Quantifications and water quality implications of minerogenic particles in Cayuga Lake, New York, and its tributaries

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Abstract

An individual particle analysis technique, scanning electron microscopy interfaced with automated image and X-ray analyses (SAX), was applied to characterize the minerogenic particle populations of Cayuga Lake (New York) and its primary tributaries and quantify their effects on common water quality metrics. The primary summary metric of SAX results is demonstrated to be the total projected area of minerogenic particles per unit volume of water (PAVm). PAVm is documented to be linearly related to the minerogenic components of particulate phosphorus (PPm), turbidity (Tnm), and the light scattering coefficient, and inversely related to Secchi depth (SD). SAX is demonstrated to support partitioning of PAVm into contributions of multiple size and geochemical classes. Clay mineral particles dominated in the tributaries and the lake, although they shifted somewhat to smaller sizes (1–15 µm) in the lake. Levels of PAVm were higher in a lake area that adjoins the tributary inputs than in pelagic waters, particularly after runoff events. This increased PAVm degraded water quality, including higher PPm and Tnm and lower SD relative to the pelagic waters, although diminished (still recognizable) signatures are documented lake-wide. Advantages of SAX over gravimetric analyses for the minerogenic particle populations of lakes include (1) improved analytical performance, (2) insights from the more robust size and composition information, (3) theoretical advantages for optical impacts, and (4) stronger relationships with water quality metrics.

Key words: clarity, lakes, minerogenic (inorganic) particles, phosphorous, stream, turbidity

Introduction

Minerogenic particles (e.g., clay minerals, quartz, calcite) can have important water quality and ecological implications in lakes and reservoirs. Specific issues include (1) net sediment accumulation (Ziegler and Nisbet 1995, Gelda et al. 2013); (2) metabolic activity and composition of biological communities (Philips et al. 1995, Newcombe 2003); (3) transport, cycling, and apportionment of forms of nutrients (Hupfer et al. 1995, Effler et al. 2014) and contaminants (O’Connor 1988, Chapra 1997); and (4) the level of light scattering and thereby optical metrics of water quality (Peng et al. 2009b, Peng and Effler 2010, Effler and Peng 2014) and the remote sensing signal (Binding et al. 2007, 2012). These particles have 3 potential general sources: terrigenous (allochthonous) inputs delivered primarily by tributaries (Kirk 1985, Peng et al. 2009b, Peng and Effler 2012), autochthonous production (Weidemann et al. 1985, Homa and Chapra 2011), and sediment resuspension (Peng and Effler 2010). Large fractions of annual sediment loads delivered by tributary streams are often input over relatively brief intervals during major runoff events (Longabucco and Rafferty 1998, Prestigiacomo et al. 2007). Short-term autochthonous production of calcium carbonate (CaCO3, or calcite, precipitation), described as whiting events, occurs in summer in the epilimnia of many hardwater lakes (Homa and Chapra 2011). Predictive capability for these particles in lacustrine systems would be invaluable to quantitatively address related features of water quality issues and provide support for insightful management deliberations.

Advancement of the understanding and quantification of the effects of minerogenic particles in aquatic
ecosystems has primarily been limited by the analytical protocols available for quantification of this particle population. The primary metric has been the gravimetric measure of the inorganic (including minerogenic) fraction of suspended particulate material (ISPM; abbreviations and symbols for parameters listed in Table 1) left after exposure to high temperatures (e.g., 500–550 °C; commonly conducted according to Clesceri et al. 1998). This process provides a coarse and imperfect fractionation of inorganic versus organic SPM (ISPM vs. OSPM; Clesceri et al. 1998). Accuracy of SPM and ISPM measurements depends on their concentrations, being generally reliable at the higher concentrations common to most lotic systems but less so for the more dilute conditions of most lacustrine systems (Peng and Effler 2012, Effler et al. 2013). Moreover, there is potential for the inclusion of nonmineral inorganic particles (e.g., diatom frustules) within ISPM, particularly in lacustrine systems, which is particularly problematic in the context of lake management to resolve the targets for reduction (e.g., nutrients vs. erosion). Further, the optical impacts (Bowers and Braithwaite 2012, Effler et al. 2013), and arguably the adsorption–desorption potential for nutrients and contaminants (Chapra 1997, Effler et al. 2014), are more dependent on particle-projected (or surface) area rather than a gravimetric attribute. Perhaps most important, the single aggregate bulk measurement of ISPM fails to represent the effects of the polydispersed (i.e., multiple sizes) character of minerogenic particle size distributions (PSDs) responsible for the observed wide distributions of dependent bulk measurements in time and space in receiving lakes and reservoirs (Gelda et al. 2009, 2013, Effler and Peng 2014).

The features of natural minerogenic particle populations that determine both their optical and gravimetric impacts include the number concentration \( N \), PSD, the composition of individual particles, and, to a lesser extent, their shapes (Babin et al. 2003, Effler and Peng 2014). Particle counters (e.g., Coulter type) have generally been successful in quantifying \( N \) and PSD for particles >1 µm; however, without compositional characterization capabilities, such measurements cannot support apportionment of the most basic components (minerogenic vs. organic) of the heterogeneous particle populations of natural systems. Recently, an individual particle analysis (IPA) technique, scanning electron microscopy interfaced with automated image and X-ray analyses (SAX), has been successfully used to directly measure \( N \), PSD, elemental composition, and shapes of natural minerogenic populations in fresh waters and thereby resolve their effects on bulk optical and water quality metrics.

Table 1. List of acronyms and parameters.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Description</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>CDOM</td>
<td>chromatic dissolved organic matter</td>
<td></td>
</tr>
<tr>
<td>IPA</td>
<td>individual particle analysis</td>
<td></td>
</tr>
<tr>
<td>PSD</td>
<td>particle size distribution</td>
<td></td>
</tr>
<tr>
<td>SAX</td>
<td>scanning electron microscopy interfaced with automated image and X-ray analyses</td>
<td></td>
</tr>
<tr>
<td>Chl-a</td>
<td>Chlorophyll a concentration</td>
<td>µg L(^{-3})</td>
</tr>
<tr>
<td>(I)SPM</td>
<td>(inorganic) suspended particulate material concentration</td>
<td>mg L(^{-3})</td>
</tr>
<tr>
<td>PA</td>
<td>projected area of a particle</td>
<td>µm(^2)</td>
</tr>
<tr>
<td>PAV(_{m})</td>
<td>total projected area of minerogenic particles per unit volume of water</td>
<td>m(^{-1})</td>
</tr>
<tr>
<td>TP (TDP)</td>
<td>total (dissolved) phosphorus concentration</td>
<td>µg L(^{-3})</td>
</tr>
<tr>
<td>PP (PP(<em>{m}) or PP(</em>{o}))</td>
<td>particulate (mineral or organic component) phosphorus concentration</td>
<td>µg L(^{-1})</td>
</tr>
<tr>
<td>PV</td>
<td>individual particle volume</td>
<td>mm(^3)</td>
</tr>
<tr>
<td>PVV(_{m})</td>
<td>minerogenic particle volume concentration</td>
<td>mm(^3) L(^{-1}) (ppm)</td>
</tr>
<tr>
<td>SD</td>
<td>Secchi disk transparency depth</td>
<td>m</td>
</tr>
<tr>
<td>(Q_f)</td>
<td>stream flow rate</td>
<td>m(^3) s(^{-1})</td>
</tr>
<tr>
<td>(&lt;Q_{b,m})&gt;</td>
<td>average scattering efficiency factor of mineral particles</td>
<td>dimensionless</td>
</tr>
<tr>
<td>(T_n) ((T_{n,m}) or (T_{n,o}))</td>
<td>nephelometric (mineral or organic component) turbidity</td>
<td>NTU</td>
</tr>
<tr>
<td>(c_p) (660)</td>
<td>attenuation (due to particles and gelbstoff) coefficient at 660 nm</td>
<td>m(^{-1})</td>
</tr>
<tr>
<td>(b_p) ((b_{m}) or (b_{o}))</td>
<td>particulate (mineral or organic component) scattering coefficient</td>
<td>m(^{-1})</td>
</tr>
<tr>
<td>(b_{bp}) ((b_{b,m}) or (b_{b,o}))</td>
<td>particulate (mineral or organic component) backscattering coefficient</td>
<td>m(^{-1})</td>
</tr>
</tbody>
</table>
SAX measures of these light-scattering attributes of minerogenic particles have served as inputs to Mie theory calculations to support forward estimates of the minerogenic components of scattering and backscattering coefficients \( (b_m, b_{nm}) \). Earlier research with the SAX–Mie approach had appropriately focused on the estimates of scattering coefficients (Table 2; also see summaries of SAX-supported analyses in Peng and Effler 2012). The credibility of the approach for fresh waters has been established through the pursuit of optical closure with bulk measurements of particulate scattering \( (b_p, \text{or its surrogates}) \) and backscattering coefficients \( (b_{np}) \) in several cases. These efforts have addressed both lacustrine and lotic systems and 2 broad scattering cases: (1) systems where minerogenic particles dominate particle assemblages and (2) those where phytoplankton make noteworthy contributions, the more common case for lacustrine systems (Table 2). A 2-component partitioning of \( b_p \) has been adopted for the second case (with one exception: 3 components for Skaneateles Lake, NY):

