Long-term study of minerogenic particle optics in Cayuga Lake, New York

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Abstract

The dynamics of light scattering by minerogenic particles in the upper waters of Cayuga Lake, New York, were characterized for the spring–autumn interval of 8 yr (1999–2006) at pelagic and nearshore sites with a scanning electron microscope interfaced with automated image and x-ray analyses (SAX). SAX results were used to estimate the minerogenic scattering coefficient \( b_m \) through Mie theory calculations. SAX–Mie supported a two-component model for particulate scattering \( b_p \) that included an organic component of scattering \( b_o \), estimated from a bio-optical model. The credibility of the \( b_m \) estimates and the two-component modeling approach was demonstrated through good closure of the modeling results with bulk values of \( b_p \) (estimated from measurements of the beam attenuation coefficient at 660 nm). The average of the ratio \( b_p : (b_m + b_o) \) was 1.03 (average relative error 19.4%). Two minerogenic particle types were important in regulating the dynamics of \( b_m \)—clay minerals that increased in concentration in response to runoff events, and calcium carbonate precipitated mostly on small organic particles during short-term late-summer whiting events. \( b_m \) was attributed to particles in the size range of 1–10 \( \mu \)m. Variations in \( b_m \) dominated the overall variations in \( b_p \) and Secchi disk depth; differences in \( b_p \) explained well those observed in \( b_p \) during dry weather intervals of low \( b_m \). Higher \( b_m \) values, mainly associated with clay mineral particles, were observed at the nearshore site as opposed to the pelagic location; there was a positive linkage between these levels and tributary flow rate.

Light scattering by particles, a fundamental process regulating radiative transfer in water (Kirk 2011), is important in determining apparent optical properties (AOPs, depend on geometry of the light field) of interest, including clarity (Preisendorfer 1986) and the remote sensing signal (Woźniak and Stramski 2004). The total scattering coefficient \( b \) (\( \text{m}^{-1} \)), corresponding to the integration of the volume-scattering function over all directions (Kirk 2011), quantifies a central feature of the light-scattering regime. \( b \) is an inherent optical property, independent of the geometry of the light field. The magnitude and spectral features of the particulate component of scattering, \( b_p \) (which greatly exceeds that due to water), depend on multiple attributes of a particle population, including the number concentration \( N \), the particle size distribution (PSD), the composition of the individual particles and their shapes (Babin et al. 2003).

The particle populations of aquatic ecosystems are heterogeneous, varying in time and space and differing greatly among systems in response to an array of drivers (Stramski et al. 2004, 2007; Peng and Effler 2011). Protocols for resolving the various components of light scattering are needed to understand these differences and dynamics, and to identify their origins and drivers, objectives that are consistent with the reductionist approach advocated by Stramski and co-workers (Stramski et al. 2001, 2004, 2007). Inorganic, or minerogenic, particles are of particular interest in coastal and inland (so-called Case 2) waters because of their relatively greater contributions to \( b_m \) compared with the open oceans (i.e., Case 1; Babin et al. 2003; Bowers and Binding 2006; Woźniak et al. 2010). Minerogenic particles have increasingly been reported to be important in influencing common optical metrics of water quality for inland waters, including Secchi depth \( (Z_{SD}) \) (Swift et al. 2006; Peng and Effler 2011) and turbidity (Peng et al. 2009a, 2009b; Peng and Effler 2010). These particles have three general origins: terrigenous (allochthonous) inputs (Kirk 1985; Peng et al. 2009b), re-suspension (Peng and Effler 2010), and autochthonous production (Weide- mann et al. 1985).

The reductionist approach has recently been advanced (Peng et al. 2009a) through forward estimates of the minerogenic component(s) of \( b_p \) (i.e., \( b_m \)) for inland waters based on an individual particle analysis technique, scanning electron microscopy interfaced with automated image and x-ray analyses (SAX). SAX measures the light-scattering attributes of minerogenic particles \( (N, \text{PSD}, \text{elemental x-ray composition, and shapes}) \) that serve as inputs (exclusive of shape) to Mie theory calculations of the scattering efficiency factor \( (Q_{b_m,i}) \) for the individual particles (Peng and Effler 2007). The estimates of \( b_m \) are made according to

\[
b_m(\lambda) = \frac{1}{V} \sum_{i=1}^{N_m} Q_{b_m,i}(m_i, \lambda, d_i)PA_{m,i}
\]

where \( V \) is the sample volume, \( N_m \) is the number of minerogenic particles in a sampled volume of water, and \( PA_{m,i} \) is the projected area \( (\text{m}^2) \) of minerogenic particle \( i \). \( Q_{b_m,i} \) depends on the complex refractive index \( (m_i) \) (function of composition) and size \( (d_i) \) of the particle, and the wavelength of light \( (\lambda) \). This SAX–Mie approach supports further partitioning of \( b_m \) into contributions according to size and particularly composition (e.g., clay minerals, quartz, and calcite) of particles (Peng and Effler 2010, 2011).

Early research with the SAX–Mie approach had appropriately focused first on testing the credibility of the forward estimates of \( b_m \) for a range of particle assemblage conditions (see review of Peng and Effler 2012), before

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applying it to characterize patterns and establish linkages with drivers and AOPs. Credibility has been tested through the pursuit of optical closure with bulk measurements of $b_p$ or its surrogates. These efforts have addressed two cases: systems where minerogenic particles dominate (i.e., phytoplankton contributions can be ignored), and those where phytoplankton make noteworthy contributions, the more common lacustrine case. A two-component partitioning of $b_p$ (i.e., the simplest reductionist scheme; Peng et al. 2009a) has been adopted for the second case

$$b_p = b_m + b_o$$

where $b_o$ is the scattering associated with organic particles. $b_o$ has been attributed to phytoplankton and their particulate retinue (Peng et al. 2009a), and has been estimated with chlorophyll $a$ (Chl $a$)–based, empirical bio-optical models developed for open oceanic waters (Loisel and Morel 1998; Huot et al. 2008). The performance of the SAX–Mie approach has been reasonably good in earlier studies in supporting a substantial degree of closure with bulk measurements, including those applying the above two-component model (Peng and Effler 2012).

There have been limitations in the robustness of the testing of the SAX–Mie approach and the two-component model to date with respect to (1) the small population sizes of SAX characterizations, (2) temporal dynamics covered, and (3) range of minerogenic particle composition considered. This paper addresses these robustness issues and makes the important transition to application to evaluate patterns, origins, and linkages with drivers and an AOP. The overarching goal of this paper is to advance both the testing and application of the SAX–Mie and reductionist approaches for $b_m$, based on the robust variations in conditions encountered in an 8 yr study of Cayuga Lake, New York.

Key features of the presentation include the following: (1) documentation and comparison of the dynamics of near-shore vs. pelagic distributions of the light-scattering attributes of minerogenic particles, (2) presentation of the temporal and spatial patterns of SAX-Mie-based $b_m$ estimates, (3) evaluation of the credibility of the $b_m$ estimates and the two-component model through testing the extent of closure with bulk measurements of $b_p$, (4) description of the contrasting dynamics of contributions by autochthonous calcium carbonate (CaCO$_3$) and allochthonous clay minerals, (5) resolution of the role of $b_m$ in influencing $Z_{SP}$ dynamics, and (6) establishment of the positive linkage between the dynamics of runoff and those of the allochthonous components of $b_m$.

