tributary inflow is contributed by several streams that enter the southern end. Fall Creek (Fig. 1) is the largest of these tributaries and has the longest record (since 1925) of measured flows (United States Geological Survey gauge No. 04234000). Conspicuous increases in both $T_n$ and PP have been reported during runoff events at the mouths of Fall Creek and the Cayuga Inlet tributary, the second largest of the southern tributaries (Effler et al. 2010). The southernmost 2 km of the lake that receives these inflows is shallow ($\leq$6 m) and is described as the southern shelf (Effler et al. 2010). The shelf also receives effluent from 2 tertiary domestic waste treatment facilities and spent cooling water from a lake source cooling facility (Matthews et al. 2002).

The lake has been described as mesotrophic (Effler et al. 2010). Earlier, phytoplankton growth was reported to be P limited (Oglesby 1978). Summer (Jun–Sep) average TP values were observed to be higher and Secchi depth lower on the shelf than in pelagic waters over the 1998–2007 interval, although summer average Chl levels were similar (Effler et al. 2010). External loading estimates of P to the shelf over the same interval, partitioned according to PP and total dissolved P (TDP), established (1) large interannual differences driven by variations in tributary hydrologic loading, (2) the dominance of PP relative to TP (67% of TP load on average), and (3) decreases in the TDP loads from increased treatment at the waste treatment facilities (Effler et al. 2010).

Sampling and analyses

Sampling was conducted biweekly over the April–October interval for 8 years from 1999 through 2006. Two sites were monitored, one in near-shore waters on the shelf with a water column depth of 6 m and the other at a pelagic site in 110 m of water located 12.8 km farther north (designated hereafter as near-shore and pelagic, respectively; Fig. 1). Samples were collected as composites of equal volumes of subsamples collected from epilimnetic depths of 0, 2, and 4 m. These samples were analyzed for $T_n$ (Hach Model 2100AN nephelometer; Clesceri et al. 1998), TP, and TDP (Clesceri et al. 1998; PP = TP − TDP), Chl (Parsons et al. 1984), and PAV$^m$ with SAX (Peng and Effler 2007). The total population of coincident measurements for the 8-year study was 230.

SAX protocols, including sample handling and measurements, have been described in detail previously (Peng and Effler 2007, Peng et al. 2009a, 2009b). An abbreviated description is presented here. Particles from known volumes of the water samples were deposited onto polycarbonate membranes (0.4 μm pore size), air dried, and coated with carbon. These were then analyzed with an Aspex PSEM 2000 system controlled by automated feature analysis (AFA) software. AFA conducts image analysis on individual particles through a rotating chord algorithm, which represents a particle as a series of radiating triangles from its centroid at 11° increments to its edges formed by 16 chords. The projected area (PA, or cross-sectional area) of a particle is the sum of these triangular areas.

SAX definitively differentiates the minerogenic particles (includes organic particles with minerogenic coating) from organic ones, as well as partitions multiple mineral classes (e.g., clay minerals, quartz, calcite), based on X-ray relative intensities acquired for 16 elements for...
the individual particles (Peng et al. 2009a). More than 2000 particles were characterized in each of the samples. \( \text{PAV}_m \) is computed from the sum of minerogenic particle PAs, the fraction of filter area analyzed, and the sample volume. The precision of \( \text{PAV}_m \) is ~10% (Peng et al. 2009a). Adjustments of PA values were made to accommodate the effect of particles lying flat on the filters (Jonasz 1987), as described by Peng et al. (2009a).

Estimates of minerogenic particle volume per unit volume (\( \text{PVV}_m \)) were also made, assuming platy morphology for these clay mineral-dominated populations (Peng and Effler 2012) as an alternate predictor of their P content.

**Development of stoichiometric ratios and theoretical calculations of scattering efficiencies**

The development of the 4 stoichiometric ratios focused on analysis of those conditions with the lowest observations of Chl and \( \text{PAV}_m \). For example, when \( \text{PAV}_m \) was close to its minimum, the PP:Chl and \( T_n:\text{Chl} \) ratios represented values attributable to only bioseston particles (i.e., PP:Chl and \( T_{m:\text{Chl}} \), respectively). Similarly, when Chl was its lowest, these ratios represented values associated only with minerogenic particles (i.e., \( \text{PP}_n:\text{PAV}_m \) and \( T_{m:\text{Chl}} \), respectively). The protocol used to determine the 4 stoichiometric ratios had 2 steps. First, bounding estimates of each ratio were established. The upper bounds were represented as the medians for the lowest 15 \( \text{PAV}_m \) and Chl observations, and the lower bounds were specified as the average of the 4 lowest observations. Second, the best estimate of each of the 4 stoichiometric ratios was determined through a nonlinear optimization calibration using the generalized reduced gradient method, as embedded in Microsoft Excel software, for the overall populations of PP and \( T_n \) observations, adopting the partitioning of organic versus inorganic particle contributions as described by equations 3 and 4. The objective function was set to the minimum of average absolute error between the observed and the model-predicted values of \( T_n \) and PP.