\[
b_p = b_m + b_{np}.
\]

where \( b_a \) is the scattering coefficient associated with organic particles, attributable to phytoplankton and their particulate retinue in most lacustrine systems. The authors used chlorophyll-\(a\)–based, empirical bio-optical models developed for open oceanic waters (Loisel and Morel 1998, Huot et al. 2008) to estimate \( b_a \), although alternatives based on particulate organic carbon (e.g., Stramski et al. 2008) and OSPM (Stavn and Richter 2008) are also available. The performances of the SAX–Mie mechanistic approach in estimating the minerogenic particle components and supporting closures of the 2-component model predictions with bulk measurements have been accepted as reasonably good or better (Table 2).

A primary summary result of SAX characterizations in the context of related metrics of freshwater water quality has been demonstrated to be the projected area of minerogenic particles per unit volume of water \( (PAV_m; \text{citations in Table 2}) \). SAX has supported the resolution of contributions of both multiple size and generic geochemical type classes to \( PAV_m \) and thereby related bulk freshwater measurements of interest. The values of \( b_m \) and \( b_{nm} \) have been found to be linearly dependent on \( PAV_m \) for multiple freshwater systems; similar linear dependencies have also been demonstrated for the minerogenic components of turbidity \( (T_b) \), particulate phosphorous \( (PP_p) \), and nonalgal particle absorption (Table 2).

The overarching goal of this paper is to advance and demonstrate the effective use of SAX characterizations of minerogenic particle populations, particularly through the \( PAV_m \) metric, to quantify their effects in fresh waters. The linkage between watershed minerogenic particle inputs and lacustrine patterns based on SAX is initiated, as supported by concurrent monitoring of Cayuga Lake (New York) and its tributaries. This work makes an important transition, moving from previous successful demonstration of the SAX-supported approach (Table 2) to a focus on (1) its application to describe patterns of \( PAV_m \) in time and space, and (2) quantification of the importance of these particles on common metrics for lake water quality. Finally, a conceptual framework is presented for a mechanistic mass-balance type lake model that would be capable of simulating patterns in response to environmental drivers.

**Methods**

**System description and sampling**

Cayuga Lake (42°41′30″N; 76°41′20″W) is the fourth easternmost of the New York Finger Lakes (Fig. 1) and has the second largest surface area (172 km²) and volume (9.4 × 10⁶ m³) of this group of lakes. It has mean and maximum depths of 55 and 133 m, respectively, and an average retention time of 8 years (Gelda et al. 2015). Phytoplankton growth in the lake is phosphorus (P) limited (Oglesby 1978), and the lake is mesotrophic (Effler et al. 2010b). The shallow southern zone, demarcated as the southernmost 2 km where depths are <6 m, is designated as the “shelf” (Fig. 1). Water quality concerns for the shelf identified by government regulators include high P and sediment concentrations, which are exacerbated by elevated loads received during runoff events (Effler et al. 2010b, 2014, Prestigiacomo et al. 2015).

Nearly 40% of the total tributary inflow to the lake enters the southern end from 3 gauged streams: Fall Creek, Cayuga Inlet Creek, and Six Mile Creek (Table 3, Fig. 1). Fall Creek, the largest of the streams (nearly 18% of the total inflow), has been gauged since 1925 (the longest). Six Mile Creek passes through 2 small impoundments (separated by ~1.5 km) located ~6.5 km upstream of its mouth. Another noteworthy gauged stream, Salmon Creek, enters farther north along the eastern shore (Fig. 1). Approximately 30 smaller streams drain ~40% of the overall watershed, but each is relatively small (<3.5% of the total inflow).

Sampling of the lake and tributaries was conducted over the April–October interval of 2013. Stream samples were collected near the mouths of the 4 study tributaries (Fig. 1) that together account for ~50% of the lake’s watershed. This sampling had 2 components: (1) biweekly fixed frequency manual collections and (2) runoff event collections with automated sampling equipment. Target thresholds of stream flow \( (Q_f) \) for events were guided by
Table 2. Summary of closure or consistency† demonstrated by SAX-based approach (PAV_m) for North America fresh waters.

<table>
<thead>
<tr>
<th>System</th>
<th>Closure (✓) or Consistency (✗)</th>
<th>No. of Components</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>New York City (NYC) Reservoir Systems (9)</td>
<td></td>
<td>b_p b_i b_i (×)</td>
<td>Peng et al. (2002, 2004)</td>
</tr>
<tr>
<td>Finger Lakes (NY)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schoharie Creek (NY)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schoharie Reservoir and Schharie Creek (NY)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Central NY lakes (4) and a river</td>
<td>✓ ✗ ✗</td>
<td></td>
<td>Peng et al. (2007)</td>
</tr>
<tr>
<td>Lake Superior</td>
<td>✓ ✓ ✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NYC Reservoir Systems (6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lake Erie</td>
<td>✓ ✓ ✗</td>
<td></td>
<td>Peng et al. (2009b)</td>
</tr>
<tr>
<td>Lake Ontario</td>
<td>✓ ✓ ✗</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Onondaga Lake (NY)</td>
<td>✓</td>
<td></td>
<td>Effler and Peng (2012)</td>
</tr>
<tr>
<td>Ashokan Reservoir and Esopus Creek (NY)</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Great Lakes (3) and Central NY lakes (4)</td>
<td>✓</td>
<td></td>
<td>Effler et al. (2013)</td>
</tr>
<tr>
<td>Lake Erie</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Skaneateles Lake (NY)</td>
<td>✓ ✗</td>
<td></td>
<td>Peng and Effler (2013a)</td>
</tr>
<tr>
<td>Cayuga Lake (NY)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cayuga Lake (NY)</td>
<td>✓ ✓</td>
<td></td>
<td>Effler and Peng (2014)</td>
</tr>
<tr>
<td>Great Lakes</td>
<td>✗</td>
<td></td>
<td>Peng and Effler (2015)</td>
</tr>
</tbody>
</table>

† Closure = optical modeling closure (equation 1); Consistency = high level of correlation between a SAX-based metrics and bulk optical or water quality parameter
‡ particulate component(s): 1 = mineral dominant; 2 = mineral and organic (excluding diatom); 3 = mineral, organic (excluding diatom), and diatom
§ consistency with SD−1
‖ absorption coefficient of nonalgal particles (m−1)

Table 3. Sediment-based characteristics of 4 Cayuga Lake tributaries for the study period of 2013.

