Advancing two-component partitioning of light scattering in Cayuga Lake, New York

Feng Peng* and Steven W. Effler

Upstate Freshwater Institute, P.O. Box 506, Syracuse, New York 13214

*Correspondence: fpeng@upstatefreshwater.org

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Abstract

The particulate scattering and backscattering coefficients ($b_p$ and $b_{bp}$) were partitioned into the additive contributions of minerogenic ($b_m$ and $b_{b,m}$) and organic ($b_o$ and $b_{b,o}$) particles for the near-shore and pelagic areas of Cayuga Lake, New York, over a seven month period in 2013. The analysis was based on paired measurements of (1) bulk $b_p$ and $b_{bp}$, (2) light-scattering properties of mineral particles, with an individual particle analysis (IPA) technique, and (3) concentrations of two proxies of organic particle scattering, chlorophyll-$a$ ([Chl]) and particulate organic carbon (POC). $b_m$ and $b_{b,m}$ were estimated through Mie theory calculations with IPA results as inputs. $b_o$ and $b_{b,o}$ were estimated with both system-specific and oceanic bio-optical models parameterized on [Chl] or POC. POC performed better than [Chl] as the proxy for both $b_o$ and $b_{b,o}$. The averages of the ratios ($b_m + b_o$) : $b_p$ and ($b_{b,m} + b_{b,o}$) : $b_{bp}$ at 660 nm, were 1.02 and 1.03, respectively; the average relative errors were 18.2% and 15.6%. Multiple empirical bio-optical models developed for Case 1 oceanic waters (for $b_o$ and $b_{b,o}$ estimates) approached the closure performance of the system-specific relationships. Terrigenous minerogenic particles made greater contributions to both $b_p$ and $b_{bp}$ in the near-shore area proximate to tributary inputs, than in pelagic waters. These particles were demonstrated to make systematically greater contributions to $b_{bp}$ than $b_p$. A strong positive dependency of the backscattering ratio ($b_{bp} : b_p$) on the $b_m : b_p$ ratio was observed for both near-shore and pelagic waters.
Light scattering by suspended particles in aquatic systems is an important physical process regulating the underwater light field and the emergent flux signal available for remote sensing. The magnitude and spectral character of particulate scattering are controlled by four features of the particle population: number concentration \((N)\), size distribution, composition, and shapes. Important light scattering properties are the scattering and backscattering coefficients \((b\) and \(b_b\); in m\(^{-1}\)) that represent integrations of the volume scattering function over the angular ranges of 0–\(\pi\) and \(\pi/2–\pi\), respectively. These coefficients are inherent optical properties (IOPs), independent of the geometry of the light field. The contribution of water to scattering is well defined and negligible is lacustrine systems; accordingly, the focus of optics studies has been on the particulate components of scattering and backscattering \((b_p\) and \(b_{bp}\)).

A diverse array of particle types makes up the particle populations of natural systems (Stramski et al. 2007). Resolution of the contributions of these types, described as the ‘reductionist approach’ (Stramski et al. 2001, 2007), offers the opportunity to identify the drivers of optical variability among systems and dynamics within individual systems. Progress in the partitioning of \(b_p\) and \(b_{bp}\) for lacustrine waters has been reported recently (Peng et al. 2009a; Peng and Effler 2011; Effler and Peng 2014) through a two-component modeling approach:

\[
b_p = b_m + b_o
\]

(1)

where \(b_m\) and \(b_o\) are the scattering coefficients of minerogenic and organic (of biogenic origin) particles, respectively (\(b_{bp}\) is partitioned analogously with the backscattering coefficients of the two components, \(b_{b,m}\) and \(b_{b,o}\)). Central to this partitioning has been the development of a protocol to make forward estimates of \(b_m\) and \(b_{b,m}\). An individual particle analysis (IPA) technique, by scanning electron microscopy coupled with automated image and X-ray analyses (SAX), provides light-scattering attributes of minerogenic particles that serve as inputs for Mie-
theory-based estimates of \( b_m \) and \( b_{b,m} \) (e.g., Peng et al. 2009a; Peng and Effler 2011). \( b_o \) and \( b_{b,o} \) have been attributed primarily to the scattering effects of phytoplankton and their retinue. Their magnitudes have heretofore been estimated from chlorophyll-\( \alpha \) concentrations ([Chl]; Peng et al. 2009) through application of empirical bio-optical models developed for open oceanic (so called Case 1) waters (Loisel and Morel 1998; Morel and Maritorena 2001; Huot et al. 2008).

The credibility of the SAX–Mie protocol and the two-component partitioning has been evaluated through closure analyses with paired bulk measurements of \( b_p \) and \( b_{bp} \) at 650 (or 660) nm (e.g., Peng et al. 2009a; Peng and Effler 2011; Effler and Peng 2014). Closure performance has been demonstrated to be reasonably good for a number of systems, with agreement mostly within 20% for both \( b_p \) and \( b_{bp} \). Due to their higher refractive indices relative to those of organic particles, minerogenic particles contribute systematically more to \( b_{bp} \) than to \( b_p \) (Stramski et al. 2004). Indeed, the particulate backscattering ratio, \( b_{bp} : b_p \) (\( \delta_{bp} \)), has been used as a diagnostic to infer composition of particle assemblages (Boss et al. 2004; Loisel et al. 2007; Peng et al. 2009a).

A wide range of contributions of minerogenic vs. organic particles to \( b_p \) and \( b_{bp} \) have been reported on the basis of two-component partitioning supported by SAX–Mie for an array of systems, including the case of dominance by each (see reviews in Peng and Effler 2012; Effler et al. 2013). Yet, \( b_o \) and \( b_{b,o} \) have received secondary attention relative to \( b_m \) and \( b_{b,m} \). There are at least two noteworthy questions related to the performance of the organic components: (1) Is there a better proxy than [Chl], and (2) To what extent are relationships reported for Case 1 systems transferrable to lacustrine (Case 2) systems? Particulate organic carbon (POC) concentrations have been reported to be strongly correlated with \( b_p \) and \( b_{bp} \) for Case 1 waters (Cetinić et al. 2012, and references therein). This suggests that POC may be an alternate proxy to [Chl] to estimate \( b_o \) and \( b_{b,o} \) in Case 2 waters and to support evaluation of the dependency of \( \delta_{bp} \) on particle
composition. Bulk measurements of $b_p$ and $b_{bp}$ with paired estimates of $b_m$ and $b_{b,m}$ can support the development of system-specific relationships for the organic particulate component(s) based on [Chl] or POC (i.e., analyses of $(b_p - b_m)$ vs. organic proxy).

The overarching goals of this paper are to advance the two-component closure for, and partitioning of, $b_p$ and $b_{bp}$, and the composition dependency of $\bar{b}_{bp}$ for a lacustrine system (Cayuga Lake, New York), through improved representation of the scattering effects of organic particles. The analysis is based on field measurements and laboratory analyses of the following parameters for the upper waters over a seven month study period: (1) bulk measurements of $b_p$ (and a proxy) and $b_{bp}$, (2) SAX characterizations of minerogenic particles, and (3) [Chl] and POC, as indices of organic particle scattering levels. Features of the presentation include (1) estimates of $b_m$ and $b_{b,m}$ from the forward SAX–Mie protocol, (2) development and testing of system-specific [Chl]–$b_o$ (and $b_{b,o}$) and POC–$b_o$ (and $b_{b,o}$) relationships, (3) evaluation of the comparative performance of [Chl]- vs. POC-based oceanic bio-optical models in supporting closures with bulk measurements of $b_p$ and $b_{bp}$, and (4) evaluation of the dependencies of $\bar{b}_{bp}$ on multiple indicators of the composition of particle populations.