Turbidity is linearly coupled to the side-scattering coefficient, \( b_s \), which can be calculated from detailed particle information according to:

\[
b_s(\lambda) = \frac{1}{V} \sum_{i=1}^{N} Q_{bs,i}(m_i, \lambda, d_i) \text{PA}_i, \tag{5}
\]

where \( \lambda \) is the wavelength of light, \( V \) is the sample volume (m\(^3\)), \( N \) is the number of particles in \( V \), \( Q_{bs,i} \) is the side-scattering efficiency of particle \( i \), and \( \text{PA}_i \) is the projected area of particle \( i \). \( Q_{bs} \) depends on the complex refractive index \( (m = n-n' i) \), where \( n \) and \( n' \) are the real and imaginary parts of \( m \), \( \lambda \), and particle size (\( d \)). The value of \( m \) is a function of composition, differing substantially for organic versus inorganic particles (Kerr and Rogers 1977). Analogous expressions can be cast for the scattering (\( b_s \)) and backscattering (\( b_b \)) coefficients, with corresponding efficiencies (\( Q_{bs} \) and \( Q_{bb} \), respectively; Stramski and Kiefer 1991, Peng and Effler 2012, Effler et al. 2013).

The relative effects of minerogenic versus organic particles on \( T_n \) were represented through Mie theory calculations of \( Q_{bs} \) for these particle types. Calculations for \( Q_{bs} \) and \( Q_{bb} \) were also made to provide context with respect to other optical metrics in limnology. Values of these 3 efficiencies were calculated with the BHMie algorithm (Bohren and Huffman 1983), based on Mie theory for homogeneous spheres. Values of \( m \) (i.e., \( n \) and \( n' \)) were specified for clay mineral \( (m = 1.17 - 0.0001 i) \) and organic particles \( (m = 1.05 - 0.0004 i) \) based on related literature (Kerr and Rogers 1977) and as adopted in recent calculations for the efficiency of backscattering (\( Q_{bb} \), Effler et al. 2013). Values of \( Q_{bs} \) were determined through integration of the differential angular scattering cross-section over the angular range of 85–95°, whereas \( Q_{bb} \) correspond to integrations over the 0–180° and 90–180° ranges, respectively. Calculations were conducted for a wavelength of 660 nm (common reference \( \lambda \); Peng and Effler 2012) for \( d \) values extending from 0.1 to 100 µm, bracketing the sizes of interest for these particle types.

**Results**

**Distributions of bulk measurements**

Distributions of the measurements of \( T_n \) (Fig. 2a and b), \( \text{PP} \) (Fig. 2c and d), Chl (Fig. 2e and f), and \( \text{PAV}_m \) (Fig. 2g and h) for the 8-year study are compared for the near-shore and pelagic locations. The distributions for the near-shore site for \( T_n \) and \( \text{PAV}_m \) were distinctly nonnormal; therefore, the statistic adopted to test for significant differences between the 2 sites was the Mann-Whitney U test on medians. The distributions for these metrics at pelagic site were also skewed, especially for \( T_n \) and \( \text{PAV}_m \), although PP was more normally distributed than the near-shore location. The distribution for \( T_n \) at the near-shore site was heavily right-skewed with a mean value (2.41 NTU) that was 2 times greater than the median (1.17 NTU). The near-shore site was significantly higher for \( T_n \) and PP compared with the pelagic site (\( p < 0.001 \)). As in the cases of \( T_n \) and PP, \( \text{PAV}_m \) was significantly (\( p < 0.001 \)) greater at the near-shore site than at the pelagic location. The Chl populations approached normality at both sites (Fig. 2e and f). In contrast to the other 3 parameters, however, Chl levels were slightly higher at the pelagic site, but the differences were not statistically significant (\( p = 0.15 \)).

Features of the distributions of the 4 parameters for the
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2 sites are represented for each of the 8 years in a box-whisker plot format (Fig. 3a–d; statistics include median, mean, 5, 25, 75, and 95 percentiles). Although no conspicuous long-term trends were observed, systematic spatial differences emerged for 3 of the metrics that differed in extent between the years. Means, medians, and temporal variability were greater in each of the years at the near-shore site than at the pelagic location for \( T_n \) (Fig. 3a), PP (Fig. 3b), and \( \text{PAV}_m \) (Fig. 3d). The smallest spatial differences for these were in 1999, the year with the third lowest average flow for the 89-year (Apr–Oct) record of Fall Creek. A limited number of particularly high values for \( T_n \), PP, and \( \text{PAV}_m \) were observed at the near-shore site in most years but only in 2006 for the pelagic site. Years of particularly high observations roughly corresponded to high runoff years; for example, Fall Creek average flow rankings for the April–October interval of 2000, 2002, 2004, and 2006 were 18, 30, 2, and 21, respectively (1 the highest). Similarity, the Chl populations of the 2 sites prevailed for each of the 8 years (Fig. 3c).