<table>
<thead>
<tr>
<th>Tributary</th>
<th>Watershed Area (km²)</th>
<th>% ISPM_1 for High Q_f</th>
<th>ISPM : SPM</th>
<th>% T_m1 for High Q_f</th>
<th>Flow-weighed ISPM_3 (mg L⁻³)</th>
<th>Flow-weighed T_m (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fall Creek</td>
<td>330.9</td>
<td>94</td>
<td>0.90</td>
<td>91</td>
<td>111</td>
<td>64.7</td>
</tr>
<tr>
<td>Cayuga Inlet Cr.</td>
<td>240.1</td>
<td>99</td>
<td>0.92</td>
<td>98</td>
<td>250</td>
<td>272</td>
</tr>
<tr>
<td>Salmon Creek</td>
<td>233.8</td>
<td>97</td>
<td>0.87</td>
<td>95</td>
<td>46.7</td>
<td>55.3</td>
</tr>
<tr>
<td>Six Mile Creek</td>
<td>134.1</td>
<td>96</td>
<td>0.90</td>
<td>94</td>
<td>83.2</td>
<td>93.9</td>
</tr>
</tbody>
</table>

1 ISPM_1 denotes ISPM loading; high Q_f is the upper quartile of the flow
2 T_m1 denotes T_m loading
3 flow-weighed ISPM calculated as total ISPM_1 divided by total stream flow
4 flow-weighted T_m calculated as total T_m1 divided by total stream flow
analysis of the long-term record for Fall Creek. The automated samplers were triggered on the basis of changes in stream flow elevations. Usually, rising limb samples were collected at 2 h intervals and falling limb samples at progressively longer intervals. Samples were selected for analyses according to the goal of providing a robust representation of event hydrographs. Samples of near-surface waters of the lake were collected at 5 sites along its primary axis (Fig. 1), with 2 on the shelf (Sites 1 and 2) and 3 in pelagic areas (Sites 3, 5, and 7). Sites 1, 2, and 3 were monitored biweekly in April, May, and October but more frequently (twice per week) for the June–September interval. Sites 5 and 7 were monitored biweekly throughout the study period.

External loading conditions for ISPM and turbidity ($T_n$) for these tributaries for the study period (Table 3) were developed with the FLUX32 (2013) software, designed to support estimates for the common case of available continuous daily $Q_F$ records combined with temporally limited concentration observations. These protocols tracked those recently described for forms of $P$ for these streams for the same study period (Prestigiacomo et al. 2015) and relied on strong empirical concentration–$Q_F$ power-law type relationships observed for each of these streams (UFI 2014). Recurring features for the tributaries included the dominance of the inorganic component (>90%) in SPM loads and >90% of the ISPM and $T_n$ loads received during high flow intervals (upper quartile for long-term Fall Creek record; Table 3). Flow-weighted (total load divided by total $Q_F$) ISPM and $T_n$ levels were in general high for all 4 tributaries, with levels the highest for Cayuga Inlet (Table 3).

**SAX characterizations and geometric calculations**

Protocols for IPA by SAX have been described in detail previously (Peng and Effler 2007, Peng et al. 2009b). Briefly, suspended particles were deposited onto polycarbonate membranes (0.4 µm pore size), air dried, and coated with carbon. SAX assesses the composition and morphology of individual minerogenic particles. IPA by SAX was conducted with an Aspex PSEM 2000 System controlled by Automated Feature Analysis (AFA) software. AFA conducts 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 area (PA) of a particle is the sum of these triangular areas; particle size ($d$) is defined as the circular area equivalent diameter. The value of PA $V_m$ is computed from the sum of the measured PAs of minerogenic particles, the fraction of analyzed filter area, and the sample volume.

Mineral particle volume concentration (PV $V_m$, ppm) was determined analogously through the summation of individual particle volumes (PVs), to support testing of consistency with tributary ISPM. The value of PV was estimated according to Peng and Effler (2012) as:

$$PV = (L_{max} \times W) \times \left(\frac{1}{6} \times (L_{max} \times W)\right), \quad (2)$$

and

$$PV = (4\pi/3)(L_{max}/2)(W/2)^2, \quad (3)$$

for 2 morphological shapes, platelet (typical of clay minerals; equation 2) and spheroid (for all other minerogenic types; equation 3), where $L_{max}$ is the length of the longest chord and $W$ is the length of its orthogonal chord (or width). The second term in equation 2 represents the thickness of clay mineral platelets. Size distributions of minerogenic particles are presented as the density function, $F(d)$, with numbers of particles in size bins (equally spaced on log-scale) normalized by the bin widths. To demonstrate the utility of the size apportionment in pattern analyses, the polydispersed populations of this study were segmented into 4 broad size classes: <2 µm, 2–5.6 µm, 5.6–11 µm, and ≥11 µm.
SAX assesses the composition of minerogenic particles on the basis of X-ray relative intensities acquired for 16 elements (including Al, Si, K, Ca, Fe, Mn). The particles are sorted into predefined generic particle types according to their elemental X-ray composition (e.g., Peng and Effler 2007). Minerogenic particle classes adopted for this system correspond to those used for other hardwater lakes (Peng et al. 2007, Peng and Effler 2011) and Cayuga Lake previously (Effler and Peng 2014). These types include clay minerals (Clay), quartz (Quartz), silica-rich (Si-rich), CaCO$_3$ (Calcite), Ca-aggregates (CaCO$_3$-coated particles; Ca-agg), and miscellaneous (not specifically defined; Misc.). Quartz particles were differentiated from diatoms on the basis of their higher X-ray densities (Peng et al. 2002). More than 2000 individual particles were analyzed for each of the samples.

**Auxiliary measurements**

A series of auxiliary measurements were made to support depiction of the effects of minerogenic particles on common water quality metrics. Paired stream samples (with those analyzed with SAX) were analyzed for SPM and ISPM concentrations following standard procedures (Clesceri et al. 1998) with Whatman 934AH glass microfiber filters (nominal pore size 1.5 μm); concentrations of ISPM were determined through loss-on-ignition at 550 °C. The average coefficient of variation for SPM and ISPM triplicate analyses of selected creek samples was ~23%. Turbidity ($T_d$; in nephelometric turbidity unit, NTU) measurements (Clesceri et al. 1998) were made on both stream and lake samples with a Hach 2100AN turbidimeter (90° side-scattering detector, precision from triplicate analyses of samples with $T_d$ < 1.5 NTU ~15%).