Methods

**Study system, sampling, and field measurements**—Cayuga Lake ($42^\circ 41'30"$N, $76^\circ 41'20"$W) is the fourth easternmost, and has the second largest surface area (172 km$^2$) and volume ($9.4 \times 10^9$ m$^3$), of the New York Finger Lakes (Fig. 1; Schaffner and Oglesby 1978). The mean and maximum depths are 55 m and 133 m, respectively. This alkaline hardwater mesotrophic lake stratifies (strongly) only in summer (i.e., warm monomixis; Oglesby 1978). The average retention time of the lake is about 10 yr (Schaffner and Oglesby 1978), with overall water transport from south to north. The City of Ithaca and its suburbs, the primary bordering urban area, are located at the southern end of the lake. Approximately 40% of the tributary inflow is contributed by several streams that enter at the southern end. The largest of these tributaries, Fall Creek (Fig. 1), has the longest flow record (since 1925; United States Geological Survey gage No. 04234000 adjoining its mouth). The southernmost 2 km of the lake that receives these inflows is shallow ($\leq 6$ m), and is described as the shelf.

Sampling and field measurements were conducted bi-weekly over the April–October interval from 1999 to 2006. Two sites were monitored, one was a nearshore location on the shelf, and the other a pelagic site (depth of 110 m) 12.8 km further north (Sites 2 and 3, respectively, designations from a lake-wide monitoring program; Fig. 1). Sample composites were made of equal volumes of sub-samples collected from depths of 0, 2, and 4 m for [Chl $a$] analyses through acetone extraction (Parsons et al.
1984; coefficient of variation (CV) ~ 8% for triplicate samples) and SAX (subsequently).

Measurements of \(Z_{SD}\) were made with a black-and-white Secchi disk of 20 cm diameter (between 10:00 h and 14:00 h). Values of \(Z_{SD} > 5\) m were not collected at Site 2 because of its shallowness (108 of potentially 136 observations reported). Interferences from the bottom at this site were not an issue because it was not reflective (covered with periphyton and attached algae). Measurements of temperature (\(T, ^\circ C\); Seabird SBE 25) and the beam attenuation coefficient (associated with particles and dissolved substances) at 660 nm (\(c_{pg}(660), m^{-1}\); Web Labs C-Star) were made since 2000 with sensors mounted in a cage that was lowered through the upper layers of water. The transmissometer (path-length 10 cm, acceptance angle 1.2°) was calibrated according to the manufacturer’s protocol.

**SAX protocols**—Light-scattering attributes of minerogenic particles were characterized for each sample with SAX. SAX protocols, including sample handling and measurements, have been described in detail elsewhere (Peng et al. 2009a,b). An abbreviated account is presented here. Suspended particles from known volumes of the water samples were deposited onto polycarbonate membranes (0.4 μm pore size), air dried, and coated with carbon. Analyses were conducted with an Aspex Personal Scanning Electron Microscope 2000 system controlled by Automated Feature Analysis (AFA) software. AFA conducted image analysis through a rotating chord algorithm, which draws 16 chords through the centroid of a particle at 11° increments and delineates it as a series of radiating triangles formed by its centroid and the chords. The projected (or cross-sectional) area of a particle is the sum of these triangular areas. Particle size (\(d\)) is calculated as the circular area equivalent diameter. The total projected area of minerogenic particles per unit volume of water sample (\(P AV_m, m^{-1}\)) is computed from the sum of the measured PAs of minerogenic particles, the fraction of analyzed filter area, and the sample volume. \(P AV_m\) is a useful bulk property because it is, at least for inland waters, linearly related to \(b_m\) (Peng and Effler 2007, 2012). Particle shape is represented by the aspect ratio (ASP)—the ratio of the length of the longest chord to that of its orthogonal chord (the ASP of a sphere is 1). Size distributions of minerogenic particles are presented as the density function, \(F(d)\), with numbers of particles in size bins (logarithmically equally spaced) normalized by the bin width.

SAX assesses the composition of minerogenic particles on the basis of x-ray relative intensities acquired for 16 elements (Al, Si, K, Ca, Fe, etc.). The particles are then sorted into predefined generic particle types according to their elemental x-ray composition (Peng and Effler 2007; Peng et al. 2009a). Minerogenic particle classes adopted for this system correspond to those used for another hardwater lake where the whiting phenomenon occurs (Peng and Effler 2011). These include clay minerals ('Clay'), Quartz, 'Silica-rich ('Si-rich'), Calcite, Ca-aggregates ('Ca-agg'; partially CaCO3 coated), and miscellaneous ('Misc'; not specifically defined). Quartz particles were differentiated from diatoms on the basis of their higher x-ray densities (Peng et al. 2002). Selected samples enriched with particles of high Ca content were reanalyzed following an acid (2 mol L\(^{-1}\) HNO\(_3\)) treatment, intended to selectively dissolve CaCO3 coatings (differential individual particle analysis or DIPA; Johnson et al. 1991; Peng and Effler 2011). Approximately 2000 individual minerogenic particles were analyzed for each of the 250 samples.

**Calculations and bio-optical model**—Forward estimates of \(b_m(660)\) were made on the basis of SAX results (Eq. 1). Values of \(Q_{bam,i}\) were calculated with the BHMie algorithm (Bohren and Huffman 1983), based on Mie theory for homogeneous spheres. Values of complex refractive indices of individual particles \((m = n_p - in_p'\); \(n_p\) and \(n_p'\) are the real and imaginary parts of \(m)\) were specified according to their respective classes (listed in Peng et al. 2009a), as guided by literature listings (Kerr and Rogers 1977; Woźniak and Stramski 2004). Adjustments of PA values (Peng et al. 2009a) were made to accommodate the effect of particles lying flat on the filters (Jonasz 1987). Average scattering-efficiency factors of the minerogenic particle populations, reflecting the combined effects of composition and PSD, were calculated for each sample (\(<Q_{bam,i}> = b_p/PAV_m\)).

\(c_{pg}(660)\) is widely used as a surrogate measure of \(b_p\) (at 660 nm; Babin et al. 2003). Estimates of bulk \(b_p(660)\) were made from the \(c_{pg}(660)\) observations according to

\[b_p(660) = k_1 \times c_{pg}(660)/k_2\]

where \(k_1 (0.97)\) and \(k_2 (0.85)\) are adjustment factors for the contribution of absorption to \(c_{pg}(660)\) and the diminished response of the C-Star transmissometer associated with its acceptance angle (Boss et al. 2009a). The value of \(k_1\) adopted here is consistent with that used in marine studies (Loisel and Morel 1998) and with systemspecific absorption measurements (Perkins et al. 2009). The value of \(k_2\) depends to some extent on the composition and PSD of the particle population (Boss et al. 2009a); the specified value is consistent with a mix of inorganic particles (Peng and Effler 2012) and phytoplankton.

The empirical bio-optical model based on [Chl a], developed by Loisel and Morel (1998; subsequently referred to as L98) for Case 1 waters, was adopted to estimate \(b_0(660)\) in Cayuga Lake,

\[b_0(660) = 0.347[\text{Chl } a]^{0.766} \times 0.97\]

Reference to the wavelength of 660 nm is henceforth omitted for brevity.