The mean (3.3) and median (2.5) values of the PP:Chl ratio at the near-shore site were 51 and 35% greater than for the pelagic site, respectively (Fig. 4). The more right-skewed character of the distribution for the near-shore site reflects the reported differences in the PP populations for these locations (Fig. 2c and 2d).

The highest values of \( T_n \), PP, and \( \text{PAV}_m \) were observed at the near-shore site after runoff events, establishing a linkage to allochthonous inputs, while Chl levels were not unusual at those times. The 10 highest \( T_n \) observations, their timing, and associated antecedent event peak flows (\( Q_p \)) in Fall Creek are presented, along with the paired values of PP, \( \text{PAV}_m \), and Chl and their rankings (Table 1); 9 of these observations were at the near-shore site. The rankings of \( \text{PAV}_m \) tracked those of \( T_n \) well (Table 1). The coupling of PP to these rankings was somewhat less strong, while no interplay with Chl was apparent.

**Performance of two-component models**

The stoichiometric ratio values that resulted in the best match of observations from the calibration process are presented, along with the initial bounding values (Table 2). The representativeness of the calibrated stoichiometric ratios for the organic and minerogenic particle components of \( T_n \) (equation 3) and PP (equation 4) was...
established through the performance of the predictions of the 2-component models compared with the observations (Fig. 5). The general consistency of the 2-component partitioning of $T_n$ and PP is supported by the strong relationships between observations and predictions achieved through calibration (Fig. 5a and b). The 2-component model predictions of $T_n$ explained 93% ($p < 0.001$) of the variations in $T_n$ observations according to linear least-squares regression (Fig. 5a). The 2-component model predictions of PP explained 56% ($p < 0.001$) of the variations in PP observations (Fig. 5b) and remained significant ($p < 0.001$) for concentrations <20 µg L$^{-1}$ (inset of Fig. 5b).

The extent of the observed scatter indicates that the resolution of the contributions of bioseston versus minerogenic particles for individual bulk observations has substantial uncertainty; however, performance was better (higher $r^2$, slopes ~1) at the time step of the study interval of the individual years (Fig. 5c and d). The average of the ratios of observations to predictions for that interval for the 8 years for $T_n$ for both the near-shore and pelagic sites approached unity (1:1 for both sites). Similar performance was observed for PP, with average ratio values of 1.3 and 1:1 for the near-shore and pelagic sites, respectively. The predicted partitionings for these mean values also performed well in representing the observed differences among the years, explaining 95 and 62% of these variations in $T_n$ (Fig. 5c) and PP (Fig. 5d), respectively.

Table 1. The 10 highest $T_n$ observations, their timing, antecedent Fall Creek flow conditions, paired PP, Chl, and PAV$^m$ values, and rankings.

<table>
<thead>
<tr>
<th>Rank$^a$</th>
<th>Date</th>
<th>$T_n$ (NTU)</th>
<th>PP (µg L$^{-1}$)</th>
<th>Chl (µg L$^{-1}$)</th>
<th>PAV$^m$ (m$^3$)</th>
<th>Qp$^b$ (m$^3$ s$^{-1}$)</th>
<th>Q%$^c$</th>
<th>$\Delta d^d$ (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29 Jun 2006</td>
<td>42.4</td>
<td>48.5 (1)$^e$</td>
<td>8.0 (16)$^e$</td>
<td>8.0888 (1)$^e$</td>
<td>57.5</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>5 Apr 2001</td>
<td>26.7</td>
<td>31.8 (2)</td>
<td>1.5 (215)</td>
<td>5.5305 (2)</td>
<td>36.0</td>
<td>95</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>16 May 2002</td>
<td>15.4</td>
<td>26.6 (4)</td>
<td>2.7 (183)</td>
<td>2.6791 (3)</td>
<td>53.5</td>
<td>99</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>28 Jun 2001</td>
<td>11.7</td>
<td>14.0 (39)</td>
<td>4.5 (101)</td>
<td>1.0089 (10)</td>
<td>32.3</td>
<td>95</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>27 Jun 2002</td>
<td>10.3</td>
<td>28.9 (3)</td>
<td>8.5 (13)</td>
<td>2.0238 (5)</td>
<td>34.3</td>
<td>95</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>13 Jul 2006</td>
<td>9.7</td>
<td>17.5 (14)</td>
<td>12.1 (3)</td>
<td>2.2914 (4)</td>
<td>23.9</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>6 Apr 2000</td>
<td>7.9</td>
<td>12.9 (46)</td>
<td>1.9 (200)</td>
<td>1.7745 (6)</td>
<td>37.4</td>
<td>95</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>5 Oct 2006</td>
<td>7.7</td>
<td>20.6 (7)</td>
<td>5.1 (79)</td>
<td>1.4200 (8)</td>
<td>4.7</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>15 Jul 2004</td>
<td>5.6</td>
<td>19.6 (9)</td>
<td>6.5 (35)</td>
<td>0.7793 (13)</td>
<td>16.9</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>14 Apr 2005</td>
<td>5.0</td>
<td>15.3 (24)</td>
<td>0.7 (228)</td>
<td>1.0160 (9)</td>
<td>141.9</td>
<td>99</td>
<td>11</td>
</tr>
</tbody>
</table>