The concentration of chlorophyll-$a$ (Chl-$a$), often an index for organic particle scattering effects in bio-optical models (e.g., Loisel and Morel 1998) as well as the most commonly used surrogate of phytoplankton biomass, was measured for lake samples fluorometrically after acetone extraction (Arar and Collins 1997). Lake and stream samples were analyzed for the concentrations of total P (TP) and total dissolved P (TDP; Clesceri et al. 1998). Particulate P (PP) was calculated as the difference between TP and TDP (PP = TP – TDP). Measurements of the beam attenuation coefficient (associated with particles and dissolved material) at 660 nm (denoted as $c_{pp}$ (660), in m$^{-1}$) were made in situ with a WETLabs C-Star transmissometer fitted inside a Seabird profiling package. The particulate scattering coefficient ($b_p$) at 660 nm was estimated as 1.14 × $c_{pp}$ (Effler and Peng 2014), taking into account the effect of acceptance angle of the instrument (underestimation of total attenuation by ~15%; Boss et al. 2009a) and the dominant contribution of $b_p$ to $c_{pp}$ ($b_p = 0.97 \times c_{pp}$) at this wavelength (Babin et al. 2003). For limited lake sites, a WETLabs ac-s meter was deployed for measurements of spectral absorption and attenuation coefficients. The results showed that, on average, absorption by particles and gelbstoff (i.e., chromatic dissolved organic matter [CDOM]) contributed ~0.5 and ~3–4% to $c_{pp}$ (660), respectively, supporting our adoption of the 0.97 factor in estimating $b_p$ from C-Star $c_{pp}$ (subsequently applied to the bio-optical model in estimating organic component scattering as well). Wavelength notation is henceforth omitted for brevity. Measurements of Secchi transparency depth (SD) were made in the lake (except Site 1, which was too shallow) with a 20 cm diameter black and white quadrant Secchi disk.

**Minerogenic particles: effects on bulk measurements and closure analyses**

The slope of the ISPM vs. PVV$_m$ linear regression for the minerogenic particle-dominated streams represents an estimate of the effective density of the material that can be checked against mineral-specific information (Peng and Effler 2012). Analyses of optical closure with bulk measurements of $b_p$ in the lake were made according to the 2-component model (equation 1).

Based on previous SAX characterizations followed by Mie scattering theory calculations, the light-scattering efficiency of minerogenic particles in multiple lakes (including Cayuga Lake) has been found to be uniform, supporting the following simple expression for estimating $b_m$:

$$b_m = <Q_{b,m}> \times \text{PAV}_m,$$

where $<Q_{b,m}>$ is the average scattering efficiency factor (= 2.3; Effler and Peng 2014) of the minerogenic particles. The value of $b_m$ was estimated here with the Chl-$a$-based, empirical bio-optical model of Loisel and Morel (1998):

$$b_m (660) = 0.347 [\text{Chl-a}]^{0.766} \times 0.97.$$

Reasonably good closure of these 2-component summations with bulk $b_p$ measurements (Table 2) demonstrated the credibility of these 2 estimates. Moreover, the relative role of each in regulating bulk $b_p$ conditions is thereby quantified. The regulation of SD primarily by $b_p$ prevails widely in lacustrine systems (Davies-Colley et al. 2003). A strong ($R^2 = 0.74$) system-specific, empirical relationship between SD$^{-1}$ and $b_p$ (660), based on earlier paired measurements (Effler and Peng 2014),

$$\text{SD}^{-1} = 0.16 \times b_p (660) + 0.004,$$

forms a basis (along with equation 1) to quantify the effects minerogenic particles impart on water clarity.
The 2-component (minerogenic particles and phytoplankton) approach was extended specifically for Cayuga Lake for $T_n$ and PP (Effler et al. 2014), with the same drivers of $PAV_m$ and Chl-$\alpha$, as described by:

$$T_n = (T_{n/o} \cdot \text{Chl-}a) \cdot \text{Chl-}a + (T_{n/m} \cdot PAV_m) \cdot PAV_m, \quad (7)$$

$$PP = (PP_{o} \cdot \text{Chl-}a) \cdot \text{Chl-}a + (PP_{m} \cdot PAV_m) \cdot PAV_m, \quad (8)$$

where $T_{n/o}$ and $T_{n/m}$ are the organic and minerogenic particulate components of $T_n$, and $PP_o$ and $PP_m$ analogously the 2 corresponding components of PP. Both partitionings depend on stoichiometric ratios ($T_{n/o} \cdot \text{Chl-}a = 0.08$ and $T_{n/m} \cdot PAV_m = 4.80$ for $T_n$; $PP_{o} \cdot \text{Chl-}a = 1.53$ and $PP_{m} \cdot PAV_m = 7.10$ for PP) developed and successfully tested specifically for Cayuga Lake (Effler et al. 2014) and adopted in this study. These expressions provide a basis to represent the contributions of minerogenic particles to lake $T_n$ and PP levels.

**Results**

**Tributaries**

Short-term dynamics of features of minerogenic sediment inputs from before (6 Aug) and through (8–10 Aug) a major runoff event (return interval 3.5 yr; Fig. 2a) are presented for Six Mile Creek. Positive and rapid responses were observed for $T_n$, ISPM, $PAV_m$, and $PVV_m$ (Fig. 2b–e). The qualitative features of these responses were recurring. The highest average $PAV_m$ was observed for Cayuga Inlet Creek (Table 4), as reported for ISPM and $T_n$ (Table 3). Variations in this metric over the study period, driven by those in $Q_F$, were high, as indicated by the standard deviation values (Table 4). The basic composition of the minerogenic particle populations was similar for the 4 tributaries, as represented by the respective type contributions to $PAV_m$ (Table 4). Clay minerals were dominant (>82%), with Quartz and Ca-agg classes making much smaller contributions. The adopted classification scheme worked well; only a small fraction (~2% on average) remained poorly defined (in the Misc. grouping).

PSDs of minerogenic particle populations are presented for 3 samples from Fall Creek collected over the August high runoff period, representing conditions before, during (close to peak $Q_F$), and after the event (Fig. 3a). The general PSD pattern was recurring for the streams, with number densities generally decreasing as particle sizes increased (but not in a straight-line pattern). The $N$ values were shifted higher for the more turbid samples (Fig. 3a). The calculated size dependencies of $PAV_m$ and $PVV_m$ are presented in a cumulative format (Fig. 3b). Submicron particles and those >30 $\mu$m did not make noteworthy contributions to $PAV_m$ or $PVV_m$. These size dependencies for the 3 samples, describing much of the differences of the event, were generally similar. The size dependency was shifted substantially toward larger sizes for $PVV_m$ compared with $PAV_m$ (Fig. 3b) as a result of the fundamentally different dependencies of these metrics on particle geometry (Peng and Effler 2012).

![Fig. 2. Example (Six Mile Creek in Aug 2013) of observed temporal patterns for runoff events in study tributaries: (a) $Q_F$, (b) $T_n$, (c) ISPM, (d) $PAV_m$, and (e) $PVV_m$.](image-url)
Table 4. Minerogenic particle population characteristics, in terms of contributions to $PAV_m$ by geochemical and size classes, for 4 Cayuga Lake tributaries and lake monitoring sites in 2013.