**Methods**

**Study system, sampling, and in situ measurements**

Cayuga Lake (42°41′30″ N, 76°41′20″ W) is the fourth easternmost of the New York Finger Lakes (Fig. 1). It has the second largest surface area (172 km²) and volume (9.4 ×10⁹ m³) of this group of lakes, with mean and maximum depths of 55 m and 133 m, respectively (Schaffner and Oglesby 1978). This alkaline hardwater, mesotrophic lake (Effler et al. 2010) has an average residence time of 5.5 yr (Upstate Freshwater Institute, 2014). Nearly 40% of the total tributary
inflow from three of the largest streams enters the southern end of the lake. The southernmost 2 km of the lake that receives these inflows is shallow (≤ 6 m), and described as the ‘shelf’ (Fig. 1). Large quantities of minerogenic sediment are delivered to the shelf during runoff events.

Near-surface samples were collected (at ~0.5 m) from five sites along the primary axis of the lake (Fig. 1) over the Apr–Oct interval of 2013. Lake-wide sample collections were conducted bi-weekly at all sites. The frequency increased to twice per week for Sites 1, 2, and 3 over the Jun–Sep interval. Measurements of the spectral attenuation and absorption coefficients ($c_{t-w}(\lambda)$ and $a_{t-w}(\lambda)$; ‘t–w’ indicating total minus pure water attenuation) were made with an ac-s meter (WETLabs; 0.93° acceptance angle, 400–730 nm) at Sites 2, 3 and 5 for a subset of the samplings (N = 52). $b_p(\lambda)$ was determined as the difference between $c_{t-w}(\lambda)$ and $a_{t-w}(\lambda)$.

Coincident measurements of $b_p$ were made at nine wavelengths with a BB9 meter (WETLabs); values at 532 nm and 660 nm were used in analyses here. In addition, the beam attenuation coefficient at 660 nm associated with particles and gelbstoff ($c_{pg}$) was measured with a C-Star transmissometer (WETLabs; 10 cm path length, 1.2° acceptance angle) at the times of all sample collections.

**Laboratory analyses and SAX–Mie protocol**

Concentrations of chlorophyll-a ([Chl]) were determined fluorometrically after acetone extraction (Arar and Collins 1997). Concentrations of particulate organic carbon (POC) were determined according to Rice et al. (2012), based on analysis of particles retained on a 0.7-μm GF/F membrane filter after acid treatment to dissolve inorganic carbon. The detection limit of this method is 0.05 mg C L$^{-1}$. 
Detailed descriptions of the SAX methodology (sampling handling, instrument analysis, and data processing) for characterizing the light-scattering attributes of individual mineral particles have been presented previously (e.g., Peng and Effler 2007; Peng et al. 2009a,b). A brief account, closely related to its application in this paper, is presented here. Known volumes of water samples were pressure filtered through 0.4-µm pore sized polycarbonate membranes with suspended particles retained on the filters (non-overlapping monolayer). The filter membranes were air dried and coated with a thin layer of carbon (40–60 nm) under high vacuum before being subject to instrumental analyses, conducted with an Aspex Personal Scanning Electron Microscope (PSEM) 2000 system. Particles composed of elements with average atomic number >11 (i.e., inorganic or mineral particles) are differentiated from the polycarbonate membrane substrate, subsequently recognized and imaged as ‘features’ and then analyzed by the ‘Automated Feature Analysis’ (AFA) software of the PSEM system. AFA conducted image analysis of individual particles 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 area (PA; i.e., geometric cross-section) of a particle is the sum of these triangular areas, and particle size \( (d, \mu m) \) is defined as the circular area equivalent diameter. The total projected area of minerogenic particles per unit volume of water \( (PAV_m, m^{-1}) \) is computed from the sum of the measured PAs of minerogenic particles, the fraction of analyzed filter area, and the sample volume. 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). Approximately 2000 individual minerogenic particles were analyzed for each of the ~150 samples.
X-ray microanalysis conducted by PSEM AFA acquires X-rays of 16 user designated elements (Na and elements of higher atomic numbers, including Mg, Al, Si, K, Ca, and Fe) from a particle and evaluates its composition in terms of the relative intensities of elemental X-rays. The elemental composition of particles provides the basis for classification of particles into generic particle types, such as clay minerals (aluminosilicates), quartz (minerogenic SiO₂), and calcite (CaCO₃), based on which the complex refractive indices (relative to water) of particles are specified (Table 1).

**Calculations and bio-optical models**

SAX characterizations and results support the calculations of bulk $b_m$ and $b_{b,m}$ based on the single-particle optics principle through summation of the contributions from individual particles (Mobley 1994). This is described below for $b_m$:

$$b_m(\lambda) = \frac{1}{V} \sum_{i=1}^{N_m} \sigma_{m,i} = \frac{1}{V} \sum_{i=1}^{N_m} (Q_{bm,i}(m_i, \lambda, d_i) \times PA_{m,i})$$  \hspace{1cm} (2)

where $V$ is the sample volume, $N_m$ is the number of mineral particles in a sampled volume of water, and $\sigma$ is a particle’s scattering cross-section, which is the product of its scattering efficiency factor ($Q_b$) and projected area (PA); $b_{b,m}$ is calculated similarly with the backscattering efficiency factor, $Q_{bb,m}$. The magnitude of $Q_b$ ($Q_{bb}$) depends on a particle’s composition (i.e., complex refractive index, $m$) and size ($d$) as well as the wavelength of light ($\lambda$), and was computed here from Mie theory (i.e., assuming particles are homogenous spheres; BHMIE routine from Bohren and Huffman 1983). For this study, results were reported for $b_m(660)$ and $b_{b,m}(532)$ as well as $b_{b,m}(660)$ to facilitate comparisons of system-specific bio-optical models with those reported in literature for Case 1 oceanic waters (e.g., Stramski et al. 2008; Cetinić et al. 2012). Values of the refractive indices ($m = n - in'$, where $n$ and $n'$ are the real and imaginary...
parts relative to water; Table 1) were specified on the basis of particle type classification and literature listings (e.g., Babin et al. 2003; Woźniak and Stramski 2004) and a recent study of the spectral absorbing properties of mineral particles in Lake Erie (Peng and Effler 2013). The \( n \) (real part, considered spectrally flat) values were consistent with earlier SAX–Mie applications (e.g., Peng et al. 2007, 2009a), including the long-term study of Cayuga Lake minerogenic particle optics (Effler and Peng 2014). The adopted values of \( n' \) were lower than those used in earlier studies (e.g., \( 10^{-4} \) instead of \( 10^{-3} \) at 660 nm for clay minerals), based on new absorption information (Peng and Effler 2013). The average scattering and backscattering efficiencies of minerogenic particles were calculated as \(<Q_{b,m}> = b_m/PAV_m\) and \(<Q_{bb,m}> = b_{bb,m}/PAV_m\).

Given our focus on closure analyses for the two-component models, bulk measurements of \( c_p \) needed to be adjusted upwards for the acceptance angle effect, to accommodate the underestimation due to the fraction of scattering captured by the detectors (as transmitted light) with finite angles. The effect is noteworthy for the instruments used in this study (Boss et al. 2009b) because of the highly peaked volume scattering function near 0°. The adjustments adopted here are consistent with the results of instrument comparisons presented by Boss et al. (2009b) for the Darling Marine Center, accepting the LISST-100-B instrument (acceptance angle 0.0269°) as the reference. The adjusted \( b_p \) values \((b'_p)\) based on ac-s measurements were calculated as:

\[
b'_p = \left( \frac{b_{p,ac-s}}{0.8} \right)
\]

(3a)

Those based on C-Star measurements were calculated according to:

\[
b'_p = \left[ \left( 0.97 \times c_{pg}^{C-Star} \right) / 0.9 \right] / 0.8
\]

(3b)

Three adjustment steps are embedded in Eq. 3b: (1) the 0.97 factor adjusts for the contribution of gelbstoff to \( c_{pg}(660) \) (e.g., Babin et al. 2003), (2) the 0.9 factor adjusts for the larger acceptance
angle of C-Star (1.2°) compared with the ac-s (0.93°), and (3) the 0.8 factor adjusts for the larger acceptance angle of the ac-s compared with the LISST-100-B (as in Eq. 3a). We observed an average of $c_{pg}^{C-Star} : b_{p}^{ac-s}$ ratio of 0.93 (CV = 16%) for the 43 paired deployments of these two instruments for this study, supporting our selections of adjustment factors from the observations of Boss et al. (2009b; their fig. 3).

