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ONONDAGA LAKE MONITORING REPORT, 1993

by

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SUMMARY: 1993 MONITORING PROGRAM

Tributaries and Discharges

Review of the monthly flows reported for Onondaga Creek at Dorwin Avenue, from the perspective of the 40 year record available for that gauging site, shows that the runoff to the lake in April of 1993, which caused substantial flooding, was the highest recorded to date. Flows in the summer months were near the median values observed over the 40 year record.

Comparison of chloride (Cl^-) concentration/flow observations for Ninemile Creek at Lakeland in 1991 and 1992 to the relationship established in 1989/1990 indicates the "loading potential" for Cl^- and related materials from the waste bed area has remained unchanged over this period.

About a 70% increase in total phosphorus (TP) loading from METRO occurred in 1993 associated with the increased "by-pass" of incompletely treated wastewater from the facility to the lake. Most of it was associated with the unusually high flow received by the facility during spring; although about 20% of the additional load was associated with construction upgrade, that was distributed more evenly through the year. Comparison of soluble reactive phosphorus to total phosphorus (SRP/TP) ratios observed for various sources over the 1991-1993 interval indicates the bioavailability of the P loads from METRO and Ley Creek is greater than the inputs received from Onondaga Creek and Ninemile Creek.

Concentrations of total Kjeldahl nitrogen (TKN) and total ammonia ($T\text{-}NH_3$) were unusually low in the METRO effluent in the

spring of 1993 because of the very high runoff. Seasonal nitrification during summer and early fall was less continuous and complete, than in recent years, and nitrite (NO_2^-) concentrations in the facility's effluent became high during this period.

Standards

The status of the lake with respect to water quality standards and the TP guideline was reviewed for several parameters for the late 1980's to 1993 interval. The monitoring program for Onondaga Lake for 1993 has documented the continuing violations of state standards for clarity, dissolved oxygen (DO), NO_2^-, and free ammonia (NH_3), and the exceedance of the TP guideline. The margins of the violations for NO_2^- and NH_3, and the exceedance of the TP guideline, are quite large. The NO_2^- violations appear to be largely coupled to inputs received from METRO. Clarity conditions have improved dramatically since 1986, but this is attributed largely to "top-down" (e.g., food web) effects, not management of nutrient loading (i.e., "bottom-up"). The stability of those conditions is unknown. No clear trend in the annual lake-wide oxygen depletion emerges from review of the last nine years of observations.

Stratification and Vertical Mixing

Onondaga Lake failed to completely turnover in the spring of 1993 because of salinity stratification, that was set up under the ice-cover by the plunging of ionically enriched inflow from Ninemile Creek, and exacerbated by the unusually high runoff of April. This represents a reversion to conditions before closure

of the soda ash/chlor-alkali facility, in that failure of spring turnover was observed in a number of years before closure of the facility. Unpublished data from 1994 indicates that the lake is again not experiencing complete spring turnover. A conspicuous manifestation of this phenomenon is the unusually low bottom water temperatures that are maintained through stratification compared to years in which complete turnover occurs. The recent failures of spring turnover are not attributed to changes in ionic loading, rather, they reflect an impact of the continuing saline pollutant loadings from the most recently active wastebeds along Ninemile Creek, that are manifested only under certain meteorological conditions (i.e., irregularly).

Estimates of vertical mixing in 1993, based on analysis of successive temperature profiles, were of the same general magnitude, and had the same general seasonal structure as reported previously for the 1987-1992 period. Minimum coefficient values were calculated for the peak stratification interval of mid-summer.

Trophic State

Changes in summer average epilimnetic TP concentrations in the lake in recent years have largely been regulated by changes in loading from METRO. Improvements in clarity and chlorophyll concentrations in recent years are instead coincident with reductions in lake concentrations of Cl^-, which preceded substantial reductions in TP loading from METRO. No worsening in clarity and chlorophyll was observed in 1993, despite the increase in TP concentrations.

Dissolved oxygen was already depleted from the lower waters at the start of the monitoring program in mid-April of 1993 because of the failure of spring turnover to occur. This represents a reversion back to conditions commonly observed before closure of the soda ash/chlor-alkali facility. The failure to replenish the oxygen resources of the lower layer in spring prohibited estimation of the "area hypolimnetic oxygen deficit "(AHOD) for 1993. As observed in previous years, oxygen-demanding reduced species accumulated progressively in the hypolimnion following the onset of anoxia, and the concentrations of the primary by-products of anaerobic metabolism, methane (CH_4) and hydrogen sulfide (H_2S), increased with depth in the anoxic layers. The accumulation rate of CH_4 was ~15% lower than observed in 1989 and 1990, but the accumulation rate of H_2S, and the total lake content of this specie, was greater.

Strong temporal variations were observed in chlorophyll, SRP, and dissolved organic P (DOP) concentrations in the upper waters of the lake in 1993, as documented in recent years. The "clearing event" following the spring phytoplankton bloom appeared to be uncoupled from nutrient limitation. Concentrations of SRP increased abruptly during clearing events. Analysis of the paired time series of these constituents indicates the utilization of the DOP pool by the lake's phytoplankton in late summer to sustain the rather high biomass concentrations in that interval, and thereby the inadequacy of SRP as a sole indicator of P availability in the lake. These findings are consistent with those reported for recent years.

CaCO3

Precipitation of calcium carbonate ($CaCO_3$) from the upper waters of the lake was depicted during the summer of 1993 by a conspicuous decrease in the concentration of DIC. The corresponding signal from the distribution of calcium (Ca^{2+}) was modified by the continuing waste inputs of this material; concentrations increased progressively and then "leveled-off" during the interval of decrease in DIC. As observed in other years before and after closure of the soda ash/chlor-alkali facility, essentially the entire water column remained oversaturated with respect to calcite ($CaCO_3$) over the spring to fall interval of 1993; a condition described as extraordinary in the literature. Thus there was no tendency for dissolution of deposited $CaCO_3$.

Optics

Pronounced temporal variations in the concentrations of light attenuating materials, and thereby measures of light penetration, were observed over the spring-fall interval of 1993. These dynamics were regulated largely by the timing of runoff events and phytoplankton growth and loss processes. Particularly low light penetration was observed during the high runoff/flood period of April, apparently as a result of the influx of large quantities of terrigenous particles. Very high clarity (Secchi disc values of about 7 m) was observed during two "clearing events".

CHAPTER 1

PROGRAM STATEMENT: ONONDAGA LAKE MONITORING, 1993

Background

Onondaga Lake is located in metropolitan Syracuse, New York, the most urbanized area of central New York. The lake is oriented along a northwest - southeast axis (Figure 1-1). The length along this axis is 7.6 km; it has a maximum width of 2 km. The lake has two basins. The surface area of the lake is 12.0×10^6 m^2, the volume is 131×10^6 m^3, the mean depth is 10.9 m, and the maximum depth is 19.5. The watershed area of the lake is 642 km^2; it lies almost entirely within Onondaga County. The climate within the watershed can be described as continental, and somewhat humid. Substantial year-to-year variations in rainfall are experienced in the watershed. The lake discharges to the Seneca River through a single outlet. The Seneca River combines with the Oneida River at the Three Rivers junction to form the Oswego River. The Oswego River flows into Lake Ontario at the City of Oswego.

The early development of the NaCl industry adjoining Onondaga Lake was largely responsible for the growth of Syracuse in the late 1700's and 1800's. Local salt and limestone deposits and the availability of Onondaga Lake for the disposal of related wastes fostered the establishment of the soda ash industry. Production by the Solvay Process began on the western shore of the lake in 1884. Later this facility expanded into a larger and more diverse chemical manufacturing operation, described here as the soda ash/chlor-alkali facility. Large quantities of ionic

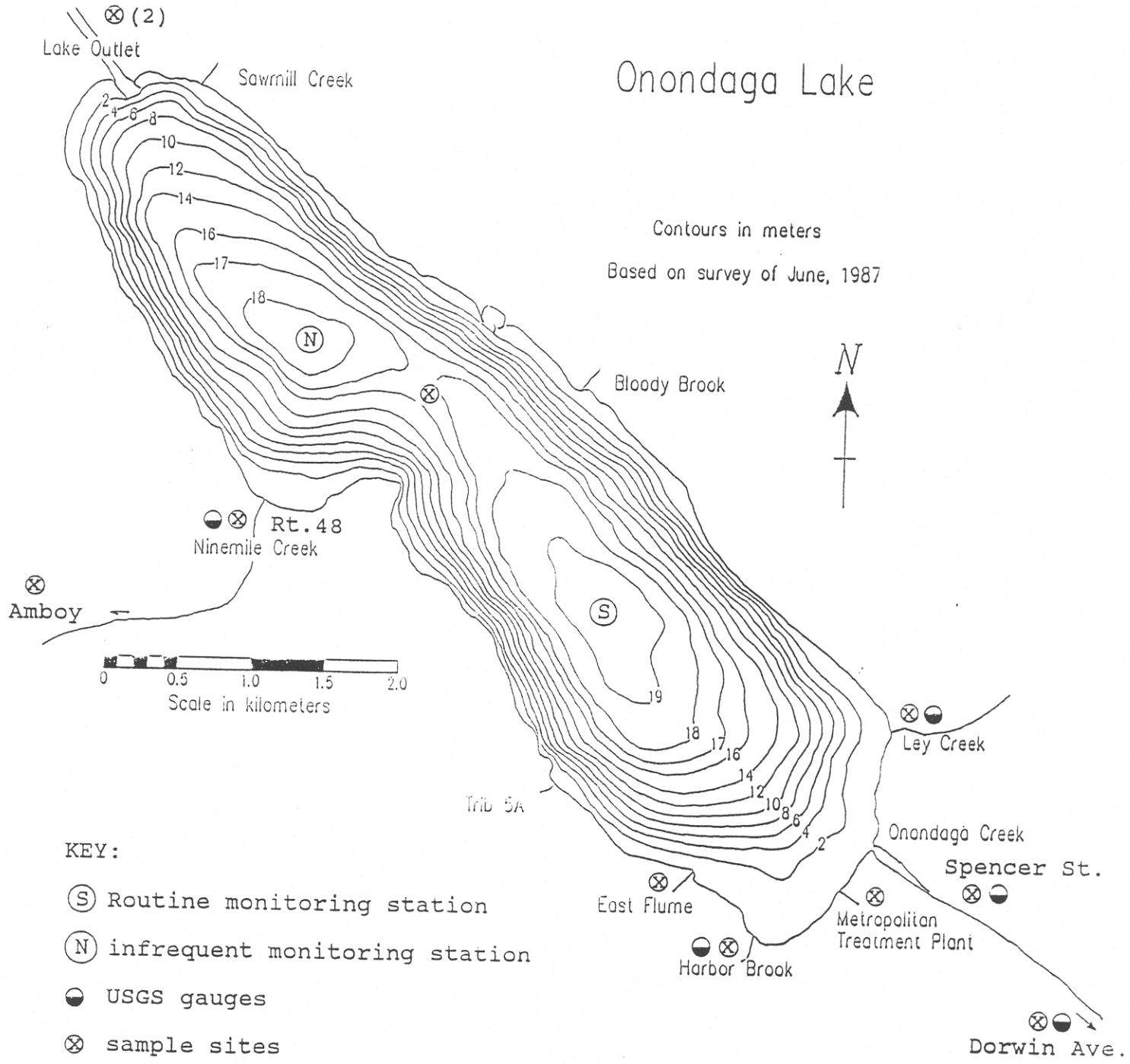


Figure 1-1. Bathymetric map of Onondaga Lake (Owens 1987), with tributaries, gauging stations, and monitoring locations identified.

(Cl^-, Na^+, and Ca^{2+}) waste drained off the waste beds (now cover about 2000 acres) from soda ash production and entered the lake. The average daily loading of this ionic waste to the lake over the 1970-1980 period was 2.5×10^6 $kg \cdot d^{-1}$. Also approximately 75,000 kg of mercury were discharged to the lake from the facility, over the 1946-1970 period. The soda ash/chlor-alkali facility closed in 1986.

Onondaga Lake has received the municipal effluent and a large portion of the industrial waste of the region for more than a century. By the turn of the century pollution already had a profound impact on the lake. By the late 1890's the lake lost its commercially valuable cold water fishery. Ice harvesting was banned for health reasons in 1900. Untreated sewage entered the lake via its tributaries until after 1900. Swimming in the lake was banned in 1940. Fishing was banned in the lake in 1970, after discovery of high concentrations of mercury in fish flesh.

A combined sewer system conveyed both sanitary and stormwater flows to treatment facilities on the southern shore of the lake in the early 1900's. Domestic waste treatment in the surrounding metropolitan area has been consolidated, and increasing levels of treatment (presently tertiary treatment for phosphorus removal) have been applied over the years, though the effluent continues to be discharged to the southern end of the lake. Dilute raw sewage continues to enter tributaries to the lake during runoff events via hydraulic relief structures in the sewer system known as combined sewer overflows.

Monitoring Program Goals

The goals of the Onondaga Lake Monitoring Program are:

1) to determine the status of Onondaga Lake with respect to water quality standards,
2) to identify significant changes in lake and tributary water quality,
3) to establish natural variability in environmental forcing conditions and implications for water quality of the lake,
4) to quantify key processes for water quality model development, testing, and application,
5) to assure continuity in key features of the long-term (since late 1960's) monitoring data base for the lake, and
6) to support testing and enhancements of water quality models, including the total phosphorus model, the ammonia model, the dissolved oxygen model, and the chloride model.

1993 Monitoring Program Statement

General. Features of the 1993 monitoring program for the lake are described below. Much of the evolution of, and justification for, this program is documented in UFI's contributions to the peer-reviewed literature concerning this system (Appendix I), and in the "State of Onondaga Lake" report prepared by UFI for the Onondaga Lake Management Conference. A number of features of the program have evolved from development of water quality models for the lake. Note that features of

long-term monitoring have been included to maintain continuity in the program that was initiated in the late 1960's. Despite several data problems of the earlier program (e.g., Walker 1991), portions of it have been continued to support identification of long-term trends. However, the scope of the earlier long-term monitoring program is not capable of addressing a number of important lake processes and phenomena, and of supporting continued testing and enhancements of the existing water quality models.

Lake Program. The parameters included in this Onondaga Lake monitoring program are presented in Table 1-1. The proposed program focuses on the environmental problems of the lake, including: potentially toxic concentrations of nitrogen species, depletion of oxygen resources, poor clarity, ionic pollution, and excessive sedimentation. Linkages between the program parameters and the environmental problems of the lake are identified in Table 1-1.

Meteorological conditions, including incident irradiance, wind direction , and rainfall, were also included because of the importance of natural variations in these environmental forcing conditions in causing substantial year-to-year (stochastic) and seasonal variations in stratification (Owens and Effler 1989), material loading (Heidtke and Auer 1992, Effler and Whitehead 1995), and water quality (e.g., Canale et al. 1993). A full compliment of field limnological and meteorological instrumentation and research vessels were utilized to conduct the monitoring program (Table 1-2).

TABLE 1-1: Justification for Lake Parameters for Onondaga Lake Monitoring Program

Parameter	Linkages to Water Quality Issues/Standards					Comments	References
	Dissolved Oxygen	Clarity	Nitrogen/ Toxicity	Mercury	Ionic Poll./ Sediment		
DO	x			x		anoxia, violations	Effler et al. 1986a, Effler et al. 1988
temperature	x	x	x			Lake stratification, vertical mixing estimates	Effler et al. 1985a, Effler et al. 1990, Wodka et al. 1985, Owens and Effler 1989
pH			x	x	x	free ammonia, over-saturation $CaCO_3$	Effler and Driscoll 1985a, Effler et al. 1990
specific conductance					x	-	-
redox potential	x	x		x		sediment-water interactions, anoxia	Driscoll et al. 1995
Secchi disc		x				violations	Field and Effler 1983a, Effler et al. 1984, Auer et al. 1990, Effler and Perkins 1995, Perkins and Effler 1995
underwater irradiance		x				partitioning light absorbing and scattering components	Effler et al. 1991b, Effler and Perkins 1995, Perkins and Effler 1995
TP, SRP, TDP	x	x				eutrophication, P-cycle, limiting nutrient	Effler et al. 1985a, Devan and Effler 1984, Connor et al. 1994, Auer et al. 1990
total ammonia, NO_3, NO_2, total nitrogen, TKN, particulate N	x		x			free ammonia and NO_2 violations, N-cycle, N/P ratio	Effler et al. 1990, Brooks and Effler 1994

chlorophyll, POC	x	x	x		x	phytoplankton biomass, total microbe biomass	Field and Effler 1983b, Auer *et al*. 1990, Effler 1995d
gelbstoff		x				light absorbing component	Effler *et al*. 1984, Effler and Perkins 1995
turbidity (total and acidified)		x			x	estimation of $CaCO_3$ turbidity/scattering	Effler 1987b, Effler *et al*. 1991b, Effler and Perkins 1995
TSS		x		x	x	solids budget	-
alkalinity					x	charge balance, $CaCO_3$ precipitation	Effler and Driscoll 1985, Driscoll et al. 1995
Cl				x	x	charge balance, surrogate measure of salinity and ionic strength, hydrologic budget, industrial pollution	Effler *et al*. 1985b, Owens and Effler 1989, Effler and Driscoll 1986, Effler *et al*. 1991a
Ca, Na					x	charge balance, industrial pollution, $CaCO_3$ precipitation, P-cycling	Effler and Driscoll 1985, Effler 1987, Driscoll *et al*. 1993, Driscoll et al. 1994
CH_4, gas ebullition	x					fall DO depletion, anaerobic metabolism	Effler *et al*. 1988, Addess and Effler 1995
Fe^{2+}, Fe (dissolved)	x	x				anaerobic metabolism, P-cycling	Driscoll *et al*. 1993, 1995
DOC, POC	x			x		organic C cycle, microbial	Effler 1995d, Driscoll et al. 1994

TABLE 1-2: Field Measurements, Instrumentation and Boats, UFI

Field Instrumentation

Parameter	Instrument	Detection Limit	Accuracy
dissolved oxygen	Hydrolab Surveyor 3	0.0 mg/1	± 0.2 mg/1
temperature	Hydrolab Surveyor 3	- 5.0 °C	± 0.15 °C
pH	Hydrolab Surveyor 3	-	± 0.2 pH units
specific conductance	Hydrolab Surveyor 3	0 mS/cm	± 1% of range (0-100 mS/cm)
redox potential	Hydrolab Surveyor 3	-	± 1% of range
irradiance downwelling PAR	LI-COR Model LI-192 SB	-	1% full range
X-Y location	GPS	-	± 30 ft.
depth	SITEX Depth Finder HE32MK2	-	± 0.5 ft.
clarity	Secchi disc	-	-

Boats

Boat	Length	Engine
Boston Whaler	20 ft	150 HP YAMAHA
RV SISU	23 ft	140 HP VOLVO
Sea Ray	17 ft	131 HP VOLVO

Meteorology

Parameter	Instrument
Wind direction and speed	NRG Data Logger 9000/Anemometer - No.40/Direction - No.200P
incident light	LI-COR LI 1000 Data Logger/Sensors: LI-200s and LI-190s

Two sites were monitored, located approximately in the middle of the south and north basins of the lake (Figure 1-1). The south basin site is the primary station; the north basin site was monitored on four occasions. This design is supported by the lack of recurring horizontal gradients for most water quality parameters (e.g., Field 1980, Effler and Driscoll 1986, Effler et al. 1991c). This is reflected in the design of several of the water quality models, that treat the epilimnion of the lake as a single homogeneous segment. The effort at the north basin site was included as a continuing test of this important model assumption, and as a measure of the degree of random spatial variability ("patchiness", common to all lakes) that occurs. The south basin site had a marked buoy during the spring-fall interval. The south and north basin sites correspond to the sites used by UFI and the Onondaga County program for many years.

The frequency of monitoring varied somewhat for the different parameters and with the time of year. The spring to fall (turnover) interval received the most intensive coverage because it has the greatest potential recreational resource value, and it is the interval over which the degraded conditions of the system are most clearly manifested (Effler 1995a). The long-term monitoring program was conducted bi-weekly, and has usually been limited to the April-October interval. UFI has found it necessary to monitor at least weekly over the late spring (e.g., late March to early April) to fall turnover (e.g., third week in October) interval, to achieve a more complete understanding of the system's important characteristics and

regulatory processes. This frequency is particularly desirable to resolve the highly dynamic conditions common to the lake's epilimnion (e.g., Auer et al. 1990, Effler et al. 1990) and the rapid transformations that occur in the hypolimnion (e.g., Effler et al. 1986a, 1988, Driscoll et al. 1995), and to recognize important changes in the system as they occur The basic weekly program was at times augmented by additional monitoring for certain parameters in response to events (e.g., phytoplankton clearing events), or to better delineate processes (e.g., gas ebullition, loss of hypolimnetic oxygen, and loss and recovery of dissolved oxygen during fall turnover).

The onset of complete fall turnover since closure of Allied in 1986 has been the second or third week of October. Recall that the water in the lake at this time is largely flushed out by the critical water quality period of the following spring because of the high flushing rate (Effler and Whitehead 1995). However, the recovery of depleted oxygen concentrations (Effler et al 1988, Gelda et al. 1995) in this period is an important issue. This period is challenging for personnel, boats, and field equipment. The lake was monitored for Hydrolab parameters (see Table 1-3) at a depth interval of 2 m on ten occasions from late October to the first week in December. It was not possible to sample during much of December for safety reasons.