**Results**

**Light-scattering attributes of minerogenic particles**—The composition of the minerogenic particle population is presented in a light-scattering context based on the contributions of the six classes to \(P AV_m\). Average percentages, along with \(P AV_m\), are presented for each year, with the CVs included as a metric of variations within the monitored interval (Table 1). The adequacy of the classification strategy in categorizing these populations is manifested by the low contributions of the Misc class (<5%). Clay minerals dominated \(P AV_m\) at both sites in each
Table 1. Light-scattering attributes of mineral particles as characterized by SAX (mean along with CV in parentheses).

<table>
<thead>
<tr>
<th>Year</th>
<th>Site 2</th>
<th>Clay</th>
<th>Calcite</th>
<th>Quartz</th>
<th>Si-rich</th>
<th>Ca-agg</th>
<th>Misc</th>
<th>ASP&lt;sub&gt;m&lt;/sub&gt;</th>
<th>&lt;i&gt;Q&lt;sub&gt;b,m&lt;/sub&gt;&lt;/i&gt;</th>
<th>df&lt;sub&gt;q&lt;/sub&gt; (μm)</th>
<th>Whiting count</th>
<th>b&lt;sub&gt;m&lt;/sub&gt; (m&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>b&lt;sub&gt;m&lt;/sub&gt;:b&lt;sub&gt;p&lt;/sub&gt; (%)</th>
<th>b&lt;sub&gt;p&lt;/sub&gt;: (b&lt;sub&gt;m&lt;/sub&gt; + b&lt;sub&gt;c&lt;/sub&gt;)</th>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>1999</td>
<td>0.173(0.96)</td>
<td>70.6(0.21)</td>
<td>8.3(1.14)</td>
<td>6.2(0.47)</td>
<td>1.6(0.71)</td>
<td>10.0(0.65)</td>
<td>3.3(0.68)</td>
<td>2.08(0.11)</td>
<td>2.28(0.04)</td>
<td>3.59(0.23)</td>
<td>1</td>
<td>0.387(0.91)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2000</td>
<td>0.318(1.29)</td>
<td>70.8(0.25)</td>
<td>9.5(2.20)</td>
<td>7.5(0.36)</td>
<td>2.3(0.89)</td>
<td>7.2(0.49)</td>
<td>2.7(0.44)</td>
<td>1.89(0.05)</td>
<td>2.31(0.04)</td>
<td>3.13(0.28)</td>
<td>2</td>
<td>1.280(2.33)</td>
<td>26.8(0.61)</td>
<td>1.22(0.24)</td>
</tr>
<tr>
<td>2001</td>
<td>0.562(2.32)</td>
<td>76.2(0.18)</td>
<td>7.4(1.68)</td>
<td>7.3(0.25)</td>
<td>1.1(0.44)</td>
<td>5.0(0.49)</td>
<td>3.1(0.65)</td>
<td>2.00(0.06)</td>
<td>2.24(0.03)</td>
<td>4.18(0.21)</td>
<td>1</td>
<td>1.258(2.33)</td>
<td>39.3(0.55)</td>
<td>1.08(0.24)</td>
</tr>
<tr>
<td>2002</td>
<td>0.577(1.40)</td>
<td>68.3(0.35)</td>
<td>15.6(1.42)</td>
<td>5.6(0.54)</td>
<td>0.8(0.52)</td>
<td>7.2(0.85)</td>
<td>2.5(0.60)</td>
<td>2.06(0.14)</td>
<td>2.21(0.04)</td>
<td>4.90(0.33)</td>
<td>4</td>
<td>0.615(0.82)</td>
<td>31.1(0.43)</td>
<td>1.10(0.25)</td>
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<tr>
<td>2003</td>
<td>0.279(0.62)</td>
<td>77.3(0.17)</td>
<td>6.1(1.75)</td>
<td>6.5(0.30)</td>
<td>1.2(0.53)</td>
<td>6.7(0.86)</td>
<td>2.3(0.31)</td>
<td>1.98(0.07)</td>
<td>2.29(0.04)</td>
<td>3.60(0.29)</td>
<td>2</td>
<td>0.643(0.64)</td>
<td>35.1(0.41)</td>
<td>1.07(0.23)</td>
</tr>
<tr>
<td>2004</td>
<td>0.265(0.78)</td>
<td>76.2(0.23)</td>
<td>5.2(1.62)</td>
<td>6.4(0.35)</td>
<td>1.2(0.37)</td>
<td>8.3(1.33)</td>
<td>2.6(0.54)</td>
<td>1.95(0.05)</td>
<td>2.28(0.04)</td>
<td>3.40(0.32)</td>
<td>2</td>
<td>0.615(0.82)</td>
<td>31.1(0.43)</td>
<td>1.10(0.25)</td>
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<td>2005</td>
<td>0.231(1.09)</td>
<td>73.0(0.20)</td>
<td>9.2(1.32)</td>
<td>6.3(0.42)</td>
<td>1.4(0.57)</td>
<td>6.6(0.67)</td>
<td>3.6(0.66)</td>
<td>1.97(0.07)</td>
<td>2.27(0.03)</td>
<td>3.67(0.22)</td>
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<td>0.532(1.13)</td>
<td>29.3(0.55)</td>
<td>1.03(0.20)</td>
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<td>2006</td>
<td>0.665(2.99)</td>
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<td>6.5(1.64)</td>
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<td>7.9(1.03)</td>
<td>3.7(0.60)</td>
<td>1.99(0.05)</td>
<td>2.29(0.03)</td>
<td>3.46(0.24)</td>
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<td>1.537(3.00)</td>
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<td>Mean</td>
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<td>8.4</td>
<td>6.5</td>
<td>1.4</td>
<td>7.3</td>
<td>3.0</td>
<td>1.99</td>
<td>2.27</td>
<td>3.71</td>
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<td>15.7(0.75)</td>
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<td>1.93(0.08)</td>
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<td>15.6(1.37)</td>
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<td>8.5(1.06)</td>
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<td>1.89(0.06)</td>
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<td>3.1(0.46)</td>
<td>1.91(0.08)</td>
<td>2.28(0.04)</td>
<td>3.43(0.21)</td>
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<td>0.265(0.78)</td>
<td>21.7(0.95)</td>
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<td>2.05(0.11)</td>
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<td>0.95(0.32)</td>
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<td>5.3(0.47)</td>
<td>1.5(0.45)</td>
<td>6.8(0.74)</td>
<td>2.4(0.39)</td>
<td>1.95(0.07)</td>
<td>2.27(0.04)</td>
<td>3.81(0.29)</td>
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<td>0.327(1.27)</td>
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<td>0.99(0.24)</td>
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<td>8.8(1.38)</td>
<td>2.8(0.55)</td>
<td>2.01(0.08)</td>
<td>2.30(0.04)</td>
<td>3.47(0.25)</td>
<td>4</td>
<td>0.655(1.90)</td>
<td>23.2(0.83)</td>
<td>0.90(0.18)</td>
</tr>
<tr>
<td>Mean</td>
<td>0.160</td>
<td>67.3</td>
<td>14.0</td>
<td>5.6</td>
<td>1.6</td>
<td>8.6</td>
<td>3.0</td>
<td>1.96</td>
<td>2.30</td>
<td>3.33</td>
<td>2</td>
<td>0.366</td>
<td>22.5</td>
<td>0.97</td>
</tr>
</tbody>
</table>
of the 8 yr, and demonstrated the least relative variability of the six classes annually. The second and third most important components were both associated with CaCO3, the Calcite and Ca-agg classes. Wide temporal variations in their contributions are indicated within the monitored intervals of each year by their much higher CV values. Occurrences of prominent contributions by CaCO3-based particles (i.e., during whiting events) were represented as counts of those sampling days when the contribution from the combined Calcite and Ca-agg classes to PAVm was 40% of the total. These conditions were observed at both sites, but more often at Site 3 (Table 1). The contribution of clay minerals was shifted lower and those of Ca-based classes higher at pelagic Site 3 compared with nearshore Site 2 in all years. The average contributions for the 8 yr at Site 3 were 67% and 23% for Clay and the combined classes of Calcite and Ca-agg, respectively, compared with 73% and 16% at Site 2. PAVm was on average higher in each year at the nearshore site than at the pelagic location (2.4-fold greater for the 8 yr period) and more variable in 6 of the 8 yr.

