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Changes in Deposition of Phytoplankton Constituents in a Ca^{2+} Polluted Lake†

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Systematic reductions in the deposition rate of organic C, N, P, and chlorophyll (Chl) are documented for Ca^{2+} polluted, culturally eutrophic, Onondaga Lake, NY, based on analyses of weekly sediment trap collections over the May–October interval for 10 years of the 1980–1992 period. Inputs of both nutrient-rich domestic waste and industrial salt waste (including Ca^{2+}) decreased over this period. Constituent ratios of the collected sediment indicate phytoplankton biomass was the dominant source of the deposited organic C, N, and Chl. Substantial decreases in downward fluxes of these constituents occurred starting in 1987: 37, 42, 25, and 54%, on average, for organic C, N, P, and Chl, respectively. These reductions were driven primarily by the decreases in the lake's salinity and Ca^{2+} concentration, that resulted from the closure of a soda ash manufacturing facility (1986), rather than decreases in water column P concentrations from reductions in domestic waste loading. Three different mechanisms for the decreased deposition, related to the reductions in salinity and Ca^{2+} concentration, are considered: (i) decrease in coating of phytoplankton with $CaCO_3$ precipitate, (ii) increased grazing of phytoplankton by large cladocerans, and (iii) decreases in coagulation of phytoplankton. The greater loss of phytoplankton biomass through deposition, driven by salt waste inputs from the industry, exacerbated the lake's problem of high primary production. This response is consistent with ecological theory for nutrient saturated phytoplankton growth but has not previously been demonstrated on a whole-lake basis.

Introduction

Deposition is a major pathway by which nutrients and organic carbon are removed from the productive layers of stratifying lakes and reservoirs. Quantifying downward flux (or deposition rate; units of g m^{-2} d^{-1}) is recognized as fundamental to representing this feature of the cycles of these constituents (*1*) and invaluable in the development of related mechanistic water quality models (*2, 3*). The three approaches to quantify sedimentation rates are the analysis of sediment trap collections, application of sediment dating techniques, and material budget calculations (*4*). The use of sediment traps represents the only viable and widely available means of resolving the short-term (interannual and seasonal) dynamics of deposition and thereby its interaction with various ecosystem drivers (*5*). Protocols for trap studies, such as design and deployment, have approached a standardization over the last two decades (see reviews (*1, 5*)).

Sinking flux is regulated by the standing crop of particles as well as particle characteristics such as size, shape, and density and ambient physical characteristics, including viscosity and turbulence (*6*). These primary variables are influenced by the composition and physiological condition and rate of production of plankton (*7–9*) and by water chemistry (*10–12*). Solution chemistry influences deposition by regulating particle stability (*12*), and thereby coagulation (aggregation of particles), mediating the precipitation of insoluble materials, and influencing the composition of plankton communities (*13, 14*). Coagulation increases particle sizes and thus settling velocities, thereby increasing downward flux (*11, 12*). Divalent cations such as Ca^{2+} are particularly effective in destabilizing particles, mostly through compression of the double-layer (*13*), thereby promoting coagulation, while dissolved natural organic substances act as stabilizing agents (i.e., retard coagulation (*11, 12*)). High Ca^{2+} concentrations may also lead to oversaturation with respect to calcite and promote $CaCO_3$ precipitation and deposition of other particle types that serve as heterogeneous nucleation sites (*15*). The zooplankton community is known to be particularly sensitive to salinity (*13*). Fecal pellets of the various zooplankton groups may have widely different settling properties (*16*).

Long-term (multiple year) sediment trap data sets for systems where forcing conditions for deposition have changed are rare. Here we document the systematic reductions in the downward fluxes of organic C, N, P, and chlorophyll (Chl) in a salt polluted, culturally eutrophic, lake based on 10 years of sediment trap collections. Potential causes for the reductions are identified and evaluated based on attendant water column and process information for the same interval. The broader implications are considered within the context of related ecological theory.

Study System

General. Onondaga Lake is a dimictic system located within metropolitan Syracuse, NY. It has an area of 12.0 km^2, a volume of 131 × 10^6 m^3, a mean depth of 12 m, and a maximum depth of 20 m. The lake flushes rapidly, e.g., the average for the 1971–1998 period was 4.0 flushes y^{-1} (*17*), on a completely mixed basis. Onondaga Lake is an alkaline system (alkalinity ~ 3 mequiv L^{-1} at spring turnover; 18), naturally enriched in Ca^{2+}, Na^+, and Cl^-, as the watershed has extensive deposits of limestone and gypsum, and NaCl brines (*19*). Paleolimnological evidence indicates the lake was oligomesotrophic before European settlement in the late 1700s (*20*). The lake is presently highly polluted (e.g., several numeric standards are routinely violated) because of inputs of domestic and industrial waste (*21*).