A breakdown of the depths analyzed/sampled for the various parameters is presented for the spring-fall interval Table 1-3. Justification for the depths monitored appears in Table 1-4. Strong vertical gradients in the concentration of a number

TABLE 1-3: Depths and Frequency of Measurements, Spring - Fall Turnover Interval: Onondaga Lake Monitoring Program

Parameter	Depths[1]	Frequency[2]
Field		
DO	1 m int.[3]	weekly
temp	1 m int.	weekly
pH	1 m int.	weekly
spec. cond.	1 m int.	weekly
redox potential	1 m int.	weekly
Secchi	-	weekly
underwater irrad.	variable[4]	weekly
position (lat./long.)	-	weekly
Laboratory		
TP	all depths[5]	weekly
SRP	all depths[5]	weekly
TDP	0,3,6,9,12,15,18 m	biweekly
$T-NH_3$	all depths[5]	weekly
NO_3	all depths[5]	weekly
NO_2	all depths[5]	weekly
TN	all depths[5]	weekly
TKN	0, 15 m	biweekly
Cl	0,3,6,9,12,15,18 m	weekly
H_2S	anoxic depths	weekly
CH_4	anoxic depths	weekly
Fe^{2+}	anoxic depths	weekly
pH	all depths[5]	weekly
alkalinity	all depths[5]	weekly
turbidity (T/A)[6]	all depths[5]	weekly
gelbstoff	1 m	weekly
POC*	0, 15 m	biweekly
Particulate N	0, 15 m	biweekly
chlorophyll	0,1,2,3,4,6,8,9,10,12,15 m	weekly
TSS	0,3,6,12,18 m	weekly
Na*	0,3,6,9,12,15,18 m	biweekly
Ca*	0,3,6,9,12,15,18 m	biweekly
DOC*	all depths[5]	biweekly
gas ebullition	18 m	-[7]

foot notes/Table 4a

* - C.T. Driscoll
1 - triplicate samples at 0 and 18 m
2 - for south station; north station sampled in mid-April, June, August and October
3 - 1 m depth interval
4 - varies according to clarity, downwelling irradiance measured

5 - "all depths" - z,y,w and x of Table 5
6 - total turbidity and turbidity on sample acidified to pH = 4.3
7 - checked at least weekly; needs to be more frequent at times - volume of gas collected is measured, % CH_4 of total is established (Addess 1990)

TABLE 1-4: Sampling Depth Justifications: Onondaga Lake Monitoring Program, Spring to Fall Turnover (see Table 4b).

Depth	Basic Monitoring/Process Program to Support Models	Long Term Data Base
0	z	x
1	y	
2	z	
3		x
4	z	
5		
6	z	x
7		
8	z	
9	v	x
10	z,v	
11	v	
12	z,v	x
13	v	
14	z,v	
15	v	x
16	z,v	
17	v	
18	z,v	x
19	w,v	

Key: z - basic program, oxic water column; supports lake content calculations and certain process studies
y - near surface heterogeneity
w - sediment - water interactions
v - depths sampled for reduced species during anoxia; support for estimates of sediment fluxes and partitioning of sediment oxygen demand (vertical interval depends on interval of anoxia)
x - long-term (late 1960's) monitoring program (most parameters)

of important constituents develop within the hypolimnion during summer, requiring close vertically spaced samples and analyses to support reliable estimates of the total lake content of these constituents. Further, strong vertical gradients in a number of important constituents also occur irregularly in the upper layers during calm periods and following storm events. This program design (Table 1-3) has been found to adequately accommodate these vertical distribution characteristics and to support identification and analysis of key lake processes and the development and testing of the Onondaga Lake water quality models (e.g., Canale et al. 1995a, Doerr et al. 1995, Gelda et al. 1995).

Tributaries. The location of the tributaries to Onondaga Lake are shown in Figure 1-1. It is important to monitor the tributaries of the lake to support estimates of material loading. These loads are used in mass balance/material budget analyses, and those for certain constituents drive the existing water quality models for the lake (e.g., Canale et al. 1995a, Doerr et al. 1994, 1995, Gelda et al. 1994). Tributary monitoring also supports the evaluation of pollutant sources along Onondaga and Ninemile Creeks, evaluation of flow/concentration relationships, and identification of temporal changes in loading of certain constituents (Effler and Whitehead 1995). Note that analyses conducted by the laboratory at the Metropolitan Sewage Treatment Plant (METRO) form a key component of the nitrogen and phosphorus tributary monitoring data base. In recent years this facility has contributed approximately 90% of the ammonia and 60% of the

total phosphorus loads received by the Lake (Effler and Whitehead 1995). These constituents are measured daily as part of the facility's permit; TKN is measured twice per week. Other parameters monitored at the facility as part of its permit requirements include: BOD_5, TSS, fecal coliform bacteria, pH, TDS, settleable solids, and residual chlorine. Detailed effluent flow data are also available for METRO.

Four tributaries of the lake are continuously gauged for flow near their mouths, Ninemile Creek, Onondaga Creek, Ley Creek, and Harbor Brook (Figure 1-1). Only about 10% of the surface inflow to the lake (exclusive of the Seneca River inflow) is ungauged.

The tributaries were monitored biweekly (i.e., 26 occasions) over the January-December interval of 1993. Additionally, the METRO effluent was monitored twice per week for nitrate (NO_3^-) and nitrite (NO_2^-), a practice that should be continued until these analyses are added to the facility's permit requirements. A listing of the parameters analyzed at each of the monitored tributary locations is presented in Table 1-5. As with the in-lake program, the tributary program focuses on the prevailing environmental problems of the lake. The Amboy (an upstream) site is included for Ninemile Creek to estimate material loadings from the waste bed area (by difference, e.g., Effler et al. 1991). The Dorwin (an upstream) site is included to partition the rural and urban loads from Onondaga Creek (e.g., Heidtke and Auer 1992, Effler and Whitehead 1995). The two outlet stations are included to assess the occurrence of the bidirectional flow phenomenon

TABLE 1-5: Proposed Onondaga Lake Tributary Program, 1993

Parameter	Tributary Site[5]									
	METRO[1]	ONON/DOR[1]	ONON/SPEN[1]	NINE/AM[1]	NIN/RT48[1]	LEY[1]	HAR[1]	EASTFL[1]	OUT1[1]	OUT3.5[1]
Field										
DO	x	x	x	x	x	x	x	x	x	x
temp	x	x	x	x	x	x	x	x	x	x
pH	x	x	x	x	x	x	x	x	x	x
spec.cond.	x	x	x	x	x	x	x	x	x	x
Laboratory										
Cl	x	x	x[3]	x	x	x	x	x	x	x
TP	x[2]	x	x[3]	x	x	x	x	-	x	x
SRP	x	x	x[3]	x	x	x	x	-	x	x
NO_2	x[4]	x	x[3]	x	x	x	x	x	-	-
NO_3	x[4]	x	x[3]	x	x	x	x	x	-	-
TN	x	x	x[3]	x	x	x	x	x	-	-
$T\text{-}NH_3$	x[2]	x	x[3]	x	x	x	x	x	-	-
TSS	x	x	x[3]	x	x	-	-	-	-	-
pH	x	x	x[3]	x	x	x	x	x	-	-
alkalinity	x	x	x[3]	x	x	x	x	-	-	-
DOC*	x[3]	x	x	x	x	x	x	-	-	-

* - by C.T. Driscoll/SU; monthly

1 - Tributary Monitoring Sites/Key: see Figure 1
- METRO -
- ONON/DOR - Onondaga Cr. at Dorwin Ave.
- ONON/SPEN - Onondaga Cr. at Spencer St.
- NINE/AM - Ninemile Cr. at Amboy
- NINE/RT48 - Ninemile Cr. at Rt. 48
- LEY - Ley Cr. at Park St.
- HAR - Harbor Brook at Hiawatha
- EASTFL - East Flume
- OUT1 - Lake outlet at bridge, 1 m depth
- OUT3.5 - Lake outlet at bridge, 3.5 m depth

2 - checks on parameters measured routinely as part of METRO permit

3 - triplicate field samples analyzed at this location

4 - sampled twice per week,to document extent and seasonality of nitrification at METRO

5 - all samples are grab-type, collected from mid-channel, except METRO which as a flow-weight composite

(Owens and Effler 1995) in the outlet, and support estimates of material export.

CHAPTER 2

TRIBUTARIES AND DISCHARGES

Background

Recently Effler and Whitehead (1995) reviewed the hydrology of Onondaga Lake and pollutant concentrations and loading conditions of the lake's discharges and tributaries. Selected features of this analysis are reviewed in this section.

Hydrology. A hydrologic analysis of the lake was conducted based on a comprehensive twenty year record of continuous gauging of the principal inflows and lake level. The average surface inflow for the 1971-1989 period was estimated to be 16.5 $m^3 \cdot s^{-1}$. Less than 10% of this inflow was not continuously gauged. The net inflow/loss associated with precipitation/evaporation processes is very small by comparison, and there is no evidence that exchange with the groundwater system is a significant component of the lake's hydrologic budget. The largest sources of water annually to the lake are Ninemile Creek and Onondaga Creek; together they contributed nearly 65% of the surface flow received over the 1971-1989 interval. The third largest source of water (19%) has been the METRO effluent; much of this water comes from outside of the Onondaga Lake watershed. Substantial interannual variations in tributary flows are observed due to year-to-year differences in runoff.

Strong seasonal variations in hydrologic loading from the fluvial inputs are observed, however, the METRO discharge remains uniform by comparison. The highest rates of tributary inflow occur in March and April. The minimum usually occurs in the

July-September interval. Thus the METRO discharge contributes relatively more to total inflow during the critical water quality period of summer (25% on average over the June-September interval). The METRO discharge was the single largest source of water to the lake for the month of August in 7 years over the 1971-1989 period. Lake level, on both an annual and seasonal basis, is strongly positively correlated to total inflow. This is largely a manifestation of the regulation of the lake's level by dam control of the level of the Seneca River.

Onondaga Lake is a high flushing rate lake; the average flushing rate for the 1971-1989 period (assuming a completely-mixed system) was 3.9 flushes$\cdot$yr^{-1}. This greatly exceeds rates of flushing reported for the Finger Lakes. The average annual flushing rate of the lake would have been about 3.2 flushes$\cdot$yr^{-1} without the METRO discharge. The high flushing rate has important implications for remediation efforts, as it causes the response time (the time it takes to reach a new steady state) to be short (< 1 year). On average, the lake flushes through more than once during the March-April period. During the summer stratification period, the epilimnion is flushed through about three times under average flow conditions.

<u>Pollutant Loading</u>. Tributaries and METRO are enriched in waste constituents. Fecal contamination enters the lake primarily from CSO's which discharge, during runoff events, mostly to Onondaga Creek, but also to Ley Creek and Harbor Brook. The METRO discharge is enriched in domestic waste constituents; particularly noteworthy are the very high loads of ammonia

($T\text{-}NH_3$) and total phosphorus (TP) discharged to the lake. Localized inputs of ionic waste (Cl^-, Na^+, and Ca^{2+}) and $T\text{-}NH_3$, materials common to Solvay Process waste, continue to be received by Ninemile Creek, in the area of the waste beds, and subsequently by the lake. The relationships between concentrations of Cl^-, Na^+, and Ca^{2+} below the most recently active wastebeds on Ninemile Creek have remained largely unchanged since before closure of the soda ash/chlor-alkali facility, and similar to those documented for the Solvay waste bed overflow during the facility's operation (i.e., inconsistent with the ionic composition of natural NaCl brines in the watershed), thereby establishing the industrial waste origins of these materials. Concentrations of these materials are linearly proportional to the inverse of flow in Ninemile Creek; such relationships are described as dilution curves. Dilution curve characteristics are usually manifested downstream of localized continuous inputs such as wastewater discharges are groundwater seeps.

The major source of suspended solids is Onondaga Creek (Effler et al. 1992). In contrast to the dilution curve constituents, suspended solids (SS) concentrations increase in the creek with increasing flows, associated largely with the "scouring" of upstream deposits, much of which originated from sediment discharges from the mud boils in the Tully Valley. There is no evidence that the SS load from Onondaga Creek has systematically changed since the early 1980's. Total phosphorus concentrations in the tributaries have not demonstrated strong

concentration/flow relationships. Total phosphorus concentrations increase in Onondaga Creek as the stream passes from upstream rural areas to the downstream urban area. Particularly dramatic increases were documented during a low flow period when an adjoining sewer line was broken.

Daily time series of loads have been developed from both special intensive and routine monitoring programs to support predictive lake water quality models for Cl^-, TP, and nitrogen (N) series (Effler and Whitehead 1995). METRO is the major source of all the N species to the lake. Nearly 75% of the total N load, and 90% of the T-NH_3 load, to the lake is from METRO. The second largest source of T-NH_3 is the waste bed area of Ninemile Creek. Approximately 60% of the TP load received by the lake since the late 1980's is from METRO. This corresponds to an average effluent TP concentration of 0.6 $mg \cdot L^{-1}$. The second largest source of TP to the lake is Onondaga Creek, mostly because of the substantial inputs received by the urban portion of the stream (Heidtke and Auer 1992). The continuing discharge from the Solvay waste beds is estimated to represent about 55, 40, and 30%, respectively, of the current total loadings of Cl^-, Na^+, and Ca^{2+} to Onondaga Lake.

<u>1993</u>. We will extend here certain features of the tributary/discharges analysis of Effler and Whitehead (1994) to include 1993. Specific features to be addressed include:

1. review of the seasonal hydrology of Onondaga Lake, in 1993,
2. evaluation of the extent of change since 1989 in the

ionic waste loading "potential" from below the Allied waste beds,

3. development of daily time series of TP and N species loads from METRO in 1993 from plant-operating records and supplemental sampling,

4. development of estimates of daily time series of total loading from all surface inflows in 1993 of Cl^-, TP, and N species; capable of supporting the extension of water quality model testing to 1993.

Hydrology

Wide interannual and seasonal variations in hydrologic loading to Onondaga Lake are experienced because of the strong variability in precipitation common to this region (Effler and Whitehead 1995). High hydrologic loading provides dilution benefits for several pollutants in Onondaga Lake, while it exacerbates the problem of terrigenous loading of suspended solids (Effler and Whitehead 1995).

Comparison of the Onondaga Creek flows at Dorwin Avenue (proximate to the boundary of the City of Syracuse) in 1993 to the documented period of record is valuable in placing the 1993 conditions in a historic perspective. First, the USGS gage at Dorwin is the longest operating station in the watershed (about 40 years). Second, the rating (i.e., credibility) of the station is high. Finally, flows at this location have been found to reflect well those measured in other portions of the watershed. For example, daily flows at Dorwin have been used as a basis to estimate daily flows at other stations in the watershed for

periods when there were missing data (Devan and Effler 1984, Effler and Whitehead 1995). We have expanded this form of correlation analysis to monthly (instead of daily) flows in Figure 2-1, where relationships based on linear least squares regression analysis have been evaluated for the three largest fluvial inputs and the estimated total inflow (including METRO and minor tributaries). The poorest relationship was observed for Ley Creek (Figure 2-1a), the smallest of the three tributaries evaluated. Not surprisingly, the strongest relationship was between Dorwin flow and the downstream Onondaga Creek flow at Spencer Street (Figure 2-1b). The performance for Ninemile Creek was rather strong, intermediate between the other two (Figure 2-1c). Finally the monthly flow at Dorwin is a good predictor of the total monthly inflow to the lake (Figure 2-1d).

The seasonality (monthly) of inflow into Onondaga Lake for 1993 is depicted from the perspective of the 40 year period of record provided by the Dorwin Avenue data base in Figure 2-2. Inflow to the lake in January was higher than normal (10 highest over the 40 year record), but unusually low in February and March. The most striking feature of the hydrology of 1993 was the extremely high inflow in the month of April, the highest inflow for that month for the 40 year period of record. Severe flooding was observed in the region during this period. Inflows in the summer period were generally near the centers of each of the monthly populations (n = 40) for the period of record (e.g., typical).

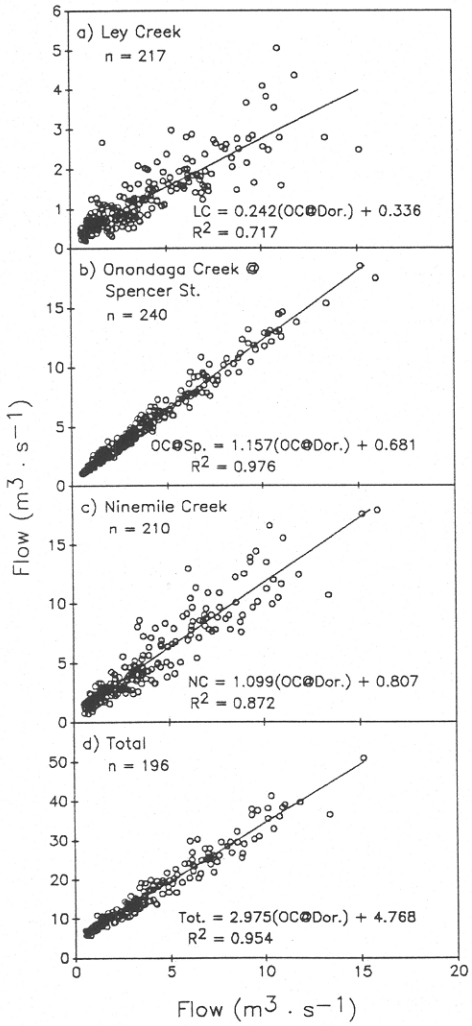


Figure 2-1. Evaluation of relationships between Dorwin/Onondaga Creek monthly flows and other monthly flows to the lake: a) Ley Creek, b) Onondaga Creek at Spencer Street, c) Ninemile Creek, and d) estimated total surface inflow to lake.

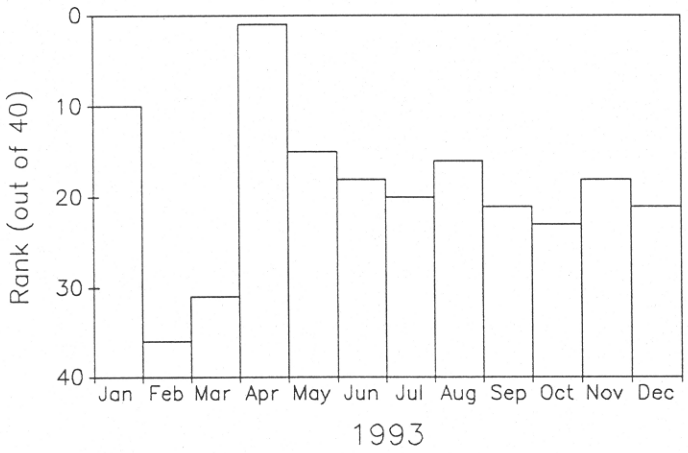


Figure 2-2. Comparison of monthly flows at Dorwin in 1993 to forty year record of monthly flows.

Ninemile Creek Chloride Loading Potential

Large quantities of ionic waste continue to enter Ninemile Creek in the area of the waste beds. At times the creek enters the lake as a plunging inflow (Owens and Effler 1995), which was in part responsible for the failure of spring turnover in 1993 (see Chapter 4). The Ninemile Creek Cl^- load represents approximately 50% of the total to the lake (Doerr et al. 1994, Effler and Whitehead 1995). This source of salinity is largely responsible for the continuing elevated density of the lake compared to the river (Owens and Effler 1995) that results in density stratification and violation of oxygen standards in the river (Canale et al. 1995b).

A strong relationship was found between Cl^- concentration and flow at the Lakeland station of Ninemile Creek (Effler et al. 1991a, Effler and Whitehead 1995), based on nearly daily sampling over a 19 month period of 1989 and 1990. The determined inverse flow (also referred as "dilution model") relationship,

$$[Cl^-] = 1756\ Q^{-1} + 288 \qquad (1)$$

in which $[Cl^-]$ concentration of Cl^- ($mg \cdot L^{-1}$), and Q = flow ($m^3 \cdot s^{-1}$), is presented in Figure 2-3 as the line. This reflects dilution of continuing inputs from the waste bed area (e.g., as leachate and contaminated groundwater) with the stream flow. As a test of potential changes in loading from this area, monitoring data from the Lakeland site obtained in 1991 and 1992 have been added to Figure 2-3. Both years of data continue to fit the same "dilution model". This indicates that the "loading potential" of

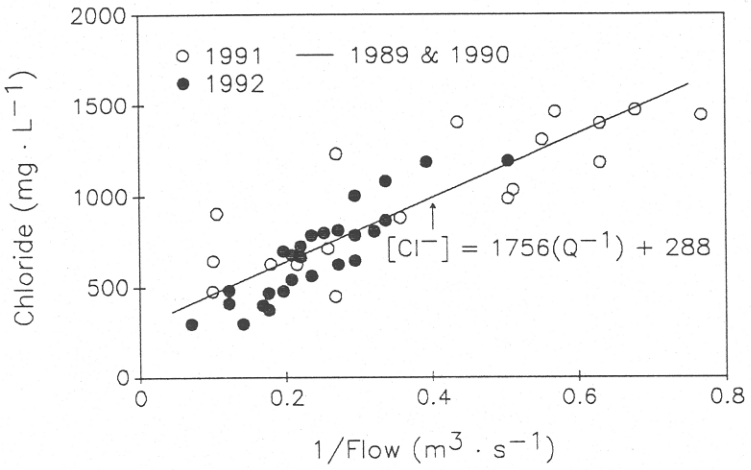


Figure 2-3. Chloride concentration - flow relationship in Ninemile Creek at Lakeland. Line is best fit relationship for intensive 1989/1990 data base; points are observations in 1991 and 1992.

Cl^-, and coupled materials (Effler et al. 1991a, Effler and Whitehead 1995), from the waste bed area along Ninemile Creek has remained essentially unchanged since 1989/1990.

METRO Loading: Phosphorus and Nitrogen Species

There was a noteworthy increase in pollutant loading (particularly TP) from the METRO facility due to increased discharges of incompletely treated wastewater (e.g., "by-pass" of the effluent of primary treated wastewater directly to the lake). There were two components to the increases in the discharge of "by-pass" waste water. The first was associated with the unusually high runoff in the watershed in spring (Figure 2-2). METRO is designed to fully treat up to 120 MGD. Flows that exceed that level receive only primary treatment before being "by-passed" to the lake. Since these "by-pass" events are linked to runoff for this combined sewer system, the discharge of incompletely treated wastewater to the lake from the facility was unusually great in the spring of 1993. The second component of the increased "by-pass" loading to the lake in 1993 was associated with the mandated construction upgrades of the facility, that irregularly diminished the upper bound of the flow that received full treatment.