The minerogenic particles were aspherical, with average ASP values close to 2 (Table 1). Variations in the average ASP values within years were modest. A platelet shape was observed for most Clay particles (Fig. 2a), whereas the calcite particles had more three-dimensional shapes during whiting events (Fig. 2a,b). Acid treatment of a whiting sample (14 August 2003, Site 3) resulted in the elimination of the bright CaCO3 features as compared with (a) before acid treatment, and (d) revealed the deformed organic particles (low BSE strength; imaged with secondary electron image mode mainly showing the surface structures of particles) that served as nuclei for calcite precipitation.

PSDs for the minerogenic fraction are presented for three samples (Fig. 3a), selected as generally representative of prominent cases. The Site 3 sample (April 2004), typical of the most common case during a dry weather interval, was dominated by clay minerals with respect to PAVm. The Site 2 sample (June 2006) also reflects Clay dominance, but following a high runoff interval. The third PSD is for a whiting event sample (14 August 2003). These PSDs are quantitative for particles with \( d \leq 0.4 \mu m \), but are considered only qualitatively representative (e.g., for shapes of PSDs) for the lower range of 0.2–0.4 \( \mu m \) (Peng et al. 2009b). Similar PSDs have been observed with 0.2 \( \mu m \) and 0.4 \( \mu m \) pore-size filters (Peng et al. 2009b). Moreover, effective retention of particles smaller than the nominal
pore size has been reported elsewhere (Atteia et al. 1998). Similar PSD patterns, with distinct curvature and peaks between 0.4 and 0.5 μm, were observed for the most common cases of clay mineral dominance, though higher concentrations prevailed throughout the range of sizes for the high runoff case (Fig. 3a). The shape for the whiting case differed, having a broad plateau-type maximum extending over the 0.4–2 μm range, with lower relative contributions from larger particles compared with the Clay-dominated populations. Clear curvature was observed in all of the minerogenic PSDs. These patterns are inconsistent with the Junge function (or power law), for which monotonic increases in the number density \( (F/d) \) with decreases in size are observed instead (Babin et al. 2003).

Calculated size dependencies of \( b_m \) are presented in a cumulative format for the same three samples (Fig. 3b). Submicrocon particles did not make important contributions to \( b_m \) \( (\leq 5\%) \) for the most common case of Clay dominance, and represented only 10% for the whiting event. Particles with \( d > 10 \mu m \) did not contribute for these samples, and were rarely noteworthy (only following major runoff events). The size range of particles contributing to \( b_m \) (Fig. 3b) was the narrowest for the whiting event sample (particles in the 1–2 μm size range responsible for 60% of \( b_m \)), intermediate for the dry weather case with Clay dominance, and the widest following a runoff event when fine particles \( (<2 \mu m) \) made < 25% contribution. The size that corresponds to the 50th percentile of \( b_m \) \( (d_{50}) \) is a useful summary metric of the size dependency of \( b_m \) (and \( b_p \); see Fig. 3b) for natural polydisperse populations (Babin et al. 2003; Peng et al. 2009a); higher \( d_{50} \) values reflect greater contributions by larger particles. Average annual values of \( d_{50} \) ranged from 3.0 μm to 4.9 μm with substantial temporal variations within the years (Table 1). The overall mean \( d_{50} \) for Site 2 (3.7 μm) was significantly (paired \( t \)-test, \( t = 4.2, \) degrees of freedom \( [df] = 122, p < 0.0001 \)) larger than for Site 3 (3.3 μm). The lower \( d_{50} \) value during the whiting event was associated with the small sizes of the organic particles that were coated with CaCO₃ (Fig. 2b,d).

\[ \text{PAV}_m \text{ and } b_m \text{ were very strongly correlated } \left( r = 1.0, \ p < 0.0001 \right) \text{ as a result of fairly uniform } <Q_{b,m}> \text{ values (Table 1). Annual averages of the } b_m \text{ estimates were in the } 0.39–1.54 \text{ m}^{-1} \text{ and } 0.24–0.67 \text{ m}^{-1} \text{ ranges at Sites 2 and 3, respectively, with these bounds corresponding to 1999 and 2006 conditions in both cases (Table 1). The overall mean } b_m \text{ value for Site 2 (0.87 m}^{-1} \text{) was significantly (paired } t \text{-test, } t = 2.8, \text{ df } = 123, \ p < 0.01 \right) \text{ greater than for Site 3 (0.37 m}^{-1} \text{). The overall population of the } b_p:b_m \text{ ratio values for the study had a right-skewed distribution (Fig. 4), where ratio values } > 0.4 \text{ corresponded to observations following runoff events. The average } b_m:b_p \text{ for the nearshore site for the 7 yr (0.30) was 23% greater than for the pelagic location (0.23; Table 1).}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.png}
\caption{Distribution of the \( b_m:b_p \) values for the study (SD–standard deviation).}
\end{figure}

**Bulk measurements, hydrology, and \( b_m \) dynamics—**Bulk measurements and tributary flow conditions are summarized on an annual study-interval basis for the two sites (Table 2), with temporal details illustrated as time series for a single year (2003; Fig. 5). The flow rates at Fall Creek \( (Q_F) \) are considered generally indicative of overall tributary inputs (Effler et al. 2010). The average \( Q_F \) for the April–October interval for the study years covered a wide range of the 88 yr record, from the 85th (1999) to the 2nd highest (2004). Average [Chl \( a \)] ranged from \(~ 4 \text{ to } > 6 \text{ mg m}^{-3} \) with substantial seasonal variation. The means of the [Chl \( a \)] populations for the 8 yr period for Sites 2 and 3 were not significantly different (\( t \)-test, \( t = 1.0, \text{ df } = 245, p = 0.32 \)). Values of \( Z_{SD} \) varied substantially at multiple time scales for both sites (Table 2). Occurrences of \( Z_{SD} < 4 \text{ m} \) were annually more frequent at the nearshore shallow Site 2. Based on the days of paired \( Z_{SD} \) observations (sample size \( n = 90 \)), the average for Site 3 was significantly \((p < 0.0001) \) higher than that at Site 2 for the entire study.