System-specific, bio-optical models for the organic particle components were developed through evaluating the dependence of the residual between bulk measurements and minerogenic component estimates on the organic proxy of [Chl] or POC, for example, $b_{o} (= b_{bp} - b_{o,m}) \propto f(POC)$. Empirical bio-optical models originally developed for open oceanic waters (where [Chl] or POC was used as the single index of total $b_{p}$ and $b_{bp}$) were selected (listed with designations in Table 2 for $b_{o}$ and Table 3 for $b_{o,o}$) to check consistency with system-specific relationships and provide alternate tests of closure with bulk measurements. These literature bio-optical models for $b_{o}$ were also adjusted to reflect the acceptance angle effect of the employed instrumentation (see footnotes of Table 2), to enable comparisons with the system-specific expressions for which the same factors were applied (Eq. 3a,b).

**Results**

**Patterns of bulk measurements of $b_{p}$ and $b_{bp}$ and estimates of $b_{m}$ and $b_{o,m}$**

Summary population statistics of the bulk optical measurements ($c_{pg}$, $b_{p}$, $b_{bp}$) for the near-shore shelf (Sites 1 and 2) and pelagic (Sites 3, 5, and 7) areas are presented (Table 4). Values were generally higher and ranges broader in the shelf area, which is proximate to tributary inputs of terrigenous material (Fig. 1). The smaller differences between these two lake areas for $b_{bp}$
were an artifact of less frequent observations and saturation of the BB9 sensor for shelf observations after major runoff events.

Temporal patterns of $b'_p$ and $b_{bp}$ (at 660 nm; the former estimated from the $e_{pg}$ observations, Eq. 3b) are presented for selected shelf (Site 2) and pelagic (Site 3) locations (Fig. 2b–e), along with the dynamics of tributary flow ($Q$) for Fall Creek (Fig. 2a). The $Q$ dynamics of this stream are a good proxy for overall tributary inputs (Effler et al. 1989) and minerogenic sediment (Effler and Peng 2014). Particularly large increases in scattering levels were observed at the shelf site after runoff events (e.g., early July event; Fig. 2b,d); corresponding increases at Site 3 were much smaller and somewhat delayed (Fig. 2c,e).

The summary statistics for SAX observations (Table 4) depict large variations in the magnitudes of $\text{PAV}_m$, but rather uniform features of composition (percent contribution of clay minerals to $\text{PAV}_m$, Clay%), shape (ASP), and light-scattering efficiency factors ($<Q_{b,m}>$ and $<Q_{bb,m}>$, see CV values). The mean $\text{PAV}_m$, particularly for the shelf, was greater than the median, because of the effects of runoff event inputs (Effler and Peng 2014). The dominant contribution of clay minerals is manifested in the high values of Clay%, though their contributions in pelagic waters were somewhat diminished, reflecting the effects of brief intervals of autochthonous formation of calcite. Other features of the minerogenic particle assemblages observed during this study, also reported from earlier characterizations (Effler and Peng 2014), included (1) PSDs with distinct curvature (peak density at ~0.4 $\mu$m, not the linear Junge pattern), and (2) associated $b_m$ and $b_{bm}$ estimates dominated by particles in the 1–10 $\mu$m size range.

The time series of the $b_m$ and $b_{bm}$ estimates are presented along with the bulk measurements of $b_p$ and $b_{bp}$ (Fig. 2b–e). Increases in the bulk measurements and estimates of the minerogenic component coincided in several instances after runoff events. The contributions of minerogenic
particles were greater on the shelf for both $b_p'$ and $b_{bp}$, and for $b_{bp}$ vs. $b_p'$ for both sites. The mean and median $b_m : b_p'$ ratio values were 0.22 and 0.16 for Site 2, compared with 0.15 and 0.14 for Site 3. Changes in $b_m$ explained only a modest but significant portion of the observed variations in $b_p'$ ($R^2 = 0.21$, $p < 0.01$ for Site 2, not including the peak of early July; $R^2 = 0.19$, $p < 0.01$ for Site 3). In contrast, variations in $b_{m,m}$ were primarily responsible for those in $b_{bp}$ ($R^2 = 0.70$, $p < 0.0001$ for Site 2; $R^2 = 0.55$, $p < 0.001$ for Site 3). The mean and median $b_{m,m} : b_{bp}$ ratio values were 0.51 and 0.46 for Site 2, and 0.41 and 0.43 for Site 3.

[Chl] and POC, and their relationships with $b_o$ and $b_{bo}$

The precision of [Chl] and POC observations for triplicate samples from Site 5 was good (average CVs of 5.4% and 10.5%, respectively). On average, [Chl] levels were relatively uniform spatially (Table 4) but varied substantially on a temporal basis. These levels exceeded the upper bounds of the H08 ($\sim 2 \mu g L^{-1}$) model development most of the time and that of the MM01 ($\sim 6 \mu g L^{-1}$) frequently, but remained well within the bounds of LM98 (Tables 2 and 3). POC concentrations were higher on average and more variable on the shelf. Cayuga Lake POC levels exceeded the upper bounds of the Case 1 bio-optical models for the vast majority of observations, and often by a wide margin (e.g., by an order of magnitude), depending on the specific model considered. Overall, the two proxies of organic particle concentration were poorly correlated ($r = 0.31$) for all observations. The [Chl] : POC ratio demonstrated major (7-fold) seasonal changes, as illustrated for Site 5 (Fig. 3, mean ± one SD from triplicate analyses). The ratio was on average significantly lower ($p < 0.001$) for shelf vs. pelagic sites (Table 4), reflecting higher POC levels in that near-shore area following runoff events.
Estimates of $b_o$ and $b_{b,o}$ were calculated as residuals of bulk measurements and minerogenic component estimates, $(b'_p - b_m)$ and $(b_{bp} - b_{b,m})$, respectively. These residuals appear as the $Y$-axes in evaluations of their dependencies on [Chl] or POC (Fig. 4). The adopted graphic formats (logarithmic for [Chl], linear for POC) are consistent with the related literature. Bulk determinations of $b_p$ by the ac-s meter were used in the system-specific evaluation of $(b'_p - b_m)$ vs. [Chl] (Fig. 4a). The best-fit relationship was significant ($p < 0.0001$), but not strong, though it was similar to the LM98 model (designations in Table 2). Predictions of the H08 model were shifted lower. The best-fit relationship between $(b_{bp} - b_{b,m})$ and [Chl] was weak (Fig. 4b); while demonstrating some consistency with the two open ocean expressions for [Chl] > 1 $\mu g$ L$^{-1}$, it was distinctly higher for lower concentrations.

A strong dependency of $(b'_p - b_m)$ (i.e., $b_o$) on POC was observed for the ac-s determinations of $b_p$ ($R^2 = 0.82$, $p < 0.0001$), with a $y$-intercept approaching zero (Fig. 4c). Predictions based on three models reported for oceanic waters (Table 2) were included for comparison. The closest of these (O05) has a slope value within 4%. The slope values from two other relationships (S08-1, including higher POC concentrations, and S08-2, excluding upwelling data; Table 2) are within 16% (lower) and 17% (higher) of that of the system-specific relationship. A validation test of the system-specific $b_o$–POC relationship was conducted for a separate dataset for which values of $b'_p$ were estimated instead from C-Star $c_{pg}(660)$ measurements (Eq. 3b) (i.e., no overlap with the dataset involved in Fig. 4c for model development). These two system-specific relationships agreed well with each other; the best-fit slope values were within 10% (Fig. 4d).

A reasonably strong relationship was observed between $(b_{bp} - b_{b,m})$ at 660 nm and POC ($R^2 = 0.62$, $p < 0.0001$), with a $y$-intercept approaching zero (Fig. 4e). This relationship matched well
with S08B-1 (Table 3), with slope values agreeing within 4%. The slopes from two other
literature expressions deviated, to different degrees, 17% for S08B-2 and more than 2-fold for
C12 (Table 3). The system-specific relationship for 532 nm was similarly strong ($R^2 = 0.62, p < 0.0001$), but the $y$-intercept (0.0017 m$^{-1}$) was significantly different from zero (Fig. 4f); it was
most closely approached by the S08-2 relationship over most of the observed range of POC
values for Cayuga Lake.