Loading estimates from METRO to the lake were based primarily on operating and monitoring records provided by the facility to the NYSDEC. These included final effluent concentrations as well as estimated flows and concentrations of the "by-passed" wastewater. Nitrate (NO_3^-) and nitrite (NO_2^-) concentrations were measured by UFI on the fully treated portion

of the METRO discharge. The TP concentrations of the "by-pass" discharge were in general much greater than the fully treated discharge (Figure 2-4). The average concentration of the fully treated discharge (0.6 $mg \cdot L^{-1}$) is similar to those observed in recent years.

The time course of estimated annual loadings from METRO to the lake is presented for the 1977-1993 period in Figure 2-5; this represents an update of the analysis conducted for the 1970-1990 interval by Effler and Whitehead (1994). Estimated loads had leveled off at the period minimum over the 1990-1992 interval, but the 1993 load represented a conspicuous increase. The 1993 load includes the estimated "by-pass" load, while earlier annual estimates do not. In an analysis of "by-pass" loads from the facility over the 1986-1990 interval, Stearns and Wheler (1991) concluded the contribution from this source was minor, less than 8% of the annual METRO load in 1989 and 1990 (Effler and Whitehead 1994). The "by-passed" flow only represented ~2% of the METRO discharge over the 1986-1990 interval. In sharp contrast, the by-passed flow represented nearly 22% of the total discharge flow in 1993, most of this occurring over the late March through early May interval (Figure 2-6a), when runoff in the watershed was extremely high (See April of Figure 2-2). Approximately 35% of the "by-pass" flow in 1993 was associated with the construction upgrade, the remainder was a result of high runoff. The vast majority of the "by-pass" contribution was made during the high runoff period of spring (Figure 2-6b). The estimated increase in TP load in 1993

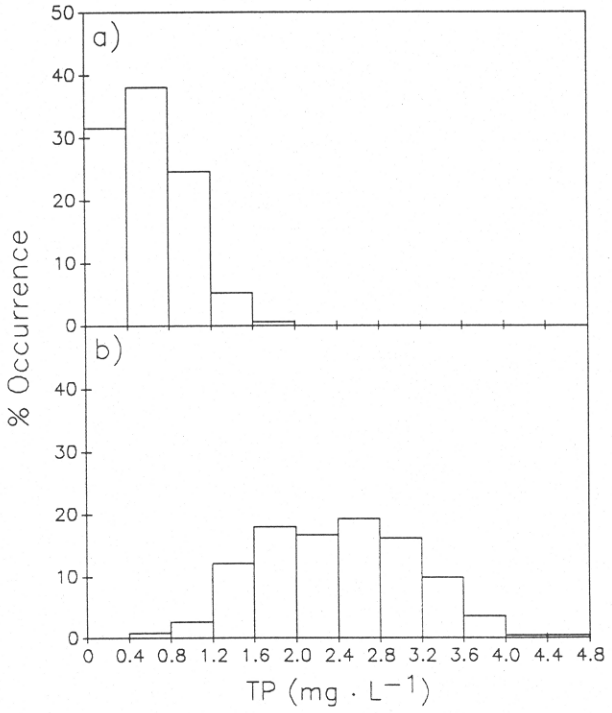


Figure 2-4. Comparisons of total phosphorus (TP) concentration distributions in discharges to Onondaga Lake from METRO in 1993: a) fully treated effluent, and b) "by-pass" discharges.

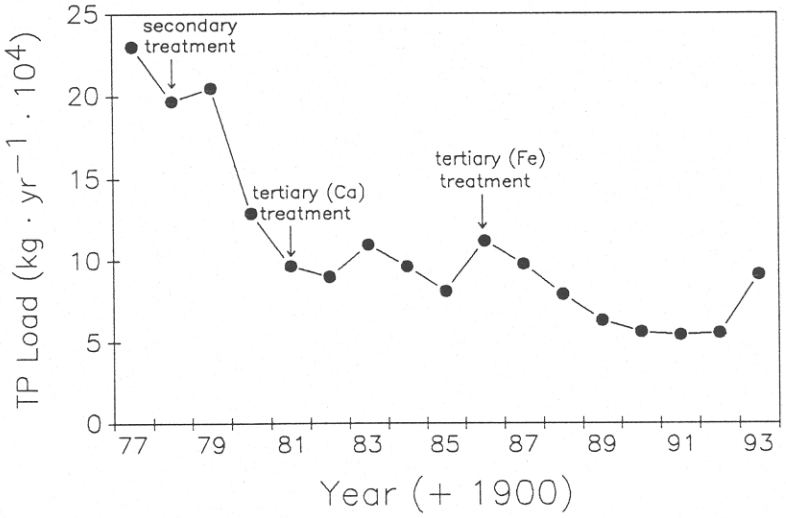


Figure 2-5. Annual total phosphorus (TP) loading rates from METRO, 1977-1993.

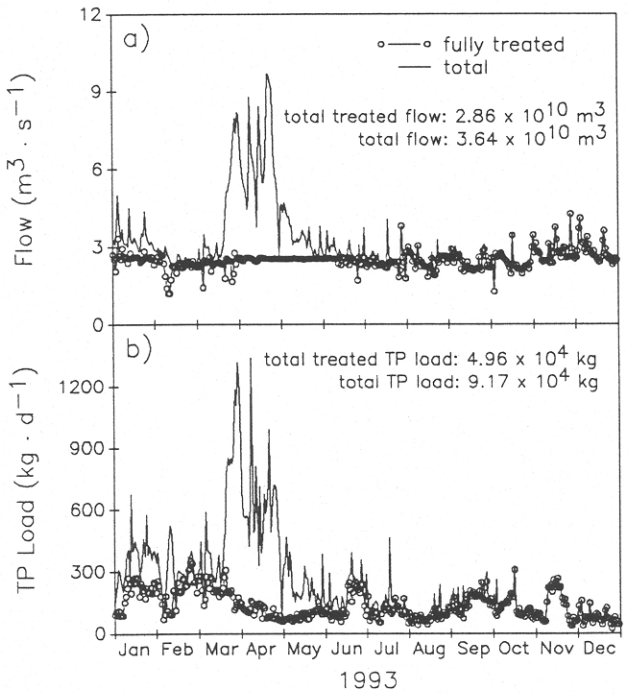


Figure 2-6. Time series of daily inputs to Onondaga Lake from METRO, 1993: a) flow, and b) total phosphorus (TP) load.

associated with the facility upgrade was at least 11,800 kg, or about 13% of the total load from the facility. The "by-passed" portion of the TP load represented an even greater fraction of the total load from the facility (~46%), because it is enriched in TP (Figure 2-4).

Time series of N species in the fully treated effluent of METRO in 1993 are presented in Figure 2-7 (a-d). These temporal distributions were different from those documented in recent years for this discharge (Effler and Whitehead 1995) in at least two ways. First, the concentrations of TKN (Figure 2-7a) and T-NH_3 (Figure 2-7b) were unusually low during the late March to early May period when runoff (Figure 2-2) and the volume of wastewater by-passed at the facility (Figure 2-6a) were very high, undoubtedly reflecting a dilution effect. Second, the seasonal nitrification achieved in summer and early fall was less continuous and complete (Figure 2-7 (a and b)) than observed in recent years (e.g., 1988 and 1989; Effler and Whitehead 1995). The NO_2^- specie has not previously been routinely monitored in the facility's effluent, instead the sum of NO_3^- and NO_2^- has been reported. Nitrite was a significant component of this summation throughout the monitored interval (Figure 2-7c and d); at times representing as much as 30% of the total. The dynamics of NO_2^- largely tracked those of NO_3^-. The progressively increasing concentrations of NO_2^- in METRO's effluent in summer (Figure 2-7d) undoubtedly contributed to the increasing concentrations observed in the upper waters of the lake over the same period (see Chapter 3; also see Brooks and Effler 1995).

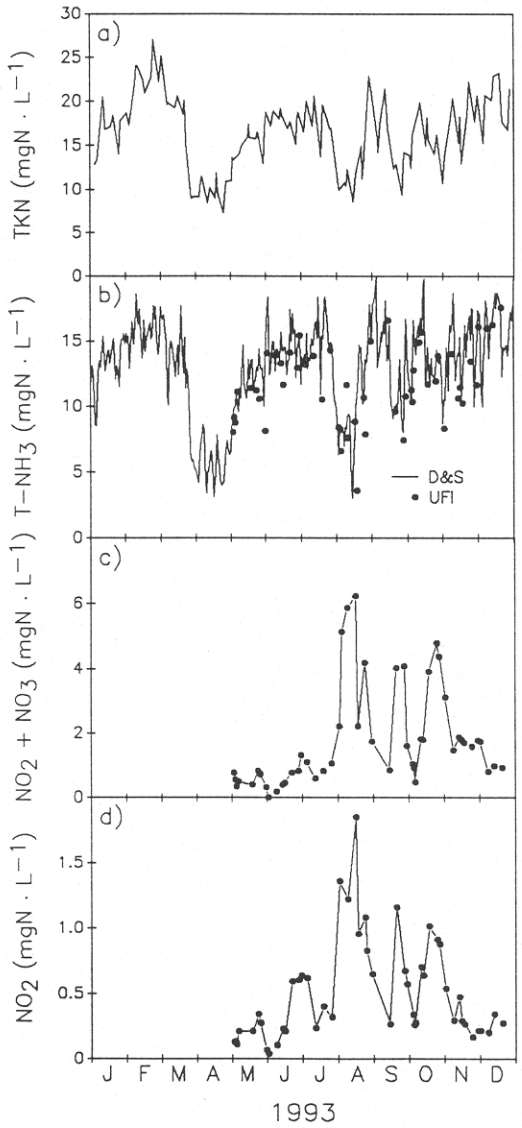


Figure 2-7. Time series of nitrogen species in METRO's effluent in 1993: a) TKN, b) T-NH_3, c) NO_2^- + NO_3^-, and d) NO_2^-,

Time series of daily estimates of loading of N species from METRO are presented in Figure 2-8(a-c). These generally track the dynamics observed for concentrations in fully treated effluent (Figure 2-7), except during the high runoff period of spring. During the spring period total loads (fully treated plus by-pass) remained unchanged for T-NH_3 (Figure 2-8b). The "by-pass" component was based on daily monitoring of T-NH_3 in that waste stream. The "by-pass" TKN load was bracketed by the estimates presented here (Figure 2-8a); the lower bound considers only the T-NH_3 component, while the upper bound assumes a TKN concentration in the "by-pass" equal to that of the influent to the facility. Approximately 14% of the total T-NH_3 load from the facility in 1993 entered via the "by-pass". These time series of loads are consistent with the input needs of the nitrogen model for the lake (Canale et al. 1995a).

Indication of Relative Availability of Phosphorus in Sources

The potential for inputs to support phytoplankton growth is reflected in each source's phosphorus (P) loading rate (e.g., $kg \cdot d^{-1}$) and the availability of the P to support algal growth. The form of P is critical to its availability. For example, SRP is considered to be immediately available to support algal growth, and a substantial fraction of the dissolved organic P pool appears to be ultimately available (e.g., after enzymatic breakdown) to the phytoplankton of Onondaga Lake (Connor et al. 1995). Further, P loosely bound to particles is also ultimately available, while certain forms of P (e.g., tightly bound to particles) are not available. Thus the relative bioavailability

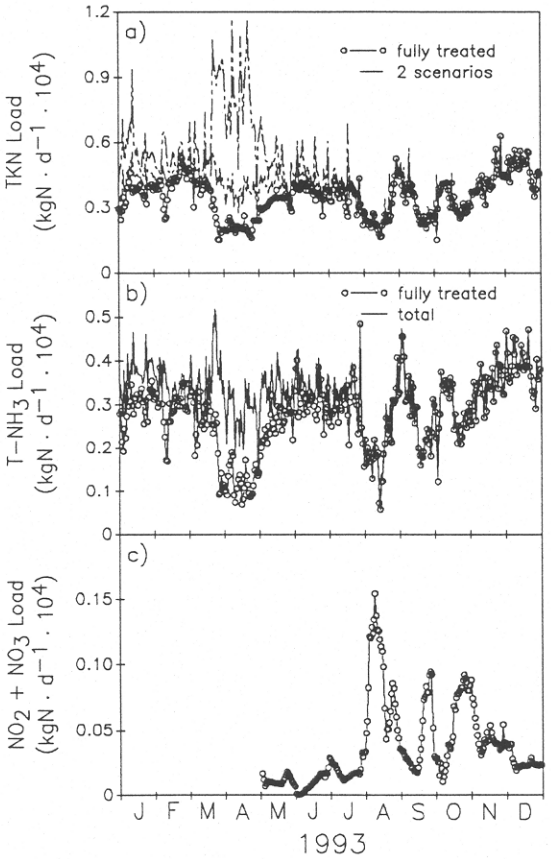


Figure 2-8. Time series of daily inputs of nitrogen species to Onondaga Lake from METRO, 1993: a) total Kjeldahl nitrogen (TKN) (two scenarios for total load, see text), b) total ammonia ($T\text{-}NH_3$), and c) nitrate (NO_3^-) plus nitrite (NO_2^-).

of P from various sources in a lake's watershed may differ substantially. For example, the availability of P in municipal effluents is often greater than in tributaries (DePinto et al. 1981, Young et al. 1981). Several different approaches have been used to indicate the relative bioavailability of a P source, including simple ratios of widely measured P fractions, ratios which include a specie of P analyzed after selective extraction techniques have been utilized, and the use of bioassay techniques (DePinto et al. 1981, Young et al. 1981). Here the most crude approach has been adopted as a preliminary indicator of relative availability, the ratio of soluble reactive P (SRP) to TP (SRP/TP).

Distributions of the SRP/TP ratio for the various sources for the 1991-1993 interval are presented in Figure 2-9(a-e). The lowest ratios (indicative of the least relative availability), and the narrowest distributions were observed at Dorwin Avenue (Figure 2-9a), which bounds the rural portion of the watershed. A shift to higher ratios (e.g., greater availability) is observed further downstream of Spencer Street (Figure 2-9b), reflecting urban inputs of SRP. The distribution of ratios in Ninemile Creek (at Lakeland; Figure 2-9c) was similar to that observed at the downstream Onondaga Creek location. Substantially greater availability is indicated for Ley Creek and METRO (Figure 2-9d and e). The METRO source is of course of greater concern because of the much greater magnitude of its load (~5x the Ley Creek load; Effler and Whitehead 1995).

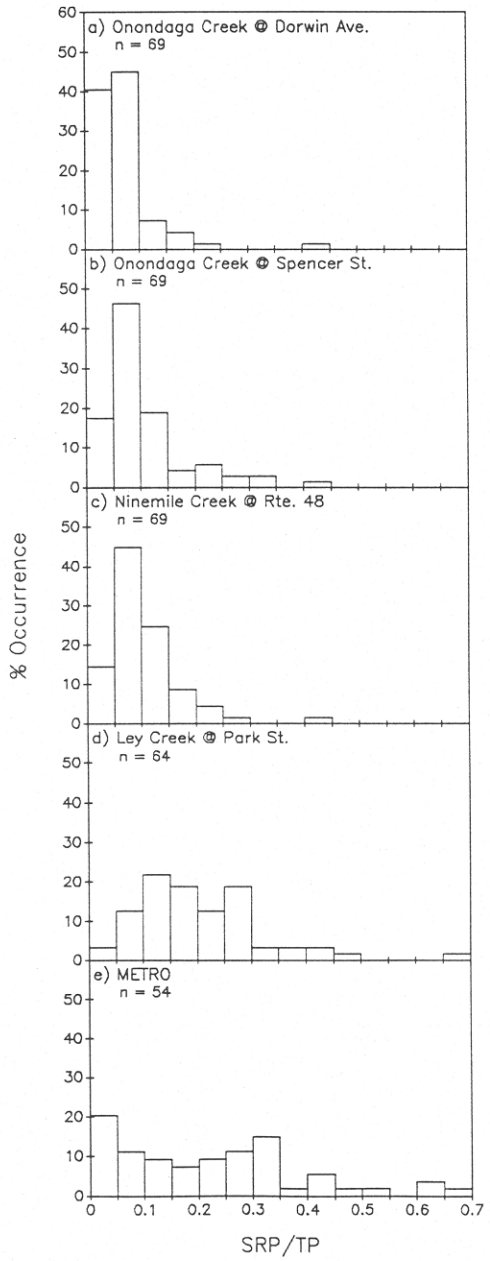


Figure 2-9. Distributions of the ratio of SRP/TP for tributaries to Onondaga Lake, for the 1991-1993 interval: a) Onondaga Creek at Dorwin Ave., b) Onondaga Creek at Spencer St., c) Ninemile Creek at Lakeland, d) Ley Creek at Park St., and e) METRO.

Daily Loadings: Cl, TP, T-NH_3 and T-NO_x

Time series of daily estimates of external loads of Cl^-, TP, T-NH_3 and T-NO_x to Onondaga Lake for 1993 are presented in Figure 2-10(a-d). These loads are appropriate to support model testing for 1993 conditions for the Cl^- (Doerr et al. 1994), TP (Doerr et al. 1995), and N (Canale et al. 1995a) models. The contributions of METRO to the TP and N species loads are depicted (Figure 2-10 b-d). The greatest TP input occurred during the spring runoff period. Tributaries made significant contributions during this interval (Figure 2-10b). Inputs of TP during the critical water quality period of summer were dominated by METRO. The variations in TP loading rate during summer largely reflect variations in the performance of METRO in P removal (i.e., effluent TP concentration).

Some reduction in T-NH_3 loading from METRO was achieved for portions of the summer period (Figure 2-10c), associated with the operation of the nitrification process. This seasonality was identified and described previously by Effler and Whitehead (1995). Note the increases in T-NO_x loading (the product of nitrification; Figure 2-10d) coincident with the decreases in T-NH_3 loading (Figure 2-10c), that provides a clear signature of the operation of the nitrification process. The seasonality reflects the influence of temperature on the rate of nitrification (Bowie et al. 1985). The extent of nitrification achieved at METRO in 1993 was substantially less than documented in earlier years (Effler and Whitehead 1995), undoubtedly at least in part due to plant modifications that were underway

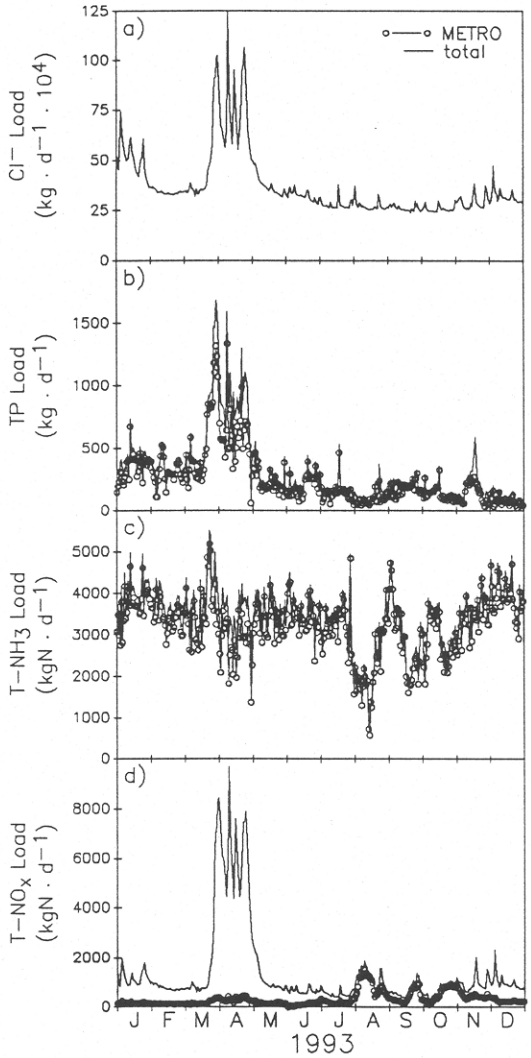


Figure 2-10. Time series of daily external loads to Onondaga Lake in 1993: a) Cl^-, b) TP, c) $T\text{-}NH_3$, and d) $T\text{-}NO_x$.

during 1993. The conspicuously high estimates of T-NO_x loading in spring (Figure 2-10d) correspond to the extremely high runoff at that time.

METRO Contributions to Total Annual Loads

Contributions of METRO versus the summation of the tributaries to annual external TP, T-NH_3 and T-NO_x loading to Onondaga Lake are depicted by pie-charts in Figure 2-11, 2-12, and 2-13 respectively. METRO's contribution to TP loading was the greatest in 1993 (~80%), for the 1987-1993 (7 y) interval (Figure 2-11). This is a manifestation of the extremely high by-pass flow from the facility (and associated loads) in 1993, associated with both the unusually high spring runoff and construction upgrades. This represents a temporary reversion to the contributions made by METRO (e.g., 1987 and 1988; Figure 2-11) before the improved tertiary treatment performance levels from $FeSO_4$ treatment were established (see Effler and Whitehead 1995). Approximately 95% of the tributary load was contributed about equally by Ley Creek, Onondaga Creek, and Ninemile Creek.