Ionic Waste, Lake Concentrations, and Dry Weight Deposition. Soda ash (Na_2CO_3) was produced along the western shore of the lake by the Solvay Process over the period 1884–1986. Large quantities of ionic waste (primarily Cl^-, Ca^{2+}, and Na^+) were generated and discharged to the lake (*21*). Approximately 1.5 kg of this waste reached the lake for every kilogram of Na_2CO_3 produced (*22*). The annual average load of this salt waste to the lake for the past decade

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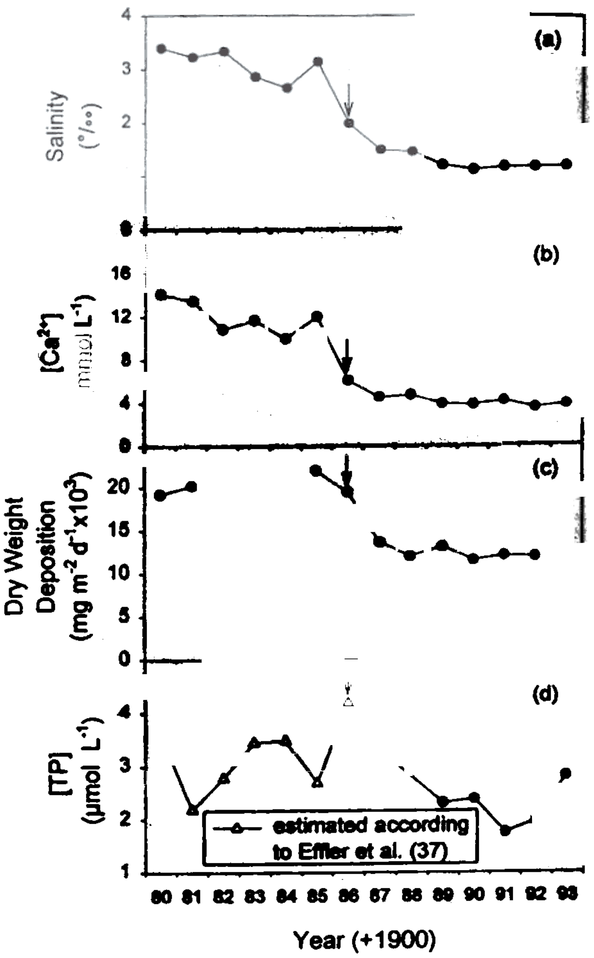


FIGURE 1. Time series for Onondaga Lake for the 1980–1993 period, average values for April–October interval except as noted: (a) salinity (21), (b) Ca^{2+} concentration (21), (c) average dry weight downward flux (May–October) (29), (d) TP concentration (May–September) (34). Arrows depict closure of soda ash facility in 1986.

of the industry's operation was ~1 million metric tons (*21*). The residual (postclosure) load from soda ash production through the early 1990s was about 13% of the preclosure load (*21*). Approximately 30% of the present total Ca^{2+} load to the lake is residual waste from this industry (*23*).

Salinity and concentrations of Ca^{2+} were extremely high in the lake before closure of the soda ash facility because of the salt waste inputs (*21*). The annual average salinity of the lake was about 3°/₀₀ before closure of the plant (Figure 1a); the average Ca^{2+} concentration was ~12 mmol L^{-1} (Figure 1b). Major decreases in salinity and Ca^{2+} concentrations occurred abruptly following closure (Figure 1a,b) because of the abrupt reduction in waste input (*21*) and the rapid flushing of the lake (*24*). The average postclosure values of salinity and Ca^{2+} (starting in 1987) were about 1.1°/₀₀ (Figure 1a) and 4 mmol L^{-1} (Figure 1b), respectively. Seasonal variations in these features occur, primarily associated with the seasonality in the diluting influences of runoff (*23*). Seasonal average levels of salinity and Ca^{2+} would decrease to about 0.7°/₀₀ (*25*) and 2.8 mmol L^{-1} (*26*), respectively, in the absence of the residual waste input. The only other divalent cation present in substantial concentrations is Mg^{2+}; levels of this cation have remained relatively uniform at ~0.8 mmol L^{-1} (*21*). Summer average epilimnetic DOC concentrations have been ~5 mg L^{-1} following closure of the industry (*27*). Limited data available for before closure suggest similar DOC concentrations prevailed in that interval (*28*).

