Factors Diminishing the Effectiveness of Phosphorus Loading from Municipal Effluent: Critical Information for TMDL Analyses

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ABSTRACT: Factors that diminish the effectiveness of phosphorus inputs from a municipal wastewater treatment facility (Metro) in contributing to phosphorus levels and its availability to support algae growth in a culturally eutrophic urban lake (Onondaga Lake, NY) were characterized and quantified. These factors included the bioavailability and settling characteristics of particulate phosphorus from this effluent, the dominant form (70%) of phosphorus in this input, and the plunging of the discharge to stratified layers in the lake. Supporting studies included: (1) chemical and morphometric characterization of the phosphorus-enriched particles of this effluent, compared to particle populations of the tributaries and lake, with an individual particle analysis technique; (2) conduct of algal bioavailability assays of the particulate phosphorus of the effluent; (3) conduct of multiple size class settling velocity measurements on effluent particles; and (4) determinations of the propensity of the discharge to plunge, and documentation of plunging through three-dimensional monitoring of a tracer adjoining the outfall. All of these diminishing effects were found to be operative for the Metro effluent in Onondaga Lake and will be integrated into a forthcoming phosphorus "total maximum daily load" analysis for the lake, through appropriate representation in a supporting mechanistic water quality model. The particulate phosphorus in the effluent was associated entirely with Fe-rich particles formed in the phosphorus treatment process. These particles did not contribute to concentrations in pelagic portions of the lake, due to local deposition associated with their large size. Moreover, this particulate phosphorus was found to be nearly entirely unavailable to support algae growth. While substantial differences are to be expected for various inputs, the effective loading concept and the approaches adopted here to assess the diminishing factors are broadly applicable. *Water Environ. Res.*, **84**, 254 (2012).

KEYWORDS: phosphorus, loads, bioavailability, settling velocity, plunging inflows.

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Introduction

Many surface waters continue to suffer water quality impacts associated with cultural eutrophication from reception of anthropogenic phosphorus loads, despite advancements in wastewater treatment and control of non-point inputs over the last four decades (Cooke et al., 2005). The most acute and challenging related problems persist in urban areas with dense populations, where municipal wastewaters contribute importantly to phosphorus budgets (Effler et al., 2009b). Rehabilitation programs for these "water quality limited" receiving waters are guided by the total maximum daily load (TMDL) analysis process (U.S. EPA, 1991). Water quality models that quantify cause and effect for impacted systems (Chapra, 1997) are embedded in TMDL analyses to provide an objective basis to establish the reductions in constituent loading (e.g., phosphorus) necessary to reach regulatory goals. Partitioning external loads of phosphorus from noteworthy sources is fundamental information to support related TMDL analyses and the development of effective strategies to achieve rehabilitation goals (Effler et al. 2009b; James et al. 1994; U.S. EPA, 1991).

Earlier, phosphorus loading was represented in terms of annual *total* phosphorus loading, based on measurements of total phosphorus concentrations and flow rates of inputs (Chapra, 1997). Such total phosphorus loads were consistent with the structure of simple empirical models used in that era to predict lake trophic state (Larsen and Mercier, 1976; Vollenweider, 1976). Phosphorus exists in a wide array of chemical forms (Bradford and Peters, 1987; Dodds, 2003) with extensive conversions and cycling amongst some of these forms (Wetzel, 2001). It is now well recognized that all phosphorus is not immediately (Dodds, 2003), nor ultimately (DePinto et al., 1981; Young et al., 1982), available to support algae growth (e.g., bioavailable). It is valuable to consider the bioavailability issue in the context of the forms of phosphorus that are commonly measured in contemporary monitoring programs focused on the cultural eutrophication issue; total phosphorus, total dissolved phosphorus (TDP), and soluble reactive P (SRP). Two additional forms are calculated, particulate phosphorus (particulate phosphorus = total phosphorus − TDP) and dissolved organic phosphorus (DOP = TDP − SRP). SRP is considered to be immediately available (Effler and O'Donnell, 2010; Reynolds, 2006), while most of DOP is made available to support growth (Auer et al. 1998; Young et al., 1982) over longer time scales through enzymatic and mineralization processes (Currie et al., 1986). However, the particulate phosphorus fraction is known to have generally lower bioavailability (e.g., needs to be converted to dissolved forms) that can differ widely amongst tributaries, and between the effluents of different municipal wastewater treatment facilities (Ekholm and Krogerus, 2003; Young et al.,

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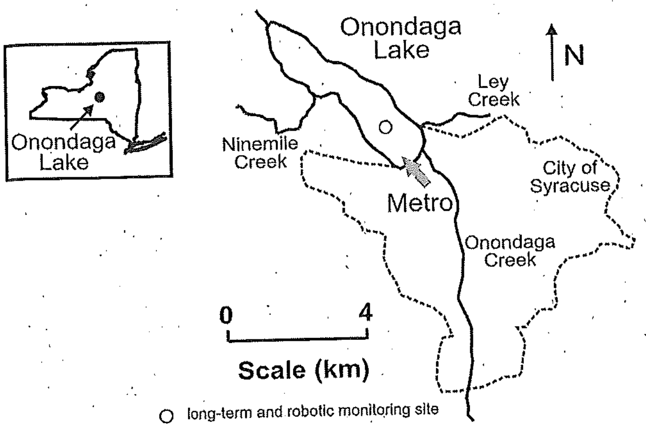

Figure 1—Onondaga Lake: with robotic monitoring site and the locations of Metro, City of Syracuse, and selected tributaries.

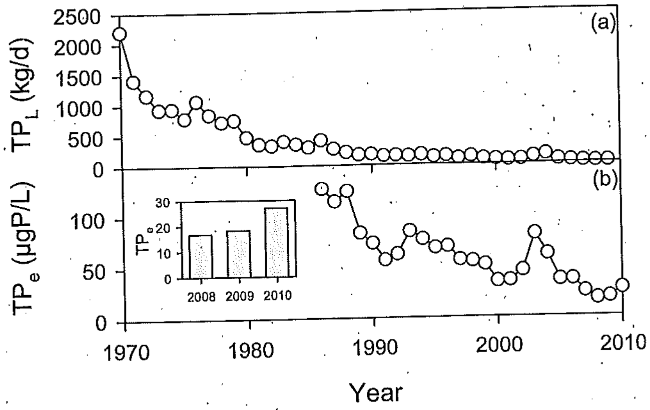

Figure 2—Time series of: (a) annual average total phosphorus (TP) loading rates from Metro 1970–2010, and (b) summer average epilimnetic total phosphorus concentrations, 1986 to 2010.

1982). Thus, the partitioning of external phosphorus loads adjusted for bioavailability can differ widely from that based on total phosphorus (Effler et al., 2002).