$^a$ according to $T_n$ values
$^b$ antecedent daily average flow peak
$^c$ percentile of occurrence of $Q_p$
$^d$ number of days to antecedent flow peak
$^e$ only pelagic observations in the top 10
$^f$ ranking according to this parameter

Table 2. Stoichiometric ratios developed to support partitioning of bioseston and minerogenic particle contributions to $T_n$ and PP.

<table>
<thead>
<tr>
<th>Stoichiometric Ratio</th>
<th>Upper Bound</th>
<th>Lower Bound</th>
<th>Best Estimate</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_n$:Chl</td>
<td>0.20</td>
<td>0.07</td>
<td>0.08</td>
<td>NTU L µg$^{-1}$</td>
</tr>
<tr>
<td>$T_n$:PAV$^m$</td>
<td>6.48</td>
<td>2.65</td>
<td>4.80</td>
<td>NTU m$^3$</td>
</tr>
<tr>
<td>PP$_o$:Chl</td>
<td>1.85</td>
<td>0.43</td>
<td>1.53</td>
<td>dimensionless</td>
</tr>
<tr>
<td>PP$_m$:PAV$^m$</td>
<td>28.0</td>
<td>7.10</td>
<td>7.10</td>
<td>mg m$^{-2}$</td>
</tr>
</tbody>
</table>

Fig. 4. Distributions of the PP:Chl ratio for the 1999–2006 study period compared for 2 sites in Cayuga Lake, with median and mean values presented (solid vertical line is near-shore site median, dashed vertical line is pelagic site median).
Application of the two-component models

The relative importance of minerogenic particles versus bioseston predicted for the 2 sites by application of the 2-component models are presented in terms of predicted distributions of the minerogenic fractions (Fig. 6a and b). The distributions for those populations were broad, indicating that the relative roles of these particle types were dynamic over the study period. Minerogenic particles made significantly (p < 0.001; Mann Whitney U test for medians) greater contributions to both $T_n$ and PP at the near-shore site, as the median fractional values for the minerogenic component to total were 25 and 67% higher at the near-shore site compared to the pelagic site for $T_n$ and PP, respectively. Minerogenic particles were relatively more important for $T_n$ (Fig. 6a) than PP (Fig. 6b). These particles were always at least important, and usually the dominant (e.g., >65%), component of $T_n$. In contrast, their contribution to PP ranged from usually noteworthy (~10%), to often substantial (~20%), and occasionally dominant (~60%).

The 2-component PP model was used to apportion the contributions of minerogenic and bioseston particles to the observed PP values for the 2 sites for each of the 8 years (Fig. 7). The analysis was conducted in the context of the prevailing regulatory limit of a summer (specified as Jun–Sep) average concentration of TP of 20 µg L$^{-1}$ in the upper productive layers. PP was the dominant component (~70%) of TP at both sites in all 8 years, with TDP representing only approximately 20% of TP. Average TDP concentrations were slightly higher (average 0.5 µg L$^{-1}$) at the near-shore site in all but one (2004) of the years. The average TP was higher at the near-shore site in each of the years (average difference of 3.6 µg L$^{-1}$, range 1.0–7.3 µg L$^{-1}$). Interannual differences in PP between the sites explained much of the year-to-year differences in TP between sites (48%, p = 0.04), as well as nearly all of the year-to-year variations in TP at both sites (71%, p < 0.001) according to linear least-squares regression.