<table>
<thead>
<tr>
<th>Stream or Lake Site</th>
<th>Avg. $PAV_m$ ($m^{-1}$)</th>
<th>% Contributions by Particle Types to $PAV_m$</th>
<th>% Contributions by Size ($\mu m$) Classes$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Clay</td>
<td>Quartz</td>
</tr>
<tr>
<td>Fall Creek</td>
<td>23.94 (40.64)$^1$</td>
<td>86.5</td>
<td>6.9</td>
</tr>
<tr>
<td>Cayuga Inlet Cr.</td>
<td>129.30 (359.74)</td>
<td>83.8</td>
<td>7.7</td>
</tr>
<tr>
<td>Salmon Creek</td>
<td>19.68 (68.25)</td>
<td>82.2</td>
<td>5.7</td>
</tr>
<tr>
<td>Six Mile Creek</td>
<td>26.30 (41.60)</td>
<td>84.8</td>
<td>6.1</td>
</tr>
<tr>
<td>Site 1</td>
<td>2.74 (13.92)</td>
<td>83.2</td>
<td>6.6</td>
</tr>
<tr>
<td>Site 2</td>
<td>0.35 (1.39)</td>
<td>82.5</td>
<td>6.4</td>
</tr>
<tr>
<td>Site 3</td>
<td>0.071 (0.063)</td>
<td>74.6</td>
<td>5.4</td>
</tr>
<tr>
<td>Site 5</td>
<td>0.053 (0.034)</td>
<td>70.7</td>
<td>5.6</td>
</tr>
<tr>
<td>Site 7</td>
<td>0.058 (0.035)</td>
<td>67.1</td>
<td>5.5</td>
</tr>
</tbody>
</table>

$^1$ standard deviation in parentheses

$^2$ reported for tributaries with higher than average $Q_F$ conditions; averaged over the entire study period for lake sites.

Fig. 3. Examples of minerogenic particle size distributions and size dependencies of $PAV_m$ and $PVV_m$ in the Cayuga Lake system: (a) PSDs for 3 Fall Creek samples for different $T_n$ conditions in August 2013 (selected over the course of a runoff event); (b) corresponding size dependency pattern of cumulative $PAV_m$ and $PVV_m$; (c) and (d) same as (a) and (b), respectively, but for 3 selected lake site samples.
Strong linear relationships were observed between common bulk measurements of water quality and SAX-based metrics of the minerogenic particle populations for all 4 streams (Fig. 4). The general character of the relationships was similar for these tributaries, although the details differed. The details, including the observations for a selected tributary and the linear least-squares regression relationships, are presented for ISPM vs. PVV_m (with Six Mile Creek observations; Fig. 4a), T_n vs. PAV_m (Fall Creek; Fig. 4b), and PP vs. PAV_m (Salmon Creek; Fig. 4c). The trajectories of the regression fits for the other tributaries are also included. Although a limited number of particularly high values influenced the apparent strength of the relationships, deletion of those did not alter their trajectories substantially.

The dependence of PAV_m on Q_f was found to be strong for each stream for overall PAV_m (Fig. 5a) as well as that associated with each of the 4 specified size classes (Fig. 5b), illustrated here for the 2–5.6 µm size class. The observations and linear least-squares regression fits are shown for Fall Creek in the commonly adopted log-log format, with just the regression fits shown for the other streams (Fig. 5). The power-law relationships (PAV_m = A × Q_f^B) were all reasonably strong (R^2 > 0.52) and highly significant (Table 5), with the strongest observed for Cayuga Inlet Creek, which is the most sediment-enriched among the study streams (Table 3). The positive dependence of exponent ‘B’ on particle size class (Table 5) for Salmon Creek indicates that larger sizes are preferentially mobilized in this stream during runoff events. The slope of the trajectory of the increase for the largest size class was lower than the other 3 size classes for Six Mile Creek while comparable in all the other stream–size-class combinations. The larger ‘A’ values for Six Mile Creek are consistent with the generally higher T_n levels manifested in this stream during low Q_f intervals. Similarly strong PVV_m – Q_f relationships were observed.

Fig. 4. Evaluation of the dependencies of water quality parameters on SAX-based metrics of the minerogenic particle populations for the 4 tributaries of Cayuga Lake: (a) ISPM vs. PVV_m, (b) T_n vs. PAV_m, and (c) PP vs. PAV_m. Linear least-squares regressions are shown for all tributaries, but only one set of observations is presented for a selected creek along with details of the linear regression (intercept [int.] significance or not is noted).

Fig. 5. Evaluation of the power-law dependencies of PAV_m on Q_f for 4 tributaries of Cayuga Lake: (a) overall PAV_m, and (b) PAV_m apportioned in size class 2 (2–5.6 µm). Only observations from Fall Creek are shown (symbols); fitting results are detailed in Table 5.
Temporal patterns of PA \( V_m \) were considered in the context of the dynamics of stream \( Q_F \), with the use of Fall Creek conditions as a proxy for overall tributary inflow, a role supported by the similarly successful use of this tributary’s flow in lake-wide modeling (Effler et al. 1989). Wide variations in \( Q_F \) (Fig. 6a) and PA \( V_m \) at multiple lake sites (Fig. 6b–d) occurred over the study period (note the logarithmic \( y \)-axes). The highest PA \( V_m \) levels occurred on the shelf (Fig. 6b) immediately following major runoff events (Fig. 6a). Levels were usually higher at Site 1, the closest monitoring location to the local tributary inputs (Fig. 1), than at Site 2 (Fig. 6b); the average PA \( V_m \) values were 2.74 and 0.35 m\(^{-1}\), respectively (Table 4). Relatively large increases were also observed after the larger events at the pelagic Site 3, although these were substantially smaller and somewhat delayed compared with the shelf observations (Fig. 6c, Table 4; study PA \( V_m \) average of 0.071 m\(^{-1}\)). The observations for the other 2 pelagic sites were generally similar to those at Site 3 (Fig. 6d), suggesting that the more frequent observations of Site 3 were generally representative of lake-wide pelagic conditions. On average, a PA \( V_m \) gradient prevailed that extended across the shelf to Site 3.

Review of the average contributions of the 4 size classes at the lake sites suggests similar conditions throughout the lake but a substantial shift to smaller sizes compared with inputs from 3 of the streams, the exception being Six Mile Creek (Table 4). Substantial temporal and spatial structure within the lake, however, was embedded within the relatively uniform average contributions by these size classes, illustrated in the comparison of the contributions of these size classes for Sites 1 and 3 (Fig. 7a and b) for a 2-week interval in August that bounded a major runoff event.

**Table 5.** Dependencies of \( PAV_m \) (total and in 4 size classes; m\(^{-1}\)) on stream flow (\( Q_F \); m\(^3\) s\(^{-1}\)) according to power law relationships (\( PAV_m = A \times Q_F^B \)) for 4 Cayuga Lake tributaries for the study period of 2013.

<table>
<thead>
<tr>
<th>Stream</th>
<th>PA ( V_m ) Total or by Size Class</th>
<th>Power Law Coefficients</th>
<th>Performance†‡</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( A )     ( B )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>Fall Creek</td>
<td>1</td>
<td>0.013       1.344</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.032       1.447</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.049       1.381</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.076       1.248</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>0.188       1.336</td>
<td>0.66</td>
</tr>
<tr>
<td>Cayuga Inlet</td>
<td>1</td>
<td>0.036       1.497</td>
<td>0.82</td>
</tr>
<tr>
<td>Creek</td>
<td>2</td>
<td>0.074       1.611</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.074       1.614</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.052       1.673</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>0.263       1.592</td>
<td>0.80</td>
</tr>
<tr>
<td>Creek</td>
<td>1</td>
<td>0.016       1.394</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.026       1.678</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.019       1.936</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.020       2.095</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>0.090       1.834</td>
<td>0.67</td>
</tr>
<tr>
<td>Salmon Inlet</td>
<td>1</td>
<td>0.157       1.234</td>
<td>0.61</td>
</tr>
<tr>
<td>Creek</td>
<td>2</td>
<td>0.342       1.369</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.248       1.331</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.226       1.117</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>1.017       1.304</td>
<td>0.67</td>
</tr>
</tbody>
</table>