Annual average values of \( b_p \) (not available in 1999) ranged from 1.2 m\(^{-1}\) to 2.1 m\(^{-1}\) at Site 3 (Table 2), whereas at Site 2 they fell in the 1.5–3.9 m\(^{-1}\) range, higher than at the pelagic site by 50% on average. The highest average \( b_p \) values were observed for 2006, the second highest runoff year of the study.

Daily average \( Q_F \) values for five runoff events in 2003 (indicated by arrows on Fig. 5a) were in the upper 5% of values for the entire record. The seasonal \( T \) pattern (Fig. 5b) is included because of its known interplay with whiting events (Homa and Chapra 2011). [Chl \( a \)] varied \(~ 10\)-fold over the interval, with similar patterns for the two sites: low levels in April and early May, a peak in late July, and modest variations around the mean through the remainder of the interval (Fig. 5c). In contrast, wide differences in \( Z_{SD} \) were observed between these sites in April–July and October, with values at Site 3 exceeding those for Site 2 on all but one day of paired observations (Fig. 5d). \( Z_{SD} \) at Site 3 was initially high in April and early May and demonstrated two well-defined minima in early June and mid-August (Fig. 5d), a pattern that was uncoupled from that of [Chl \( a \)]. The patterns for \( b_p \) were roughly inversely related to the \( Z_{SD} \) observations, with similar patterns for the two sites for the May–September interval (Fig. 5e,f), though the August peak was shifted somewhat later for the pelagic site.
Table 2. Auxiliary flow data (Fall Creek; study period mean) and bulk measures; mean along with CV in parentheses.

<table>
<thead>
<tr>
<th>Year</th>
<th>Flow (m³ s⁻¹)</th>
<th>Site</th>
<th>Mean (m)</th>
<th>% &lt; 4 m</th>
<th>[Chl a] (mg m⁻¹)</th>
<th>bₚ (m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999</td>
<td>1.92(1.35)</td>
<td>2</td>
<td>3.5(0.25)</td>
<td>60.0</td>
<td>3.8(0.29)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>4.7(0.28)</td>
<td>46.2</td>
<td>4.5(0.23)</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>5.40(1.16)</td>
<td>2</td>
<td>2.5(0.46)</td>
<td>84.6</td>
<td>4.2(0.62)</td>
<td>1.70(0.31)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>4.0(0.31)</td>
<td>31.2</td>
<td>4.3(0.44)</td>
<td>1.32(0.27)</td>
</tr>
<tr>
<td>2001</td>
<td>3.46(2.14)</td>
<td>2</td>
<td>2.5(0.46)</td>
<td>81.8</td>
<td>3.8(0.39)</td>
<td>2.86(1.43)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>4.8(0.27)</td>
<td>13.3</td>
<td>4.3(0.46)</td>
<td>1.34(0.40)</td>
</tr>
<tr>
<td>2002</td>
<td>4.88(1.34)</td>
<td>2</td>
<td>2.6(0.42)</td>
<td>92.9</td>
<td>4.5(0.45)</td>
<td>2.53(0.78)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>4.5(0.33)</td>
<td>26.6</td>
<td>4.4(0.40)</td>
<td>1.49(0.37)</td>
</tr>
<tr>
<td>2003</td>
<td>5.36(1.10)</td>
<td>2</td>
<td>3.0(0.36)</td>
<td>76.9</td>
<td>4.7(0.62)</td>
<td>1.84(0.36)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>5.2(0.37)</td>
<td>20.0</td>
<td>4.6(4.58)</td>
<td>1.34(0.41)</td>
</tr>
<tr>
<td>2004</td>
<td>7.27(1.03)</td>
<td>2</td>
<td>2.8(0.46)</td>
<td>83.3</td>
<td>4.1(0.59)</td>
<td>1.52(0.37)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>4.4(0.35)</td>
<td>40.0</td>
<td>4.6(0.61)</td>
<td>1.19(0.45)</td>
</tr>
<tr>
<td>2005</td>
<td>4.48(2.67)</td>
<td>2</td>
<td>3.4(0.37)</td>
<td>42.8</td>
<td>3.8(0.46)</td>
<td>1.48(0.52)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>4.9(0.35)</td>
<td>37.5</td>
<td>3.8(0.46)</td>
<td>1.25(0.42)</td>
</tr>
<tr>
<td>2006</td>
<td>5.38(1.21)</td>
<td>2</td>
<td>2.8(0.37)</td>
<td>81.8</td>
<td>5.5(0.76)</td>
<td>3.86(1.96)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>4.2(0.50)</td>
<td>57.1</td>
<td>6.7(0.56)</td>
<td>2.14(1.04)</td>
</tr>
<tr>
<td>Study mean</td>
<td>—</td>
<td>2</td>
<td>2.9(0.42)</td>
<td>75.5</td>
<td>4.3(0.59)</td>
<td>2.19(1.44)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>4.7(0.36)</td>
<td>33.3</td>
<td>4.6(0.49)</td>
<td>1.39(0.62)</td>
</tr>
</tbody>
</table>

The corresponding dynamics of the SAX–Mie-based estimates of $b_m$ in 2003 are presented in two panels, first along with the bulk measurements of $b_p$ (Fig. 5e,f), for comparison and to support depiction of the extent of closure with the two-component model (subsequently) and then as the sum of particle class contributions (Fig. 5g,h). The six type classes have been compressed to four here, combining Calcite and Ca-agg into Ca-rich, and Si-rich and Misc into ‘Other’ because of their small contributions. Variations in $b_m$ contributed significantly to the observed $b_p$ dynamics at both sites in 2003, explaining 47% ($p < 0.01$) and 72% ($p < 0.0001$) of the variations in $b_p$ (linear least-squares regression) for Sites 2 and 3, respectively. Clay minerals dominated $b_m$ throughout the monitored interval except in August (Fig. 5g,h), when $T$ was at its seasonal maximum (Fig. 5b) and Ca-rich dominated. $b_m$ levels at Site 2 exceeded those at the pelagic site throughout the monitored interval. The whiting signature (magnitude of $b_{Ca-rich}$) was greater and longer at the pelagic Site 3. Minerogenic PSDs varied substantially over the monitored interval as depicted in $d_{50}$ patterns, ranging from $< 2 \mu m$ (whiting event) to 5 $\mu m$ (Site 2 in late October; Fig. 5i). The $d_{50}$ patterns for the two sites roughly tracked each other until October.

Closure considerations—Temporal details of the extent of closure are illustrated for a single year (2003) as time series of ($b_m + b_o$) in comparison with $b_p$ (Fig. 5e,f). The modeled and measured values of $b_p$ matched reasonably well in this year, with the greatest deviations in April and late October. Closure was quantitatively evaluated at longer time scales in two formats: as the $b_p$ ($b_m + b_o$) ratio, and through linear regression with $b_p$ and ($b_m + b_o$) as the dependent and independent variables, respectively. Ratio and slope (with near-zero intercepts and high $R^2$) values that approach one are indicative of good closure of the modeled and measured $b_p$.