Yet other processes that operate within receiving waters can further diminish or attenuate the phosphorus input that actually reaches productive zones and supports algae growth in lakes and deep rivers, including settling losses of bioavailable particulate phosphorus and plunging of dense inputs to deep layers below productive depths (Effler et al., 2009a). Loads that are adjusted for all of these attenuating effects (bioavailability, settling, plunging) have been described as "effective" phosphorus loads (Effler et al., 2002). Contemporary mathematical models for phosphorus and associated features of cultural eutrophication (such as would be used in TMDL analyses) are generally mechanistically robust, providing a high degree of realism in representing the complexities of phosphorus cycling and algae growth (Chapra, 1997; Omlin et al., 2001). These modern frameworks accommodate, or can be modified to represent, the various attenuating effects for the availability (i.e., potency) of phosphorus inputs embedded in the effective phosphorus loading concept, based on findings from studies that target resolution of these effects.

This paper presents findings of studies directed at identification, characterization and quantification of attenuating effects on the availability of phosphorus inputs from a municipal wastewater treatment facility where upgraded phosphorus treatment has recently been implemented, and that had been responsible for the severe cultural eutrophication of the receiving urban lake, Onondaga Lake, N.Y. These studies included: (1) characterizations of inorganic (minerogenic) particles from the effluent with an individual particle analysis (IPA) technique; (2) the conduct of algal bioavailability assays of particulate phosphorus from the effluent; (3) the conduct of settling velocity measurements on effluent particles; and (4) evaluations of propensity for the effluent to plunge, based on density calculations, and observations of plunging, based on three-dimensional monitoring adjoining the facility's outfall. This case study is particularly valuable because: (1) the effective phosphorus loading issue influences the development of representative phosphorus budgets and related management strategies for many systems, (2) the protocols presented here to assess the various attenuating effects are broadly applicable, (3) key findings for this facility are transferable to others where similar advanced treatment technologies for phosphorus have been implemented, (4) findings presented here will be used to guide the appropriate representation of these effects in a water quality model that is supporting a phosphorus TMDL analysis for the lake, and (5) a large investment has been made in the rehabilitation of Onondaga Lake from the effects of municipal wastes.

System Description

Municipal Wastewater Treatment Facility. The Metropolitan Syracuse Wastewater Treatment Plant (Metro) discharges (average flowrate (Q_{Metro}) of ~3 m^3/s, largely unchanged over the last 40 years) into the southern end of Onondaga Lake (Figure 1). The contribution of Q_{Metro} to the lake's overall hydrologic budget is extraordinary (Rucinski et al., 2007), representing nearly 20% on an annual average basis (Effler, 1996) and 25% on average for the critical summer interval. This is the largest contribution by municipal waste effluent for a lake in the United States. Metro has three points of discharge to the lake, a shoreline discharge (maximum flow of 5.25 m^3/s) and two smaller outfalls (each with maximum flows of 2.6 m^3/s; entry depths of near-surface and 7 m). Treated effluent was discharged primarily through the subsurface outfalls, a common practice for lake discharges, until 1980. However, thereafter the discharge was switched to the shoreline outfall to compensate for the negative buoyancy (i.e., plunging) effects of Ca-rich saline industrial waste water that was received from 1981 to 1986 as part of a cotreatment strategy to remove phosphorus from the municipal waste and diminish the load of saline waste to the lake (Effler, 1996).

Mostly progressive decreases in Metro's effluent total phosphorus concentration (TP_{Metro}) and load occurred since 1971 (Figure 2a) in response to a series of management actions including a ban on high phosphorus content detergents in the watershed (Murphy, 1973) and treatment upgrades in 1979 (secondary treatment), 1981 (tertiary, from addition of industrial waste), over the interval 1989 to 2002 (more common tertiary treatment optimization), and in 2005 (advanced tertiary treatment, Actiflo®). The total phosphorus load from Metro has been reduced about 99% since 1970 (Effler and O'Donnell, 2010). The most recent reduction in TP_{Metro} was mandated as part of a phosphorus TMDL analysis (NYSDEC, 1998). The mandated TP_{Metro} limit of 0.12 mg/L by 2006 was met. This upgrade in phosphorus treatment, along with the addition of year-round nitrification to eliminate problems associated with high ammonia levels (Effler et al., 2010), cost approximately 150 million dollars. The mandated TP_{Metro} of 20 µgP/L by 2012, developed in the phosphorus TMDL analysis (NYSDEC, 1998), has feasibility issues based on existing technologies. This effluent concentration has yet to be routinely met for a facility the size of Metro. The phosphorus TMDL analysis for Onondaga Lake was criticized for failing to embrace the effective phosphorus loading approach in its development (Effler et al., 2002). A revised TMDL analysis is to be prepared that will incorporate insights from the lake response to date (e.g., Figure 2b) and adopt the effective phosphorus loading approach for Metro and the tributaries.

Actiflo® is a micro-sand ballasted process that was implemented in 2005. The micro-sand serves as a seed for floc formation after coagulant (ferric chloride at Metro) addition, providing a large surface area for suspended solids to bond to, and promoting subsequent rapid settling. Settled solids are passed through a hydrocyclone where the lighter iron (Fe)–enriched chemical sludge is separated from the ballast. Performance in removal of suspended solids at Metro has been particularly effective since implementation of Actiflo®; the average effluent total suspended solids concentration (TSS) since 2006 has been 6 mg/L. The average summertime (mid-May to mid-September) TP_{Metro} for the 2008 to 2010 interval was 103 µgP/L (Figure 2a). The dominant phosphorus fraction for this recent interval has been particulate phosphorus, representing approximately 65% of the total (average particulate phosphorus = 67 µgP/L). Most of the dissolved phosphorus has been in the form of DOP (86% of TDP; 29% of TP_{Metro}). The average SRP concentration over this interval was 5 µgP/L, representing only 5% of TP_{Metro}.

Onondaga Lake. This lake is located (lat. 43° 06′ 54″; long. 76° 14′ 34″) in metropolitan Syracuse, N.Y. (Figure 1). The lake has a volume of 131×10^6 m^3, a surface area of 12 km^2, and a maximum depth of about 20 m. Onondaga Lake is a hard water, alkaline, dimictic system, strongly stratifying during summer months (O'Donnell et al., 2010). The lake flushes rapidly, about four times per year on average (Effler, 1996), and thus responds rapidly to changes in external loading (Doerr et al., 1994). The lake was oligomesotrophic before European settlement in the late 1700s (Rowell, 1996) and supported a cold-water fishery in the early years of development of the region (Tango and Ringler, 1996). Inputs of industrial and domestic wastes to the lake increased as the urban area developed that led to severe degradation and the loss of resources, including the cold-water fishery in the late 1800s (Effler, 1996).