† particle size classes: 1 = <2 µm; 2 = 2–5.6 µm; 3 = 5.6–11 µm; 4 = ≥11 µm
‡ \( p < 0.0001 \) for all relationships

**Cayuga Lake**

Patterns of minerogenic particles

Temporal patterns of \( PAV_m \) were considered in the context of the dynamics of stream \( Q_F \), with the use of Fall Creek conditions as a proxy for overall tributary inflow, a role supported by the similarly successful use of this tributary’s flow in lake-wide modeling (Effler et al. 1989). Wide variations in \( Q_F \) (Fig. 6a) and \( PAV_m \) at multiple lake sites (Fig. 6b–d) occurred over the study period (note the logarithmic \( y \)-axes). The highest \( PAV_m \) levels occurred on the shelf (Fig. 6b) immediately following major runoff events (Fig. 6a). Levels were usually higher at Site 1, the closest monitoring location to the local tributary inputs (Fig. 1), than at Site 2 (Fig. 6b); the average \( PAV_m \) values were 2.74 and 0.35 m\(^{-1}\), respectively (Table 4). Relatively large increases were also observed after the larger events at the pelagic Site 3, although these were substantially smaller and somewhat delayed compared with the shelf observations (Fig. 6c, Table 4; study \( PAV_m \) average of 0.071 m\(^{-1}\)). The observations for the other 2 pelagic sites were generally similar to those at Site 3 (Fig. 6d), suggesting that the more frequent observations of Site 3 were generally representative of lake-wide pelagic conditions. On average, a \( PAV_m \) gradient prevailed that extended across the shelf to Site 3.

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**Fig. 6.** Temporal patterns of stream flow and \( PAV_m \) in the upper waters of Cayuga Lake in 2013: (a) Fall Creek \( Q_F \), (b) \( PAV_m \) at Sites 1 and 2 (on the shelf), (c) \( PAV_m \) at Sites 1 and 3, and (d) \( PAV_m \) in pelagic waters at Sites 3, 5, and 7. Note \( y \)-axis is logarithmic for (a)–(c) and linear for (d).
Three minerogenic PSDs of lake samples (Fig. 3c) demonstrated qualitatively similar size dependencies to those observed for the streams (Fig. 3a). The size patterns of cumulative PA\textsubscript{m} and PVV\textsubscript{m} demonstrate a noteworthy shift to smaller sizes in the lake, however, with contributions by particles >10 µm being decidedly less than in the streams (Fig. 3b and d). Temporal and spatial structure is suggested by the contrasting cumulative patterns for the August 15 (after a major runoff event) sample at Site 3, depicting greater contributions by larger particles within the 1–15 µm size range compared with the other 2 lake samples.

Clay minerals remained the dominant type class of PAV\textsubscript{m} throughout the lake over the study period (Table 4), establishing the watershed origins of that material; however, there were increased contributions by the classes of Calcite and Ca-agg, on average, particularly at the pelagic site. This increase was manifested primarily as short-term peaks, or events, in mid-July and late August to early September (Fig. 8; those 2 classes were combined as Ca-rich), although other intervals also had contributions of this type class that exceeded those in the tributaries (Table 4). The Quartz contribution at pelagic sites was about 10% lower than in the streams.

**Water quality implications of minerogenic particles**

The summer (Jun–Sep) average TP concentration, a regulated water quality metric in New York State, was partitioned into contributions of TDP and PP, and the results are presented for Sites 1, 2, and 3 (Fig. 9). The values of PP correspond to those determined analytically (i.e., PP = TP − TDP). The partitioning of PP into PP\textsubscript{m} and PP\textsubscript{o} (Fig. 9) was based on their predicted relative contributions to the sum (equation 8). The summer average TP concentrations were 35.2, 18.9, and 13.3 µg L\textsuperscript{-1}, for Sites 1, 2, and 3, respectively. The value for Site 1 exceeded the New York State guidance value of 20 µg L\textsuperscript{-1}. Although TDP levels were higher on the shelf, particularly for Site 1, compared with the pelagic Site 3, the differences in PP were greater (Fig. 9). These higher PP concentrations were due to the higher PP\textsubscript{m} levels because PP\textsubscript{o} levels were nearly equivalent, consistent with the spatially uniform Chl-\textalpha concentrations. Accordingly, the P associated with minerogenic particles was a primary cause of the higher TP concentrations on the shelf.

Minerogenic particles contributed to degradations of optical features of water quality. Predictions of summertime SD are presented for the cases of (1) the combination of minerogenic particles (b\textsubscript{m}; equation 4) plus organic (i.e., phytoplankton) particles (b\textsubscript{o}; equation 5), and (2) organic particles only (Fig. 10). The difference represents the effect of minerogenic particles. Reasonably good closure of the predicted summation with the observed b\textsubscript{p} values (average [b\textsubscript{m} + b\textsubscript{o}] : b\textsubscript{p} = 1.07 [±0.37]) supports the representativeness of the predictions (Fig. 10). The effect of minerogenic particles was greater...
on the shelf where PAVm levels were higher. On average, the SD values would have been 27% (2 m) greater than observed at Site 2 in the absence of minerogenic particles (Fig. 10a), compared with 15% (0.9 m) at Site 3 (Fig. 10b).

The effects of minerogenic particles on Tn were even greater than for SD, particularly for the shelf sites (note the logarithmic y-axis for Sites 1 and 2, linear instead for Site 3; Fig. 11). Reasonably good closure of the 2-component model (equation 7) predictions with observations (average $T_{n/o} + T_{n/m}:T_n = 0.78 [±0.20]$) supports their representativeness (Fig. 11). The $T_{n/o}$ component, as estimated from Chl-a observations, was generally inconsequential on the shelf (Fig. 11a and b), with study means of 0.32 NTU for both Site 1 and Site 2 and median values of 0.26 and 0.30 NTU, respectively. $T_{n/m}$ was dominant at these sites even in the context of median values (1.21 and 0.44 NTU for Sites 1 and 2, respectively). Even in pelagic waters, minerogenic particles made an important contribution to $T_n$ (Fig. 11c), representing 48% of the total on average for the study period.

**Discussion**

The goals of our analyses were to (1) continue the advancement of the characterization of minerogenic particle populations in fresh waters; (2) demonstrate the consistency of the SAX-based IPA information for minerogenic particles, particularly as represented by PAVm, with common bulk measurements; and (3) consider the advantages of SAX-based information in identifying and quantifying the effects of these particles on common metrics of lacustrine water quality. Successful SAX-based characterizations (e.g., closure demonstrated) have been reported for streams and a number of lacustrine systems (Table 2). This is the first effort to integrate such information in evolution of related seasonal trends in tributaries and a receiving lake.

**Minerogenic particle population characteristics**

Clay mineral particles, which have inherently terrigenous origins, are ubiquitous in surface waters (Davies-Colley et al. 2003, Stramski et al. 2007). The dominance of this particle type with respect to PAVm (and PVVm) in both the study streams and Cayuga Lake (Table 4) is consistent with findings from previous applications of SAX for other systems (Table 2 citations; also see review by Peng and Effler 2012). Certain features of the clay mineral particle populations characterized here are recurring (e.g., Peng and Effler 2007, 2013a, Effler and Peng 2014), including the general curvature of the PSDs (Fig. 3a and c) and the finding that submicron particles do not make noteworthy
contributions to PAV$_m$ and PVV$_m$ (Fig. 3b and d). Although the polycarbonate filter membranes used had a nominal pore size of 0.4 µm, they were also effective in retaining smaller particles (Atteia et al. 1998). Limited paired measurements of samples collected on 0.2 and 0.4 µm pore-sized filters were conducted for this study, and we found that the PSD and PAV$_m$ results were generally comparable (e.g., PAV$_m$ results within ~15%) and that finer pore-sized filters did not necessarily result in higher particle number and area concentrations. An exponential (i.e., straight-line) decrease throughout the range of particle sizes, described as a Junge function, has often been assumed in the absence of direct measurements for overall particle populations (Babin et al. 2003). The observed minerogenic PSDs (Fig. 3a and c) cannot be adequately described by the Junge distribution.