Performance is first considered on an annual basis (Fig. 6). The average $b_p$ ($b_m + b_o$) ranged from 0.88 (Site 3, 2006) to 1.22 (Site 2, 2001), and the average values for Site 2 were greater than for Site 3 in each year. The 7 yr averages for these sites were 1.09 and 0.97, respectively (Table 1). Substantial variability was manifested for the ratio within each year (Fig. 6a), with the CVs in the 0.11–0.40 range for the available data. The slope was not systematically higher for Site 2 compared with Site 3; these ranged from 0.5 (Site 2, 2004) to 1.4 (Site 2, 2001; Fig. 6b). The y-intercepts from regression analyses for each year by site differed significantly from zero only once (Site 3 in 2006, $p = 0.04$). The linear regression fits were highly significant for all cases ($R^2 = 0.57–1.0$; Fig. 6c). Values of $R^2 \geq 0.95$ were manifestations of a limited number of much higher $b_m$ observations associated with runoff events in those years.

The distribution of $b_p$ ($b_m + b_o$) is presented for the combined population from both sites as a metric of the extent of closure for the entire study (Fig. 7). The means of the populations from the two sites (1.09 and 0.97 for Sites 2 and 3, respectively) were significantly different. The combined population had a modest right-skewed appearance, but the mean and median values were similar. Regression analyses to evaluate closure performance were conducted for three groupings of the population based on $b_m$ values: the full range, $< 3 \text{ m}^{-1}$, and $< 0.25 \text{ m}^{-1}$. The first two populations differ only by six high observations (five at Site 2) following runoff events. Strong linearity between $b_p$ and ($b_m + b_o$) was observed for the overall population (Fig. 8a); however, several very high values disproportionately influenced the slope value. The population for the $b_m < 3 \text{ m}^{-1}$ grouping, which represented the vast majority (98%) of the total, was more evenly distributed (Fig. 8b) and retained strong closure performance. The
grouping for $b_m < 0.25 \, m^{-1}$ represented about 45% of the observations; closure performance was only modestly diminished for this subset (Fig. 8c). There was reasonable consistency between the central metric of the distribution of ratio values (Fig. 7) and the slopes of the regressions (Fig. 8b,c). The extent of the correlation between $b_p$ and the individual components provide insights concerning their relative roles in closure performance and regulation of bulk conditions. The role of $b_o$ increased as the $b_m$ threshold decreased, making no significant contribution to $b_p$ variation when the extremely high $b_m$ values were included (Fig. 8d), representing only a minor contribution when $b_m, 3m^{-1}$ (Fig. 8e), but becoming dominant for $b_m, 0.25 \, m^{-1}$ (Fig. 8f). The opposite trend for the role of $b_m$ was manifested for these three groupings (Fig. 8g–i).

Fig. 5. Temporal patterns of study parameters at the two lake sites (except for tributary flow) for 2003: (a) daily average flows in Fall Creek ($Q_F$), with arrows indicating days of five largest runoff events; (b) temperature (T) of the upper waters; (c) [Chl a]; (d) Secchi depth ($Z_{SD}$); (e,f) $b_m$ along with modeled (mod.) and measured (mea.) $b_p$; (g,h) $b_m$ partitioned into contributions by Clay, Ca-rich (Calcite plus Ca-agg), Quartz, and Other (Si-rich plus Misc); (i) $d_{50}$ values (see Fig. 3b).

Fig. 6. Metrics of closure of the two-component models (Eq. 1), on a yearly basis for Sites 2 and 3: (a) $b_p : (b_m + b_o)$, vertical bars are one standard deviation, and (b,c) slope value and $R^2$ (along with level of $p$-value: * $p < 0.01$, ** $p < 0.001$, *** $p < 0.0001$) from linear least-squares regression.
Sources of uncertainty in the SAX characterizations include (1) potential transformations in samples from handling protocols, (2) precision of the analyses (~ 10%; Peng et al. 2009a), (3) the lying-flat effect (particularly clay platelets) on the effective \( \text{PAV}_m \) (~ 5%; Peng and Effler 2007), and (4) imperfect specification of \( m \) (Eq. 1) according to x-ray compositional characterization. The last of these is a minor effect, because Mie theory estimates of \( b_m \) have been demonstrated (fig. 9a of Peng et al. 2007) to be insensitive to reasonable variations in \( m \) for the PSDs that prevailed in this study. Uncertainties in \( n_p \) are also a minor effect at the red wavelength considered here but could be an issue for blue wavelengths (McKee et al. 2009).

Samples for laboratory analysis may be imperfect representations of conditions measured by field instrumentation because of the acknowledged patchy distribution of particles (Babin et al. 2003; Reynolds 2006). The noteworthy differences in laboratory \( c_{\text{rag}} \) analyses of replicate samples (CV = 0.09) have been attributed in part to this effect (Peng and Effler 2012).

Particle aggregation is a ubiquitous phenomenon (Weillemann et al. 1989), which complicates the light-scattering effects of the involved particles (Boss et al. 2009b). This effect is much more prominent in the high-divalent-cation-concentration environments of marine waters, particularly in coastal waters (Bowers et al. 2011; Hill et al. 2011; Neukermans et al. 2012), compared with the much lower divalent cation levels of freshwaters (Peng and Effler 2012). Moreover, the scattering effects of aggregates are to some extent represented by the SAX–Mie approach, though imperfectly; aggregated small particles may either be represented as a single particle, or by the summation of imaged smaller particles due to the porosity (void spaces) of the aggregate (Peng and Effler 2010).

The Mie theory stipulations of sphericity and particle homogeneity were not met by the minerogenic particle populations of this study, nor in the earlier applications of the SAX–Mie approach (Peng and Effler 2012). Moreover, the ASP values (~ 2) and contributions by heterogeneous particles (e.g., Ca-agg) observed here are recurring features of these studies. The SAX protocol for calculation of \( d \) from detailed morphological information may amend the effects of non-sphericity. Mie theory remains the practical framework to support forward estimates of \( b_m \) from characterizations of the light-scattering attributes of thousands of diverse individual minerogenic particles in natural aquatic systems. The appropriateness of Mie theory calculations for real particle populations, beyond applications for idealized populations (Stramski et al. 2001; Babin et al. 2003; Woźniak and Stramski 2004), should be evaluated on the basis of performance, while acknowledging its potential shortcomings and the values of more robust frameworks in the future. The uniformity of the \( <Q_{b,m}> \) values (2.15–2.35) reported from all implementations of the SAX–Mie approach to date indicates that whatever the potential bias may be from the use of Mie theory, it has remained uniform for the various test systems (Peng and Effler 2012). Moreover, these values approach the limiting value of 2 for polydisperse particle populations (Bricaud et al. 1983; Jonasz 1987).

**Fig. 7.** Distribution of the \( b_p : (b_m + b_o) \) values (as a metric of the extent of closure of the two-component model) for the study.

**Linkages to Secchi depth and hydrology**—The dependence of \( Z_{\text{SD}} \) (inverse format, \( Z_{\text{SD}}^{-1} \)) on \( b_p \) was strong and highly significant (Fig. 9a) for \( Z_{\text{SD}} \) observations \( \geq 1.4 \) m (several lower observations of \( Z_{\text{SD}} \) demonstrated a similar relationship; not shown). The relationship between \( Z_{\text{SD}} \) and the estimates of \( (b_m + b_o) \) was also noteworthy (Fig. 9b), though diminished by comparison. The relationship between \( Z_{\text{SD}}^{-1} \) and \( b_o \) was not significant (Fig. 9c). However, the dynamics of \( b_m \) were important and significant in regulating those of \( Z_{\text{SD}} \) (Fig. 9d).