METRO continued to represent more than 90% of the external T-NH_3 load to the lake in 1993, as it has since at least 1987 (Figure 2-12). The average estimated contribution of the facility for the 7 y period represented in Figure 2-12 is 93%. METRO's discharge represented about 23% of the T-NO_x load to the lake in 1993, very similar to the 1992 contribution (Figure 2-13). This represents the lowest contribution over the 7 y period, and is largely a manifestation of the relatively low degree of nitrification achieved within METRO, associated with

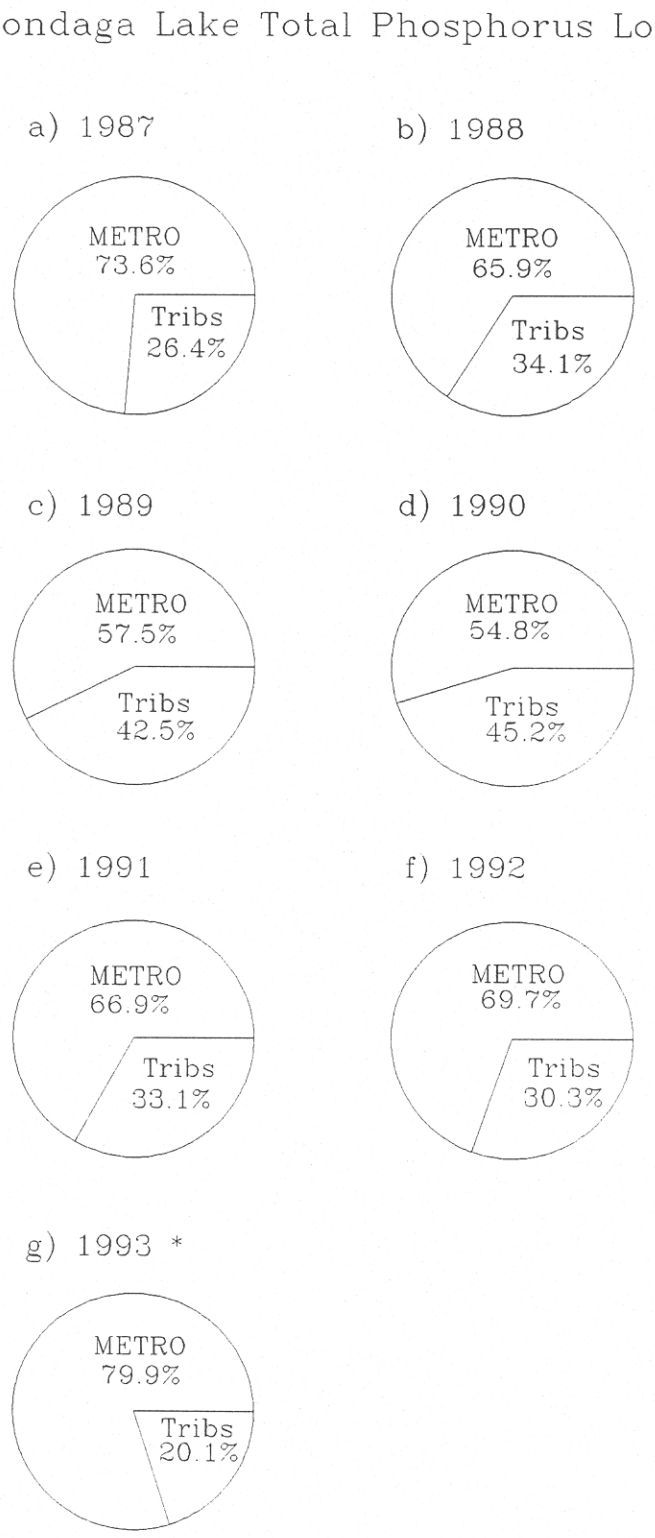


Figure 2-11. Contributions of METRO and tributaries to external TP loading to Onondaga Lake: a) 1987, b) 1988, c) 1989, d) 1990, e) 1991, f) 1992, and g) 1993.

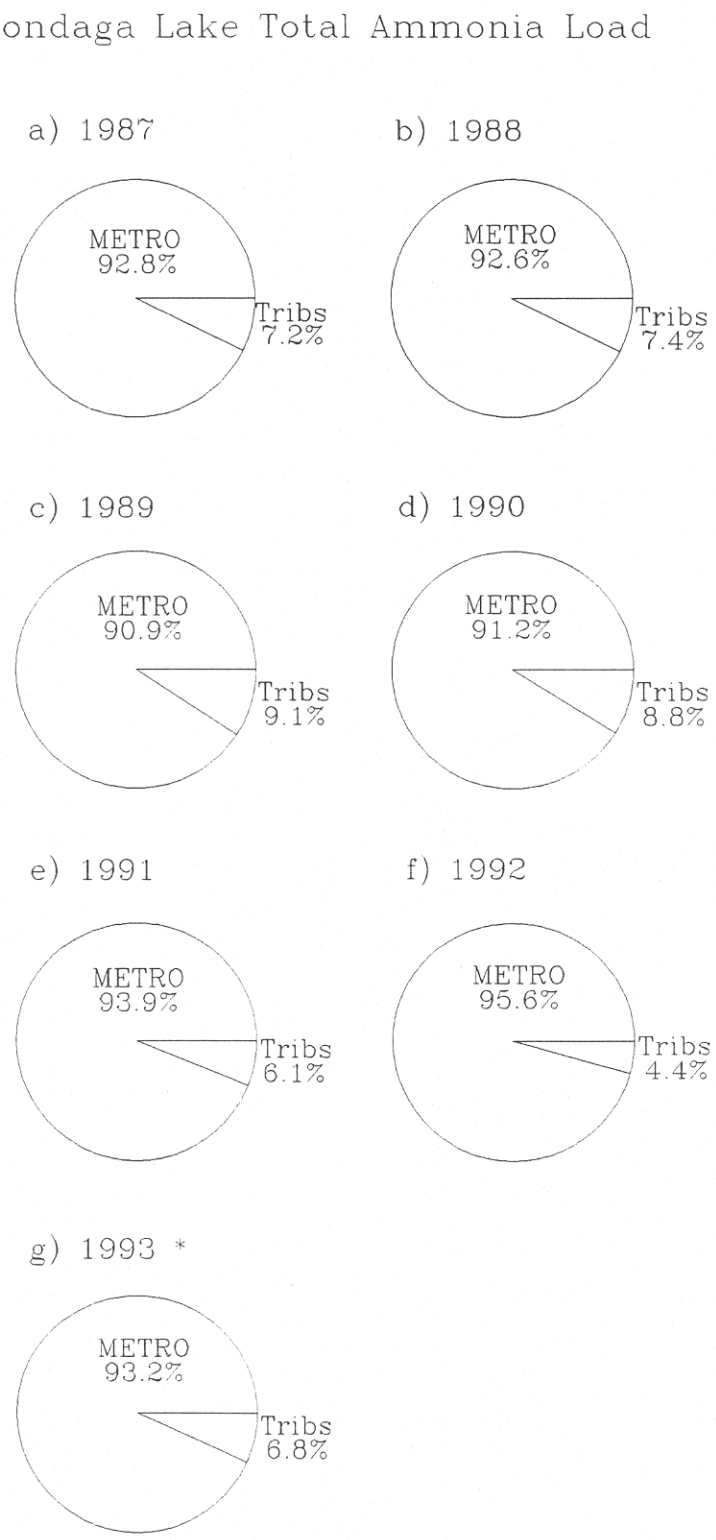


Figure 2-12. Contributions of METRO and tributaries to external T-NH_3 loading to Onondaga Lake: a) 1987, b) 1988, c) 1989, d) 1990, e) 1991, f) 1992, and g) 1993.

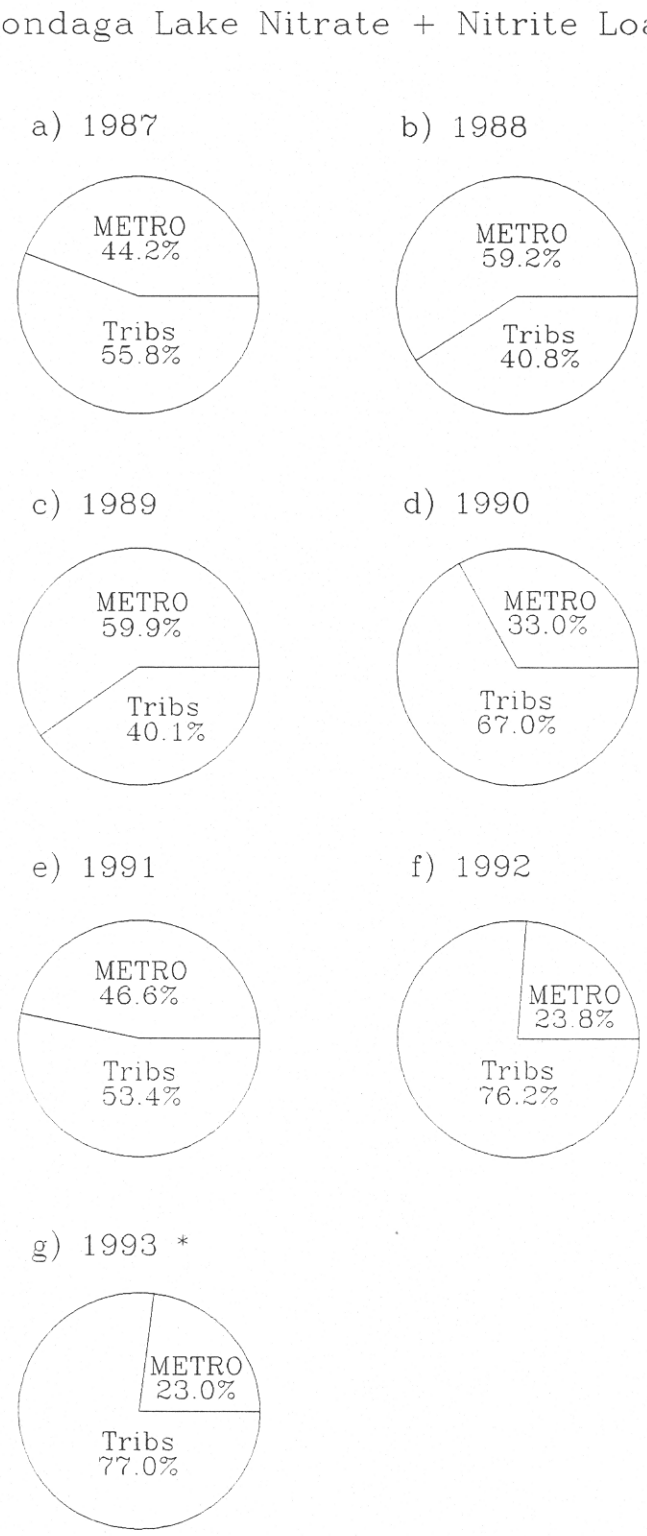


Figure 2-13. Contributions of METRO and tributaries to external NO_3+NO_2 loading to Onondaga Lake: a) 1987, b) 1988, c) 1989, d) 1990, e) 1991, f) 1992, and g) 1993.

the construction upgrades. Note the much higher contributions made by the facility to the T-NO_x load in several of the years (e.g., 1987, 1988, 1989 and 1991), associated with the much greater nitrification achieved within the facility in those years (e.g., Effler and Whitehead 1995). The low contribution from METRO in 1993 is also in part a manifestation of the very high T-NO_x load estimated for the tributaries (see Figure 2-10d), associated with the unusually high runoff in spring.

CHAPTER 3

STATUS WITH RESPECT TO WATER QUALITY STANDARDS

Background

An impressive list of numerical standards, intended to protect the fishing and contact recreation resources of surface waters, has been demonstrated to be violated in recent years in Onondaga Lake (Effler 1995a). These standards/violations are summarized in Table 3-1. The lake's problems of high total

TABLE 3-1: Violations/Exceedance of Numerical Standards/Guidance Value for State of New York, in Onondaga Lake

Constituent/Attribute	Resource/ Use	Standard/Guideline	Primary Responsibility	Support Documentation
free ammonia (NH_3)	fishing	toxicity; standard function of pH and temperature; differ for salmonid and non-salmonid fisheries	METRO	Chapters 3, 5, and 9
nitrite (NO_2^-)	fishing	toxicity; < 100 $\mu g\ NO_2^- \cdot L^{-1}$ for non-salmonid, 20 < $\mu g NO_2^- \cdot L^{-1}$ for salmonid	METRO	Chapter 5
dissolved oxygen (DO)	fishing	≥ 5 $mg \cdot L^{-1}$, daily average; ≥ 4 $mg \cdot L^{-1}$, minimum within a day	METRO	Chapters 3, 5, 6, and 9
mercury (Hg) in fish flesh	fishing	FDA standard of < 1 ppm	?	Chapters 5, and 6
clarity (Secchi disc transparency, SD)	swimming	standard for opening a public bathing beach; ≥ 4 ft (or 1.2 m)	METRO	Chapters 3, 5, 6, and 7
fecal coliform (FC) bacteria	swimming	log mean ≥ 200 $FC \cdot 100\ ml^{-1}$ over 5 days, single observations < 1000 $FC \cdot 100\ ml^{-1}$	combined sewer over-flows (CSO's)	Chapters 3, 6, and 9
total phosphorus (TP)	swimming	guidance value; epilimnetic summer average ≤ 20 $\mu g \cdot L^{-1}$	METRO	Chapter 3, 5, 6, 8, and 9

* Chapters State of Onondaga Lake (Effler 1994a)

phosphorus (TP) concentrations (guidance value), poor clarity (Auer et al. 1990), and low dissolved oxygen (DO) concentrations (e.g., lake-wide during fall turnover (Effler et al. 1988)) are manifestations of cultural eutrophication caused by excessive phosphorus (P) loading emanating principally from METRO (Effler and Whitehead 1995). Violations of the free ammonia (NH_3) standard (e.g., Effler et al. 1990) have been attributed almost entirely to the METRO discharge of total ammonia (T-NH_3; Canale et al. 1995a), that represents about 90% of the external load (Effler and Whitehead 1995). There is less detailed evidence linking the lake's NO_2^- problem to METRO, but there appears to be little question concerning this facility's responsibility (Brooks and Effler 1990).

Here we document the status of Onondaga Lake in 1993 with respect to the numerical standards for clarity, DO, NH_3 and NO_2^- and the guideline for TP, and review the recent history of violations in the lake for each of these parameters. Responsibility for monitoring and reporting findings concerning Hg fish flesh contamination is assumed by the NYSDEC. Violations of fecal coliform bacteria public health standards occur after runoff events (Table 3-1; Canale et al. 1993). The status of the lake with respect to these standards can only be quantitatively assessed by an event-based monitoring effort (e.g., Canale et al. 1993), that is outside of the scope of this monitoring program.

Total Phosphorus

The time distributions of the volume-weighted concentration of TP in the 0-8 m depth interval (good representation of

epilimnion) of Onondaga Lake for the mid-May to mid-September (e.g., summer) interval over the period 1987-1993 are presented in Figure 3-1(a-g). Concentrations were generally highest in May and decreased during summer, reflecting loss rates (e.g, phytoplankton uptake and subsequent deposition) exceeding sources. Concentrations decreased after 1988, associated largely with improved treatment at METRO (Doerr et al. 1995, Effler and Whitehead 1995; and repair of sewer line breaks in 1988), but increased in 1993, due mostly to the bypass of primary effluent from METRO directly into the lake associated with the unusually high runoff of April (see Chapter 2) and plant modification. The margin of exceedance of the NYSDEC guideline value of 20 $\mu g \cdot L^{-1}$, as a summer epilimnetic average, was a factor of 4.5 in 1993. The margins were somewhat lower (~3 to 4) over the 1989-1992 interval, but greater in 1987 and 1988. The TP concentration in all the years was substantially above levels described as indicative of eutrophy in the literature (e.g., Auer et al. 1986, Chapra and Dobson 1981, Vollenweider 1975, 1982).

Clarity

A significant shift to increased transparency followed the closure of the soda ash/chlor-alkali plant in 1986 (Auer et al. 1990), that has been attributed to increased grazing losses of light attenuating particles (particularly phytoplankton), associated with coupled reductions in lake salinity (Seigfried et al. 1995). Distributions are compared for 1968-1986 and 1987-1993 intervals in Figure 3-2. The distribution since closure is much broader, including Secchi disc (SD, m) observations that

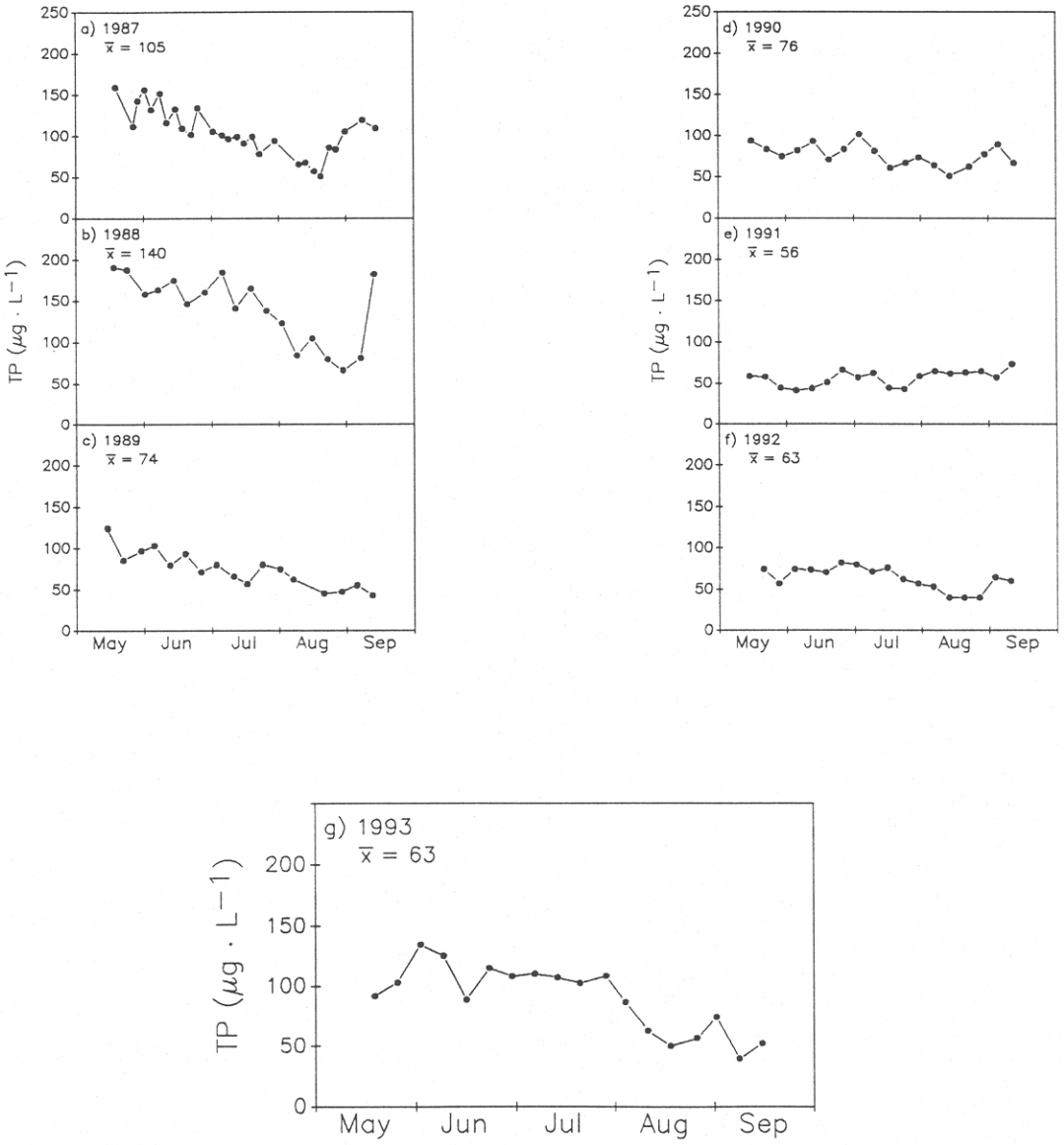


Figure 3-1. Time series of epilimnetic volume-weighted total phosphorus (TP) concentrations for Onondaga Lake: a) 1987, b) 1988, c) 1989, d) 1990, e) 1991, f) 1992, and g) 1993. Summer average concentrations included.

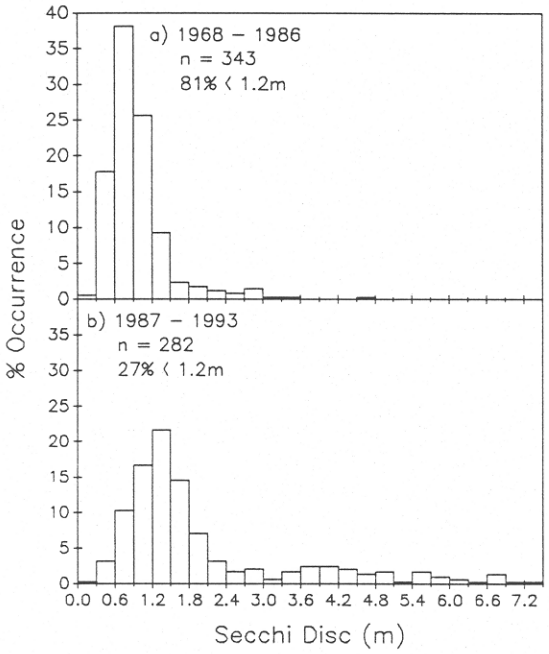


Figure 3-2. Distributions of summertime Secchi disc (SD) observations in Onondaga Lake: a) 1968-1986, and b) 1987-1993.

exceed 7 m. Before closure the lake failed to meet the 1.2 m standard for more than 80% of the summertime observations. Since closure only about 25% of the SD observations have been less than the standard (Figure 3-2).

The detailed time structures of summertime SD values are presented for the 1985-1993 interval in Figure 3-3. Clarity values failed to meet the standard for essentially the entire summer of 1985 (Figure 3-3a) and 1986 (Figure 3-3b). An abrupt increase of SD was observed in mid-July of 1987 (Figure 3-3c). These events, described as "clearing events" (Auer et al. 1990, Lampert et al. 1986), became more pronounced in magnitude and duration in subsequent years (Figure 3-3(d-i)). The events have terminated by mid-July and been followed by periods of relatively constant (and poor) clarity conditions that approach the standard. In 1992 all observations were above or equal to the 1.2 m standard (Figure 3-3h). The standard was not met for only 2 of 21 weekly observations in 1993, and the peak SD value exceeded 7 m.