**Extent of closure for the two-component models**

Distributions of the populations of $(b_o + b_m) : b_p'$ and $(b_{b,o} + b_{b,m}) : b_{bp}$ (at 660 nm) for the
study, based on system-specific POC relationships for the organic component (Fig. 4a,e), are
presented (Fig. 5a,b) to represent the extent of closure obtained with the two-component
approach. The average ratio values approached unity. However, substantial variances in the
degree of closure were observed, with CV values of 23% and 19% for $b_p'$ and $b_{bp}$, respectively.

The implications of not considering the minerogenic component are represented by the
distributions of $b_o : b_p'$ and $b_{b,o} : b_{bp}$ (Fig. 5a,b) for comparison. The effects of minerogenic
particles were substantial for $b_p'$ (mean ratio 0.82), but major for $b_{bp}$ (mean ratio 0.6). Moreover,
variances were greater (CV ~36%) for these cases of not including the contributions of
minerogenic particles.

The same ratio format was adopted to compare the performances of the oceanic bio-optical
models with the system-specific relationships, with either POC or [Chl] as the proxy for $b_o$ and
$b_{b,o}$ estimates, to represent the extent of closure (Fig. 6). Based on system-specific relationships,
POC performed better than [Chl] as the organic particulate proxy, with respect to the average
degree of closure and variance for both $b_p$ (Fig. 6a) and $b_{bp}$ (at 660 nm and 532 nm; Fig. 6b,c).
Selected oceanic bio-optical models based on POC had similar benefits compared with [Chl]-based expressions. Still, reasonable levels of closure (i.e., within 15% on average) could be achieved with relationships based on both proxies. All three of the literature $b_o$–POC relationships performed better than the two $b_o$–[Chl] bio-optical models (Fig. 6a). However, unlike the two S08B relationships the C12 $b_{b,o}$–POC model predicted much higher values than the two [Chl]-based models, MM01 and H08B (Table 3; Fig. 6b,c). The performance levels of different models at two different wavelengths were comparable, though the [Chl]-based $b_{b,o}$ models supported slightly better closure at 532 nm than at 660 nm.

Contributions of minerogenic and organic particles to scattering, and $\tilde{b}_{bp}$

We used the two-component models to contrast the contributions of minerogenic vs. organic particles to $b_p$ and $b_{bp}$, for the shelf and pelagic waters (Fig. 7). The fractional contributions were calculated on the basis of estimated values of $b_m$ and $b_{b,m}$, and predicted values of $b_o$ and $b_{b,o}$ according to system-specific POC-based relationships. Minerogenic particles were relatively more important on the shelf, which was proximate to tributary inputs (Fig. 1), for both $b_p$ and $b_{bp}$ (Fig. 7a,b), compared with pelagic waters (Fig. 7c,d). $b_m$ exceeded $b_o$ on the shelf on several occasions after runoff events; such a case was not observed in pelagic waters. The contributions of $b_{b,m}$ to $b_{bp}$ (Fig. 7b,d) were systematically greater than those of $b_m$ to $b_p$ (Fig. 7a,c). $b_{b,m}$ contributed 60% and 41% to $b_{bp}$ on average on the shelf and in pelagic areas, respectively, in contrast to $b_m$ accounting for 30% and 14% of $b_p$.

The dependency of $\tilde{b}_{bp}$ on composition of the particle assemblages was evaluated with three ratios (Fig. 8) representing the relative contributions of organic and minerogenic particles, [Chl] : $b'_p$, POC : $b'_p$, and $b_m : b'_p$. These were evaluated separately for the shelf and pelagic waters, as
well as together as one population. No significant relationships were observed for the ratios involving the organic particle proxies (Fig. 8a,b). However, strong and spatially uniform dependencies of \( \tilde{b}_o \) on \( b_m : b'_p \) prevailed (Fig. 8c); overall, changes in this ratio explained 77% of the variations in \( \tilde{b}_o \) \((p < 0.0001)\).

**Discussion**

**Advancing two-component partitioning of \( b_p \) and \( b_{bp} \)**

Heretofore, implementation of the two-component scattering model for lacustrine waters has involved adopting empirical, oceanic bio-optical models based on [Chl] for the organic component (Tables 2 and 3). The justification for this approach has been performance-based, that is, the use of these relationships in combination of SAX–Mie based estimates of the minerogenic component resulted in a substantial degree of closure with bulk measurements (Peng and Effler 2012). Representation of the organic particle component has been advanced here by (1) testing empirical, POC-based oceanic models, and (2) developing system-specific relationships of the same forms. The reasonably good closure of oceanic model predictions of \( b_o \) and \( b_{o,o} \) (Fig. 4c,e,f) with the estimates (calculated as residuals, \( b_o = b_p - b_m \)) from Cayuga Lake observations further supports the concept and performance of the two-component partitioning. In addition, our system-specific \( b_o \)--POC relationship is in very good agreement with the reported \( c_p(660) \)--POC for Crater Lake, Oregon (Boss et al. 2007). This convergence provides early support for the transferability of certain Case 1 bio-optical models to estimate \( b_o \) and \( b_{o,o} \) in lacustrine waters, despite the higher proxy concentrations of these inland waters. The potential for broad applicability is appealing, serving as a welcome parsimonious element in addressing the complexity of the optical regimes of lacustrine systems (Kirk 2011).
It is convenient to consider the two-component partitioning in the context of the Case 1 vs. Case 2 classifications (Morel and Prieur 1977; Morel 1988), while acknowledging their limitations in representing the wide variety of noteworthy cases (Mobley et al. 2004). In broad terms, the two-component model accommodates the fundamental differences in scattering between these two cases (Morel and Prieur 1977), by quantifying the noteworthy contributions of minerogenic particles ($b_m$ and $b_{b,m}$). The overly simplistic Case 2 descriptor for this lake fails to differentiate the multiple minerogenic scattering cases associated with (1) scattering vs. backscattering (e.g., $b_m : b_p < b_{b,m} : b_{bp}$; Figs. 5,7), (2) temporal and spatial variations in their contributions (e.g., runoff events, shelf vs. pelagic waters; Figs. 2,7), and (3) the relative importance of allochthonous (clay minerals) vs. autochthonous (calcite) sources (Table 4; Effler and Peng 2014).

$[\text{Chl}]$ is accepted as a proxy of phytoplankton biomass in the oceanic bio-optical models for scattering. Moreover, the effects of an attendant retinue of covarying constituents (including bacteria, protozoans, and associated organic detritus), and even a small amount of minerogenic particles, are implicitly embedded in those relationships (Loisel and Morel 1998; Huot et al. 2008). The observed substantial variances in the system-specific $b_{o,-} \text{ and } b_{b,o,-}[\text{Chl}]$ relationships for Cayuga Lake (Fig. 4a,b) are not unexpected as similar levels of dispersion were manifested in the development of the oceanic relationships. These short-comings in performance of $[\text{Chl}]$ reflect fundamental limitations of this pigment concentration as a proxy of phytoplankton biomass and associated light-scattering attributes, and the potential non-covariation of the retinue components (Loisel and Morel 1998; Huot et al. 2008). This includes the dependence of the cellular content of chlorophyll-$a$ on the composition of the phytoplankton assemblage and
ambient conditions (Reynolds 2006), alternatively described as taxonomic and physiological
dependences (Behrenfeld and Boss 2006).