Onondaga Lake experienced extreme cultural eutrophication and severe coupled impacts on water quality, primarily as a result of the input of large quantities of phosphorus from Metro (Effler and O'Donnell, 2010). Water quality manifestations of cultural eutrophication included: (1) high concentrations of phytoplankton and severe blooms of nuisance forms (Effler, 1996); (2) low water clarity (Secchi disc values; Effler et al., 2008b); (3) high rates of deposition of organic material from the epilimnion to the hypolimnion (Effler et al., 2001); (4) rapid loss of oxygen from the hypolimnion (Matthews and Effler, 2006b); (5) high hypolimnetic accumulation rates of oxygen-demanding reduced by-products of anaerobic metabolism (Matthews et al., 2008); and (6) depletion of oxygen in the upper waters during the approach to fall turnover (Matthews and Effler, 2006a) and the coupled exodus of fish from the lake (Tango and Ringler, 1996). However, internal loading of phosphorus from the hypolimnion, related to these redox conditions, has not been noteworthy because of limited vertical mixing during the summer and the subsequent rapid flushing of the lake following the onset of fall turnover (Effler et al., 2002).

Major reductions in summertime concentrations of total phosphorus in the lake's upper waters, a widely accepted metric of trophic state (Chapra, 1997), have been achieved (Figure 2b; reliable data for 1987 to 2010) in response to decreased phosphorus loading from Metro (Figure 2a). The regulatory limit for the summer average epilimnetic total phosphorus concentration (TP_e), specified as part of a TMDL analysis (NYSDEC, 1998), is 20 µgP/L, a level consistent with mesotrophy (Chapra, 1997). This limit was met in 2008 and 2009, but not in 2010 (inset of Figure 2b). Corresponding substantial improvements in other metrics of trophic state, including concentrations of chlorophyll **a** (primary photosynthetic pigment, common surrogate of phytoplankton biomass), Secchi disc (water clarity), and rates of hypolimnetic oxygen depletion, were also observed in recent years (Effler and O'Donnell, 2010). The lake had remained highly eutrophic until the most recent treatment upgrade at Metro. Since this most recent upgrade the upper waters of the lake have been in a distinctly phosphorus-limited state (nitrogen concentrations remain well above limiting levels; Effler et al., 2010) with respect to algae growth during the critical summer months (Effler et al., 2008a). Accordingly, the lake is poised for further reductions in algae growth and improvements in related features of water quality from additional reductions in effective phosphorus loading.

Methods

Individual Particle Analysis (IPA) with SAX. Scanning electron microscopy interfaced with automated image and X-ray analyses (SAX) provides both morphometric and chemical (elemental) composition characterizations of particle populations through analyses of large numbers of individual particles. Metro effluent particle populations were characterized by SAX and contrasted with those from the major tributaries and the upper waters of the lake at the long-term monitoring site (Figure 1). Grab-type samples were collected weekly from these sites in 2010. Sample preparation and instrumentation protocols for SAX have been described previously (Peng and Effler, 2007). The SAX instrumentation was an Aspex PSEM 2000 system controlled by automated feature analysis (AFA) software (Aspex®). About 2000 individual particles were analyzed for each sample. The total particle projected area per unit volume of water (PAV) is a valuable bulk property available from SAX (Peng and Effler, 2007; 2010) that can be expected to be positively correlated with the adsorptive capacity of certain inorganic particle types for phosphorus (e.g., a surface area-based phenomenon; House 1990).

SAX conducts compositional analysis of a particle by acquisition of X-rays of sixteen elements (sodium and heavier elements). A particle's chemical composition is represented by elemental X-ray counts normalized to relative intensities. Aquatic particles generally have distinctive and source-dependent compositional signatures that can be identified by X-ray analysis (Peng and Effler, 2007). Accordingly, particles were sorted into eight predefined generic types based on their elemental X-ray composition, including clay-minerals, quartz (SiO_2), Si-containing minerals, calcium carbonate ($CaCO_3$, calcite), calcium carbonate aggregates (Ca-agg), iron and calcium (Fe/Ca) aggregates, miscellaneous inorganic particles, diatoms (biogenic SiO_2), and organic (e.g., phytoplankton and bacteria). With the exception of the Fe/Ca class, these particle classes generally coincide with those successfully adopted to characterize particle populations in other fresh water systems where SAX has been employed (Peng and Effler, 2007; 2010).

Bioavailability Algal Assays. These bioassays were conducted using modifications of the Dual Culture Diffusion Apparatus (DCDA) developed by DePinto (1982), as applied to inputs of the Great Lakes (DePinto et al., 1981; Young et al., 1982), the New York City reservoir system (Auer et al., 1998), various receiving waters in Finland (Ekholm and Krogerus, 2003), and Onondaga Lake (Effler et al., 2002). In these bioassays, phosphorus mobilized from concentrated particulates (except Ekholm and Krogerus, 2003; dissolved and particulates not separated) diffuses across a semi-permeable membrane and is taken up by phosphorus-starved algae (*Selenastrum capricornutum*). In this study the algae cells were harvested at 3-day intervals, and the phosphorus content determined over a 30 day period.

Metro effluent samples for assays were collected by passing ~40 L of source water through a tangential flow filtration (0.45 μm pore size) apparatus, yielding ~50 mL of particulate phase slurry. Paired measurements of the total suspended solids (TSS; dry weight, DW) and total phosphorus (Methods 4500-P B., persulfate digestion and 4500 P E., ascorbic acid; Clesceri et al., 1998) content of the sample were made, yielding the total phosphorus richness (μgP/gDW) of the particulate matter. The sample was then subjected to assay, with the result being the mass of bioavailable phosphorus supplied. Division by the solids (DW) added to the assay chamber yields the bioavailability particulate phosphorus (BAPP) richness (μgP/gDW) of the particulate matter. The ratio of BAPP richness: total phosphorus richness defines the bioavailable fraction (f_{bio}) for the sample, typically presented as percent bioavailable. A fit of a first order function to the time series of cumulative BAPP production yields a bioavailability coefficient (k_{bio}, d^{-1}) that describes the rate at which phosphorus in the sample is made available to algae (Auer et al., 1998). Particulate phase concentrate from the Metro effluent was analyzed for phosphorus richness and bioavailability on samples from three dates (3 May, 1 June, and 7 July, 2010).

Density Differences and Occurrences of Plunging. The dynamics of the buoyancy of the Metro discharge relative to the lake were determined for the May-September interval of 2010 based on calculated densities that were a function of temperature (T) and salinity (Chen and Millero, 1978). Salinity was estimated from specific conductance (SC; Hill et al., 1986). Temperature and SC were measured in the effluent hourly with calibrated instrumentation (YSI 6560). In-lake measurements of T and SC were made with the same probes at 1 m depth intervals four times per day (hourly estimates from interpolation), over the same time interval, at the long-term deep-water monitoring site (Figure 1), from a solar-powered robotic monitoring platform (YSI 6955 and 6980).