Dry weight deposition before the closure of the soda ash facility was extremely high (average ~ 23 g m^{-2} d^{-1}; from analysis of sediment trap collections; Figure 1c), greater than found in the literature for any other lakes (*29*). This was primarily due to the very high precipitation and deposition rates of $CaCO_3$ (*26*), promoted by the industrial load of Ca^{2+} (lake was continuously oversaturated with respect to solubility of calcite over the spring to fall interval (*18, 30*)). Calcium carbonate represented ~70% of the dry weight deposition before closure (*26*). The summer average dry weight deposition decreased abruptly by ~45% following closure ((*29*) Figure 1c), associated mostly with the reduction in $CaCO_3$ precipitation and deposition that was brought about by the decrease in Ca^{2+} loading (*26, 30*). The postclosure rate of dry weight deposition remains high compared to most lakes (*29*), and $CaCO_3$ continues to be the dominant (60–55%) component (*26*).

A major and abrupt shift in the zooplankton assemblage of the lake was also observed soon after closure of the soda ash facility; species richness increased substantially and large-bodied cladocera (*Daphnia* spp.) replaced cyclopoid copepods as dominants (*31*). This dramatic change in the zooplankton community was attributed primarily to the reduction in salinity and the attendant precipitation of $CaCO_3$, associated with the closure (*31*). High salinity (e.g., > 1°/₀₀) is known to exert selective pressure on the zooplankton community (and particularly cladocera (*13*)), and mineral particles in general (*32*), and $CaCO_3$ particles specifically (*33*), interfere with the feeding of daphnids.

Domestic Waste, Nutrient Concentrations, and Phytoplankton Biomass. Treated domestic waste is discharged directly to Onondaga Lake from the regional treatment facility (Metro). Metro's discharge (average ~ 3.5 m^3 s^{-1}) makes an extraordinary contribution to the hydrologic load to the lake, representing nearly 20% of the total inflow on an annual basis; in many years it is the single largest source of water in late summer (*21*). Metro's effluent represented ~60% of the total annual external load of P and 80% of the N load through the early 1990s, though substantial interannual variations have occurred as a result of differences in treatment performance (*34*). This discharge is responsible for the lake's hypereutrophic state (*21*). Water quality manifestations of hypereutrophy in this system include the following: (i) severe phytoplankton blooms (*21*), (ii) poor clarity (*35*), (iii) rapid loss of oxygen from the hypolimnion (*34*), (iv) subsequent accumulation of reduced byproducts of anaerobic metabolism (e.g., NH_4^+, CH_4, H_2S) (*36, 37*), and (v) severe depletion of dissolved oxygen in the lake's upper waters during the fall mixing period associated with the oxidation of these byproducts (*38*) and the coupled exodus of fish from the lake (*39*).

Concentrations of dissolved inorganic N that can support phytoplankton growth (NH_4^+ and NO_3^-) have remained above levels considered limiting to phytoplankton growth ((*21*) i.e., saturated conditions). Summer average concentrations of total P (TP) in the lake's upper waters, a widely used indicator of trophic state (*40*), varied greatly over the 1987–1993 interval (Figure 1d), though levels remained substantially above eutrophic limits (*34*). The interannual differences were driven largely by differences in the Metro load (*3, 34*); lake concentrations presented for earlier years (Figure 1d) are estimates based on extension of an empirical expression between this load and lake concentration (*34*). Summer average concentrations of Chl, another widely used indicator of trophic state, have also remained well above eutrophic limits (*34*). These values reflect the imbalance of growth (primary production) and loss processes (e.g., grazing, deposition, death). Temporal and intersystem differences in the magnitude of the loss processes, but particularly grazing (*14, 31*), compromise Chl as a surrogate measure of primary production. The decrease in average Chl since closure of the soda ash facility has been attributed to increased grazing pressure from zooplankton (e.g., top-down control) associated with the shift to larger and more efficient feeders (*Daphnia* spp.), driven by reductions in salinity that accompanied closure (*31*), rather than increased nutrient limitation (e.g., bottom-up control).