POC has conceptual advantages over [Chl] as a proxy of scattering. First, POC directly
measures the particulate organic components of the retinue accompanying phytoplankton
(Stramski et al. 2008), rather than relying on covariation. Second, the POC content per
phytoplankton cell volume varies less than for chlorophyll-\(a\) (Fennel and Boss 2003). The poor
relationship reported here between [Chl] and POC, manifested in the 7-fold variation in [Chl] :
POC (Fig. 3), is widely observed (Fennel and Boss 2003; Mobley et al. 2004). The levels of
variance in the linear POC−\(b_o\) or \(b_{b,o}\) (Fig. 4b–f) relationships (less than those for the [Chl]-based
relationships) are generally consistent with those manifested in the development of the individual
oceanic expressions (Stramski et al. 2008; Cetinić et al. 2012).

Limitations in the \(c_p\)− and \(b_{bp}\)–POC relationships have been identified in marine studies,
manifested in part as differences in slopes (see compilation in Cetinić et al. 2012), and illustrated
by the differences in selected relationships included here (Fig. 4c,e,f). Cetinić et al. (2012)
identified two types of sources of these variations: (1) methodology based, including
measurements of \(c_p\) and \(b_{bp}\), and sampling and measurements of POC, and (2) natural variability
of organic particles. Two factors give us confidence in the POC data set, the generally high range
of concentrations (relative to that in Case 1 waters) and good precision of replicate POC analyses
for Site 5 samples. Natural variations may occur from differences in the phytoplankton
assemblage, associated with differences in their carbon content per unit volume (Menden-Deuer
and Lessard 2000; Cetinić et al. 2012). Cetinić et al. (2012) reported the POC−\(c_p\) slope was 11%
lower for the diatom vs. recycling communities in a study of Case 1 waters. We did not observe
systematic temporal shifts in our relationships over seasonal changes in the lake’s phytoplankton
community. Given the reported variations in the slopes of the Case 1 relationships, it would be prudent to extend the findings of this study to other lacustrine systems to establish the extent of variability. The extent to which the effects of minerogenic particles were embedded in the development of oceanic [Chl]- and POC-based $b_p$ and $b_{bp}$ expressions represents a ‘double-counting’ in our two-component models. However, this effect is negligible because of the much higher minerogenic particle concentrations of lacustrine waters. The POC proxy for scattering has an additional advantage for inland waters, as it can also accommodate the effects of terrigenous (vs. phytoplankton derived) organic detritus. This was likely encountered for samples collected on the shelf after runoff events when POC levels were distinctly higher. However, the scattering–POC relationships of this terrigenous material could differ substantially.

**Light scattering by minerogenic particles in Cayuga Lake**

Earlier particle optics research on Cayuga Lake (Effler and Peng 2014) pursued testing of the two-component model for $b_p$, with $b_m$ and $b_o$ estimated through the SAX–Mie approach and a Case 1 bio-optical model based on [Chl] (Loisel and Morel 1998), respectively. This have been extensively expanded here with a new data set, through (1) pursuit of optical closure for both $b_p$ and $b_{bp}$, (2) testing POC as an alternative proxy of organic particle scattering to [Chl], (3) evaluating multiple Case 1 models based on both proxies to represent the organic component, (4) developing system-specific relationships to estimate $b_o$ and $b_{o,o}$, and (5) evaluating the dependence of $\tilde{b}_{bp}$ on multiple composition indicators.

The light-scattering features of minerogenic particles in this study (reported for 660 nm; Table 4) are consistent with those reported from SAX applications elsewhere, indicating that these are broadly occurring. Clay mineral particles inherently have terrigenous origins, and they
are ubiquitous in both inland (Davies-Colley et al. 2003) and marine (Stramski et al. 2007) waters. Clay minerals have generally been found through SAX to be the dominant type in freshwater studies to date, the only exception being CaCO₃ particles during whiting events in hardwater lakes (e.g., Peng and Effler 2011). Several recurring features have prevailed for the clay mineral particle populations (Table 4), including (1) platelet morphology, with average ASP values of ~2, (2) the general curvature of the PSDs, (3) uniform values of $<Q_{b,m}>$ (2.2–2.5) and $<Q_{bb,m}>$ (0.043–0.075; increased ~10% on average when lower value of $n'$ was used in calculations, compared with early reported values in Effler et al. 2013), and (4) the importance of particles in the 1–10 µm size range to scattering (i.e., submicron particles not noteworthy).

A broad range of contributions of clay mineral particles to light scattering in lakes was bracketed in this study, relative to the other systems pursued with the two component approach to date (e.g., see review in Peng and Effler 2012), by addressing both the shelf and pelagic waters seasonally in Cayuga Lake (Fig. 7). Disproportionately large quantities of this material are delivered to most lakes, including Cayuga (Effler and Peng 2014), during runoff events (Longabucco and Rafferty 1998; Prestigiacomo et al. 2007). The clear signatures of increased $b_m$ and $b_{b,m}$ (Fig. 2b–e) from such events, even in pelagic waters, in this relatively large, slow flushing lake suggest that these effects are imparted in many lakes. The greater effects in near-shore areas, associated with their proximity to sediment-enriched inputs, may be expected to extend over larger portions of smaller rapid flushing systems (Peng et al. 2009b). Temporally limited surveys may miss or over-represent runoff event signatures because of their stochastic timing. The reported strong temporal variations in $b_m$ and $b_{b,m}$ are an important element of complexity of the optical regimes of affected lakes (Kirk 1985; Davies-Colley et al. 2003) and other Case 2 systems (Mobley et al. 2004). The effects of minerogenic particles on $b_p$ may not be
necessary to consider in certain lakes during dry weather periods (i.e., $b_m \ll b_o$) in the context of related apparent optical properties. However, the systematically greater contributions of minerogenic (vs. organic) particles to $b_{bp}$ compared with to $b_p$ (Stramski et al. 2004), as demonstrated here (Figs. 5,7), make the representation of the mineral particle effects in remote sensing retrieval initiatives important in most lakes (Binding et al. 2012; Effler et al. 2013).

Contributing uncertainties in pursuit of closure of the two-component model

Despite the substantial degree of closure demonstrated for the two-component models, and the improvement from specifying the organic particle component based on POC instead of [Chl], considerable variance was observed (Figs. 4,6), which raises questions concerning its origins. Future efforts to improve performance will be informed by consideration of the sources of uncertainty. Our treatment here represents an expansion of earlier reviews (Peng et al. 2009a; Effler and Peng 2014). The sources of uncertainty considered here are (1) SAX characterizations of light-scattering features of minerogenic particles, (2) potential effects of particle aggregates (Boss et al. 2009a), (3) potential limitations in sample representativeness, (4) the application of Mie theory to estimate $b_m$ and $b_{b,m}$, (5) bulk measurements of $b_p$ and $b_{bp}$, and (6) applications of empirical bio-optical models from Case 1 waters for the organic component.

The uncertainties associated with SAX characterizations, including precision for replicate samples (~10%), adjustments in PA for the particle lying-flat effect, and imperfect specifications of $m$ values for different clay minerals, are modest for $b_m$ estimates for the prevailing PSD shapes (Peng et al. 2009a). There is more related uncertainty for $b_{b,m}$ estimates, because of its greater dependencies on $m$ (Peng et al. 2007) and spherical morphology used to represent natural irregular particles in theoretical calculations. Aggregation of particles is a ubiquitous process,
promoted particularly by high concentrations of divalent cations (Weilenmann et al. 1989). This phenomenon complicates the light-scattering effects of affected particles (Boss et al. 2009a), and has been reported to greatly influence scattering signatures in coastal marine waters (Bowers et al. 2011; Neukermans et al. 2012). The phenomenon is not as acute in lacustrine waters where divalent cation concentrations are much lower (Peng and Effler 2012). Moreover, the scattering effects of aggregates are represented to some extent by the SAX–Mie approach (Peng and Effler 2012; Effler and Peng 2014). Samples for laboratory analyses may imperfectly represent conditions that prevailed during bulk measurements, as a result of the patchy distribution of particles (Reynolds 2006).