The observed shift to increased contributions to PAV$_m$ by smaller-sized particles in the upper waters of the lake relative to 3 of the tributaries (Table 4) is consistent with the effects of size-dependent settling (e.g., Stokes Law; Gelda et al. 2009) within the lake. The similarity of the size distribution for Six Mile Creek to the lake on average is probably a result of that stream passing through 2 upstream reservoirs, causing the preferential loss of larger particles. Other processes operating within the lake, particularly aggregation (coagulation) and disaggregation of particles (O’Melia 1985, Hofmann and Filella 1999), may have contributed to the shift in sizes from the tributaries to the lake. The increased contribution of calcium-containing particles (particularly calcite) at pelagic sites (Table 4, Fig. 8), mostly on a short-term basis, is observed widely in hardwater lakes as a result of autochthonous precipitation of CaCO$_3$ (Homa and Chapra 2011). These “whiting” events are often recurring on an annual basis and have most often been observed in August in Cayuga Lake (Effler and Peng 2014). The signature of these events was masked on the shelf by the generally high concentrations of clay mineral particles (Fig. 6c). This CaCO$_3$ precipitation usually occurs as coatings of other particles (serving as nuclei) that kinetically promote precipitation (Homa and Chapra 2011). In Cayuga Lake the primary nucleation sites are apparently phytoplankton; secondary sites include clay mineral particles (Effler and Peng 2014). The thin layer coating of calcite onto organic particles causes a disconnect between the substantial optical effects and the low gravimetric concentrations of these particles during whiting events (Effler et al. 2013).

Consistency of IPA data with bulk measurements

The slopes of the linear least-squares regressions of the ISPM vs. PVV$_m$ datasets for the tributaries represent estimates of the density of the minerogenic particles (Peng and Effler 2012) of the 4 streams (Fig. 4a). The slope values (units 10$^3$ kg m$^{-3}$) for Fall Creek, Cayuga Inlet Creek, Salmon Creek, and Six Mile Creek were 1.80, 2.86, 2.13, and 2.61, respectively, closing reasonably well with known densities of common clay minerals. Density values for 3 common clay minerals, kaolinite, illite, and montmorillonite, are 2.60, 2.85, and 2.04 × 10$^3$ kg m$^{-3}$,
respectively (Woźniak and Stramski 2004). Sources of potential uncertainty and stream-specific differences included (1) the detailed clay mineralogy of the streams, (2) deviations from the specified platelet geometry of the Clay particles (equation 2), (3) differences in the extent of inclusion of particle aggregates in the populations (i.e., void spaces), and (4) inclusion of nonminerogenic particle (e.g., diatom frustules) contributions to ISPM. Representation of the general platelet morphology of clay mineral particles (equation 2) was important to the degree of gravimetric closure reported here based on the IPA characterizations (Fig. 4a). Application of the spheroid formulation for all minerogenic particles (equation 3) instead shifted the slope values lower by about 40% for these streams. Good density closure was also reported on the basis of SPM-PPV data for kaolinite-dominated Esopus Creek, New York, where clay platelet morphology was also prevalent (Peng and Effler 2012). The platelet vs. spheroid geometry has a much smaller effect on light scattering (Effler et al. 2013).

Turbidity ($T_m$) is a measure of side-scattering of light (Kirk 2011). $\text{PAV}_m$ has been reported to be linearly related to $b_m$ and $b_{nm}$ (Table 2). The strong $T_m$-PAV$_m$ relationships obtained here for the streams (Fig. 4b) are generally consistent with those reported for other clay mineral-dominated systems. The slope values for Fall Creek, Cayuga Inlet Creek, Salmon Creek, and Six Mile Creek were 4.0, 4.3, 3.8, and 5.3 NTU·m, respectively, similar to values reported in studies of 4 other streams where minerogenic particles were dominant (range 3.7–5.3 NTU·m; Table 2 references).

Phosphorus associated with minerogenic particles may be adsorbed (Froelich 1988) or embedded within the particles (Reynolds and Davies 2001). Clay minerals have high adsorption capacity for dissolved forms of P (Reddy et al. 1999). Greater adsorption may be anticipated in systems with elevated dissolved P concentrations. Although a linear dependence of PP concentrations on $\text{PAV}_m$ is a reasonable hypothesis, the relationships for these 4 streams (Fig. 4c) are the first reported. The highest slope value for these relationships was observed for Salmon Creek, which has the highest TDP concentrations of the 4 monitored streams (UFI 2014); however, the differences in slopes for the other 3 tributaries did not track their respective TDP levels.

The power-law type dependence of overall $\text{PAV}_m$, along with its 4 size-apportioned components, on $Q_T$ (Fig. 5, Table 5) is qualitatively consistent with similar relationships reported for SPM for lotic systems (Crawford 1991, Asselman 2000). Such relationships are widely used to estimate constituent loading rates (Vogel et al. 2003) necessary to support testing of mass-balance type mechanistic water quality models for receiving lakes (Chapra 1997). The lack of, or modest, differences in these relationships for the 4 size classes for these tributaries suggests that the in-stream PSDs are influenced, or even regulated, by dynamics in PSDs of source material received rather than material mobilized from the watershed. This finding is consistent with the important contributions of eroding streamside glaciolacustrine deposits to sediment loading reported specifically for Fall Creek, Cayuga Inlet Creek, and Six Mile Creek (Nagle et al. 2007).

**Impacts of minerogenic particles on Cayuga Lake**

The $\text{PAV}_m$ signatures in time and space within the upper waters of the lake (Fig. 6b–d) are qualitatively consistent with the timing of runoff-event–driven inputs (Fig. 6a) and the position of the entry of a major fraction of the external loads onto the shelf (Fig. 1). The magnitude of variation in $\text{PAV}_m$ throughout the pelagic waters (more than 10-fold; Fig. 6d) is impressive for such a large, slow flushing rate system. Such variability should be considered probable for many lacustrine systems in response to runoff events. Smaller, more rapid flushing lakes can be expected to demonstrate even larger lake-wide signatures (Peng et al. 2009b). The extent of uniformity throughout the pelagic waters of Cayuga Lake reflects the extensive level of mixing that prevails in this lake (Effler et al. 2010b, Gelda et al. 2015). Episodic occurrences of whiting events overly simplify the perspective that the in-lake patterns of $\text{PAV}_m$ are driven entirely by external loads of clay mineral particles; however, this autochthonous source was decidedly secondary in this study (Figs. 6d and 8), as reported by Effler and Peng (2014) for earlier years. Cases have been reported where whiting events were instead responsible for the primary clarity reduction observed seasonally (Weidemann et al. 1985, Homa and Chapra 2011, Peng and Effler 2011).