Methods

Sediment Traps. Sediment trap collections were made in Onondaga Lake during the late spring to early fall (stratified) interval during the years 1980–1981 and 1985–1992. Trap design and deployment followed the unifying recommendations of a number of investigators, as reviewed by Bloesch (*5*). The traps were cylindrical PVC with an aspect ratio (height ÷ diameter) of six. The diameter of the traps was 4 cm through 1987; thereafter the diameter was 7.6 cm. Essentially equivalent dry weight deposition rates were obtained with these two trap designs for deployments made in the lake in 1993 (*29*). Three replicate traps were suspended vertically within the metalimnion (~10 m depth), except in 1980 (17 m), in 20 m of water. The metalimnetic deployment has the advantage of minimal ambient turbulence (*41*), thereby reducing the potential for compromising the efficacy of trap collections (*5*). Essentially equivalent cumulative fluxes of dry weight were obtained for deployments made over a wide range of depths (10–17.5 m) below the epilimnion in 1993 (*29*), supporting the incorporation of the 1980 results (deeper collections) in this long-term analysis. The deployment site has been found to be generally representative of lake-wide conditions for a number of limnological and water quality parameters (*21*). Trap collections were made frequently to minimize degradation during deployment (*1*), weekly since 1985, but more frequently in 1980 and 1981.

Resuspension of particles deposited in the traps is unlikely based on the findings of Lau (*42*). Further, there was no evidence of particle loss during retrieval of the traps; the traps contained relatively low turbidity water overlying the deposited solids. After collection and decanting, the solids were frozen until analysis.

Sample Handling, Analysis, and Calculations. Aliquots for analysis were taken from homogenized trap samples from each of the three cylinders. The aliquot for organic C and N analysis was acidified to a pH of 1.0 for 24 h to dissolve the collected $CaCO_3$ (*26*). The acidified aliquot was then filtered through a 1.5 μm (934AH) pore size glass fiber filter, dried (103 °C), and weighed. Carbon and N analyses were conducted with a Carlo Erba Model EA1108 elemental analyzer.

Separate aliquots were analyzed for TP (*43*) and Chl (*44*). The method for Chl did not differentiate chlorophylls from phaeophytin (chlorophyll degradation products formed primarily by zooplankton grazing and found mostly in zooplankton fecal pellets (*45*)). Paired analyses of a subset of trap collections from the lake demonstrated a near equivalence of Chl with the sum of chlorophyll *a* and phaeophytin (*21*).

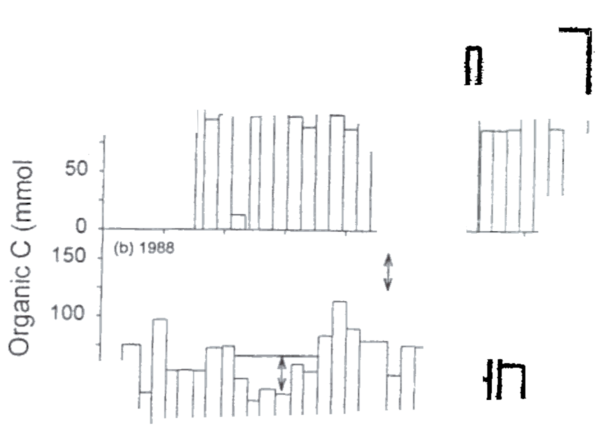
The downward fluxes (DF) of organic C, N, P, and Chl are represented as areal rates (units of mmol m^{-2} d^{-1} or mg m^{-2} d^{-1}). The fluxes were determined for the individual deployment intervals from the mass of constituents collected in the traps (W; mg), the sediment trap deployment interval (T; d), and the area of the trap opening (A; m^2), according to the relationship

$$DF = W/(A \cdot T) \qquad (1)$$

The fluxes for P for 1987 have been presented previously (*3*).

Results and Discussion

Temporal Patterns and Stoichiometry of Depositing Particles. Detailed time-series of the downward flux of organic



C are presented for 1985 (Figure 2a) and 1988 (Figure 2b) to illustrate features of the temporal patterns of deposition in the lake before and after closure of the soda ash facility. Similar levels of precision for replicate trap deployments were observed here (average coefficient of variation (CV) = 10–15%) as reported in the literature (*1*), supporting the position that substantial short-term and seasonal variations in deposition have occurred in Onondaga Lake (Figure 2). Similar patterns were generally observed for all four of the constituents within both years ($r > 0.57$). Thus, the seasonal minimum observed for organic C in June and early July of 1988 (Figure 2b) also occurred for N, P, and Chl. These minima in downward fluxes have been a recurring (annual) feature since closure of the facility, with only modest variation in timing (*21*). They coincide with minima in water column concentrations of phytoplankton biomass (and maxima of large daphnids (*21, 31*)), described as "clearing" events or phases (*46*). Clearing events are widely observed in productive lakes and are attributable to effective grazing by zooplankton, particularly by large-bodied cladocerans (*31, 46, 47*). Substantial year-to-year differences in the temporal details of downward flux occurred both before and after closure of the facility.