The Mie theory stipulations of homogenous spheres are not met by natural particle populations (such as the minerogenic particles in this study and others with SAX applications; e.g., ASP values of ~2 in Table 4). These shape deviations are in general modest compared with those common to many freshwater phytoplankton (Reynolds 2006). Mie theory remains the practical framework to support the single-particle optics approach for estimating spectral IOPs of diverse minerogenic particle assemblages characterized by SAX in natural aquatic systems (Effler and Peng 2014). The potential effects of asphericity on $b_{bp}$ are greater than for $b_p$ (Mishchenko and Travis 1994). This, together with the greater sensitivity of $b_{bp}$ to the values of $m$, results in greater uncertainty in the forward estimates of $b_{b,m}$ than those for $b_m$. The SAX protocol to calculate $d$ from the directly measured PA may in part compensate for the asphericity effects (Effler and Peng 2014). The average $<Q_{b,m}>$ value (Table 4) was within the narrow bounds reported for other lacustrine systems for which SAX–Mie approach was implemented (Effler et al. 2013; Effler and Peng 2014). These $<Q_{b,m}>$ values approach the limiting value of 2
for polydispersed particle populations (Jonasz 1987). There is no evidence of systematic bias in
the estimates of $b_m$ and $b_{b,m}$.

More complex models for aspherical particles (Mishchenko and Travis 1994; Zhang et al. 2014) may support further improvements in estimates of IOPs of mineral particles in the future. Presently, each of these models has its own sources of limitations associated with shape
specifications, speed of computations or particle size limit. None of these have been used to
make forward estimates for large data sets of natural polydispersed populations, such as
measured by SAX, for comparative performance evaluations relative to those presented here
through the SAX–Mie approach. Such comparative analyses are recommended when feasible.

Sullivan et al. (2013) recently considered uncertainties in $b_p$ measurements, made with
sensors similar to those used here; their upper bound (~10%) included comparison with sensors
of other instruments. In an evaluation of sources of uncertainty for $\tilde{b}_{b_p}$, Whitmire et al. (2007)
presented 20% as a reasonable upper bound.

The acceptance angle issue influences our analysis in two ways, by affecting the bulk
measurements of $c_p$ (and $b_p$) in Cayuga Lake, and by having associated effects on Case 1 bio-
optical models, applied here to estimate $b_o$ (Table 2). The negative bias effect on $b_p$ (i.e., false
low) associated with the acceptance angle is systematic, increasing as the angle of the instrument
increases (Boss et al. 2009b). Without adjustment this would cause corresponding
underestimates of $b_o (= b_p - b_m)$. Through modification of the forward estimates of $b_m$ to reflect
the effects of an instrument’s acceptance angle (Peng and Effler 2012; an average ~10%
reduction), the bias in $b_o$ can be reduced and the relative contributions of these two components
can still be pursued, though both estimates would remain negatively biased. Such as approach
becomes compromised by the inclusion of a second dataset, such as that in this study, with a
different acceptance angle instrument, resulting in systematically different levels of negative bias in $b_o$ and $b_m$. Moreover, such an approach fails to provide realistic estimates of the magnitudes of $b_o$ and $b_m$; instead, the values are constrained in the context the instrument used.

The adopted approach instead made upward adjustments in the bulk measurements of $c_{pg}$ and $b_p$ (for 660 nm), and literature bio-optical models, to accommodate the acceptance angle effect, consistent with our goal of testing the extent of closure of the two-component scattering models for Case 2 waters. The values of our uniform adjustment factors (Eq. 3a,b) were consistent with some of the average values reported for one system by Boss et al. (2009b) and paired ac-s and C-Star observations for Cayuga Lake. However, the adopted approach is accompanied by substantial uncertainty, particularly the variability that occurs within a given system (e.g., CV = 16% for $c_{pg}$ C-Star : $c_{ac-s}$) associated with variations in composition and size distributions of particles (Boss et al. 2009b). The protocols adopted here are in part supported by the extent of closure reported for $b_p$ (Figs. 5a, 6a; i.e., performance-based). Much of the observed variance in performance is likely attributable to the imperfect adjustments made to the $b_p$ and $c_{pg}$ measurements. Application of the same form of adjustment to the literature bio-optics models (Table 2) is acknowledged to be more tenuous and uncertain, without paired measurements with other instruments in those works. However, it supports first, albeit tentative, selection of models for $b_o$ in Case 2 systems where system-specific analyses cannot be performed.

**Backscattering ratio dependencies**

Values of $\tilde{b}_{bp}$ have been used to estimate bulk refractive indices of ocean particle populations (an indicator of general composition; Boss et al. 2004; Sullivan et al. 2005), and in modeling the shape of the volume scattering function (Mobley et al. 2002). $\tilde{b}_{bp}$ has been used as a diagnostic
of composition of particle assemblages in both marine (Boss et al. 2004; Loisel et al. 2007) and
lacustrine (Peng et al. 2009a; O’Donnell et al. 2013) waters with varying degrees of success.
Decreases in $\tilde{b}_{bp}$ are expected as the contribution of organic particles increases; the reverse effect
is anticipated as the contribution of minerogenic particles increases. Proxies of composition have
included $[\text{Chl}] : c_p$ (e.g., Loisel et al. 2007; Peng et al. 2009a), the ratio of POC to suspended
particulate material (SPM; Loisel et al. 2007), the inorganic fraction of SPM (Snyder et al. 2008;
O’Donnell et al. 2013), and $b_m : c_p$ (Peng et al. 2009a). Differences in $[\text{Chl}] : c_p$ explained 56% (Boss et al. 2004) and 26% (Loisel et al. 2007) of the
variability in $\tilde{b}_{bp}$ observed in two coastal marine studies. However, Snyder et al. (2008) observed
no significant dependence of $\tilde{b}_{bp}$ on the organic fraction of SPM in a study of US coastal waters.
Similarly, Loisel et al. (2007) did not observe significant relationships between $\tilde{b}_{bp}$ and
POC : SPM. Stronger relationships have been reported for smaller population size (single cruise),
lacustrine studies. Strong, positive dependencies ($R^2 = 0.92$) on the inorganic fraction of SPM
were observed for two sediment enriched systems, the western basin of Lake Erie following a
resuspension event (O’Donnell et al. 2010) and inner Green Bay of Lake Michigan (O’Donnell
et al. 2013). Strong, negative dependencies on $[\text{Chl}] : c_p$ were reported for single cruises of Lake
Superior ($R^2 = 0.88$; Peng et al. 2009a) and Lake Erie ($R^2 = 0.66$; Peng and Effler 2010), whereas
strong, positive dependencies on $b_m : c_p$ were reported ($R^2 = 0.67$ and 0.73, respectively). The
smaller number of observations in these lacustrine studies has been acknowledged to probably
contribute to the apparently better performance of $\tilde{b}_{bp}$ as an indicator of particle composition
compared with the cited, larger marine studies. Deterioration in the performance of these
relationships for lacustrine waters was hypothesized for seasonal studies (Peng et al. 2009a;
O’Donnell et al. 2010), particularly from shifts in the phytoplankton assemblages relative to light-scattering characteristics and cellular chlorophyll-a content.

The deterioration of the relationship between $\tilde{h}_p$ and metrics of organic particle contributions to scattering for the seasonal dynamics of Cayuga Lake for both the shelf and pelagic waters was essentially complete (i.e., no correlations; Fig. 8a,b). It is noteworthy that despite the better performance of POC vs. [Chl] as a proxy for both $b_o$ and $b_{b,o}$ (Fig. 4), the performance of POC : $b_p$ was not better than for [Chl] : $b_p$. The expectations for the shelf were diminished because of the uncoupled irregular increases in $b_m$ and $b_{b,m}$ that occur in response to runoff event inputs of clay minerals (Fig. 2; Effler and Peng 2014). Apparently, even the modulated variations in minerogenic particle scattering in pelagic waters (Figs. 2, 7c,d) were adequate to prevent the manifestation of a significant signature based on metrics of organic particle contributions (Fig. 8a,b).