A yearly summary of clarity conditions in the lake over the period of record is presented Figure 3-4. The median summertime SD value increased following closure of the soda ash/chlor-alkali facility and has leveled out in the early 1990's at somewhat less than 2.0 m (Figure 3-4a). This is a major improvement over the conditions documented for the 1977-1986 interval (≤ 1 m). We have less confidence in the representativeness of the earlier high median values reported for 1970, 1971, and 1977, because of the limited number of observations. The frequency of violation

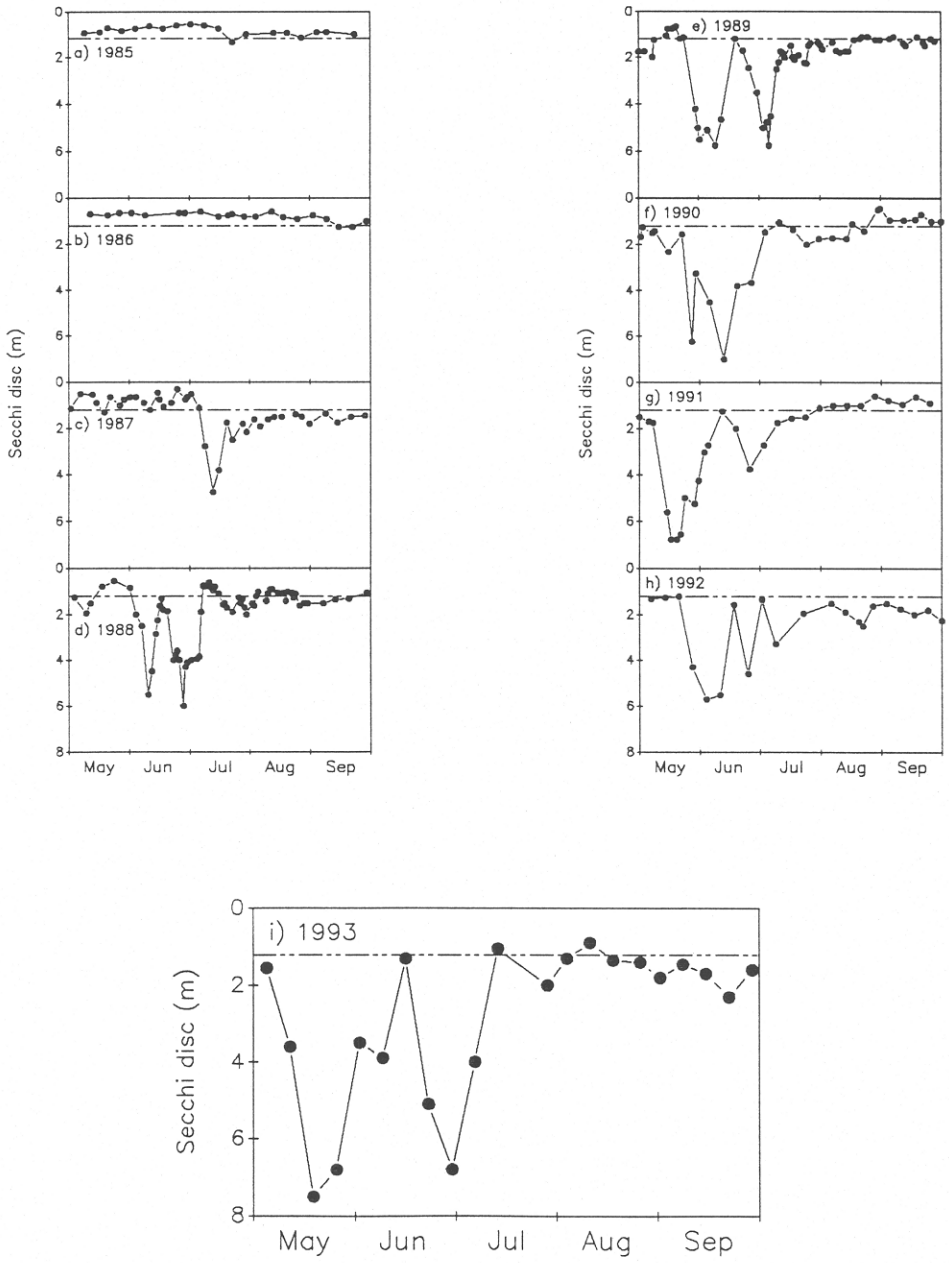


Figure 3-3. Time series of Secchi disc (SD) observations in Onondaga Lake: a) 1985, b) 1986, c) 1987, d) 1988, e) 1989, f) 1990, g) 1991, h) 1992, and i) 1993. Standard (1.2 m) for bathing beach included.

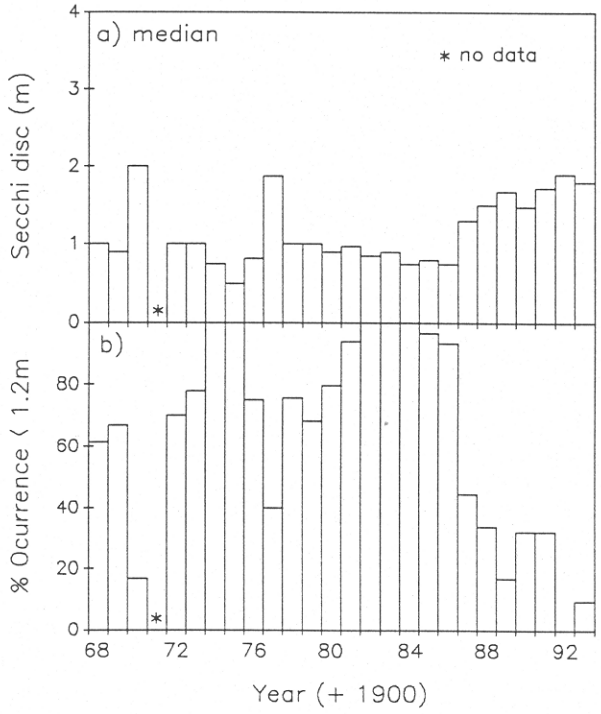


Figure 3-4. Annual summertime Secchi disc conditions for Onondaga Lake over the 1968-1993 interval: a) median, and b) percent of observations < 1.2 m.

of the 1.2 m standard has decreased greatly since the closure (Figure 3-4b). It is important to note that the substantial improvements in clarity observed in recent years is associated largely with "top-down" (grazing) effects, and not reductions in nutrient availability (e.g., nutrient loading).

Dissolved Oxygen

Severe lake-wide depletions of oxygen to concentrations representing violations for surface waters in New York State are observed almost annually in the upper waters of Onondaga Lake during the approach to fall turnover. This has been attributed to the oxidation of the hypolimnetic accumulations of reduced species, particularly H_2S (Effler et al. 1988) and CH_4 (Addess and Effler 1995), upon entrainment into the upper waters. The exodus of most fish from the lake during this period has been documented by Ringler et al. (1995).

The time course of the average DO concentration in the upper 5 m of the water column of the lake during the fall mixing period in 1993 appears in Figure 3-5i; the distributions for the 1985-1992 interval are presented in Figure 3-5a-h. A conspicuous DO "sag" in time was evident in the fall of 1993. The minimum DO standard within a day of 4.0 $mg \cdot L^{-1}$ was violated in early October, and the daily average standard of 5.0 $mg \cdot L^{-1}$ (Table 3-1) was probably violated over a longer period. Diurnal measurements would almost certainly depict more severe conditions with respect to daily minima and violations of the daily average standards. Strong depletions have been observed annually over the 1985-1993 interval. Well defined single "sags" have been observed in

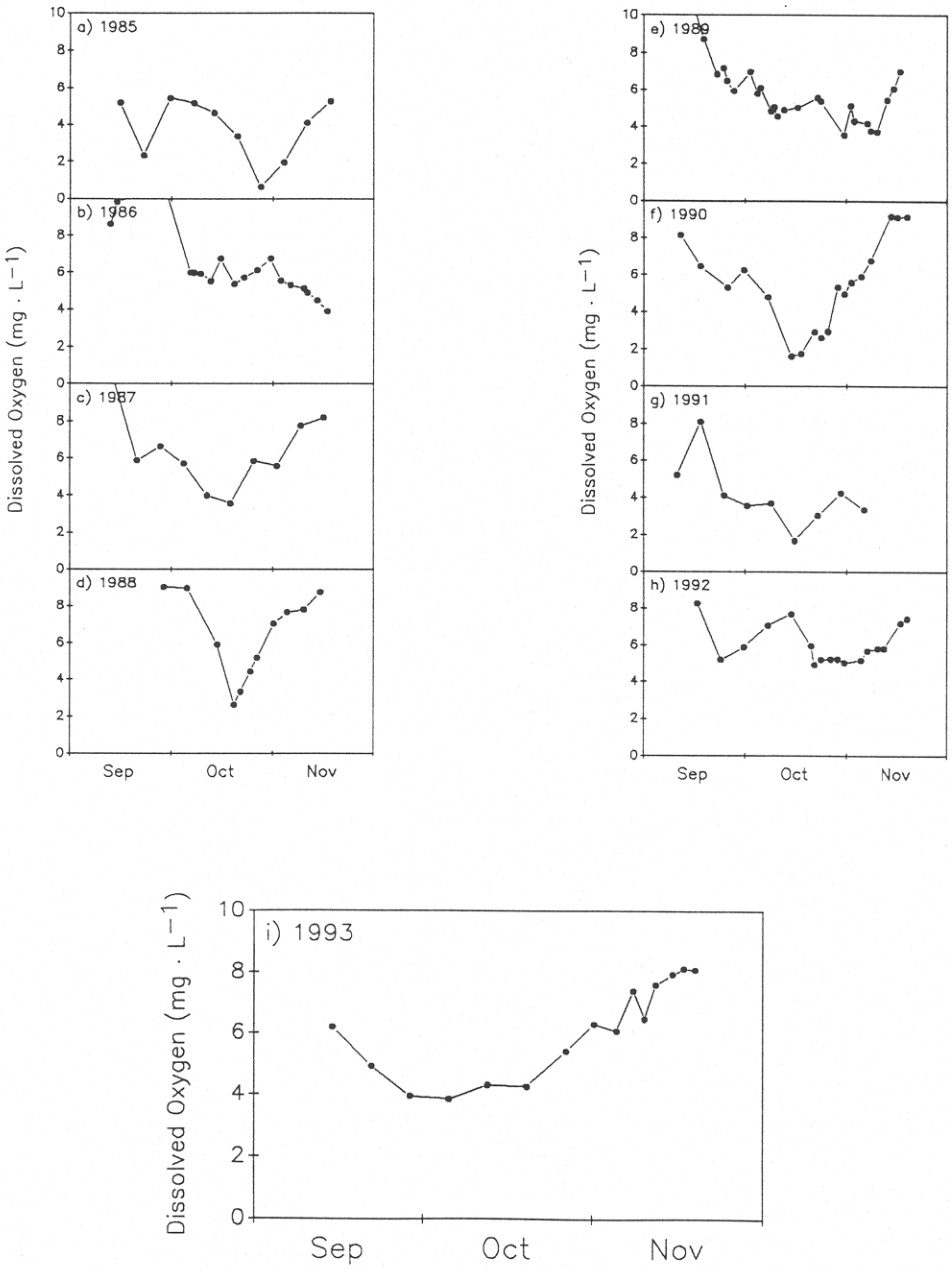


Figure 3-5. Time series of average dissolved oxygen concentrations in the upper 5 m of Onondaga Lake for the September - November interval: a) 1985, b) 1986, c) 1987, d) 1988, e) 1989, f) 1990, g) 1991, h) 1992, and i) 1993.

several years. Other years have demonstrated two distinct "sags". This and other interannual differences in the temporal structure of the sag appear to be greatly influenced by meteorological conditions, which are subject to major natural year-to-year variations (e.g., Owens and Effler 1989). For example a double "sag" may be observed if an initial significant, but incomplete, entrainment of oxygen-demanding hypolimnetic water is followed by a period of stimulated phytoplankton growth and low kinetic energy inputs (e.g., warm and calm), before additional kinetic energy inputs entrain the remainder of the pool of hypolimnetic accumulations of reduced substances.

The distribution of the fall minimum DO (upper 5 m average) measured annually for the 1985-1993 period is depicted in Figure 3-6. The lowest minimum was observed in 1985. The minima were distinctly higher over the 1986-1989 interval, but lower again in 1990 and 1991. The minima were higher again in 1992 and 1993. There is no documentation of violation of the 4.0 $mg \cdot L^{-1}$ standard in the lake in 1992. No strong evidence for a trend in this degraded feature of the lake emerges from analysis of these data (Figure 3-6).

Nitrite

Profiles of NO_2 are presented for Onondaga Lake for the April-October interval of 1993 in Figure 3-7; the non-salmonid toxicity standard is included for reference. Initially concentrations were nearly uniform with depth and less than the toxicity standard. Total depletion from the bottom anoxic (see Chapter 5) layers (e.g., denitrification (Brooks and Effler

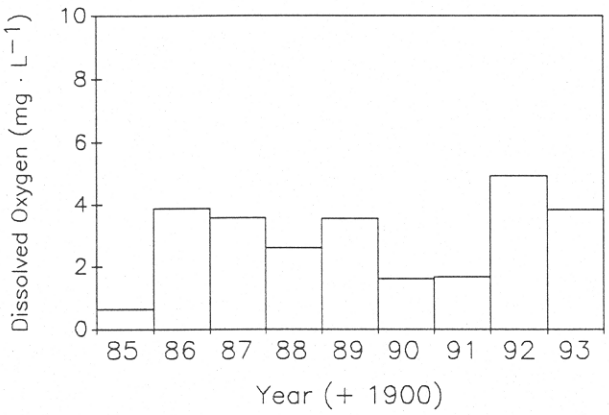


Figure 3-6. Annual minimum of dissolved oxygen concentration in the upper 5 m of Onondaga Lake during the fall mixing period for the 1985-1993 interval.

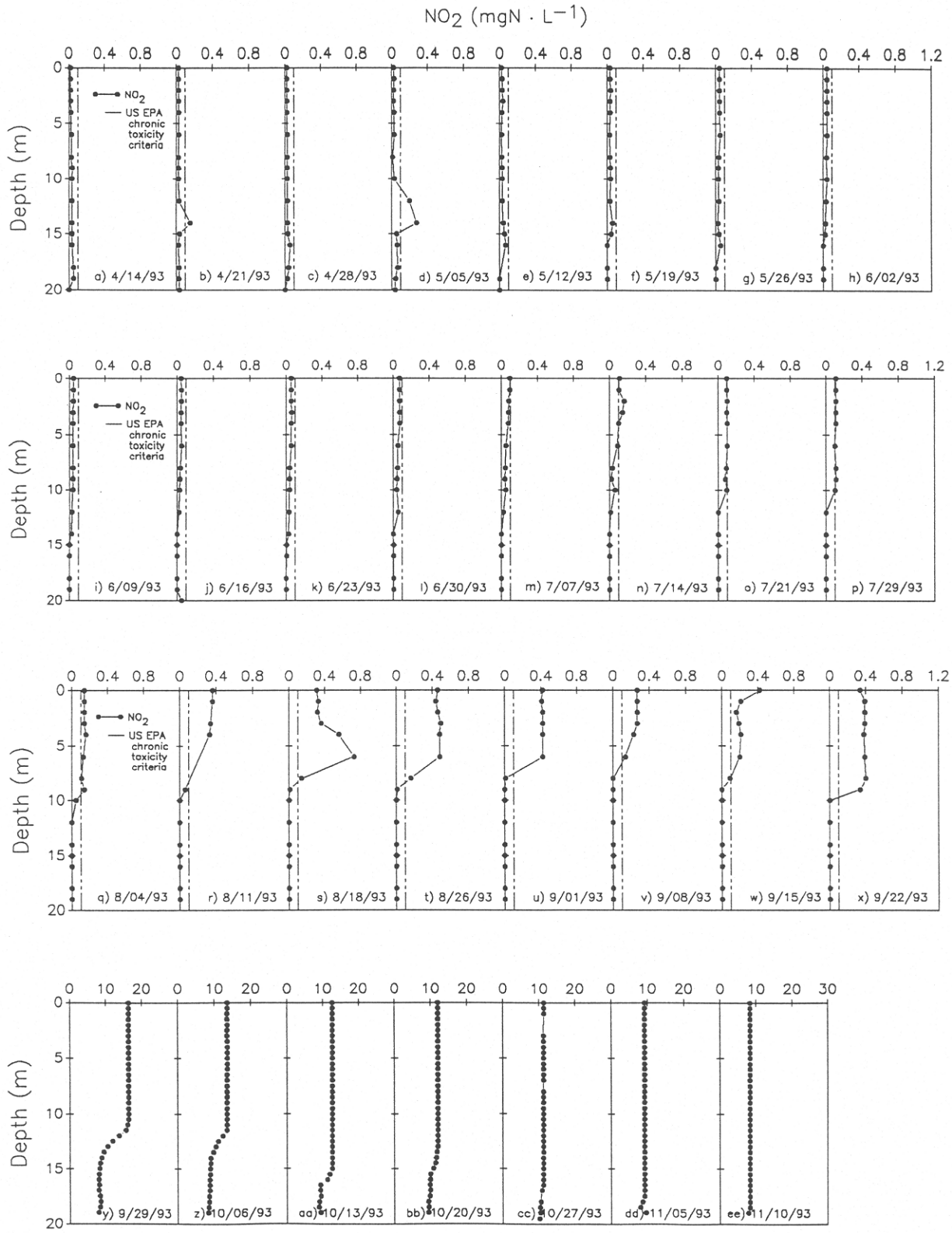


Figure 3-7. Profiles of nitrite (as N) concentrations in Onondaga Lake for the spring to fall interval of 1993 (a-ee). Standard for non-salmonid fish included.

1990)) occurred by early summer, the boundary of total depletion subsequently deepened in fall with the approach to turnover, largely tracking the boundary of anoxia. Clear increases in the upper waters, representing violations of the toxicity standard, were apparent by early August. Further increases occurred through September. The greatest margin of violation was about a factor 49. Violations of the NO_2^- standard, often by a wide margin, prevailed in the oxic layers of Onondaga Lake from early August through early October of 1993 (Figure 3-7).

Nitrite concentrations in the near-surface (1 m) waters of the lake are compared over the 1988-1993 interval in Figure 3-8, from the perspective of the non-salmonid toxicity standard. Violations of the NO_2^- standard, by a wide margin, is a recurring (annual) problem in Onondaga Lake (Figure 3-8). Maximum concentrations (and margins of violation) have been observed in September and October, though concentrations were decidedly lower in this period in 1992. The time course of lake NO_2^- concentrations through mid-September (Figure 3-8f) approximately matches that of effluent concentrations and loading from METRO (Chapter 2), but the maxium of late September can only be explained by a substantial contribution from in-lake processes. The September peak of NO_2^- was the largest observed over the 1988-1993 period (Figure 3-8). The toxic effects of NO_2^- are known to be mitigated by Cl (e.g., Lewis and Morris 1986), which is present in Onondaga Lake in unusually high concentrations (Doerr et al. 1994).

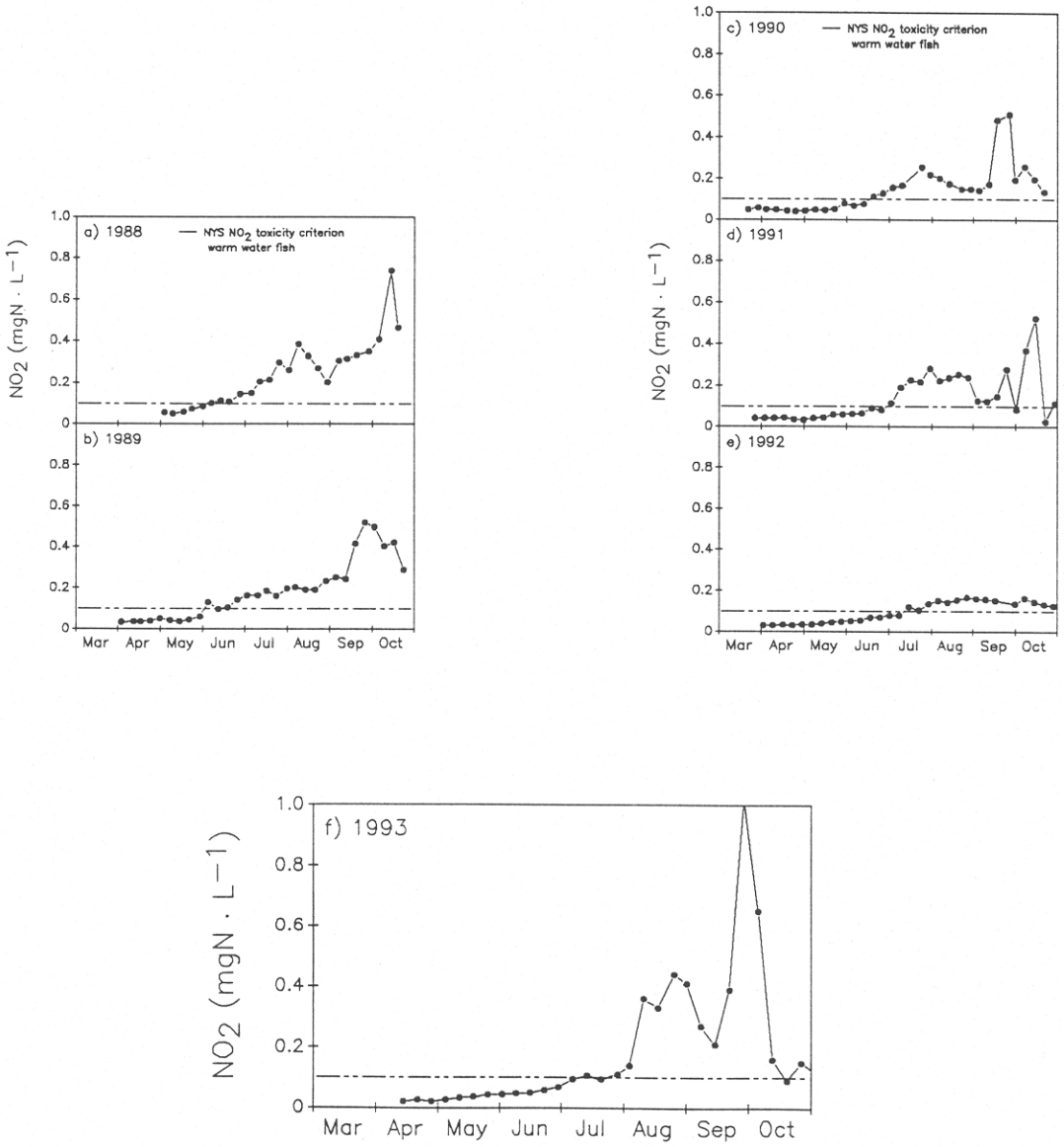


Figure 3-8. Time series of nitrite (as N) concentrations in the near surface waters of Onondaga Lake: a) 1988, b) 1989, c) 1990, d) 1991, e) 1992, and f) 1993. Standard for non-salmonid fish included.