Deposition rates of organic C were shifted distinctly lower in 1988 compared to 1985 (Figure 2a,b). Review of longer-term downward flux data (average for the May–October interval) for the period of record depicts substantial reductions in deposition rates of all the constituents starting in 1987 (Figure 3), the year following the closure of the soda ash facility. Rather uniform average annual fluxes prevailed both before and after closure of the facility except for Chl (Table 1), which decreased progressively over the 1987–1992 interval. The decreases in average fluxes from the 1980–1986 to the 1987–1992 interval for organic C, N, P, and Chl were 37, 42, 25, and 54%, respectively. These decreases are significant at the 0.01 level.

The stoichiometry of the collected particulate material, represented by constituent ratios, is valuable in identifying its origins (*48*). The average values of the ratios of organic C to N and organic C to Chl, both before and after closure of the soda ash facility (Table 2), are consistent with the composition of phytoplankton biomass (*48*), indicating that was the dominant source (e.g., rather than terrigenous detritus) of those three constituents collected in the traps. In contrast, the ratio of organic C to P was substantially lower than typically reported for phytoplankton (*48*), suggesting other types of P-bearing particles also contributed to the

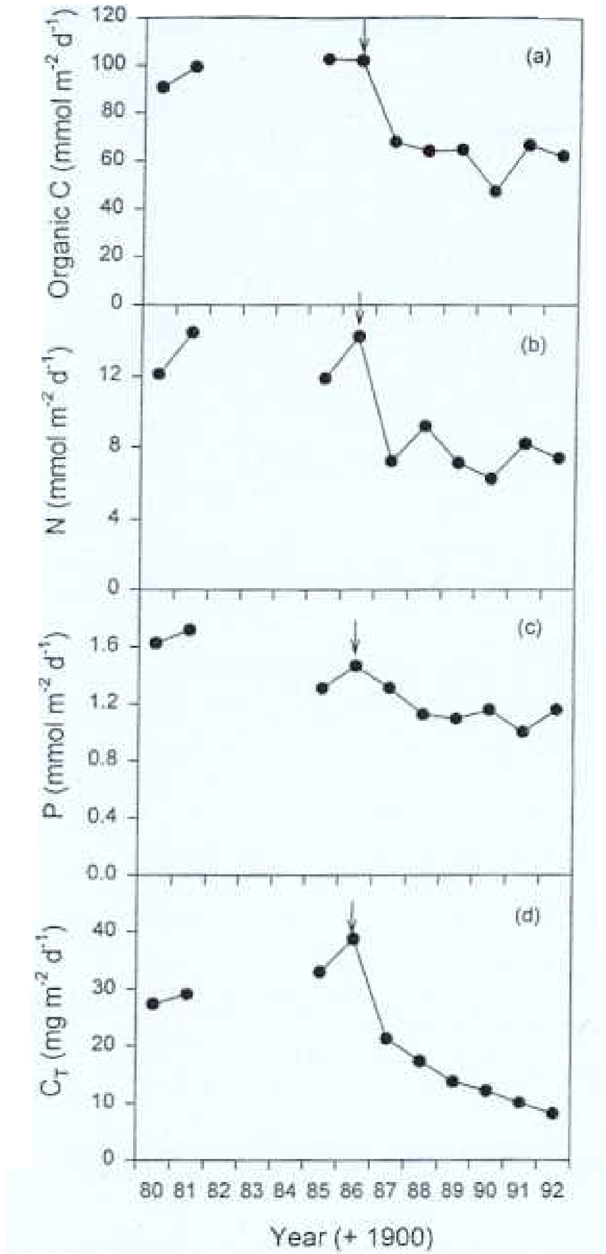


FIGURE 3. Time series for Onondaga Lake for the 1980–1992 period, average downward fluxes for the May–October interval: (a) organic C, (b) N, (c) P, and (d) Chl. Arrows depict closure of soda ash facility in 1986.

downward flux of this constituent. This was also manifested in the distinctly smaller reduction in deposition in P observed following closure compared to the other three constituents (Figure 3c). A progressive decrease in the cellular content of Chl in phytoplankton is indicated for the postclosure interval (Figure 3a,d), though the organic C to Chl ratio remained well within the range commonly reported for phytoplankton biomass (*48*). The cellular content of Chl is known to be sensitive to ambient environmental conditions, including the availability of light and nutrients (*48*).