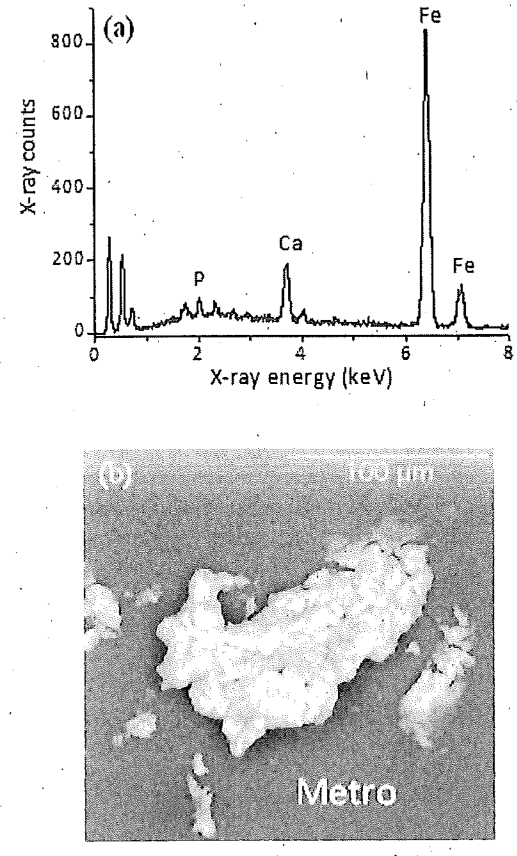

Figure 3—SAX characterizations of system particles: (a) X-ray spectrum for Fe/Ca particle from the Metro effluent; and (b) micrograph of Fe/Ca particles from the Metro effluent.

The high concentration of nitrate (NO_3^-) in the effluent (~11 mg N/L) relative to the lake (e.g., summer average for the upper waters ~2 mg N/L) provides an opportunity to track the transport of the discharge, utilizing NO_3^- as a tracer, including its effective depth of entry into the water column (Prestigiacomo et al., 2009). Vertically detailed (resolution of 0.25 m) measurements of NO_3^- were made weekly at 21 sites extending from the Metro discharge along lateral transects towards the deeper (pelagic) portion of the south basin of the lake (Figure 1), with an in situ ultraviolet spectrophotometer (ISUS; Satlantic Inc.). Measurements of NO_3^- made with this rapid profiling instrumentation have been validated for Onondaga Lake by standard laboratory wet chemistry analyses (Prestigiacomo et al., 2009). Positions of the profiles were established in the field with GPS (accurate within 3 m). These griddings were generally completed within 2 hours.

Particle Settling Velocities. Measurements of particle settling velocities (SV), and supporting determinations of number concentration and size distribution (PSD), were made for eight size classes with a LISST-ST (Sequoia Scientific Inc.) particle size analyzer. The theory and operation of the instrument were described in detail by Agrawal and Pottsmith (2000). This instrument uses the principle of laser diffraction to obtain the PSD and volume concentration of suspended particles (V_p), assuming spherical particles.

The optical detector to count and size the particles is enclosed near the bottom of a settling tube of 30 cm height and 5 cm

Table 1—Chemical characteristics of particle populations for the Onondaga Lake system from SAX analyses.

System	n*	PAV (m^{-1})	Average PAV Composition (%)								
			Clay	Quartz	Si-rich	Calcite	Ca-agg	Fe + Ca	Misc	Diatom	Org.
Metro	18	0.42±0.11	1.5	0.2	0.0	0.1	0.2	89.9	2.6	0.2	5.3
Tributaries											
Onon. Cr.	22	5.36±5.76[§]	66.7	5.5	1.6	1.9	13.8	0.3	4.5	5.5	0.2
Ninemile Cr.	21	3.43±4.82	56.5	3.8	1.3	6.9	18.1	0.3	5.3	7.0	0.6
Ley Cr.	23	2.59±1.11	60.0	2.8	1.1	3.6	18.9	0.9	7.9	4.2	0.6
Onondaga Lake	27	0.35±0.45	48.6	1.9	1.1	10.4	16.4	0.2	6.1	12.4	2.9

* number of samples.
§ mean ± std, dev.

diameter. Volume concentrations of the eight size classes are tracked based on numerous detector scans (n = 83) during each 24-hour experiment. The size classes are logarithmically spaced, with geometric mean diameters (d_g) of 1.74, 3.38, 6.56, 12.70, 24.70, 47.90, 92.90 and 180.00 μm. Estimates of SV were accepted for those size classes for which a clear trend consistent with settling was observed (Perkins et al., 2007).

Results and Discussion

Particle Characterizations by SAX. The X-ray chemistry of the Metro effluent particles (Figure 3a) was found to be quite distinctive. More than 90% of the PAV of the Metro particles were in the Fe/Ca class (Table 1). The prominent Fe signal reflects the use of $FeCl_3$ as the coagulant in the Actiflo® process. Contributions of Ca to this signature are probably associated with precipitation of $CaCO_3$ in treatment of these hard wastewaters (Effler, 1996). The inorganic particles that dominate in the Metro effluent are unrecovered floc particles from this tertiary treatment. The SAX signature for these particles is nearly unique in this system, as particles associated with this chemical class were essentially absent from the tributaries and the upper waters of the lake (Table 1). Instead, the tributaries are dominated by common terrigenous inorganic particles, particularly clay minerals, while the lake demonstrates some additional contributions from internal production of calcite (Driscoll et al., 1994; Johnson et al., 1991), Ca-agg, organic particles and diatoms (Table 1).

Consistent with the goals of the tertiary treatment, the Fe/Ca particles of the Metro effluent were enriched with phosphorus, and thereby resolvable in the X-ray spectra (Figure 3c). Essentially all the phosphorus X-rays collected were associated with the Fe/Ca particles. Accordingly, the near absence of Fe/Ca particles in the upper waters of the lake supports the position that the particulate phosphorus load from Metro does not contribute to total phosphorus concentrations in these lake layers. SAX could not be used to quantify phosphorus associated with the natural particle types, such as clay minerals and calcite (Mayer and Gloss, 1980; Wetzel, 2001), because the generally lower associated X-ray intensity contributions were inadequate to provide a reliable signal. This is consistent with the higher phosphorus content of solids from Metro compared to the tributaries, based on routine monitoring of particulate phosphorus and TSS. The particulate phosphorus/TSS ratio for the Metro effluent (~13 mgP/gDW) is 3 to 4 times greater than for tributaries (Prestigiacomo et al., 2007).