Free Ammonia

The fraction of total ammonia ($T\text{-}NH_3$; the analyte) that exists as free ammonia (NH_3) and the standards (USEPA 1985; salmonid and non-salmonid) for free ammonia are both functions of temperature and pH, and thus subject to substantial seasonal variations in north temperate systems such as Onondaga Lake. The protocols for these calculations have been reviewed by Effler et al. (1990). Both the fraction of $T\text{-}NH_3$ that occurs as NH_3 and the standard increase as pH and temperature increase, however, the fraction is more strongly influenced (Effler et al. 1990).

Profiles of the calculated NH_3 concentrations and non-salmonid standard values are presented for the April-October interval of 1993 in Figure 3-9. Little vertical structure occurred through April and concentrations of NH_3 were close to the standard. Concentrations and the standard increased thereafter in the upper waters associated largely with increases in temperature and pH. Clear violations emerged for the hypolimnion by late May and persisted through the stratification period (Figure 3-9). By mid-June clear violations emerged in the upper waters. The maximum margin of violation (about a factor of 3) was observed in mid-July (Figure 3-9n). The margin generally decreased through August. This decrease largely tracked the decrease in $T\text{-}NH_3$ concentrations (e.g, phytoplankton uptake, reduced loading from METRO). Thereafter, violations were limited to the enriched ($T\text{-}NH_3$) anoxic hypolimnion.

The status of the upper waters (1 m) of the lake with respect to NH_3 toxicity standards over the 1988-1993 interval is

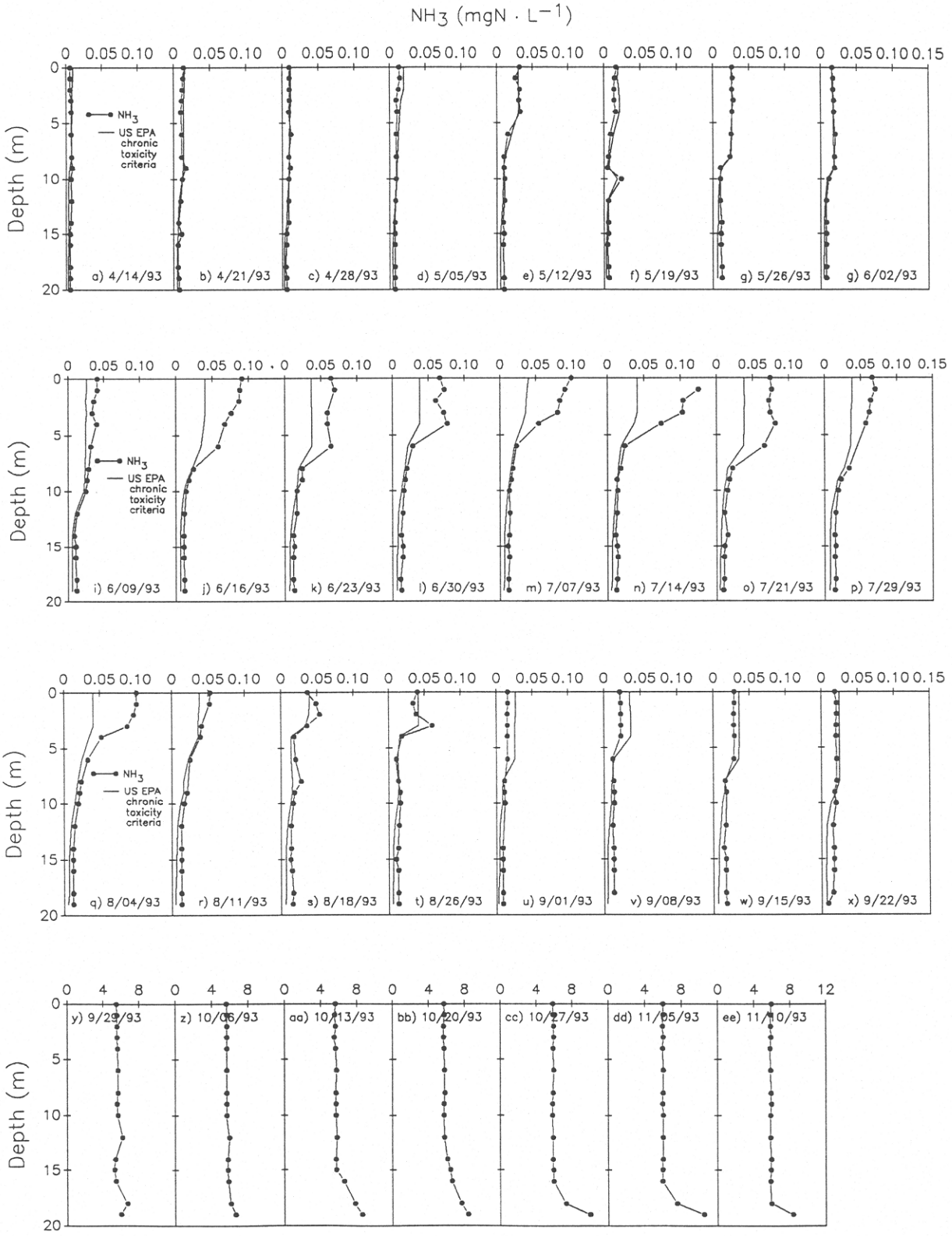


Figure 3-9. Profiles of free ammonia (as N) concentrations in Onondaga Lake for the spring to fall interval of 1993 (a-ee). Standard for non-salmonid fish included.

reviewed in Figure 3-10; both the chronic and acute non-salmonid standards are presented. Violations of the acute standard were documented in 1988 and 1989, but not in subsequent years. The least severe conditions of the six years with respect NH_3 toxicity violations (e.g., margin and duration) were observed in 1993 (Figure 3-10f). This was largely a manifestation of the unusually high spring runoff (e.g., flood) of 1993, and not a reduction in T-NH_3 loading from METRO (see Chapter 2). Violation of the NH_3 toxicity standard, by a wide margin, is a recurring problem for Onondaga Lake (Figure 3-10).

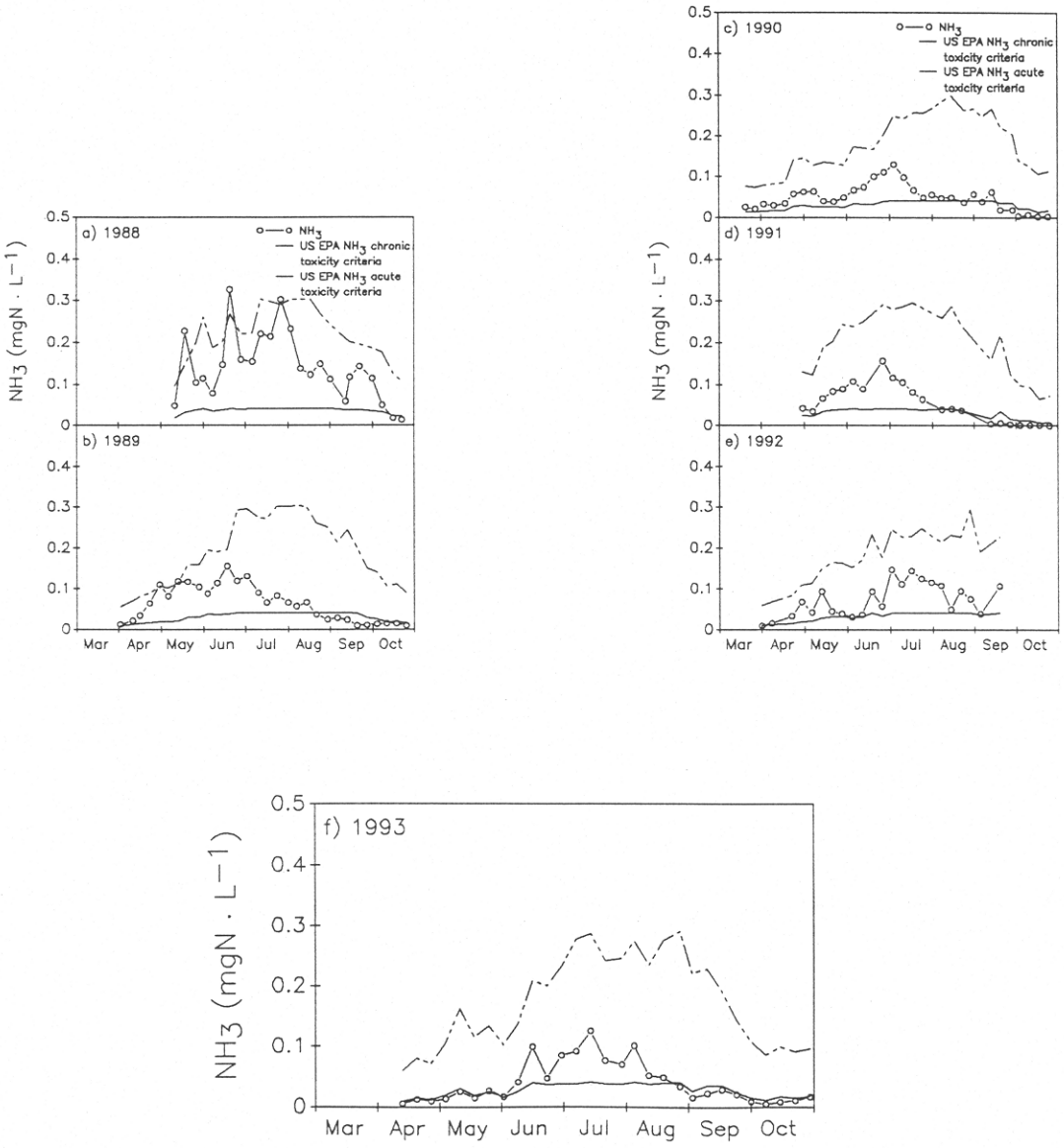


Figure 3-10. Time series of free ammonia (as N) concentrations in the near surface waters of Onondaga Lake: a) 1988, b) 1989, c) 1990, d) 1991, e) 1992, and f) 1993. Standard for non-salmonid fish included.

CHAPTER 4

STRATIFICATION AND VERTICAL MIXING

Background

Stratification. Recently Owens and Effler (1994) reviewed density stratification conditions that prevailed in Onondaga Lake over the late 1960's to 1990 interval. During the operation of the soda ash/chlor-alkali facility the ionic waste discharge and the resulting plunging inflow phenomenon caused the natural thermally-based stratification regime to be modified by contributions from salinity stratification (Effler et al. 1986b). Rather strong salinity-based stratification was initially established in early spring when the underflow(s) entered at the bottom of the lake. Late in spring, when stratification was well established, the underflow entered above the thermocline, as it could not penetrate the density gradient. As a result, the chemocline (depth of maximum density gradient due to salinity) in summer was at a depth equal to or less than the depth of the thermocline (depth of maximum density gradient due to temperature).

During the operation of the soda ash/chlor-alkali facility, the contribution of the salinity component to overall density stratification decreased progressively from spring until late summer, as a result of the seasonal progression of the thermal component of stratification and the entry of the ionic discharge into the upper layers. Rather strong year-to-year differences in the magnitude of salinity-based density stratification and its seasonal dynamics were observed during the period of operation of

the facility. The salinity component represented from 13 to 50% of the overall density stratification for the May through September interval over the 1968-1986 period; the average was 30%. Salinity-based restratification developed in periods of low ambient turbulence during fall turnover as a result of the underflow phenomenon. Salinity-based stratification developed progressively under the ice. The unusually high stability of the water column at the time of ice-out required greater kinetic (e.g., wind-based) energy inputs to achieve spring turnover. As a result, the lake either failed to turnover in the spring, or experienced a very brief turnover period, in 7 of the last 19 years of the operation of the soda ash/chlor-alkali plant.

Monitoring conducted over the 1987-1990 interval indicated the impact of the ionic waste discharge on the stratification regime of the lake has been greatly ameliorated (Owens and Effler 1995) by the loading reductions that accompanied closure of the soda ash/chlor-alkali facility (Effler and Whitehead 1995). Spring turnover was observed over the 1987-1990 interval, following closure of the facility. Further, there was no significant chemical component of stratification over this interval. Thus there was a reduction in water column stability during summer. The duration of stratification was reduced to about 5 months, similar to Otisco Lake, a nearby lake of similar morphometry. Restratification during fall turnover, resulting from the continuing underflow phenomenon, was still observed, but was less strongly manifested.

Vertical Mixing. The transport of materials between the

epilimnion and hypolimnion is determined by the magnitude of vertical mixing and the concentration gradient between the two layers (Chapra and Reckhow 1983, Wodka et al. 1983). In the fixed two-layer framework (an upper mixed layer (UML) corresponding approximately to the epilimnion, and a lower mixed layer (LML) corresponding approximately to the hypolimnion) utilized in the water quality models for Onondaga Lake (Effler 1995a), the vertical mixing coefficient, v_t ($m \cdot d^{-1}$), accommodates the net effect of all mixing processes (particularly diffusion and entrainment). It is important to quantify vertical transport, and therefore v_t, to effectively model critical water quality constituents in Onondaga Lake. The temporal distributions of v_t were determined for the spring to fall intervals of four different years, 1987, 1988, 1989, and 1990, by Doerr et al. (1995a) using a heat balance (or model) on the lower mixed layer (LML), according to

$$\Delta T_2 = \frac{[v_t \cdot A_i \cdot (T_1 - T_2)]}{V_2} \cdot \Delta t \qquad (1)$$

in which ΔT_2 = the change in the hypolimnion (LML) temperature (°C), T_1 = volume weighted temperature of the epilimnion (UML; °C), T_2 = volume-weighted temperature of the hypolimnion (LML; °C), V_2 = volume of the LML (m^3), A_i = the area of the interface between the UML and the LML, and Δt = the time interval over which v_t is to be determined (d).

A polynomial is fit to the temporal distribution of T_1 for each year. The polynomial is used as input to the heat budget

for the LML, and v_t is adjusted to match the temporal distribution of T_2. This iterative calculation procedure is an improvement on related non-iterative estimative techniques presented by other investigators (e.g., Chapra and Reckhow 1983, Wodka et al. 1983).

Profiles of Chloride and Temperature, and Components of Density Stratification

The components of density stratification are qualitatively depicted by the profiles of chloride (Cl; a good surrogate measure of salinity in the lake (e.g., Effler et al. 1986a)) and temperature (T) presented in Figures 4-1 and 4-2. The lake was stratified with respect to salinity on the first monitoring day in mid-April of 1993. This stratification was apparently established during ice-cover, as a result of the plunging of the ionically enriched (i.e., dense) Ninemile Creek inflow, and exacerbated by the unusually high runoff during April (Chapter 2), that caused the upper waters to have a unusually low salinity (Figure 4-1a). The progression of the Cl profiles (Figure 4-1) and the initially weak, but progressively increasing, T stratification (Figure 4-2) indicates Onondaga Lake did not turnover in the spring of 1993. This is also supported by water quality measurements made in early spring (see Chapter 5). Concentrations of Cl increased progressively in the epilimnion as a result of the entry of the enriched inflows into the upper layers. The modest mid-depth peaks apparent starting in late July reflect the continued propensity for "plunging" of the Ninemile Creek inflow. The peaks are manifested because the

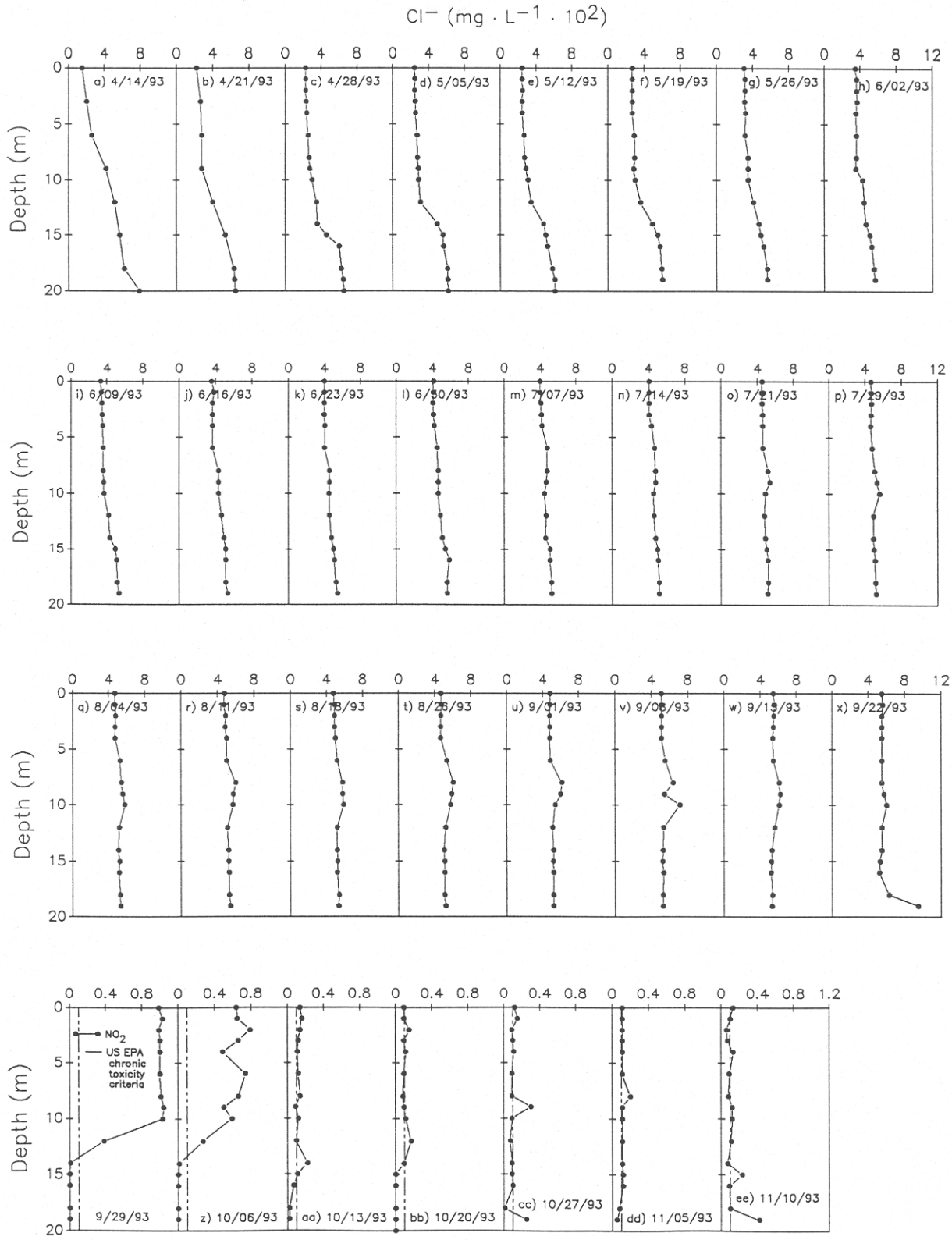


Figure 4-1. Profiles of chloride (Cl^-) concentrations in Onondaga Lake for the spring to fall interval of 1993 (a-ee).

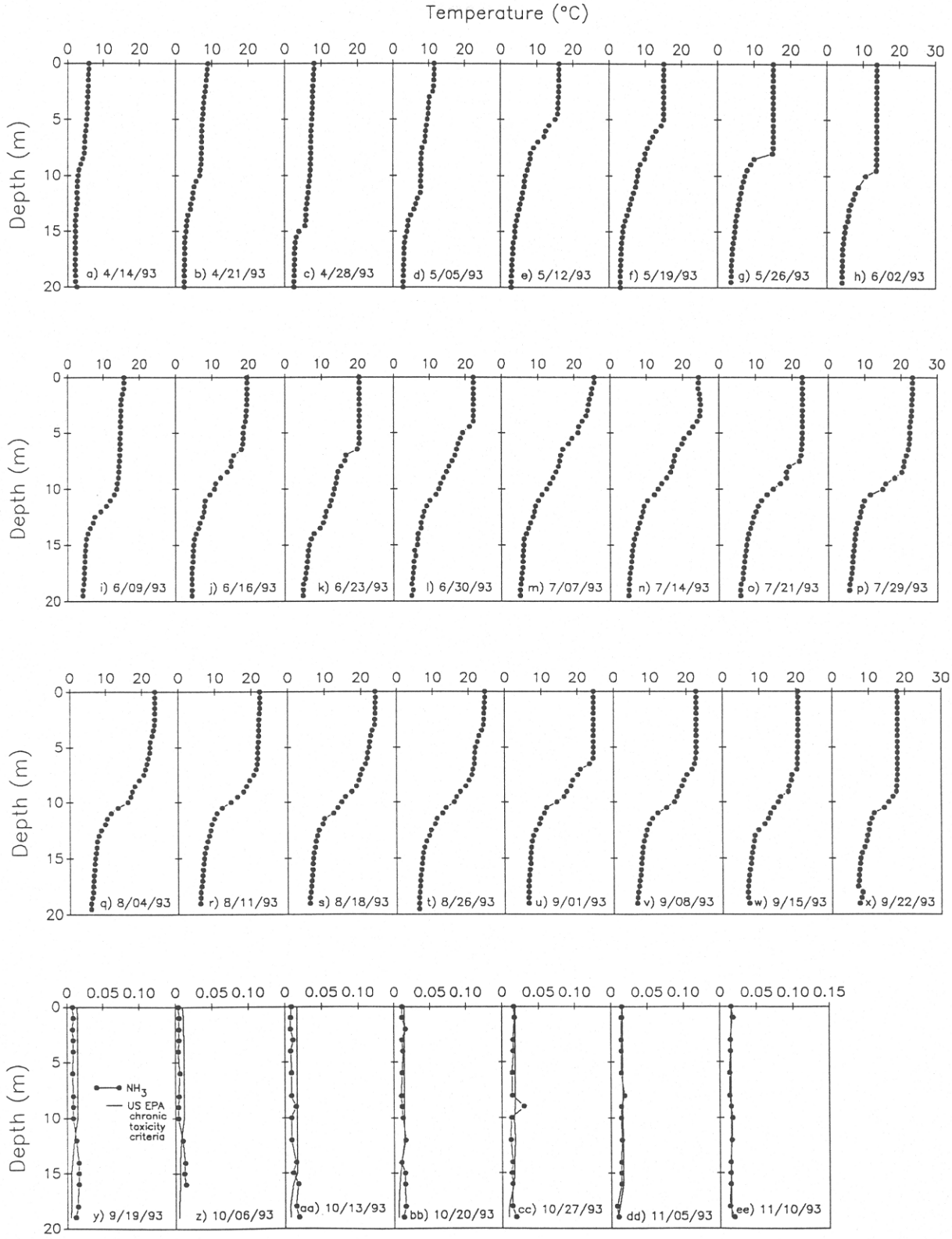


Figure 4-2. Profiles of temperature in Onondaga Lake for the spring to fall interval of 1993 (a-ee).

plunging inflow cannot penetrate the strong thermally-based (Figure 4-2) density gradient. Plunging to the lake bottom in fall was first indicated in late September (Fig. 4-1x), but was prevalent during the low water column stability period of mid-October to mid-November.