The strong relationships between $\text{PAV}_m$ and lake water quality metrics established for this lake (Effler and Peng 2014, Effler et al. 2014) supported the important implications of the $\text{PAV}_m$ levels on TP concentrations (Fig. 9), SD (Fig. 10), and $T_m$ (Fig. 11). TP is the most widely applied metric of trophic state used by the regulatory community in the United States in setting water quality goals or limits to protect against excessive cultural eutrophication (Effler et al. 2014). The large contributions of PP to TP on the shelf (Fig. 9) raises questions concerning the appropriateness of TP as a regulated metric for this particular area because this form of P generally has limited bioavailability (DePinto et al. 1981, Young et al. 1985, Auer et al. 1998, Effler et al. 2002). PP on the shelf was found to have low (1.7%) bioavailability in a sample collected soon.
after a major runoff event (Prestigiacomo et al. 2015), as determined with a bioassay protocol (Auer et al. 1998, Effler et al. 2012). Accordingly, TP values collected on the shelf after runoff events should not be integrated into assessments of the status of that area relative to the guidance value because it is not at that time a valid metric of trophic state. Exceedances identified for previous years were also the result of the inclusion of high PP\textsubscript{m} (i.e., PAV\textsubscript{m}) levels caused by runoff events (Effler et al. 2014). Moreover, such assessments are highly dependent on the timing of monitoring relative to the occurrences of runoff events. For example, a limited number of high values that occur soon after major runoff events can cause high summer average TP concentrations.

Minerogenic particles have increasingly been recognized as important in influencing common optical metrics of water quality for lacustrine waters, including SD (Swift et al. 2006, Peng and Effler 2011, Effler and Peng 2014) and T\textsubscript{n} (Peng et al. 2009b, Peng and Effler 2010, Effler et al. 2014). SD is also a metric of trophic state (Chapra 1997) and closely coupled to the public’s perception of water quality (Smith and Davies-Colley 1992). T\textsubscript{n} is particularly critical as a quality metric for water supplies. The predicted impact of PAV\textsubscript{m} levels on SD, based on an established system-specific relationship (equation 6; Effler and Peng 2014) was noteworthy, even in pelagic portions of the lake (Fig. 10). This effect is important because the minerogenic component of b\textsubscript{p} (i.e., b\textsubscript{p}m) acts to limit the extent of improvement in SD that could be achieved by nutrient management (i.e., decreases in b\textsubscript{p}) alone (Effler and Peng 2014). The dominant role played by suspended particles in affecting water quality parameters related to clarity is expected in other lacustrine systems where the contributions of particle and CDOM absorptions to light attenuation are similarly minimal, as in Cayuga Lake. The relatively greater effect of minerogenic particles on T\textsubscript{n} (Fig. 11) compared with SD (Fig. 10) is well grounded in optical theory. Effler et al. (2014) demonstrated through Mie theory calculations the much greater efficiency of side scattering (i.e., T\textsubscript{n}) for minerogenic (particles of high refractive indices) versus organic particles compared with the similar efficiencies of these 2 particle groups for overall scattering (i.e., b\textsubscript{p}).

**Advantages of SAX information and a conceptual model for PAV\textsubscript{m}**

The population of lacustrine systems for which minerogenic particle populations have been characterized by SAX, with successful related performance testing (i.e., scattering closure), has grown substantially in recent years (Table 2). The relative contribution of these particles to the overall particle assemblage of Cayuga Lake, particularly in its pelagic waters, is not unusual compared to the other ~20 characterized systems. Accordingly, the effects of these particles on water quality metrics described here should not be considered uncommon. Minerogenic particles are an important (or even dominant) feature of water quality in many surface waters and widely limit the extent of improvement that can result from nutrient management alone (Davies-Colley et al. 2003). SAX-based information is pertinent to management concerns for optical water quality and P. Specifically, PAV\textsubscript{m} information can contribute importantly in identifying management targets and establishing reasonable expectations where the effects of minerogenic particles are noteworthy. Erosion control rather than reductions in inputs of bioavailable P would be the preferred strategy for systems where clay (or other terrigenous) minerogenic particles dominate SD degradation.

SAX-based IPA characterizations have a number of advantages over the traditional gravimetric measurements of ISPM, particularly for the issues addressed here. First, SAX does not suffer from the accuracy and representativeness (e.g., contributions by diatom frustules, calcite-coated organic particles) problems of gravimetric measurements for the relatively dilute conditions that prevail in most lacustrine systems (Effler et al. 2013). The geochemical and size-class partitioning supported by SAX provides additional valuable insights concerning origins and behavior of these particles (Peng et al. 2009a, Peng and Effler 2011). Resolution of the contributions of terrigenous (e.g., clay minerals) particles, specifically, has fundamental management (e.g., erosion vs. nutrient control) value (Effler et al. 2014). The authors did not find cases of documented successful partitioning of PP and T\textsubscript{n} into minerogenic versus organic particle contributions (Fig. 9 and 11) in fresh waters that uses ISPM instead of PAV\textsubscript{m} (Effler et al. 2014) to represent minerogenic particles. The optical implications of minerogenic particles, as measured by SD, T\textsubscript{n}, the beam attenuation coefficient, and b\textsubscript{p}m depend linearly on their cross-sectional area (i.e., PAV\textsubscript{m}), not their mass (Boss et al. 2009b, Bowers and Braithwaite 2012, Effler et al. 2013). The mass-specific scattering coefficient for inorganic particles (= b\textsubscript{m}/ISPM) has been demonstrated to vary as a function of the size distribution of minerogenic particles in the optically important size range (Peng and Effler 2012). Continuing research related to the effects of aggregation and its interplay with PSDs and the evolution and performance of alternate calculation frameworks (e.g., Zhang et al. 2014) for scattering may further improve the performance of the SAX-based approach in the future.

The combined tributary (Fig. 2 and 5) and lake (Figs. 6–8) SAX datasets offer a unique opportunity to support development and testing of a first mechanistic
mass-balance type model (Chapra 1997) for minerogenic particles in a lake. A reasonable first approach is considered here (Fig. 12) in the context of the parsimony principle (Chapra 1997), which recommends that the model should only be as complex as necessary to reasonably simulate the observations. For example, the potential effect of phytoplankton metabolism (e.g., a potential coagulation pathway) would not be explicitly considered. Moreover, the whiting phenomenon would not be explicitly modeled. Instead, this secondary component could be specified, consistent with historic site-specific, SAX-based observations (Effler and Peng 2014). The model’s state variable would be $PAV_m$ (although $PVV_m$ predictions would also be produced), consistent with its central role in regulating related features of water quality (Fig. 9–11; Table 2). $PAV_m$ would be partitioned into the contributions of multiple size classes (Fig. 12) that may differ from those adopted here for data presentation, based on performance feedback from alternative classification strategies. The multiple size-class feature is a major advantage (e.g., compared with a model with ISPM as the state variable) because it enables representation of size-dependent behavior of the particles within the lake, consistent with the broad PSDs that prevail for these particles in both streams and lacustrine systems (Fig. 3a and c, Table 4). This feature of detailed size classification is necessary for representing the associated effects on the persistence and distribution of these particles in receiving waters.

External loads of $PAV_m$ would be delivered according to the chosen size classes (Fig. 12), as specified by measurements for a model calibration year (e.g., 2013) and based on the reported $PAV_m$–$Q_s$ relationships (Fig. 5) for days without observations, as well as for model validations years (Effler and Peng 2014). In-lake processes would include, as a minimum, size-dependent settling (Gelda et al. 2009), which could be expanded to include non-size–selective losses to filter feeding by the large resident dreissenid mussel population (Gelda and Effler 2000) and particle aggregation. Predictions of $PAV_m$ would also support predictions of $PP_m$, $T_{woa}$, $h_m$ (Fig. 12), and $b_{h,m}$.

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