In contrast, $\tilde{h}_p$ has been demonstrated to be strongly dependent on the of minerogenic particle contribution to scattering ($b_m : b_p$) in this lake for both the shelf and pelagic waters (Fig. 8c), matching the performance level reported for the smaller single cruise data sets (Peng et al. 2009a; Peng and Effler 2010). This metric of particle composition can be represented equivalently as $PAV_m : b_p$ (or $c_p$) that incorporate the basic SAX results instead of a predicted variable, as $PAV_m$ and $b_m$ are linearly related ($<Q_{b,m}>$ largely invariant; Table 4). The extent to which strong $\tilde{h}_p$ – ($b_m : b_p$) relationships prevail in other lacustrine systems needs broader investigation. Features suggesting that it likely prevails widely include (1) the large size and slow flushing rate of Cayuga Lake, and (2) the $PAV_m$ values in the pelagic waters of Cayuga Lake were not high relative to most of the other lacustrine systems characterized to date (Peng and Effler 2012). The prominence of minerogenic particles in influencing this optical signature...
for this and other lacustrine systems is consistent with their central role in differentiating the
References


Acknowledgments

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Figure Legends

Fig. 1. Map of Cayuga Lake (and position within New York State) with sampling and measurement sites, covering the shelf (Sites 1 and 2) and pelagic (Sites 3, 5, and 7) areas, along with the major tributary Fall Creek.

Fig. 2. Temporal patterns for study interval of 2013: (a) daily average flow rate (Q) from Fall Creek, (b,c) $b_p^t$ and $b_m$ at Sites 2 and 3, and (d,e) $b_{bp}$ and $b_{b,m}$ at Sites 2 and 3. (Back)scattering levels were reported for 660 nm; $b_o$ (i.e., $b_o = b_p^t - b_m$) and $b_{b,o}$ were calculated as residuals, as illustrated in (b,e).

Fig. 3. Temporal patterns of the [Chl]:POC ratio at Site 5 for the study interval of 2013. Vertical bars are ± SD from analyses of triplicate samples.

Fig. 4. Evaluation of the dependencies of $b_o (= b_p^t - b_m^t)$ and $b_{b,o} (= b_{bp} - b_{b,m})$ on [Chl] or POC: (a,b) $b_o$ and $b_{b,o}$ (respectively, at 660 nm) vs. [Chl], (c) $b_o(660)$ vs. POC, $b_p^t$ from ac-s, (d) $b_o(660)$ vs. POC, $b_p^t$ from C-Star (data set for model validation), and (e,f) $b_{b,o}$ vs. POC, at 660 nm and 532 nm, respectively. System-specific relationships given (solid lines) along with performance statistics (Model II linear regressions applied in c–f). Predictions with Case 1 bio-optical models are included for comparison (see Tables 2 and 3 for model designations and details).

Fig. 5. Metrics of the extent of closure of the two-component models, as distributions of the ratios of modeled values to those of bulk measurements (for 660 nm): (a) $(b_o + b_m):b_p^t$, and (b) $(b_{b,o} + b_{b,m}):b_{bp}$. The magnitudes of organic components were estimated from system-specific, POC-based relationships. Additional distributions are presented for organic fractions ($b_o:b_p^t$, $b_{b,o}:b_{bp}$) to demonstrate the importance of including the minerogenic component to approach closure.

Fig. 6. Comparisons of the extent of closure supported by POC- vs. [Chl]-based bio-optical models for the organic particle component (both Case 1 and system-specific relationships), evaluated through as distributions of the ratios of modeled values to those of bulk measurements: (a) $(b_o + b_m):b_p^t$ for 660 nm, and (b,c) $(b_{b,o} + b_{b,m}):b_{bp}$, for 660 nm and 532 nm, respectively.
Results are presented in the Box-and-Whisker format, with mean (symbol) and 10, 25, 50, 75, and 90 percentiles. Literature relationships are listed in Tables 2 (for \( b_o \)) and 3 (for \( b_{b,o} \)).

**Fig. 7.** Application of the two-component models to contrast differences in the partitioning of scattering between the shelf and pelagic areas, and relative importance of minerogenic particles to \( b'_p \) vs. \( b_{bp} \), presented as the distributions of the fractional contributions of the two components: (a,b) fractional contributions of the two components to the modeled \( b_p \) and \( b_{bp} \), respectively, for the shelf, and (c,d) same as (a,b), but for pelagic areas.

**Fig. 8.** Evaluation of the dependency of \( b_{bp} \) on indicators of the composition of the particles populations, (a) [Chl] : \( b'_p \), (b) POC : \( b'_p \), and (c) \( b_m \) : \( b'_p \), along with best-fit linear regression line.
Table 1. Values of relative (to water) complex index of refraction ($m = n - i\lambda'$) of major mineral particle types adopted for $b_m$ and $b_{b,m}$ calculations

<table>
<thead>
<tr>
<th>Mineral type</th>
<th>$n^*$</th>
<th>$n' (10^{-4})$ $\lambda = 532 \text{ nm}$</th>
<th>$\lambda = 660 \text{ nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>1.173</td>
<td>5.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Calcite</td>
<td>1.20</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Quartz</td>
<td>1.155</td>
<td>2.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Misc.</td>
<td>1.17</td>
<td>5.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Values selected on the basis of Babin et al. (2003) and Woźniak and Stramski (2004), spectrally uniform
† Study averages from Peng and Effler (2013)
Table 2. Open ocean bio-optical models parameterized on POC (mg L\(^{-1}\)) or [Chl] (mg m\(^{-3}\)) for calculations of organic particle scattering coefficient \((b_o)\) at 660 nm

<table>
<thead>
<tr>
<th>Literature bio-optical model (upper limit for model development)</th>
<th>Instrument (acceptance angle)</th>
<th>Reference</th>
<th>Adopted form for this study</th>
<th>Eq.</th>
<th>Model designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c_p = 1.76 \times \text{POC} \quad (\text{POC} &lt; 0.11 \text{ mg L}^{-1}))</td>
<td>ac-9 (0.93°)</td>
<td>Oubelkheir et al. 2005</td>
<td>(b_o = 0.97 \times (1.76 \times \text{POC})/0.8^*)</td>
<td>(4)</td>
<td>O05</td>
</tr>
<tr>
<td>POC (mg m(^{-3})) = 661.9 \times c_p (660) – 2.2 \quad (R^2 = 0.934, all data, POC &lt; 275)</td>
<td>C-Star (1.2°)</td>
<td>Stramski et al. 2008</td>
<td>(b_o = 1.968 \times \text{POC}^†) (all data)</td>
<td>(5a)</td>
<td>S08-1</td>
</tr>
<tr>
<td>POC (mg m(^{-3})) = 458.3 \times c_p (660) + 10.7 \quad (R^2 = 0.888, no upwelling, POC ≤ 150)</td>
<td></td>
<td></td>
<td>(b_o = 2.77 \times \text{POC}^‡) (no upwelling)</td>
<td>(5b)</td>
<td>S08-2</td>
</tr>
<tr>
<td>(c_p = 0.347[\text{Chl}]^{0.766} \quad ([\text{Chl}] &lt; \sim 30))</td>
<td>SeaTech transmissometer (1.03°)</td>
<td>Loisel and Morel 1998</td>
<td>(b_o = 0.97 \times (0.347[\text{Chl}]^{0.766})/0.8^*)</td>
<td>(6)</td>
<td>LM98</td>
</tr>
<tr>
<td>(b_p = 0.267[\text{Chl}]^{0.60} \quad ([\text{Chl}] \leq 2))</td>
<td>ac-9 (0.93°)</td>
<td>Huot et al. 2008</td>
<td>(b_o = (0.267[\text{Chl}]^{0.60})/0.8^‡)</td>
<td>(7)</td>
<td>H08</td>
</tr>
</tbody>
</table>

\(^*\) acceptance angle adjustment (0.8) as in Eq. 3a, and \(c_p\)-to-\(b_p\) conversion (0.97)

\(^†\) original relationships developed through Model I regressions, following adjustments were made: (1) conversion to Model II expression (Laws and Archie 1981, ignore intercept): POC (mg m\(^{-3}\)) = 684.89 \times c_p (660), (2) from \(Y\)-on-\(X\) to \(X\)-on-\(Y\), \(c_p(660) = 1.46 \times \text{POC} \quad \text{(mg L}^{-1}\)), (3) acceptance angle adjustment as in Eq. 3b