The Fe/Ca particles had diverse shapes (Figure 3b) that diverged from the common platelet morphometry of the clay minerals. Larger particles made greater contributions to the population of the Metro effluent than in the natural tributaries or the upper waters of the lake. This is depicted through comparison of the average distributions of size contributions to PAV for Metro to those for a major tributary (Onondaga Creek) and the upper waters of the lake (Figure 4). The peak of the Metro distribution was about 17 μm, approximately three times larger than for the tributary and lake. The generally greater contributions of larger sized particles to PAV in the Metro effluent (Figure 4) can be expected to be manifested in local deposition from elevated settling rates. Local deposition has also been documented adjoining the lake's two largest tributaries (Auer et al., 1996).

Bioavailability Assays. The average phosphorus-richness of Metro effluent particulate matter was found to be 11.9±3.8 mgP/gDW. Of this amount, 1.4 ±0.3% was bioavailable with a corresponding rate coefficient (k_{bio}) of 0.23±0.03 d^{-1} (Figure 5). These findings are particularly striking with respect to their implications in formulating a phosphorus TMDL. The phosphorus-richness of particulate matter in the Metro effluent was reduced by approximately one-third from historical levels (17.5 mgP/gDW in 1996; Effler et al., 2002) and the fraction bioavailable under the Actiflo® treatment regime decreased by 98%. The rate at which particulate-phosphorus became bioavailable

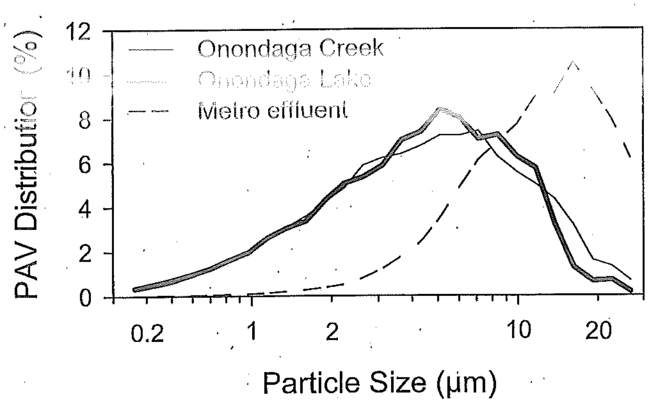

Figure 4—Comparison of the dependence of PAV (%) on particle size for Metro, a major tributary (Onondaga Creek), and the upper waters of the lake, based on averages from weekly monitoring (April to September, 2010).

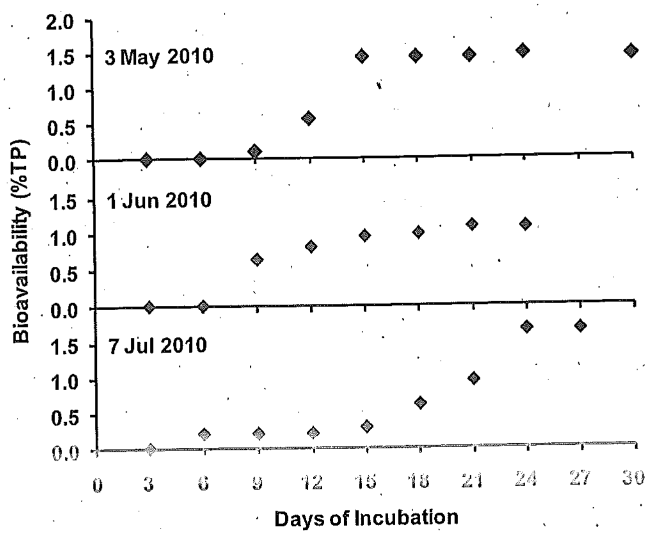

Figure 5—Bioavailability of particulate phosphorus in three Metro effluent samples as determined through assay with a Dual Culture Diffusion Apparatus.

decreased by 25%. As discussed above in relation to particle analysis, solids associated with the Actiflo® effluent are distinctive in their size, shape and SAX signature. These differences extend to their chemical composition. Effler et al. (2002) reported that most of the bioavailable phosphorus realized from particulate matter originated from the operationally-defined organic-phosphorus fraction, a class that represented 52% of the particulate-phosphorus content historically. Thus the mechanism controlling bioavailability, formerly diagenesis of particulate organic matter, is now sorption on particles with high iron content.

Buoyancy Status and Plunging. Time series of hourly estimates of the densities (ρ) of the Metro effluent and the upper waters of the lake are compared for the April to September

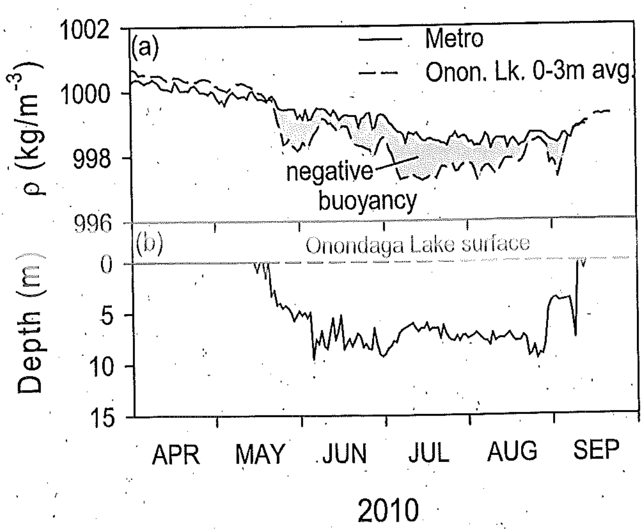

Figure 6—Buoyancy and plunging propensity for Metro for the April to September interval of 2010: (a) time series of densities of the Metro effluent and the upper waters (0 to 3 m) of Onondaga Lake, and (b) time series of the neutral buoyancy depth in the water column of Onondaga Lake.

interval of 2010 (Figure 6a). The dynamics of ρ for both the effluent and lake, at time scales from within a day to seasonal, are regulated primarily by variations in water temperature (T). Variations in air T are an important driver of the dynamics of water T (Martin and McCutcheon, 1999; Sinokrot and Stefan, 1993). Thus, natural variations in meteorological conditions can be expected to cause noteworthy year-to-year differences in the details of such patterns, as well as in the buoyancy status of the discharge (ρ difference between the effluent and the lake).

The density of the Metro effluent was lower than for the lake over the April through mid-May interval of 2010 (Figure 6a). Inflows that are less dense tend to enter across the surface of a receiving lake as overflows that are readily incorporated into the relatively well-mixed epilimnion through wind-driven turbulent mixing (Martin and McCutcheon, 1999). However, starting in late May and persisting through early September this discharge was more dense than the lake (i.e., negatively buoyant) and therefore tended to plunge. The magnitude of the density differences varied substantially over this interval of negative buoyancy, and was the greatest in early June and mid-July (Figure 6a). Analyses of more temporally limited data from earlier years indicated substantial inter-annual differences in the details of these patterns, but a recurrence of summertime negative buoyancy of the discharge.