Causes for Reductions in Deposition. The systematic changes in potential forcing conditions (Figure 1) offer an unusual opportunity to identify and evaluate the cause(s) and mechanism(s) responsible for the observed conspicuous reductions in deposition of phytoplankton constituents (Figure 3). Rarely are signatures in aquatic ecosystems so clearly manifested (Figures 1 and 3).

	flux (mg m^{-2} d^{-1})			
	1980–1986			
constituent	$\bar{x}$	CV^a	$\bar{x}$	CV^a
organic C	1185	5.7	748	12.0
N	184	10.3	106	13.3
P	49	11.6	36	9.0
Chl	32	15.8	14	35.2

^{a} CV – coefficient of variation (%) of the averages for the specified period.

The case is strong that the reductions in deposition were driven primarily by reductions in salt waste loading (lake salinity and Ca^{2+} concentration) rather than decreases in domestic waste inputs (lake TP concentration). The temporal pattern of lake TP concentration (Figure 1d) diverged from the pattern observed for the deposition of phytoplankton constituents (Figure 3). The downward flux of organic C has been used as a measure of primary production/trophic state (*49, 50*). Indeed, lake managers often seek to reduce algal growth and hence deposition of organic C, and thereby improve the oxygen resources of hypolimnia of eutrophic lakes, by reducing external loading of P (*51*). However, reduced primary production will only occur if concentrations of P are reduced to levels that limit growth. There is ample evidence that essentially nutrient saturated conditions (i.e., nonlimiting) were maintained in the productive layers of the lake throughout the study interval with respect to the availability of P to support phytoplankton growth. Under such conditions phytoplankton growth was insensitive to the variations in P loading from Metro and the coupled changes in ambient P concentrations that occurred (Figure 1d). The lowest summer average TP concentration over the study period (1.8 μmol L^{-1}; 1991; Figure 1d) was well above the level Auer et al. (*52*) found to be essentially saturating for the phytoplankton community of Green Bay, Lake Michigan. Based on detailed analysis of ambient dissolved and cellular P pools, Connors et al. (*53*) concluded only a very small degree of P limitation of phytoplankton growth occurred in Onondaga Lake over the 1989–1992 interval. Yet greater reductions in external P loading are necessary to reduce P concentrations in Onondaga Lake to levels that would limit phytoplankton growth (*53, 21*).

One feature supporting the position that the reductions in deposition flux of these constituents were driven primarily by reductions in salt waste is the similar character of the long-term patterns in salinity, Ca^{2+} concentration, and deposition. Abrupt changes following closure of the soda ash facility, with approximate uniformity both before and after (Figures 1a,b and 3), were observed for all these parameters. More importantly, there are at least three mechanisms related to the reductions in salinity and Ca^{2+}

that are consistent with the observed decrease in the downward flux of these constituents: (i) decrease in coating of phytoplankton with $CaCO_3$ precipitate, (ii) increased grazing by large cladocerans, and (iii) decreases in coagulation of phytoplankton.

Regulation of deposition of phytoplankton-based constituents by $CaCO_3$ precipitation is superficially supported by the correlated time series of downward fluxes of $CaCO_3$ (*26*). Wodka et al. (*54*) hypothesized that calcite formed on the surfaces of phytoplankton in the upper waters of the lake associated with localized elevated pH in microzones surrounding the cells, thereby enhancing the deposition of these particles (*55*). Coating of certain cyanobacteria with $CaCO_3$ (*56*) and diatom-$CaCO_3$ associations (*49*) have been documented elsewhere. However, continued application of individual particle analysis techniques (scanning electron microscopy, with and without automated image analysis and X-ray energy spectroscopy), does not support this as a major particle-type association of settling phytoplankton in Onondaga Lake (*57*). Only limited occurrences of this association were observed ((*57*) with diatoms, that have been a codominant group during spring and fall since closure of the facility). Other particle types, particularly clay minerals, are common nucleation sites (heterogeneous nucleation) for $CaCO_3$ in Onondaga Lake (*57*). We cannot eliminate the possibility that this mechanism and the observed reduction in $CaCO_3$ precipitation/deposition (*26*) contributed to the decrease in deposition in phytoplankton constituents (Figure 2), though it seems unlikely that it was a major factor.