The thermal component of stratification (Figure 4-2) demonstrated features common to deep lakes in this region, with only minor anomalies associated with the salinity component of stratification. Thermal stratification became progressively stronger through August associated with solar radiation and air temperature-based inputs of heat. Subsequently heat loss and wind-driven kinetic energy inputs resulted in reduced thermal stratification and deepening (e.g., via entrainment) of the upper mixed layer. Nearly vertically uniform temperatures were observed from late October to mid-November (Figure 4-2cc,dd, and ee), a period during which lakes of this size in this region experience complete fall turnover. However, a minor degree of salinity and thermally based stratification persisted in Onondaga Lake. Minor temperature inversions (e.g., reincreases in lower waters, Figure 4-2x and dd) were observed. These may appear superficially anomalous. However, they were consistent with the attendant salinity stratification conditions (Figure 4-1); i.e., no decrease in density with depth occurs.

A particularly clear signature on the temperature regime from the failure of spring turnover to occur is the unusually low bottom water temperatures that were maintained through summer stratification (also see Owens and Effler 1989). This is

illustrated in Figure 4-3; bottom (19 m) water temperatures in 1993 were decidedly lower than observed in two earlier years that experienced spring turnover. Note the heating rate of the bottom waters was higher in 1989 and 1992 during turnover, and decreased dramatically during stratification. The rate of heating was greater during summer stratification in 1993 (Figure 4-3), at least in part because of the higher vertical temperature gradient that attended the reduced hypolimnion temperature of that year. The reduced bottom water temperature effect of the failure of turnover has potential water quality implications, as the kinetics of decomposition processes are known to be influenced by temperature (lower rates expected for lower temperatures; Bowie et al. 1985).

The partitioning of density stratification according to the components of salinity and temperature in 1993 is presented and compared to two other years in Figure 4-4 (a-c). The example for before closure of the soda ash/chlor-alkali plant, 1980 (Figure 4-4a), demonstrates the much greater role salinity played in overall stratification during the operation of the facility (because of much higher ionic waste loads (Effler and Whitehead 1995) and much greater tendency for plunging (Owens and Effler 1995)). Onondaga Lake did not turn over in the spring of 1980 (Owens and Effler 1994). The partitioning for 1989 (Figure 4-4b) is generally representative of the 1987-1992 interval, following closure of the facility. There was no significant salinity component of density stratification during non-ice-cover periods over this interval, except irregularly during the fall turnover

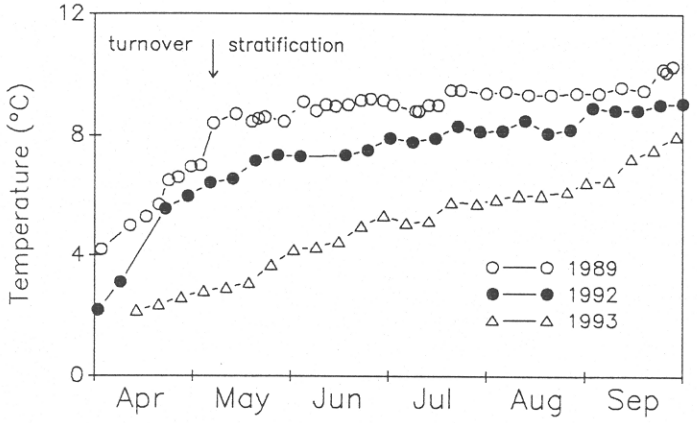


Figure 4-3. Comparison of time series of bottom water (19 m) temperatures in Onondaga Lake, for 1989, 1992, and 1993.

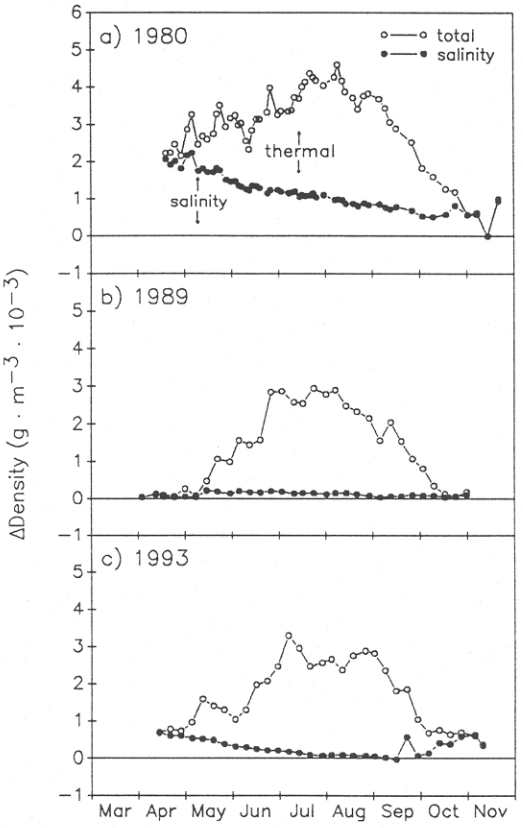


Figure 4-4. Temporal distributions of the total watercolumn differences in density and the salinity component of density: a) 1980, b) 1989, c) 1993.

period (e.g., Figure 4-1). The 1993 partitioning (Figure 4-3c) represents a reversion back towards pre-closure conditions. Though the magnitude of chemical stratification was initially lower and was largely eliminated by mid-summer, clearly it was great enough to eliminate spring turnover (also see Chapter 5). Data collected as part of the 1994 monitoring effort again reflected the persistence of salinity stratification in spring. The negative impact failure of spring turnover has on hypolimnetic oxygen resources has been described by Effler and Perkins (1987), and is documented for 1993 in Chapter 5. The recent failures of spring turnover are not attributed to changes in ionic pollutant loadings. Rather, they reflect the impact of the continuing saline pollutant loadings from the most recently active waste beds along Ninemile Creek, that are manifested only under certain meteorological conditions (i.e., irregularly). For example the hydrologic loading (dilution) was unusually high in the spring of 1993 and ice cover persisted into the spring of 1994 later than usual.

Vertical Mixing

The polynomial fit to the time distribution of T_1 in 1993 is shown in Figure 4-5a. The fit of the time distribution of T_2 achieved by the iterative calculation technique for v_t in 1993 is presented in Figure 4-5b. The calculated distributions of v_t for the 1987-1993 interval are presented in Figure 4-6. The distributions have the recurring temporal features widely reported elsewhere for north temperature lakes (e.g., Chapra and Reckhow 1983, Effler and Field 1983, Thomann and Mueller 1987,

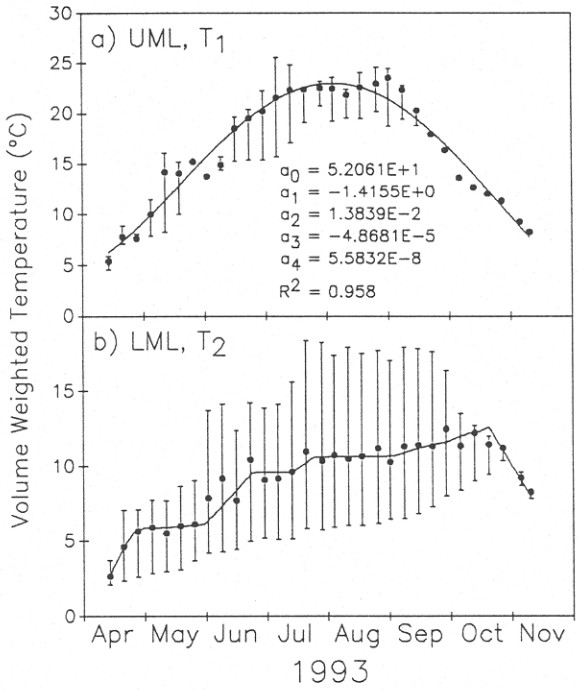


Figure 4-5. Calculation of the vertical mixing coefficient (v_t) for Onondaga Lake: a) polynomial fit to time series of the volume-weighted epilimnetic temperature in 1993, and b) match of observed volume-weighted hypolimnetic temperature in 1993 to that calculated from the distribution of v_t.

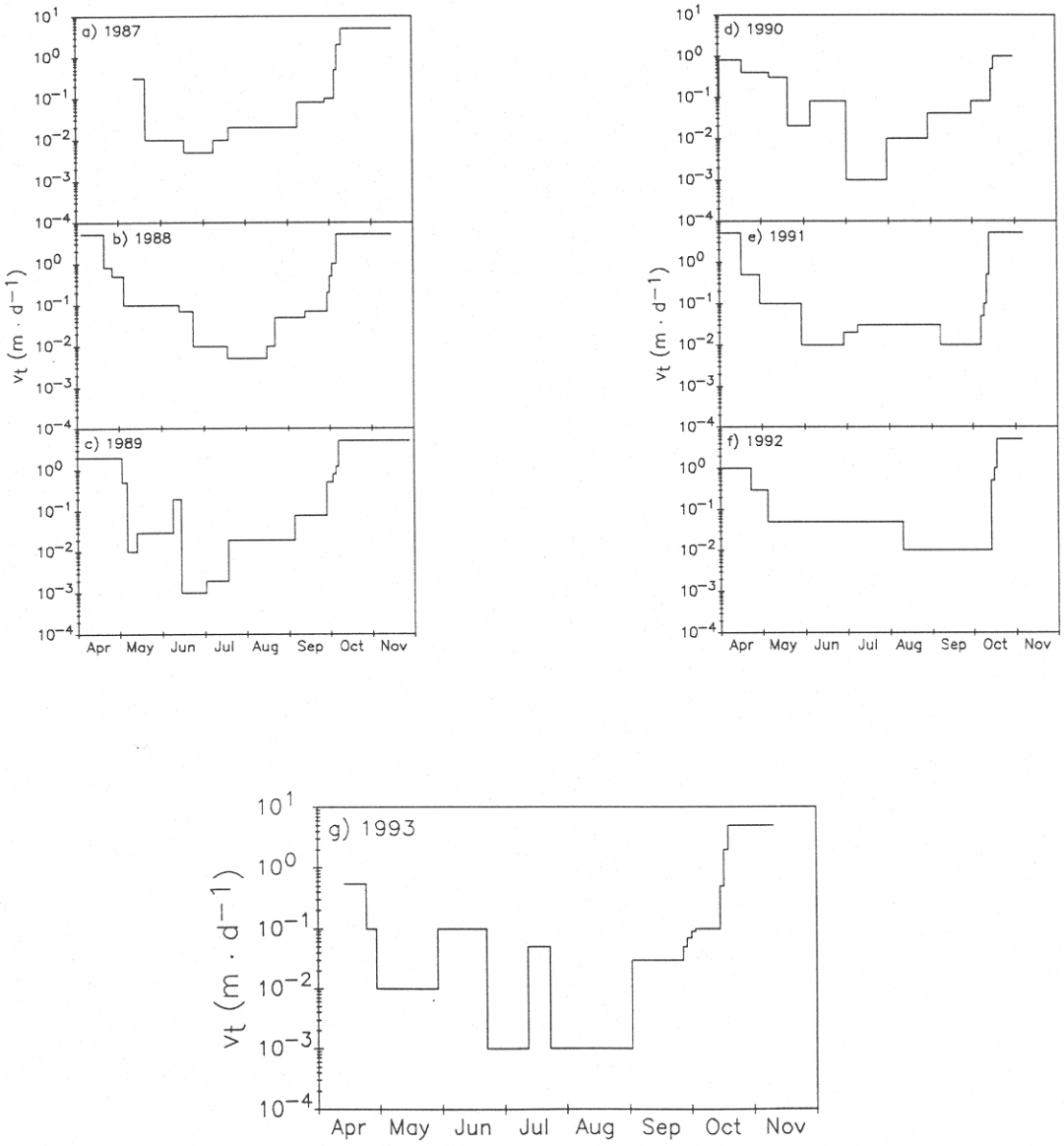


Figure 4-6. Temporal distributions of the calculated vertical mixing coefficient (v_t) for Onondaga lake for the spring-fall interval: a) 1987, b) 1988, c) 1989, d) 1990, e) 1991, f) 1992, and g) 1993.

Wodka et al. 1983), as described for Onondaga Lake for the 1987 - 1990 interval using the fixed-layer constraint (Doerr et al. 1995), and as described for the lake, outside of the fixed-layer constraints invoked here (Owens and Effler 1995). Minimal vertical mixing is indicated in mid-summer (Figure 4-6) when stratification is strongest; vertical mixing is higher in spring and fall when stratification is weaker (Owens and Effler 1995). The details of the distributions are expected to differ from year-to-year as a result of meteorological variability (Effler et al. 1986c, and Owens and Effler 1989). The magnitude of v_t was estimated to be particularly low in spring and for much of the mid-summer period of 1993 (Figure 4-6g). The time distributions of v_t can be used directly as model inputs for updated testing of the Onondaga Lake water quality models (e.g., Doerr et al. 1995, Canale et al. 1995a, Gelda et al. 1995).

CHAPTER 5

TROPHIC STATE: RELATED CHARACTERISTICS

Background/Recent Trends in Common Indicators

Onondaga Lake is hypereutrophic (Auer et al. 1990), largely as a result of tertiary effluent (average TP concentration of about 0.6 $mg \cdot L^{-1}$) received from METRO. This domestic waste input represents, on average, nearly 20% of the total annual inflow and 60% of the annual TP load received by the lake (Effler and Whitehead 1995). Chlorophyll concentrations tended to remain high (e.g., > 30 $\mu g \cdot L^{-1}$; Auer et al. 1995a) throughout the productive period of late spring to early fall before closure of the adjoining soda ash/chlor-alkali facility. Since 1987 stronger seasonality has been observed, characterized by distinctly lower minima(e.g., < 3$\mu g \cdot L^{-1}$), of longer duration, compared to earlier years (Auer et al. 1995a). This change has been attributed to shifts in the zooplankton community (more efficient grazers), brought about by reductions in the salinity of the lake (Seigfried et al. 1995) that resulted from closure of the soda ash/chlor-alkali facility (Doerr et al. 1994). Over the 1987-1990 interval the general seasonality of phytoplankton in the lake was flagellated green algae and cryptomonads in spring, dominance of chlorococcalean green algae and flagellates in summer and fall, with increasing contributions of filamentous cyanobacteria (e.g., Aphanizomenon flos-aquae) in summer (Sze 1995). The reemergence of these nuisance organisms may be in response to increased grazing pressure (Seigfried et al. 1995).

Time distributions of the TP load from METRO over the

April-September interval (e.g., period critical for support of summer phytoplankton populations) and common indicators of trophic state as summertime means or medians, are presented, along with the annual volume-weighted Cl^- concentration of the lake, in Figure 5-1(a-e). It is important to recall that the lake has a high flushing rate, and thus responds rapidly to significant reductions in external loading (Effler and Whitehead 1995, Doerr et al. 1994). The summertime epilimnetic TP concentrations are tightly coupled to TP loading from METRO (Figures 5-1a and b, 5-2). Approximately 97% of the year-to-year differences in epilimnetic TP concentrations over the 1987-1993 interval, eliminating 1988 from the population, can be explained by changes in METRO TP loading (Figure 5-2). Treatment of 1988 as an outlier is justified because of the unusually large TP load that emanated from Onondaga Creek that year, caused by sewer line breaks (Effler and Whitehead 1995). Note that distinct improvements in clarity (Figure 5-1d) and reductions in phytoplankton biomass (Figure 5-1c) were not tightly coupled to reductions in METRO TP loading, but were coincident with the reductions in Cl^- concentration. Further, the annual summer time concentration of phytoplankton biomass and clarity were largely insensitive to the reincrease in TP loading and lake concentrations observed in 1993. The evidence is strong (e.g., Figure 5-1; Seigfried et al. 1995) that the reductions in phytoplankton and improvements in clarity are uncoupled from TP loading (e.g., "bottom-up" effects). These substantial changes instead appear to be a manifestation of increased "top-down"

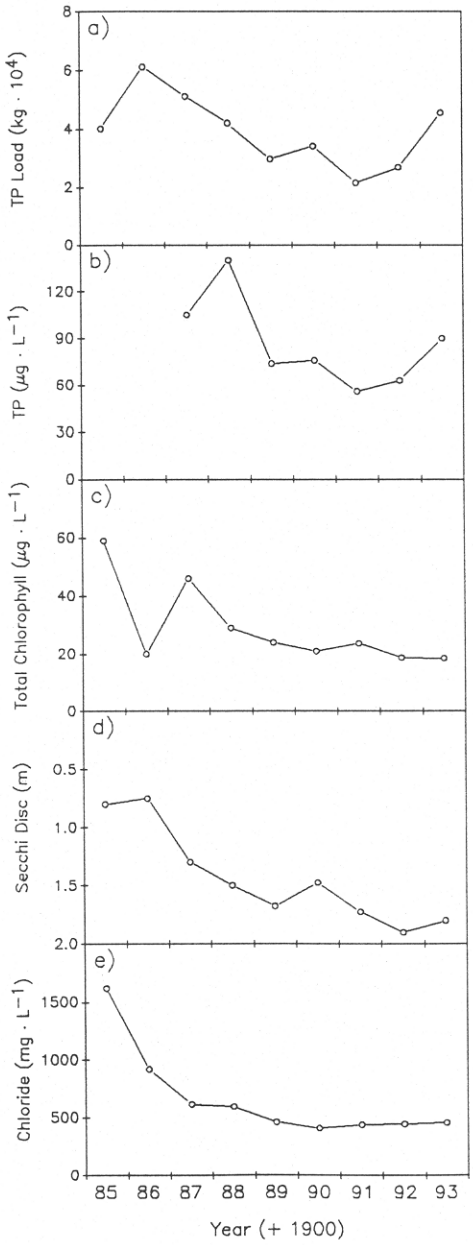


Figure 5-1. Time distributions of annual conditions for Onondaga Lake: a) total phosphorus (TP) load from METRO (April-September), b) epilimnetic summer average TP concentration, c) summer median chlorophyll concentration in upper waters, d) summer median Secchi disc transparency, and e) epilimnion chloride concentration of lake.

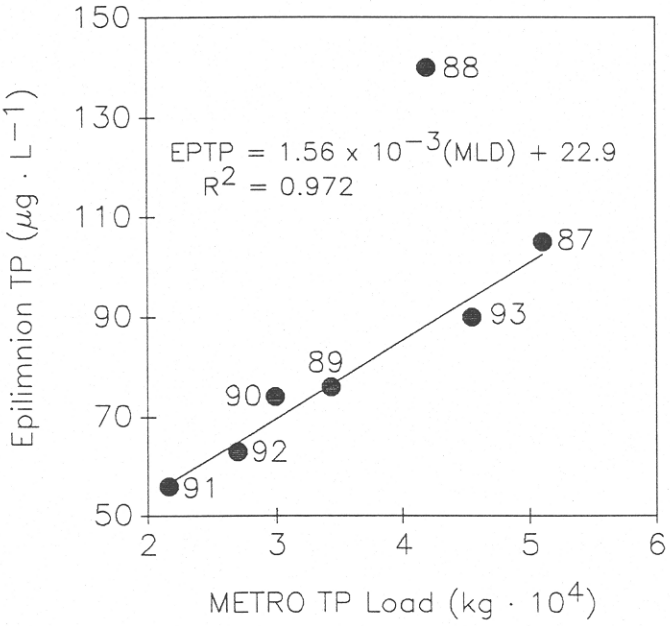


Figure 5-2. Evaluation of relationship between epilimnetic summer average total phosphorus (TP) concentration in Onondaga Lake and TP loading from METRO over the April-September interval. Individual years identified by the last two numbers.

pressure on the phytoplankton (and perhaps other particles) from zooplankton (Seigfried et al. 1995).