The extent to which a plunging tendency is manifested is dependent on multiple factors, including: (1) the magnitude of the density difference; (2) the geometry of the inflow zone; and (3) the ambient turbulence (Martin and McCutcheon, 1999). A plunging inflow, or density current, moves along the bottom of the receiving basin as an underflow, undergoing shear at the bottom and entraining ambient water (Alavian et al., 1992; Fang and Stefan, 2000). An underflow separates from the bottom as a neutrally buoyant interflow, entering the water column at a vertical position where the density is equivalent. The temporal pattern of the neutral buoyancy depth of the Metro discharge for the study interval of 2010 is presented (Figure 6b). This is the depth of the lake where the density was equal to that of the discharge. Accordingly, these are upper bound values of the neutral buoyancy depth, as natural ambient mixing processes will tend to diminish density differences, thereby shifting the effective neutral buoyancy depths upward (shallower) in the water column. Over the critical water quality months for the lake of June, July, and August the upper bound neutral buoyancy depths were usually between 6 and 9 m (Figure 6b).

The in-lake three-dimensional signatures of NO_3^- documented through ISUS gridding (A and B; Figure 7) were qualitatively consistent with the dynamics of the buoyancy status (Figure 6a) and neutral buoyancy depths (Figure 6b) of the Metro discharge. Here occurrences of NO_3^- concentrations distinctly higher than the ambient lake levels (~2 mgN/L) serve as tracers of the Metro discharge (~11 mgN/L). Features of the spatial patterns of NO_3^- obtained from selected in-lake griddings are presented along transects (A and B; Figure 7a) as length/depth contours (Figure 7b-e). An overflow signature of elevated NO_3^- concentrations in the surface waters was manifested on 17 May along transect A (Figure 7b), during an interval when the effluent was positively buoyant (Figure 6a). The lack of lateral uniformity (e.g., transect A) in the Metro signature was recurring, including those for interflows, reflecting the details of short-term variations in transport of the discharge, mediated by the

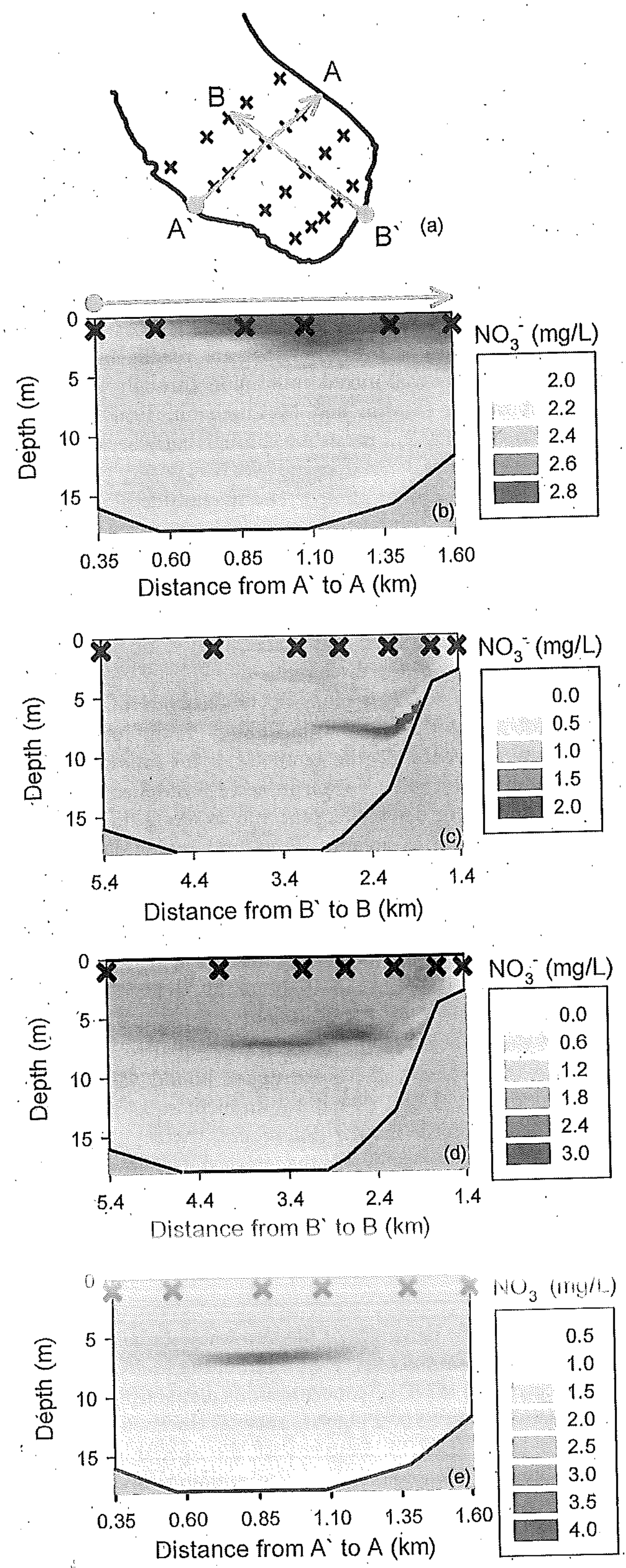

Figure 7—Gridding transects for ISUS profiling and length/depth patterns of NO_3^- for selected cases in 2010: (a) gridding transects on Onondaga Lake, with the two thick arrows depicting those used in the patterns of this figure (transects A and B); (b) length/depth patterns of 17 May along the lateral transect (A) depicting an overflow from Metro, (c) length/depth patterns of 28 June along the longitudinal transect (B) depicting an interflow from Metro, (d) length/depth patterns of 16 August along the longitudinal transect (B) depicting an interflow from Metro, and (e) length/depth patterns of 16 August along the lateral transect (A) depicting an interflow from Metro.