![Fig. 5. Closure performance of partitionings of $T_n$ and PP with bulk measurements for Cayuga Lake (both sites), as plots of observations versus predictions, with statistics, for (a) individual $T_n$ values, inset for lower range of $T_n$ values; (b) individual PP values, inset for lower range of PP; (c) yearly average $T_n$; and (d) yearly average PP.](image)

![Fig. 6. Comparisons of predicted distributions of minerogenic particle contributions in Cayuga Lake, for the 1999–2006 period for 2 sites, based on application of the 2-component models: (a) $T_n$ and (b) PP.](image)
Differences in PP$_o$ were much less important. Estimates of PP$_m$ were lower in each year at the pelagic site and less variable between the years (average 1.1 µg L$^{-1}$, coefficient of variation (cv) = 0.2), compared to the near-shore site (average 3.0 µg L$^{-1}$, cv = 0.6). Observations of TP exceeded the water quality limit at the near-shore site in 2002 (20.1 µg L$^{-1}$), and in 2006 (21.5 µg L$^{-1}$; Fig. 7), the 2 years with the highest average PP$_m$ levels over the 8-year study.

**Side-scattering efficiency and PAV$_m$ linkage to hydrology**

Predictions of the size dependency of $Q_{bs}$ differed greatly for the clay mineral and organic particles (Fig. 8a). Values for clay particles were much greater than the organic particles except for the smallest sizes considered and for $d > 20$ µm. The greatest differences were for sizes in the range of 0.6 to 5 µm.

Regressions of PAV$_m$ at the near-shore site on daily average flows (Fall Creek; Fig. 1) were conducted to test the dependence of minerogenic particle content at the near-shore site on allochthonous inputs. Various intervals of tributary flow were evaluated iteratively to represent the effect of flow, guided by earlier estimates of the residence time of tributary inputs to the southern end of Cayuga Lake (e.g., not more than several days; Effler et al. 2010). The best flow predictor was the average for the day of and one day prior to sampling ($Q_{F2}$). The relationship (log-transformed format; Fig. 9) was nonlinear, highly significant ($p < 0.0001$), and strong, with $Q_{F2}$ explaining 70% of the variation in PAV$_m$, establishing a linkage between PAV$_m$ at this site and runoff.

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**Fig. 7.** Comparisons of summer average concentrations in Cayuga Lake for 8 years of observed TP, TDP, and PP for 2 sites, and predictions of PP$_o$ and PP$_m$ based on application of the 2-component PP model.

**Fig. 8.** Mie theory predictions for idealized (monodispersed spheres) particle populations of size dependencies for clay mineral and organic particles for scattering efficiencies: (a) side-scattering (i.e., turbidity), $Q_{bs}$; (b) backscattering, $Q_{bb}$; and (c) overall scattering, $Q_b$.

**Fig. 9.** Evaluation of the dependence of PAV$_m$ at the near-shore site on the 2-day (day of the sampling and one day prior) average daily flow at Fall Creek ($Q_{F2}$) for the study period.

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Discussion

Two-component models

This is a robust first test of the stoichiometric approach adopted here to partition the contributions of minerogenic particles and bioseston to $T_n$ and PP, which succeeded in explaining near-shore versus pelagic and interannual differences caused by variations in the 2 components. Expansion of the testing of the approach for other systems is recommended to evaluate the breadth of its applicability and variability in the stoichiometric ratios. The 2-component model representations would be systematically flawed where allochthonous organic detritus (i.e., a third component) makes important contributions to $T_n$ and PP. No indications of a noteworthy missing component have been manifested in 2-component representations implemented for $b$ and $b_a$, which partitioned the contributions of organic versus inorganic particles to these metrics of light scattering, for multiple lacustrine systems to date (Peng and Effler 2012), including for $b$ for Cayuga Lake (Effler and Peng 2014). Certainly there are lakes, such as those enriched with humic substances (Wetzel 2001), for which a third component would be necessary.

The dependent variables for the 2-component models, Chl and PAV_m, differ in the extent to which these represent intrinsically unique effects. Chl in this case represents not only the effect of phytoplankton, but also its retinue (other covering particles, including bacteria, associated detritus, and viruses; Huot et al. 2008). Thus, the Chl-specific ratios developed here cannot be attributed solely to the side-scattering (Huot et al. 2008, Effler et al. 2013) and P content (Hecky et al. 1993) of phytoplankton. These features are more appropriately attributed to bioseston. Moreover, Chl is known to be an imperfect measure of phytoplankton biomass because of the dependence of its cellular content on ambient conditions and composition of the assemblage (Reynolds 2006).

In contrast, there is not known to be a covarying retinue for PAV_m that would influence either the light-scattering effects or the P content of the responsible particles. While multiple minerals contribute to the minerogenic assemblage of lakes, the most common case is dominance of clay mineral particles (Peng and Effler 2011, 2012) that is interrupted in late summer in some hard water lakes by calcite precipitation (whiting; autochthonous) events (Homa and Chapra 2011). These are the conditions that prevail in Cayuga Lake (Effler and Peng 2014).