\(^‡\) same adjustments as above were made

\(^§\) acceptance angle adjustment as in Eq. 3a
Table 3. Open ocean bio-optical models parameterized on POC (mg L\(^{-1}\)) or [Chl] (mg m\(^{-3}\)) for calculations of organic particle backscattering coefficient (\(b_{o,o}\))

<table>
<thead>
<tr>
<th>Bio-optical model (upper limit for model development)</th>
<th>Reference</th>
<th>Eq.</th>
<th>Model designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b_{o,o}(555) = 0.01311 \times \text{POC} ) (all data)</td>
<td>Stramski et al. 2008*†</td>
<td>(8a)</td>
<td>S08B-1</td>
</tr>
<tr>
<td>(b_{o,o}(555) = 0.01644 \times \text{POC} ) (upwelling data excluded)</td>
<td></td>
<td>(8b)</td>
<td>S08B-2</td>
</tr>
<tr>
<td>(b_{o,o}(700) = 0.02823 \times \text{POC} + 0.0004 ) (POC &lt; 0.34)</td>
<td>Cetinić et al. 2012†</td>
<td>(9)</td>
<td>C12</td>
</tr>
<tr>
<td>(b_{o,o}(\lambda) = \left{0.002 + 0.01\left(0.5 - 0.25\log_{10}[\text{Chl}]\right)(\lambda/550)^{0.5}\right} \times b_o(550))</td>
<td>Morel and Maritorena 2001</td>
<td>(10)</td>
<td>MM01</td>
</tr>
<tr>
<td>(v = \left{\begin{array}{ll}0.5\left(\log_{10}[\text{Chl}] - 0.3\right) &amp; \text{for } 0.02 \leq [\text{Chl}] &lt; 2 \text{ mg m}^{-3} \ 0 &amp; \text{otherwise (but } &lt; 5.5 \text{ mg m}^{-3}\end{array}\right))</td>
<td>Huot et al. 2008</td>
<td>(11a)</td>
<td>H08B</td>
</tr>
<tr>
<td>and (b_o(550) = 0.416 [\text{Chl}]^{0.766})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b_{o,o}(660) = 0.00171 [\text{Chl}]^{0.618})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b_{o,o}(532) = 0.00236 [\text{Chl}]^{0.556})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*originally reported as POC–\(b_{bp}\) converted to \(b_{bp}–\text{POC}\) expression after the original Model I slope value was transformed to that of Model II

†converted to expressions for 532 nm and 660 nm through \(b_{bp}(\lambda) = b_{bp}(\lambda_o)(\lambda/\lambda_o)^{0.41}\) (Cetinić et al. 2012)
Table 4. Population statistics for measurements in pelagic waters and shelf sites in Cayuga Lake

<table>
<thead>
<tr>
<th>Metric</th>
<th>Shelf (near-shore)</th>
<th>Pelagic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>mean</td>
</tr>
<tr>
<td>$c_{pg}(660) \text{ (m}^{-1})$</td>
<td>76</td>
<td>1.670</td>
</tr>
<tr>
<td>$b_p (660) \text{ (m}^{-1})$</td>
<td>21</td>
<td>2.278</td>
</tr>
<tr>
<td>$b_{bp}(660) \text{ (m}^{-1})$</td>
<td>18</td>
<td>0.0130</td>
</tr>
<tr>
<td>$b_{bp}(532) \text{ (m}^{-1})$</td>
<td>18</td>
<td>0.0148</td>
</tr>
<tr>
<td>$PAV_m (\text{m}^{-1})$</td>
<td>80</td>
<td>1.541</td>
</tr>
<tr>
<td>Clay%</td>
<td>82.8</td>
<td>84.5</td>
</tr>
<tr>
<td>ASP</td>
<td>2.09</td>
<td>2.07</td>
</tr>
<tr>
<td>$&lt;Q_{b,m}&gt;$</td>
<td>2.336</td>
<td>2.333</td>
</tr>
<tr>
<td>$&lt;Q_{bb,m}&gt;$</td>
<td>0.0632</td>
<td>0.0636</td>
</tr>
<tr>
<td>$[\text{Chl}] (\mu g \text{ L}^{-1})$</td>
<td>80</td>
<td>4.0</td>
</tr>
<tr>
<td>POC (mg L$^{-1}$)</td>
<td>79</td>
<td>0.658</td>
</tr>
<tr>
<td>$[\text{Chl}] : \text{POC} (\mu g : \text{mg})$</td>
<td>79</td>
<td>7.75</td>
</tr>
</tbody>
</table>
Fig. 1. Map of Cayuga Lake (and position within New York State) with sampling and measurement sites, covering the shelf (Sites 1 and 2) and pelagic (Sites 3, 5, and 7) areas, along with the major tributary Fall Creek.
Fig. 2. Temporal patterns for study interval of 2013: (a) daily average flow rate ($Q$) from Fall Creek, (b,c) $b_p'$ and $b_m$ at Sites 2 and 3, and (d,e) $b_{bp}$ and $b_{bm}$ at Sites 2 and 3. (Back)scattering levels were reported for 660 nm; $b_o$ (i.e., $b_o = b_p' - b_m$) and $b_{b,o}$ were calculated as residuals, as illustrated in (b,e).
Fig. 3. Temporal patterns of the [Chl]: POC ratio at Site 5 for the study interval of 2013. Vertical bars are ± SD from analyses of triplicate samples.
Fig. 4. Evaluation of the dependencies of $b_\alpha (= b'_p - b_m)$ and $b_{\alpha,o} (= b_{\alpha,p} - b_{\alpha,m})$ on [Chl] or POC: (a,b) $b_\alpha$ and $b_{\alpha,o}$ (respectively, at 660 nm) vs. [Chl], (c) $b_\alpha(660)$ vs. POC, $b'_p$ from ac-s, (d) $b_\alpha(660)$ vs. POC, $b'_p$ from C-Star (data set for model validation), and (e,f) $b_{\alpha,o}$ vs. POC, at 660 nm and 532 nm, respectively. System-specific relationships given (solid lines) along with performance statistics (Model II linear regressions applied in c–f). Predictions with Case 1 bio-optical models are included for comparison (see Tables 2 and 3 for model designations and details).
Fig. 5. Metrics of the extent of closure of the two-component models, as distributions of the ratios of modeled values to those of bulk measurements (for 660 nm): (a) \( b_{o} : b_{p} \), and (b) \( (b_{b,o} + b_{b,m}) : b_{bp} \). The magnitudes of organic components were estimated from system-specific, POC-based relationships. Additional distributions are presented for organic fractions \( (b_{o} : b_{p}, b_{b,o} : b_{bp}) \) to demonstrate the importance of including the minerogenic component to approach closure.
Fig. 6. Comparisons of the extent of closure supported by POC- vs [Chl]-based bio-optical models for the organic particle component (both Case 1 and system-specific relationships), evaluated through as distributions of the ratios of modeled values to those of bulk measurements: (a) $(b_o + b_m) : b_p$ for 660 nm, and (b,c) $(b_{b,o} + b_{b,m}) : b_{bp}$, for 660 nm and 532 nm, respectively. Results are presented in the Box-and-Whisker format, with mean (symbol) and 10, 25, 50, 75, and 90 percentiles. Literature relationships are listed in Tables 2 (for $b_o$) and 3 (for $b_{b,o}$).
Fig. 7. Application of the two-component models to contrast differences in the partitioning of scattering between the shelf and pelagic areas, and relative importance of minerogenic particles to $b'_p$ vs. $b_{bp}$, presented as the distributions of the fractional contributions of the two components: (a,b) fractional contributions of the two components to the modeled $b_p$ and $b_{bp}$, respectively, for the shelf, and (c,d) same as (a,b), but for pelagic areas.
Fig. 8. Evaluation of the dependency of $\bar{b}_{bp}$ on indicators of the composition of the particles populations, (a) [Chl] : $b_p'$, (b) POC : $b_p'$, and (c) $b_m : b_p'$, along with best-fit linear regression line.