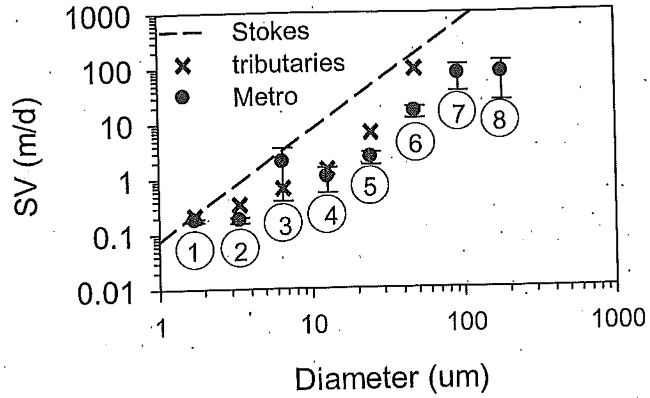

Figure 8—Relationships between determinations of SV and particle size for eight size classes (circled numbers) of Metro particles, as averages with range bars from five experiments. Stokes' Law conditions (temperature = 20°C, particle density = 2.6 g/cm^3) and mean for tributary experiment results included for reference.

dynamics of ambient mixing/transport processes (e.g., circulation currents, surface waves, interval waves, and turbulence; Martin and McCutcheon, 1999). Clear interflow (i.e., plunging) signatures of the Metro effluent were manifested along the longitudinal axis (transect B) in the lake's southern basin on 28 June (Figure 7c) and 16 August (Figure 7d), during the interval of negative buoyancy (Figure 6a). On the second of these days the interflow was laterally confined to mid-lake areas (transect A), away from the near-shore zones (Figure 7e). Moreover, the entry depths of the interflows were only slightly shallower than the neutral buoyancy depths on those days (Figures 6b, and 7c and d). The extent of this apparent closure in depth needs to be tempered by the potential effects of internal wave activity (Martin and McCutcheon, 1999) that could influence the depth of the interflow signatures. Signatures of Metro plunging were mostly recurring during the negative buoyancy interval of June through August. Clear evidence of an interflow entry of Metro effluent was found for 10 of the 14 griddings of NO_3^- collected over this interval.

Particle Settling Velocities (SVs). The results of the multiple size class (numbered, 1 to 8) SV measurements are presented as the mean values of the five experiments, with range bars to depict the variability (Figure 8). A general pattern of increasing SVs for increasing particle size (d_g, geometric mean) was observed, consistent with theory for homogeneous particle populations (Davies-Colley et al., 2003; Dietrich, 1982). The average SVs for d_g = 1.74 μm (size class No. 1), d_g = 6.56 μm (No. 3), and d_g = 180.00 μm (No. 8) were 0.18, 1.97, and 78.3 m/d, respectively. Thus the Metro particle population demonstrated a wide range of SVs that depended on the sizes of the

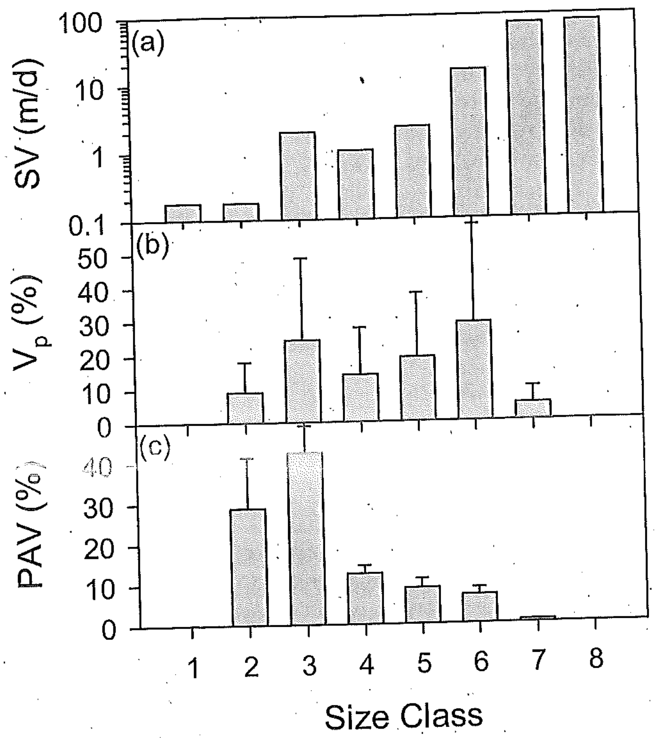

Figure 9—Results from particle characterization of Metro effluent as part of settling velocity (SV) experiments, for eight size classes: (a) SV, (b) particle volume, V_p, % of total, and (c) PAV, % of total.

individual particles. Moreover, substantial variability within the individual size classes was observed amongst the five weekly samples (Figure 8), suggesting temporal variability in the settling characteristics of unrecovered Actiflo® floc.

Stokes' Law (i.e., homogeneous spheres) SVs as a function of d_g (for a particle density of 2.6 g/cm^3; e.g., clay minerals), and observations for Onondaga Lake tributaries dominated by clay minerals, are included for reference (Figure 8). All of the experimental determinations of SVs for Metro, as well as the tributaries, were systematically lower than Stokes values. Deviations were the least for the smallest size class, while deviations for the larger classes were much greater (Figure 8). Moreover, SVs for Metro tended to be lower than those for the tributaries, deviating more from Stokes settling. The deviations from Stokes settling were qualitatively consistent with those reported previously based on this instrumentation (Agrawal and Pottsmith, 2000; Perkins et al., 2007). The smaller deviations from Stokes settling observed for the tributaries can mostly be attributed to the non-spherical morphometry of these particles, associated with the platelet shapes of clay minerals (Davies-Colley et al., 2003). The Metro particles also were generally non-spherical (Figure 3b). However, the greater deviation from Stokes settling of the Metro particles likely is attributable to the added effect of their aggregate (or floc) character, causing the effective density to be lower than solid particles because of the presence of void spaces (Droppo et al., 1997). These interpretations are consistent with the particle flocculation/aggregation that prevails in the Actiflo® process.

It is important to consider the SV results in the context of the relative contributions of the size classes to metrics of bulk characteristics. Two metrics are considered here, total particle volume concentration (V_p) and PAV. These two alternatives are presented to accommodate the fundamentally different representations of particulate phosphorus associations as being gravimetrically or particle surface area (e.g., adsorption) based (Chapra, 1997; House 1990). Paired distributions of average SV, V_p and PAV determined from the experiments are presented according to the size classes for the Metro particles (Figure 9a to c). The smallest and two largest size classes are unimportant as these did not make noteworthy contributions to total V_p (Figure 9b) or PAV (Figure 9c). Substantial variability in the contributions of the noteworthy size classes was observed (Figure 9b and c; vertical bars are ± one standard deviation). The major differences in size dependency of the V_p and PAV metrics is a result of simple geometry, as V_p depends on the cube of a particle dimension compared to the square dependency of PAV (Peng and Effler, 2007). A PAV-based approach would emphasize the effects of the smaller size classes; e.g., size classes 2 (d_g = 3.38 μm) and 3 (dg = 6.56 μm) represented approximately 75% of the total PAV (Figure 9c). In contrast, these size classes represented only about 35% of the total V_p (Figure 9b). Thus either a gravimetric or adsorption-based, multiple settling class, modeling strategy can be supported to represent this process within the lake from such settling velocity experiments.