Multiple factors establish the primary origins of PAV_m as allochthonous: (1) the inherent allochthonous origins of clay minerals (Babin and Stramski 2004, Stramski et al. 2007), (2) the higher PAV_m levels at the near-shore site proximate to tributary inputs (Fig. 2g and h), and (3) the positive dependence of near-shore PAV_m on tributary flow (Fig. 9), including abrupt increases following runoff events (Table 1). The linkage with tributary flow would likely become stronger through implementation of an appropriately robust (e.g., 3-dimensional) hydrodynamic framework (Martin and McCutcheon 1999), driven by temporally detailed particle loads (Owens et al. 2012). The effects of these allochthonous inputs were particularly strong after runoff events (Table 1). These signals reflect increased particle concentrations that occur at elevated stream flows in Cayuga Lake tributaries (Effler et al. 2010), as widely reported for other systems (Richards and Holloway 1987, Longabucco and Rafferty 1998). Year-to-year and within-year variations in PAV_m (Fig. 3d) and its effects on $T_n$ (Fig. 3a) and PP ($T_n$ (Fig. 3b) at the near-shore site reflect differences in the extent to which the effects of runoff events were encountered by the biweekly sampling program because this interval was coarse relative to the detention time of local inflows on the shelf (Effler et al. 2010).

Whiting events occur annually and last about 2 weeks (Effler and Peng 2014). A short-term, modest increase in the $T_n$;PAV_m ratio is a reasonable expectation during whiting events because of the higher refractive index of calcite compared to clay minerals, an effect demonstrated for $b$ (Peng and Effler 2011). The potential effect of these events on the PP:PAV_m ratio is more uncertain; both calcite (House 1990) and clay minerals (Reddy et al. 1999) are considered to have high potential for P adsorption. The nearly equivalent performance of the PAV_m and PVV_m metrics of the minerogenic particle assemblage with respect to explaining PP leaves unidentified the regulating association of P with these particles, which deserves further pursuit. Adoption here of PAV_m converges with the known (Peng et al. 2009b) regulation of $T_n$ by this particle attribute and has the advantage of parsimony for the combined analyses for $T_n$ and PP presented here.

The 2-component models invoke linearity between the independent variables, Chl and PAV_m, and their effects on $T_n$ and PP (equations 3 and 4), which in some cases may be an over-simplification. The strongest support for linearity is for the dependence of $T_n$ on PAV_m because it is consistent with optical theory and has been demonstrated for systems where minerogenic particles dominate (Peng et al. 2009b). This was also supported by the strong linearity demonstrated in their paired observations ($T_n = 4.93 \cdot \text{PAV}_m + 0.44$, $r^2 = 0.93$, $p < 0.0001$). In contrast, exponential relationships have been used to describe the dependences of $b$ (Loisel and Morel 1998) and $b_a$ (Morel and Maritorena 2001, Huot et al. 2008) on Chl in ocean waters. These relationships have demonstrated substantial variance relative to observations, however, in part because...
of recognized limitations of Chl as a surrogate of light scattering (Morel and Maritorena 2001). The extensive variability encountered in seston stoichiometry (Hecky et al. 1993, Sterner et al. 2008) overwhelms the linearity issue between Chl and PP, and PAV and PP, The estimates of the 4 stoichiometric ratios developed here are acknowledged to be “central values” of populations that apparently (Fig. 5a and b) are subject to substantial variation.

**PP:Chl**

Variations in the stoichiometry of seston (e.g., Fig. 5a and b) are a recognized feature for lakes; for example, “the reigning paradigm for” stoichiometric “ratios in lakes focuses on variation not constancy” (p. 1170 in Sterner et al. 2008). The populations of PP:Chl values for both Cayuga Lake sites were indeed highly variable and were shifted higher at the near-shore site (Fig. 4) because of the greater contributions of allochthonous minerogenic particles to PP at that location (Fig. 6b). A number of drivers have been identified in the literature for such variability (Bloesch and Uehlinger 1986, Harris 1986, Hecky et al. 1993, Reynolds 2006, Sterner et al. 2008), including (1) phytoplankton speciation, (2) seasonal and shorter-term shifts in nutrient status, (3) variations in other ambient conditions and relative growth rates, and (4) shifts in the relative contributions of associated detritus. Based on the results of this study, we add to this list variations in time and space of allochthonous P-containing minerogenic particles. This last factor has been demonstrated here (Fig. 6b) to also contribute to the higher PP:Chl values relative to those associated with bioseston.

Our central estimate of PP:Chl (1.5; Table 2), can be attributed to bioseston, acknowledging that the effects of detritus that attends primary production are also embedded. The observed variability in PP:Chl within various portions of the range of PAV values indicates this stoichiometric attribute of the lake’s bioseston is indeed variable, consistent with the array of drivers identified above. The literature provides some support for the general consistency of the PP:Chl estimate, although earlier works apparently did not specifically target bioseston.