Contributions of nonphytoplankton components to the downward flux of P in the lake indicated by stoichiometric considerations (Table 2) are at least in part attributable to $CaCO_3$ precipitation. Coprecipitation of P with $CaCO_3$ is known to occur in hardwater systems (*58, 59*), and its occurrence in Onondaga Lake is supported by the results of chemical equilibrium modeling (*60*) and sequential chemical extraction analyses of fractions of particulate P (*61*) collected in trap samples. Further, P mobilized through decomposition during deposition has been demonstrated to be taken up (e.g., sorbed) by particles (*62*). Findings reported by Penn and Auer (*61*) support the position that a substantial fraction of the deposited P was not associated with phytoplankton. Only about one-third of the P in sediment trap collections following closure of the soda ash facility was classified as biogenic (e.g., phytoplankton).

The shift to increased grazing pressure on the phytoplankton community by zooplankton in response to decreased salinity and $CaCO_3$ precipitation (*31*) represents an indirect food web effect from the reduction in salt waste loading that has influenced the deposition of phytoplankton constituents. Zooplankton fecal material can play a major role in the downward transport of phytoplankton constituents from productive layers (*16*). While increased grazing should be expected to convert more phytoplankton biomass to zooplankton solid waste, the settling characteristics of this material differs among the major groups of zooplankton (*16*). Copepods (dominant before closure) produce well-packaged fecal pellets that settle substantially faster than the rather diffuse egestion products of cladocerans (dominant after closure (*16*)). However, no conspicuous signature of the increased grazing (and attendant respiration) and decomposition of cladoceran fecal material (e.g., before it settles) was manifested in the CO_2 pool of the productive layers of the lake following closure of the soda ash facility. Rather, increases in pH have been reported (*30*). Restructuring of the phytoplankton community by the major shift in the zooplankton community (*31*) may also have caused changes in the settling velocities (m d^{-1}) of phytoplankton (63). The return of late summer nuisance blooms of filamentous cyanobacteria (and near elimination of more edible chlorophytes) following closure, not observed in the lake since the early 1970s (*21*), has been attributed to the shift to the more efficient grazing cladocerans (*31*), as these forms of phytoplankton are essentially inedible for daphnids (*64*). Certain cyanobacteria are known to have lower settling velocities than most other common phytoplankton (*63*).

The annual minimum in deposition in early summer since closure, coincident with the clearing event, indicates at least a modest contribution (e.g., Figure 2b) from the shift in the zooplankton community to the systematic long-term decrease in deposition (Figure 3). However, certain features of the paired short-term and long-term time series of plankton biomass and composition (*21, 31*) and deposition (Figures 2 and 3) over the study period depict uncoupled distributions, indicating changes in these features of the phytoplankton community have not been the primary mechanism for the reduced downward fluxes. For example, the seasonal patterns in deposition rates for the individual years appeared to be largely insensitive to the substantial interannual variation in seasonal patterns of plankton composition and biomass observed both before and after closure (*21, 31*). For example, systematically lower deposition rates were not observed annually during the late summer cyanobacteria blooms following closure. Further, average deposition rates remained uniform within the intervals before and after closure (Figure 3), despite substantial interannual variations in average Chl concentrations (*3, 4*) and zooplankton biomass (*31*).

The observed change in the downward flux of phytoplankton constituents is consistent with decreased coagulation that would be expected by the 3-fold reduction in the concentration of Ca^{2+} (and unchanging DOC concentrations) brought about by the closure of the soda ash facility (*15*). The decrease in the Ca^{2+} concentration represents a reduction in the destabilizing effect of this divalent ion on particles in the lake. Coagulation has been found to be a controlling mechanism in deposition elsewhere. The higher dry weight downward flux and nearly equal organic C flux in Lake Zurich ($[Ca^{2+}] \sim 1.2$ mmol L^{-1}, $[DOC] \sim 1$ mg L^{-1}), compared to more productive Lake Sempach ($[Ca^{2+}] \sim 1.2$ mmol L^{-1}, $[DOC] \sim 4$ mg L^{-1}), was attributed to more rapid coagulation in the epilimnion of Lake Zurich associated with its low DOC (i.e., low stablilizing effect on particles) concentration (*12*). Major increases in coagulation potential, as measured by the particle stability factor (*12*), were reported (*10*) for lake water in laboratory experiments where Ca^{2+} concentrations were increased over the range of values observed in Onondaga Lake. Weilemann et al. (*12*) measured stability factors in several lakes that supported the position Ca^{2+} ions act to destabilize particles and thereby promote coagulation. Zones of increased deposition are widely observed in portions of estuaries where ionic concentrations increase associated with the destabilizing influence of these ionic constituents (*65*).