Synthesis and Management Perspectives

The findings from the array of measurements and experiments presented here establish the clear operation of the diminishing effects of limited bioavailability of particulate phosphorus, plunging, and rapid settling of discharged particles that together make the effective phosphorus load substantially lower than the total load for this municipal wastewater effluent. While differences in the details and magnitude of the effects certainly will occur for various effluents and receiving water cases, the approaches and the effective loading concept described here are broadly applicable. The extra level of effort necessary to implement the effective phosphorus loading approach is justified for particularly acute problems of cultural eutrophication, with high rehabilitation costs, to guide appropriate targeting of sources and more reliable predictions of ecosystem response. In the context of phosphorus TMDL analyses, adoption of this approach dictates its application for all noteworthy phosphorus sources. For example, two major tributaries for the lake demonstrate even greater negative buoyancy than Metro and are known to plunge to stratified depths (Effler et al., 2009b). Moreover, a limited number of bioavailability experiments on the tributaries in the mid-1990s established that noteworthy fractions of these particulate phosphorus sources were bioavailable (Effler et al., 2002), in sharp contract to the present situation for Metro. Accordingly, similar studies to those reported here for Metro are underway for Onondaga Lake's major tributaries to represent effective phosphorus loading from those inputs. Those findings together with the results presented here for Metro will support the forthcoming revision of the phosphorus TMDL for Onondaga Lake.

The SAX characterizations of Metro effluent particles, contrasted to the natural particle populations of the tributaries and lake, provided compelling evidence that the particulate phosphorus in this discharge did not contribute to total phosphorus in the upper waters of the lake. The particulate

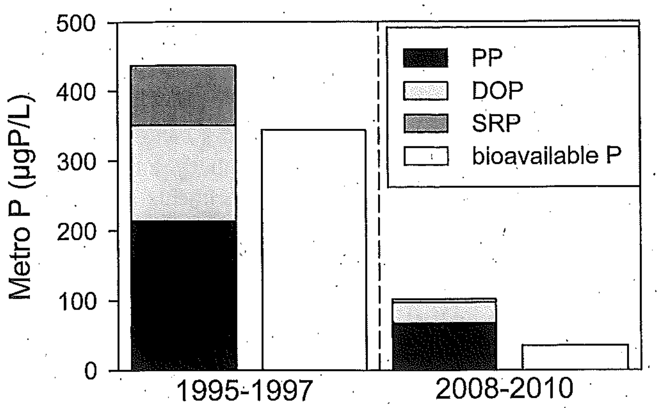

Figure 10—Metro phosphorus concentrations according to fractions and estimated bioavailable phosphorus, compared for the intervals 1995 to 1997 and 2008 to 2010.

phosphorus in the effluent was entirely associated with distinctive Fe-rich particles formed in the Actiflo® process that were not recovered in phosphorus treatment. These distinctive particles were not found in the upper waters of the lake, apparently because of local deposition losses. Such losses are generally consistent with the direct measurements of particle size and SVs reported here, that were large and rapid, respectively. Moreover, the potential recycle of phosphorus from these particulates that may reach the anoxic hypolimnion is not a concern because of limited vertical mixing in the lake in summer and rapid flushing of the lake following fall turnover (Effler et al., 2002). These findings indicate that pursuit of further optimization of phosphorus treatment at Metro, in the context of an effort to more routinely meet the receiving water goal, should focus on the dissolved fraction. Further reductions in the particulate phosphorus fraction would not contribute to reaching that goal. The non-bioavailability of the Metro particulate phosphorus is attributable to the strong chemical association (mostly $FePO_4$ precipitate; Metcalf and Eddy, 2003) established between phosphorus and iron during treatment that is not susceptible to the biochemical mobilizing processes of enzymatic conversion or mineralization that prevail in the bioassays and oxic receiving waters (DePinto, 1982). This lack of bioavailability of particulate phosphorus associated with iron-phosphorus precipitates is expected to prevail elsewhere, which likely explains similar observations of non-bioavailability reported for certain European facilities that have chemical precipitation treatment (Ekholm and Krogerus, 2003). However, discharges of such unavailable particulate phosphorus would remain a concern in cases where it is not lost to local deposition, as it could contribute directly to total phosphorus concentrations and thereby affect the status with respect to regulatory limits.

In the context of bioavailable phosphorus loading, the relative reduction in loading from Metro from the most recent treatment upgrade (Actiflo®/$FeCl_3$) was substantially more than indicated by the decrease in total phosphorus (Figure 10). A nearly 4.5-fold (77%) decrease in the average total phosphorus in the effluent was achieved from the 1995–1997 interval to 2008 to 2010. The reduction in the bioavailable phosphorus, assuming the dissolved phosphorus was, and continues to be, available (particulate phosphorus was 58% bioavailable for 1995 to 1997 interval; Effler et al., 2002), was more than 11-fold (91%). The availability of the DOP fraction has been reported to be incomplete in certain surveys (Ekholm and Krogerus, 2003), and deserves direct evaluation in the future for this effluent and the other major inputs. Presently, the Metro discharge of TDP represents approximately 38% of the estimated total TDP load to the lake (Effler et al., 2009b), a partitioning estimate that does not accommodate the effective attenuating factors of plunging or potential incomplete bioavailability. Before the recent upgrade in treatment, Metro represented approximately 86% of the total TDP load. Increasingly, the tributaries may represent appropriate targets for further reductions in effective phosphorus loads, given the approach of contemporary phosphorus treatment at Metro to existing technological limits and the increased relative contribution of the tributaries to phosphorus loading that attended the recent treatment upgrade (Effler et al., 2009b).

In general, the overall quantitative effect of the various attenuating influences is not amenable to determination without appropriate representation within a mechanistic water quality model framework that accommodates the simultaneous operation of these, as well as other, source and sink processes (Chapra, 1997). The presented findings are in appropriate forms to represent the attenuating processes and guide related simulations within such mechanistic model frameworks. In this particular case, the lack of bioavailability of particulate phosphorus from Metro and its absence from the upper waters of the lake has simplified the situation for this form of phosphorus from this source. However, the intermediate level of bioavailability of the particulate phosphorus from the tributaries (Effler et al., 2002) will require a robust representation by such a model that quantifies the simultaneous operation of each of the attenuating processes. The quantitative effects of plunging of the Metro discharge remains uncertain with respect to its extent, dynamics, and associated attenuating benefit, dictating a robust hydrodynamic analysis. Residence time of this inflow within stratified depths is a key feature, as greater duration would support potential kinetic transformations of dissolved forms to less available particulates. A return to use of a subsurface discharge(s) for the Metro effluent has potential benefit with respect to an increased plunging effect that should be quantified through application of an appropriate hydrodynamic model. Moreover, the potential for increased attenuating benefit of a deep Metro discharge through a diffuser, to further enhance retention in stratified layers (Owens and Effler, 1996), should be evaluated.

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