The modeling community has often adopted PP:Chl values in deterministic nutrient–phytoplankton models in the range of 0.5 to 1.0 for phytoplankton (Bowie et al. 1985, Chapra 1997); other components of the bioseston have generally not been explicitly considered. While Reynolds (2006) did not specifically present PP:Chl values for phytoplankton, his treatment of their composition (from cultures; e.g., full complement of non-phytoplankton components of bioseston not included) supports reasonable estimates (compare to Effler and O’Donnell 2010). A broad range of 0.33–1.8 was estimated (Effler and O’Donnell 2010), associated mostly with the extent of nutrient limitation (Reynolds 2006). Harris (1986) reported PP:Chl values centered at a value of 1.5 for seston (includes minerogenic contributions) for the various Laurentian Great Lakes. Median values of PP:Chl of 2.1–2.3 were reported for seston for the epilimnion of Onondaga Lake, New York (Effler and O’Donnell 2010), which is enriched with clay mineral and calcite particles (Effler and Peng 2012).

**Water quality context**

P and trophic state

Of the 3 common metrics of trophic state (TP, Chl, and Secchi depth; Chapra 1997, Cooke et al. 2005), TP is the most widely applied in the United States in setting water quality goals or limits to protect against excessive cultural eutrophication. The exceedance of the summertime TP limit of 20 μg L⁻¹ (New York State regulations) in certain years near-shore (e.g., Fig. 7) has been identified as a water quality limiting condition requiring remediation. The findings that PP makes a noteworthy to substantial contribution to PP (Fig. 6b) and TP, and that the exceedances at the near-shore site were primarily associated with summers of higher PP (Fig. 7), raises interesting questions related to a TP limit and its implementation for this system. Given that the intent of such a limit is to protect against cultural eutrophication-driven degradations of water quality, its implementation should be supported by TP being either completely bioavailable or the bioavailable fraction remaining uniform. Neither of these conditions seemed to have prevailed in Cayuga Lake over the study period.

Bioavailable P refers to those fractions of TP that are readily assimilable by organisms, or can be made assimilable through the activities of the organisms themselves, and the portion that has been assimilated (e.g., intracellular; Boström et al. 1988, Reynolds and Davies 2001). These can be considered in the context of the commonly measured fractions and the partitioning of PP presented here. Forms of dissolved P included in the measurement of soluble reactive P (SRP) are considered to be immediately available to support algae growth (Reynolds 2006). The residual of TDP and SRP, often described as dissolved organic P (DOP), is considered to be mostly (to entirely) available through enzymatic hydrolysis and mineralization processes (Young et al. 1982, Bentzen et al. 1992, Auer et al. 1998). The portion of P assimilated is well represented here by PP, while the P associated with minerogenic particles (here as PP) generally has limited availability.
Based on the results of bioassays conducted at other sites, usually only a modest portion of allochthonous particles (mostly <25%) is bioavailable (DePinto et al. 1981, Young et al. 1985, Auer et al. 1998, Effler et al. 2002, Ekholm and Krogerus 2003). These bioassays were mostly conducted on streams enriched with inorganic suspended solids. Much of the bioavailable fraction was probably associated with the small organic components. Two factors further diminish the availability of PP$_m$ associated with allochthonous particles within the upper waters of lacustrine systems: (1) the ongoing depositional losses of these comparatively dense particles (Hatch et al. 1999, Effler et al. 2002, Ellison and Brett 2006), and (2) the residence time since delivery and the attendant approach to equilibrium (e.g., desorption–sorption processes) with ambient conditions (Froelich 1988, Auer et al. 1998). Given these considerations, the observed interannual and spatial variations in TP, driven by year-to-year and spatial differences in PP$_m$, are not a reliable indicator of changes or differences in trophic state in Cayuga Lake. Instead, these variations have served as an indicator of differences in PAV$_m$ levels for those intervals.

The complications of minerogenic particles for the trophic state metrics of TP and Secchi depth Carlson 1977) and the stoichiometry of P with respect of other cellular constituents of phytoplankton (Hecky et al. 1993, Effler et al. 2012) have been qualitatively recognized for some time. Such interferences support Chl as the preferred trophic state metric. TP has been reported to be a poor indicator of algal availability (Ekholm and Krogerus 1998, Reynolds and Davies 2001). Differences in PP$_m$ between systems doubtless contributed to the great scatter manifested in Chl–TP relationships developed from cross-sectional surveys of multiple lakes (compare to Chapra and Auer 1999).