To test the dependence of the allochthonous component of \( b_m \) on tributary input, we regressed the summation of the Clay (C) and Quartz (Q) components of \( b_m \) (\( b_{CQ} \)) against \( Q_F \) in log-scale. Various intervals of tributary flow were evaluated to specify flow, guided by independent estimates of the residence time of tributary flows on the shelf (Effler et al. 2010). The best predictor was the 3 d (2 d prior to and the day of sampling) average of the flows. The exponential relationship for Site 2 explained 42% of the variations in \( b_{CQ} \) (Fig. 10), demonstrating a linkage between \( b_{CQ} \) and runoff. The relationship for this same 3 d \( Q_F \) for Site 3 was weaker (\( R^2 = 0.31 \)), but still significant (\( p < 0.0001 \)).

**Discussion**

**Uncertainties in forward estimates and the pursuit of optical closure**—It is valuable to consider the performance of the SAX–Mie approach and the two-component model in the context of the sources of uncertainty, to establish the extent of consistency and reasonable expectations. These uncertainties have been identified and addressed to varying extents previously (Peng et al. 2009a; Peng and Effler 2012). A review of these issues here is deemed appropriate to provide proper context for the performance reported. Sources of uncertainty considered here include (1) SAX characterizations of light-scattering attributes, (2) potential effects of particle aggregates (Boss et al. 2009b), (3) application of Mie theory, (4) use of \( c_{\text{rag}} \) measurements to estimate \( b_p \), (5) potential limitations in sample representativeness, and (6) estimates of \( b_o \) with the L98 model (Eq. 4) developed for Case I waters.
The effects of the acceptance angle of the transmissometer on the estimates of $b_p$ are subject to some variation (i.e., $k_2$ of Eq. 3 is not constant; Boss et al. 2009a). The factor is dependent on PSD and composition, and thus may vary temporally in response to changes in the particle populations, including the phytoplankton assemblage (Boss et al. 2009a). Peng and Effler (2012) reported estimates of $k_2$ for a minerogenic particle–dominated stream (0.86) and reservoir (0.94) on the basis of integration of the Mie scattering intensities over the $1.2–180^\circ$ range (acceptance angle as the lower limit). This approach was not adopted here because of the noteworthy and varying contributions of phytoplankton (with likely lower values; Boss et al. 2009a).

There are two aspects of uncertainty related to the use of the empirical bio-optical models to estimate $b_o$, the conceptual justification as well as applicability and their performance limitations. The two-component model (Eq. 2) for inland waters adds the effects of minerogenic particles to $b_o$ ($= b_{p}$ for Case 1 waters). The effects of the attendant retinue of particles associated with phytoplankton, including bacterioplankton and organic detritus, in addition to minerogenic particles of Case 1 systems are implicitly embedded, but are relatively minor and assumed to co-vary

Fig. 8. Linear least-squares regression analyses of extent of closure for $b_o$ and the relative roles of $b_o$ and $b_m$ in regulating $b_p$, for different levels of $b_m$: (a–c) $b_p$ vs. $(b_m + b_o)$, (d–f) $b_p$ vs. $b_m$, and (g–i) $b_p$ vs. $b_o$; (a,d,g) full range of $b_m$; (b,e,h) $b_m > 1$, and (c,f,i) $b_m < 0.25$ m$^{-1}$. The relationships are shown, except for (d), with equations, numbers of data points ($n$), and coefficients of determination ($R^2$); $p < 0.0001$ for all linear fits other than the one in (i) for which $p = 0.02$. 

\[
\begin{align*}
\text{(a)} & \quad y = 1.29x - 0.40 \\
& \quad n = 199 \\
& \quad R^2 = 0.96 \\
\text{(b)} & \quad y = 0.93x + 0.13 \\
& \quad n = 194 \\
& \quad R^2 = 0.65 \\
\text{(c)} & \quad y = 0.42x + 1.04 \\
& \quad n = 194 \\
& \quad R^2 = 0.09 \\
\text{(d)} & \quad y = 1.19x + 0.98 \\
& \quad n = 196 \\
& \quad R^2 = 0.58 \\
\end{align*}
\]
Any double-counting effect for minerogenic particles is negligible in the two-component model because of the much higher minerogenic particle concentrations of inland waters. There was no evidence that an important scattering component was not accommodated by this model for Cayuga Lake (e.g., \( y \)-intercept approaches zero in Fig. 8a), nor in other applications (Peng and Effler 2012). The \( b_p \)-[Chl \( a \)] relationships that supported the development of the bio-optics models for the Case 1 waters manifested substantial dispersion, which was attributed largely to the imperfect character of this pigment concentration as a surrogate of the light-scattering properties of phytoplankton (Loisel and Morel 1998; Huot et al. 2008). This fundamental limitation is exacerbated by the known dependence of the cellular content of this pigment on ambient conditions as well as composition of the assemblage (Reynolds 2006), which demonstrates strong seasonal variations in this lake (Upstate Freshwater Institute unpubl.). An alternative bio-optical model developed by Huot et al. (2008) for lower [Chl \( a \)] levels (\( \leq 2 \) mg m\(^{-3}\)) did not perform as well as the L98 model for Cayuga Lake.

This study represents the most comprehensive test of the SAX–Mie approach for \( b_m \) and the two-component model for \( b_p \) conducted to date, with the largest population of observations and a robust range of seasonal and inter-annual dynamics in the components and associated drivers. A substantial degree of optical closure for \( b_p \) was demonstrated over the long term (Figs. 7, 8a), as well as within individual years (Fig. 6a,b), consistent with the levels of performance described as good in earlier studies with much smaller populations of observations (Peng and Effler 2012).

The credibility of the SAX–Mie estimates of \( b_m \) was most clearly manifested when this component dominated following runoff events (Fig. 8a). The performance for those infrequent occurrences matched that demonstrated for other systems where minerogenic particles dominated \( b_p \) (Peng et al. 2009b; Peng and Effler 2010, 2012). The extent of closure of the two-component model observed outside of those irregular events (Fig. 8b), though somewhat diminished by comparison, was mostly attributable to the dynamics of \( b_m \) (Fig. 8h), even though it was only a modest fraction of \( b_p \) (Fig. 5). The predicted values of \( b_o \) served to support the reported levels of overall closure, but were of secondary importance, even for the population of observations that did not include the few extremes following major runoff events (Fig. 8e). The best test of performance for \( b_o \) estimates was for the low \( b_m \) grouping (\( \leq 0.25 \) m\(^{-1}\); Fig. 8f), associated with dry weather intervals. This population (\( b_o \) dominating) represents the most extensive (\( n = 92 \)) test of \( b_o \) estimates to date, and supports the use of this L98 model for \( b_p \) estimates for inland waters. Without systematic advancements in specifying and partitioning of \( b_o \), however, there is no reason to expect further improvements in \( b_o \) estimates, related partitioning of \( b_p \), and performance of the two-component model.