Several features of deposition in Onondaga Lake support this mechanism as contributing to the observed systemic reductions, though separating it conclusively from the potential effects of $CaCO_3$ precipitation is difficult. The downward fluxes of the phytoplankton constituents reported for Onondaga Lake for both before and after closure of the soda ash facility (Table 1; Figure 3) are high compared to fluxes measured in other lakes. For example the postclosure fluxes exceed the rates reported for 15 lakes in New York, Pennsylvania, and Connecticut, that represent a wide range of trophic state (*7*). The organic C fluxes in the post-closure interval exceed most values reported for other eutrophic lakes, including Rotsee (*49*), Frains Lake (*50*), Third Sister (*50*), Lake Lugano (*66*), Lake Hallwil (*67*), Lake Zug (*2*), and Lake Sempack (*12*). The only two exceptions (*68, 69*) encountered in our review of the literature were other hardwater eutrophic lakes, where high Ca^{2+} concentrations probably also promote deposition. Comparisons of settling velocities (m d^{-1}), calculated as the quotient of downward flux and the corresponding overlying water column concentration of the constituent (*2, 54*), is more valuable than flux as it represents settling characteristics of the contributing particle assemblage. Unfortunately, only a limited number of settling velocity values have been reported. The estimated settling velocity of particulate organic C (POC) in Onondaga Lake in 1989 (1.05 m d^{-1}, based on unpublished POC data for the epilimnion) substantially exceeded values reported for other lakes in the literature (*2, 7, 70*). The high settling velocity for Onondaga Lake is consistent with the unusually high Ca^{2+} concentrations that continue to prevail (Figure 1b) and the coagulation mechanism for enhanced deposition.

Coagulation probably also contributed to the regionalization of clay mineral content reported for the surficial sediments of the lake (*71*). The highest concentrations of clay minerals were documented in portions of the lake adjacent to a tributary (*71*) that contributes ~75% of the clay mineral load (*72*) but only 35% of the total hydrologic input (*21*). Concentrations of Ca^{2+} in the lake have been greater than in this tributary; ~4-fold greater before closure and about a third higher since closure. Similar localized deposition of clays has been reported in estuaries as riverine (freshwater) particles encounter the destabilizing influence of increased ionic concentrations from seawater (*65*).

Implications. Anthropogenic inputs of ionic constituents, particularly divalent ions, that cause distinctly higher ambient concentrations, can be expected to promote increased deposition of phytoplankton in lakes through increases in coagulation (*11, 12*). However, in nutrient limited systems the production and subsequent deposition of organic material is ultimately controlled by the supply (e.g., loading rate) of the limiting nutrient (usually P (*73*)). Calcium pollution would be expected to shorten the residence time of phytoplankton and other small particles (*74*), and thereby increase average clarity, in nutrient limited lakes. The systematically higher deposition rates in Onondaga Lake before closure, caused by ionic waste inputs of the industry, could only be sustained by higher levels of production of phytoplankton. Under the nutrient saturated conditions that have prevailed throughout the study period (*53*) because of domestic waste pollution (*34*), enhancement of deposition by Ca^{2+} pollution translated to the promotion of increased phytoplankton production in Onondaga Lake. This response is consistent with theory; it is axiomatic that a systematic increase in any phytoplankton loss process for a nutrient saturated system would stimulate additional production (*75*). This has been demonstrated here on a whole-lake basis for the first time through this long-term sediment trap program, that took advantage of the effects of industrial and domestic waste inputs and changes in the loading of salt waste.

The increased deposition of organic material caused by Ca^{2+} pollution during the facility's operation exacerbated Onondaga Lake's problem of degraded oxygen resources. In the absence of this added deposition, the period of hypolimnetic anoxia would have been shorter and depletion of oxygen in the lake's upper waters during fall turnover less severe (*34, 37*). Improvements in the lake's oxygen resources are anticipated from the documented reductions in deposition.

Further decreases in deposition are a reasonable expectation in Onondaga Lake for the case of the elimination of the residual Ca^{2+} pollution, based on the findings of Weilenmann et al. (*12*). They found coagulation was an important factor in deposition in Lake Sempach, where the Ca^{2+} concentration is > 3 times lower and DOC is 20% lower than in Onondaga Lake (*11*). Additional reductions in deposition may also occur if the supply of P from domestic waste is reduced adequately in forthcoming treatment upgrades to cause substantial reduction of the production of phytoplankton (nutrient limitation).

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