This study has advanced related issues through the estimated partitioning of PP. The recent expansion of minerogenic particle characterization in lacustrine systems with SAX and similar technologies (Yin and Johnson 1984, Johnson et al. 1991, Swift et al. 2006, Peng and Effler 2012, Effler et al. 2013) opens the way for broader application of this partitioning approach. Certainly the noteworthy contribution of PP$_m$ is not unique to Cayuga Lake. Wide ranges of PAV$_m$ associated mostly with differences in concentrations of clay mineral particles, have been reported within and among various lakes and reservoirs to date (Peng and Effler 2012, Effler et al. 2013). Noteworthy interferences with the TP signal for trophic state by clay mineral particles are a reasonable expectation when and where substantial concentrations are encountered.

Moreover, differences in PP:PAV$_m$ delivered by various tributaries are a distinct possibility based on watershed-specific conditions (Froelich 1988, Reddy et al. 1999). Expansion of the PP partitioning approach adopted here is recommended for other lacustrine systems for which paired PP, Chl, and PAV$_m$ data are available. New initiatives would ideally incorporate paired chemical measurements of a fraction of PP that targets specifically the PP$_m$ component (e.g., selective extraction technique; Penn and Auer 1997, Auer et al. 1998), thereby supporting an additional form of closure analysis. Such efforts would test the transferability of the presented partitioning approach and the variability of the PP$_m$:PAV$_m$ ratio as well as contribute to more informed approaches for nutrient management.

T$_n$ and other optical metrics

The dominant role of minerogenic particles in regulating T$_n$ levels in the lake is consistent with optical theory (Fig. 8a), particularly in light of the common sizes of clay mineral particles. These common sizes correspond to the most efficient side-scattering and the greatest relative differences with organic particles. Moreover, particles in the size range of 1–8 μm have been demonstrated to regulate light scattering by the minerogenic assemblage in Cayuga Lake (Effler et al. 2010, Effler and Peng 2014). Such theoretical idealized (e.g., spherical particles) calculations (Fig. 8) have been found to be consistent with bulk observations for b$_n$ (Peng and Effler 2012) and b$_n$ (Effler et al. 2013) and have supported reasonable degrees of closure with bulk measurements (Peng and Effler 2010, 2011). We know of no previous analyses of side-scattering efficiency (Q$_{bs}$) reported specifically for the collection angles of T$_n$ measurements.

Note that T$_n$ measurements have been reported to have some dependence on the instrument used (Davies-Colley and Smith 2001). Here we adopted the recommendation (Davies-Colley and Smith 2001) of reporting the instrument used. The much greater Q$_n$ of the clay mineral versus organic particles (Fig. 8a) is due to the higher n values, an effect similar to that reported for b$_n$ (Fig. 8b; Effler et al. 2013). Moreover, similar differences from organic particles prevail for other minerogenic particle types (e.g., quartz and calcite) because their n values are similar to those of clays (i.e., greater than for organic particles). Accordingly, the observed regulation of T$_n$ dynamics by PAV$_m$ both at both sites and the generally higher T$_n$ levels at the near-shore site are consistent findings. T$_n$ patterns in the lake are driven largely by allochthonous inputs of minerogenic particles, with the exception of during whiting events (Effler et al. 2010). The character of the theoretical optics analyses (Fig. 8a) suggests this is widely occurring.

All optical metrics of light scattering, and those that depend strongly on scattering, would be sensitive to
changes in the relative contribution of minerogenic particles to the overall particle assemblage; however, there are noteworthy differences in the responses of these various metrics. Similar preferential dependencies of the efficiency of backscattering ($Q_{b}$) on minerogenic particles prevail (Fig. 8b; also see figure 10c in Effler et al. 2013) as reported for $Q_{b}$ (Fig. 8a). This would be manifested in the upward reflectance from the water surface (e.g., increases in PAV would result in conspicuous increases in reflectance; O'Donnell et al. 2013). The dependence of the efficiency of overall scattering ($Q$) on clay minerals (Peng and Effler 2012) and phytoplankton (Stramski and Kiefer 1991) for their common sizes is much more balanced (Fig. 8c). Accordingly, incremental increases in PAV would cause less dramatic increases in $b$ than in $T_{n}$ and $b_{b}$ (Effler et al. 2013).

Surrogate measurements of $b$ are commonly made with a beam transmissometer (Babin et al. 2003). These differences in the response of $b$ also translate to differences in the response of Secchi depth, for which an inverse dependency on $b$ prevails for most lacustrine systems (Davies-Colley et al. 2003). Secchi depth measurements would show less sensitivity to changes in PAV than $T_{n}$. These differences in responses between the scattering metrics contribute to the imperfect correlations reported for these measurements for systems where variations in the relative amounts of bioseston and minerogenic particles prevail.

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References


Partitioning the contributions of minerogenic particles and bioseston to particulate phosphorus and turbidity