Clay minerals in Cayuga Lake and comparisons with other systems—Clay mineral particles, with inherently terrigenous origins, are ubiquitous in surface waters (Davies-Colley et al. 2003; Stramski et al. 2007). The dominance of these particles with respect to \( b_m \) on a seasonal average basis, as documented for Cayuga Lake, is consistent with findings from previous applications of SAX (Peng and Effler 2007, 2010, 2012). Certain unifying features of the clay mineral particle populations have emerged; submicron particles are not important contribu-

Fig. 9. Linear least-squares regression analyses of (a) \( Z_{SD}^{-1} \) vs. \( b_p \) and its components: (b) \( b_m + b_o \), (c) \( b_o \), and (d) \( b_m \); \( p < 0.0001 \) for all regressions.

Fig. 10. Evaluation of the dependence of the magnitude of scattering due to clay minerals and quartz (\( b_{CQ} \)) at Site 2 on the 3 d (2 d prior to and the day of the sampling) average daily flow of Fall Creek (\( Q_{F,3-d} \)) for the study period.
tors to $b_m$ (Fig. 3b), and the general curvature of the PSDs (Fig. 3a) and values of $Q_{b_m}$ ($2.15 - 2.35$) and ASP ($\sim 2$; Table 1) are recurring features. The Junge function does not fit these PSDs, yet it can still be used to obtain $b_m$ estimates of similar magnitudes, though the trajectory of the size dependency will deviate (Peng and Effler 2007). The corresponding Junge slope values ($\sim 2 - 2.5$) are generally lower than considered by Babin et al. (2003) in a large survey of coastal waters.

The positive coupling demonstrated here between in-lake (particularly Site 2) $b_{CO}$ and tributary flow (Fig. 10) is generally consistent with the terrigenous origins of clay and quartz particles and the positive dependence of the turbidity of the local streams on flow rate (Effler et al. 2010). A positive dependency of $d_{50}$ values on ambient energy levels has emerged in certain systems for which the SAX-Mie approach has been applied (Peng and Effler 2012). The lack of a strong dependency of $d_{50}$ on tributary flow here suggests that this feature may be influenced by dynamics in the PSDs of the source material received. The higher $b_m$ and $d_{50}$ values at the nearshore site compared with the pelagic location reflect its proximity to the allochthonous sources and perhaps greater exposure to re-suspension, and the effects of size-dependent settling with transport away from the source (Baker and Lavelle 1984; Stramski et al. 2007). Such $d_{50}$ patterns, while conceptually consistent with effects of allochthonous inputs and the settling process (Bowers and Binding 2006), have rarely been demonstrated for lacustrine systems.

Whiting events—Annual late-summer whiting events interrupted the dominance of $b_m$ by clay minerals in Cayuga Lake (Table 1; Fig. 5g,h). CaCO$_3$ precipitation occurs widely in oversaturated hardwater lakes (Hodell et al. 1998; Homa and Chapra 2011), though only over a portion of the oversaturation period (Hodell et al. 1998). Our bi-weekly sampling probably prevented full resolution of its occurrence within the individual years. Whiting has been linked to increases in primary production, temperature, or both (Vanderploeg et al. 1987; Homa and Chapra 2011). Nucleation sites that kinetically promote the precipitation are critical (Homa and Chapra 2011). Picoplankton have been identified as primary nucleation sites (Dittrich and Obst 2004), whereas other possibilities include clay minerals (Stumm and Morgan 1996) and diatoms (Stabel 1986). The whiting phenomenon has AOP implications, causing decreases in $Z_{SD}$ (Fig. 5d) from associated increases in $b_m$ and $b_p$ (Weidemann et al. 1985; Homa and Chapra 2011), and increases in the water-leaving radiance signal for remote sensing (Binding et al. 2007), because the higher $n_p$ value for CaCO$_3$ has a greater effect on backscattering than on $b_p$ (Peng and Effler 2011).

SAX, aided by DIPA, advanced our understanding of the interplay of CaCO$_3$ precipitation with nucleation and its role in $b_m$ dynamics and characteristics. The small organic particles coated with CaCO$_3$ during the event in Cayuga Lake in 2003 (Fig. 2b,d) were likely picoplankton. The whiting phenomenon transformed these inefficient light-scattering particles to highly efficient ones (Stramski and Kiefer 1991). Their short-term importance in regulating features of $b_m$ during the event was manifested in increases in $b_m$ (Fig. 5g,h), the unique plateau-like PSD (Fig. 3a), and the associated narrow range of sizes primarily responsible for $b_m$ (Fig. 3b). DIPA also established that clay mineral particles served as secondary nucleation sites during the events.

Clarity and hydrology linkages—Clarity is closely coupled to the public’s perception of water quality (Smith and Davies-Colley 1992). The regulation of $Z_{SD}$ by $b_p$, as reported here (Fig. 9a), is broadly occurring in lacustrine systems (Davies-Colley et al. 2003). Earlier lake studies focused on phytoplankton as the primary regulator of $Z_{SD}$ (Megard et al. 1980; Tilzer 1983); recent studies, however, have identified the importance of minerogenic particles for a number of systems (Peng and Effler 2005; Swift et al. 2006), as depicted for Cayuga Lake. The dominance of clay mineral particles in this regard links this important component of $b_p$ to watershed sources. Disproportionate increases in inputs of inorganic sediment (natural or anthropogenic origins) are widely reported during runoff events (Richards and Holloway 1987). It is noteworthy that the light-scattering signatures of such allochthonous inputs, and associated diminished $Z_{SD}$, are clearly manifested at a pelagic location of Cayuga Lake with a relatively slow flushing rate. Yet greater effects in nearshore areas, as observed here, should be anticipated. Systems with more rapid flushing would be expected to be more vulnerable to such inputs. The whiting phenomenon complicates the $b_m$ signature through its autochthonous contribution to $b_m$ (Fig. 5g,h) and the associated reduction in clarity (Fig. 5d; Koschel et al. 1983; Weidemann et al. 1985; Peng and Effler 2011).

A simple set of calculations illustrate the importance of $b_m$ to $Z_{SD}$ in Cayuga Lake. The observed average $Z_{SD}$ at Site 3 was 47.7 m. This would increase to $\sim 9.6$ m if $b_p$ was reduced by 50%, according to the system-specific relationship (Fig. 9a). However, if the 50% reduction was only for $b_s$ (e.g., from nutrient management; $b_m$ unchanged), the improvement would be diminished (7.5 m instead). Thus the $b_m$ component acts to limit the extent of improvement that could be achieved by nutrient management alone.

The empirical linkage(s) of $b_{CO}$ to $Q_F$ was not particularly strong, though the best averaging interval for the inflow was consistent with independent estimates of the typical retention time of tributary inflows on Cayuga Lake’s southern shelf (Effler et al. 2010). Failure to accommodate the effects of hydrodynamic complexities of the system limits the performance of such empirical relationships. For example, substantial lateral heterogeneity in turbidity has been documented on the shelf following runoff events, with the highest levels often observed along either the east or west shorelines (Effler et al. 2010). Inputs from other smaller tributaries that enter north of the shelf represent another complication for the pelagic site. A mechanistic model with a robust hydrodynamic framework (Martin and McCutcheon 1999), driven by well-defined external loads of these particles, would be necessary to more accurately quantify this linkage.
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