Dissolved Oxygen

Detailed Profiles. Oxygen profiles for Onondaga Lake in 1993 are presented in Figure 5-3. Severe oxygen depletion was established by the start of monitoring in mid-April (Figure 5-3a), because of the failure of spring turnover, and the absence of the related replenishment of the oxygen resources of the lower layers. Initially the lowermost 2 m of the water column were anoxic. The depth interval of anoxia expanded in the hypolimnion as stratification became stronger. Significant vertical structure in the upper waters was manifested only during calm periods; otherwise uniform concentrations were observed in the epilimnion. By late August all but the upper 5 m of water column was anoxic. Divergences from saturation in the epilimnion during summer (e.g., highly oversaturated on August 26 (Figure 5-3t)) were largely associated with phytoplankton activity. The progressive deepening of the epilimnion in fall was accompanied by progressive decreases in the concentration of DO to a level representing violation of a New York State water quality standard (i.e., $< 4\ mg \cdot L^{-1}$). This depletion has been attributed to oxygen demand exerted by hypolimnetic accumulations of H_2S (Effler et al. 1988) and CH_4 (Addess and Effler 1995) as they are entrained into the deepening epilimnion. This feature of the degraded conditions of the lake are addressed in more detail in Chapter 3. Some recovering of the oxygen resources of the lake was apparent by early November of 1993, near the onset of complete fall

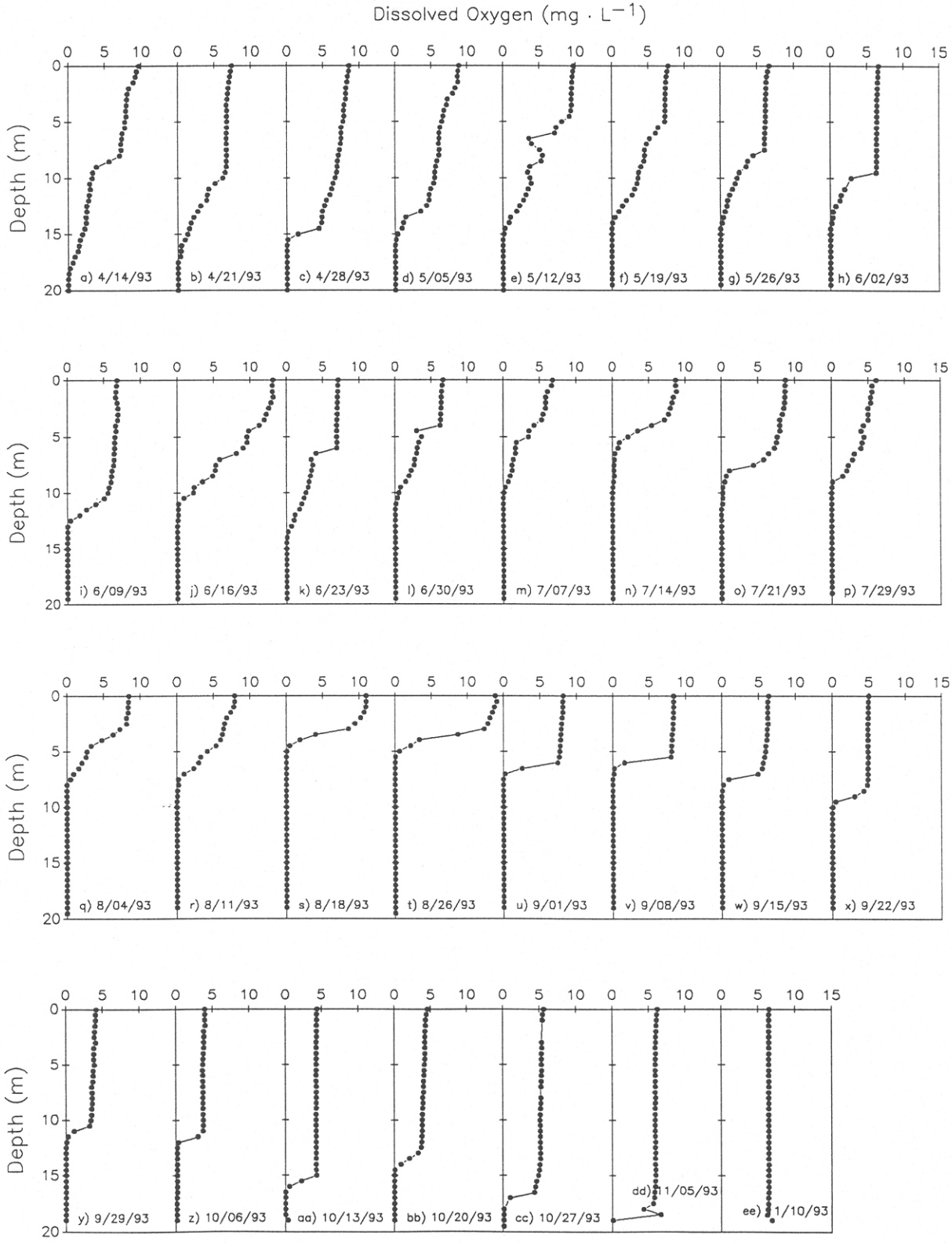


Figure 5-3. Profiles of dissolved oxygen concentrations in Onondaga Lake for the spring to fall interval of 1993 (a-ee).

turnover.

Bounds of Anoxia. The implications of the failure of spring turnover on the temporal distribution of anoxia in Onondaga Lake is illustrated in Figure 5-4(a-c). The upper depth boundaries of anoxia observed in the lake for 4 different years before closure of the soda ash/chlor-alkali facility, and the year of closure, are compared to conditions observed in the 6 years following closure in Figure 5-4(a and b). The breadth of the envelopes formed by these populations represents the substantial level of variability in this feature of the distribution of oxygen that is common to the lake. For example, note the more severe conditions observed in early summer in 1987 and in early fall in 1990 (Figure 5-4b). This variability is at least in part attributable to variations in the stratification regime associated with natural meteorological variability. The distributions for the two periods are similar in mid-summer (Figure 5-4a and b). However, the more recent distribution is clearly narrower, i.e., in general, the lower layers remain oxygenated longer in spring and early summer, and are replenished sooner in fall since the closure of the facility. This change is largely the result of decreases in the duration of stratification that accompanied the closure of the plant (Owens and Effler 1995).

The conditions of 1993 are compared to these populations, represented by the best fit polynomial curves, in Figure 5-4c. The failure of spring turnover caused this feature of the oxygen resources of the lake to revert to the preclosure conditions in spring. These conditions extended beyond the bounds of the

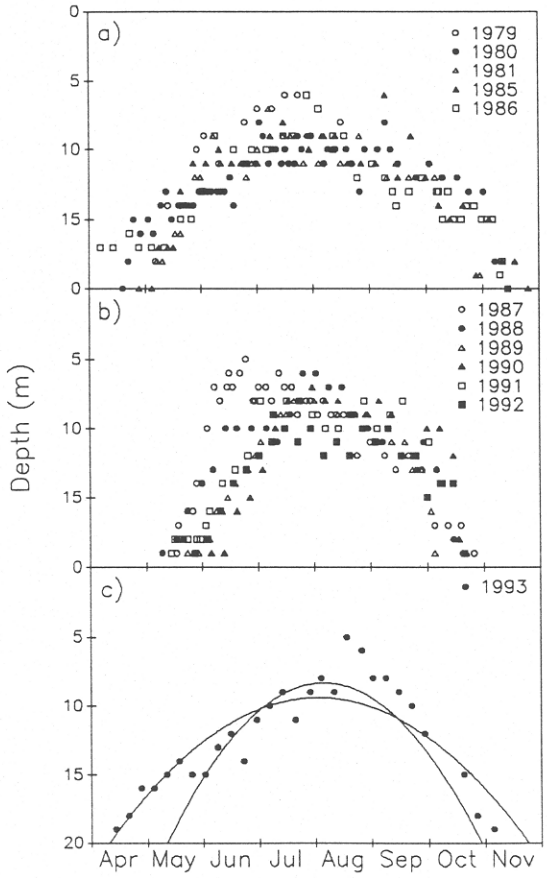


Figure 5-4. Temporal distributions of the upper depth boundary of anoxia in Onondaga Lake: a) before, and the year of, closure of the soda ash/chlor-alkali facility (1979-1981, 1985, 1986), b) 1987-1992, and c) 1993, compared to polynomial fits of the distributions from a) and b).

envelope formed by observations over the 1987-1992 period. This degradation in 1993 is attributed to the failure of spring turnover, and ultimately the continuing ionic waste input from the most recently active waste beds of the soda ash/chlor-alkali manufacturer (see Chapter 4). Note, however that the distribution in fall of 1993 tracks conditions observed in other years since closure. The spring DO conditions of 1993 reaffirm the important role duration of stratification plays in regulating the duration of anoxia in Onondaga Lake and the negative impact the ionic waste discharge from that facility had on the oxygen resources of the lake during its operation (Effler 1995c), and continues to have, albeit irregularly, since closure.

AHOD. The depletion of hypolimnetic DO is most often parametrized as the "areal hypolimnetic oxygen deficit" (AHOD; $g \cdot m^{-2} \cdot d^{-1}$). AHOD has been used as an indicator of trophic state (Hutchinson 1938, Mortimer 1941). Mortimer (1941) proposed limits of 0.25 $g \cdot m^{-2} \cdot d^{-1}$ for the upper limit of oligotrophy and 0.55 $g \cdot m^{-2} \cdot d^{-1}$ for the lower limit of eutrophy. The depletion of DO from the hypolimnion is depicted for 6 earlier years and 1993 in Figure 5-5(a-g), as the time plot of volume-weighted DO concentrations below a depth of 10 m. Each data point is based on an oxygen profile measured at a 1 m depth interval and the hypsographic data of Owens (1987). AHOD is calculated quotient of the slope of the hypolimnetic mass content time plot and the area of the hypolimnion. Linear least squares regression analysis was used to support AHOD estimates for the years before 1993 (Figure 5-5a-f). These values are presented and compared to

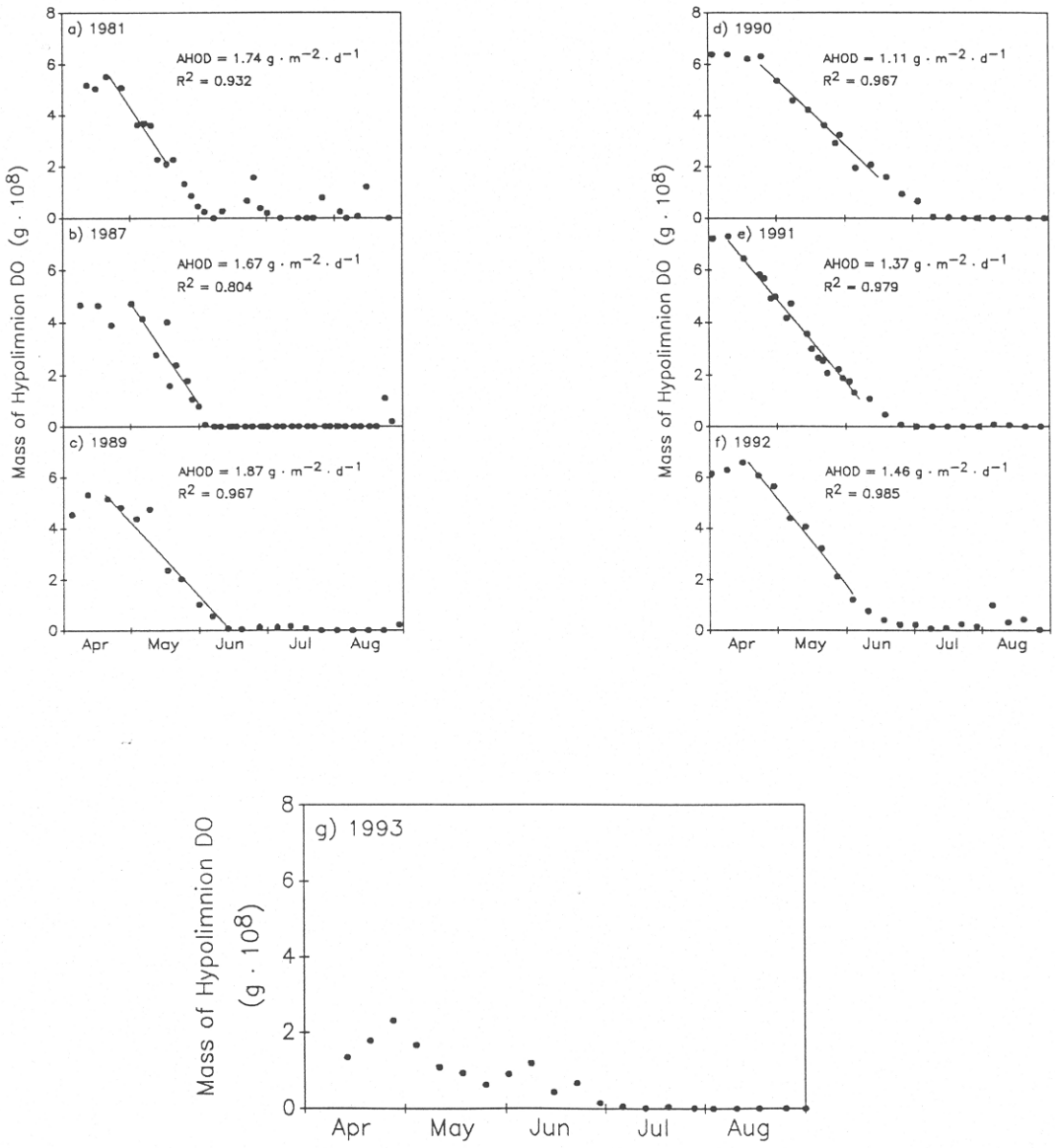


Figure 5-5. Depletion of dissolved oxygen from the hypolimnion of Onondaga Lake for 7 years, with determination of "areal hypolimnetic oxygen deficit" (AHOD): a) 1981, b) 1987, c) 1989, d) 1990, e) 1991, f) 1992, and g) 1993 (no determination because of failure of spring turnover).

estimates for nearby Otisco and Owasco Lakes in Table 5-1. The

TABLE 5-1: Comparison of AHOD Values; Onondaga Lake, Otisco Lake and Owasco Lake

Lake	Year	AHOD $g \cdot m^{-2} \cdot d^{-1}$	Source
Onondaga (hyper-eutrophic)*	1981	1.7	Figure 5-5
	1987	1.7	Figure 5-5
	1989	1.9	Figure 5-5
	1990	1.1	Figure 5-5
	1991	1.4	Figure 5-5
	1992	1.5	Figure 18
Otisco (mesotrophic)	1983	1.0	Effler et al. 1985
	1986	0.8	Effler et al. 1987a
	1988	0.8	Effler et al. 1989
Owasco (oligo-mesotrophic)	1987	0.62	Effler et al. 1987b

* trophic state

average for these years is 1.54 $g \cdot m^{-2} \cdot d^{-1}$, the range is 1.1 to 1.87 $g \cdot m^{-2} \cdot d^{-1}$. These values are indicative of a highly eutrophic system (e.g., Mortimer 1941); they approach the highest values incorporated in data bases used to develop predictive empirical expressions for AHOD (Cornett and Rigler 1979, Walker 1979, Welch and Perkins 1979). The value determined for 1990 is distinctly lower than the other years (Figure 5-5). As is the case for the DO minimum during the fall mixing period (Chapter 3), no clear trend emerges from this population of AHOD values, similarly, the year-to-year variability in this feature of the oxygen resources of the lake is attributed largely to meteorological variability. The values for Onondaga Lake are, with the exception of the 1990 estimate, substantially greater than those obtained for the other two lakes (Table 5-1), consistent with the established

differences in trophic state of the lakes, though the AHOD value for Owasco Lake is greater than expected for its trophic state.

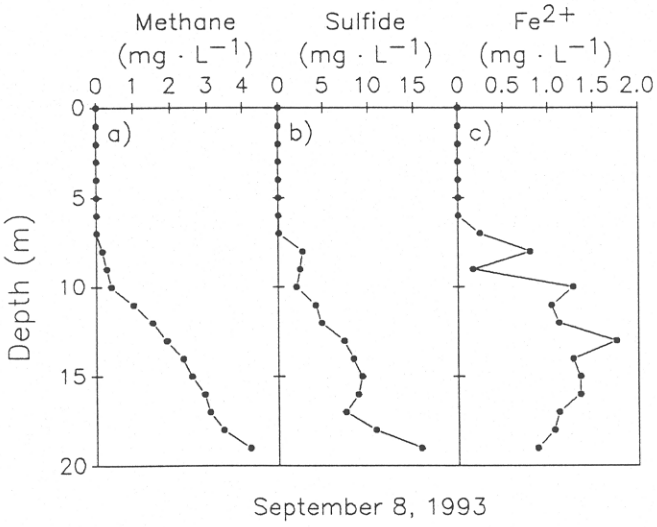
The monitoring data for Onondaga Lake in 1993 (Figure 5-5g) cannot support the estimation of AHOD because the lower waters were not replenished with oxygen in spring, as a result of the failure of the lake to experience spring turnover. Note that the maximum concentration in late April in 1993 (Figure 5-5g) was about at the lower limit of values included in analyses from the earlier years (Figure 5-5 a-f). The scarcity of estimates from before closure of the soda ash/chlor-alkali facility (Table 5-1) in part reflects the common failure of spring turnover during the plant's operation (e.g., Effler et al. 1986). Spring turnover occurred in all the years for which AHOD estimates are presented in Table 5-1.

Anaerobic Metabolism By-Products

Decomposition processes in the hypolimnion and surface sediments proceed via aerobic pathways until oxygen is depleted. Thereafter decomposition is affected by several anaerobic processes, including denitrification, Fe^{3+} reduction, SO_4^{2-} reduction, and methanogenesis. Accumulation of the by-products of anaerobic metabolism in the lake's hypolimnion during summer stratification has been documented (e.g., Addess and Effler 1995, Driscoll et al. 1995a, Effler et al. 1988). Oxidation of these materials, particularly methane (CH_4) and hydrogen sulfide (H_2S), upon entrainment into the overlying oxygenated waters is largely responsible for the lake-wide depletion of DO observed during the fall mixing period (Figure 5-3, also see Chapter 3; Gelda et al.

1995). Assessment of the summertime accumulation of the reduced species by-products of anaerobic metabolism represents a measure of these anaerobic pathways (e.g., Driscoll et al. 1995a), and ultimately primary production. Further, the accumulations and the time course of the reduction in the pools of these materials has important implications for the lake's problem of degraded oxygen resources during the fall mixing period.

Example profiles for CH_4, H_2S, and ferrous iron (Fe^{2+}) in late summer in 1993 are presented in Figure 5-6(a-c). Several features of these profiles are recurring for the lake (see Driscoll et al. 1995a). No detectable quantities of these reduced species were observed in the oxic layers of the water column (e.g., anoxia established by 7 m depth on September 8, see Figure 5-3v). Concentrations of CH_4 and H_2S generally increased with depth within the anoxic depth interval of the lake, with maximum concentrations observed proximate to the sediment-water interface (Figure 5-6(a and b)). This vertical distribution is consistent with the sedimentary sources of these materials and the limited vertical mixing that occurs in the hypolimnion. The profile for Fe^{2+} depicts a different vertical distribution, with the maximum displaced from the sediment-water interface. This disparate distribution is likely a manifestation of interaction with the high concentrations of H_2S (~ 10x, on a molar basis) that develop. This pattern is consistent with the oversaturated conditions that prevail with respect to the solubility of FeS (Driscoll et al. 1993) and the observed presence of FeS particles in the near bottom waters in late summer (Yin and Johnson 1984).



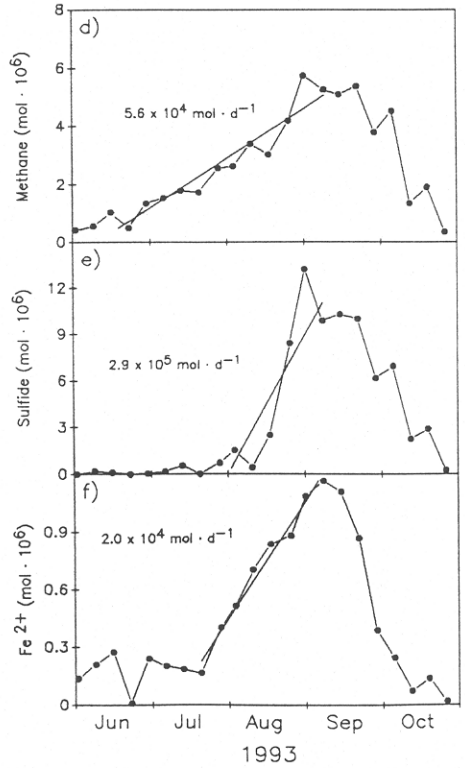


Figure 5-6. Distributions of reduced species in Onondaga Lake, example profiles from late summer: a) methane, b) hydrogen sulfide, and c) ferrous (Fe^{2+}) iron), and temporal transformations in total lake content: a) methane, b) hydrogen sulfide, and c) Fe^{2+}, with estimates of accumulation rates.

Evidently the decrease in Fe^{2+} concentrations in the deepest anoxic depths in late summer reflects the immobilization of Fe^{2+} by H_2S, to form precipitated FeS.

Seasonal distributions of the total water column content ("pool") of CH_4, H_2S and Fe^{2+} in 1993 are presented in Figure 5-6(d-f). The maximum pool size of CH_4 in late summer of 1993 was only slightly less than reported for 1989 and 1990 (Driscoll et al. 1995a). However, the accumulation rate (5.6×10^4 $mol \cdot d^{-1}$) was about 15% less than reported for 1989 and 1990 (Driscoll et al. 1995a). This may in part be a result of the lower bottom water temperatures that prevailed in 1993 because of the failure of spring turnover to occur (see Chapter 4). The maximum H_2S pool in 1993 was the greatest observed since 1987. Accumulation of H_2S started distinctly later than observed for CH_4 or Fe^{2+} (Figure 5-6), but increased much more abruptly. The estimated accumulation rate (29×10^4 $mol \cdot d^{-1}$), which is highly dependent on the selection of the time interval for the calculation, is the highest reported to date (see Driscoll et al. 1995a). The maximum Fe^{2+} pool was reduced compared to recent years, probably reflecting control by the elevated H_2S levels through FeS solubility/precipitation.

Chlorophyll and Phosphorus Pool Dynamics

Recently Connor et al. (1995) analyzed the seasonality in the P physiology of the phytoplankton assemblage of Onondaga Lake for the 1989-1992 interval, by assessing the dynamics of dissolved and cellular P pools, phytoplankton biomass (chlorophyll, C_T), and one year of alkaline phosphatase activity

(APA) assays. Evidence for luxury uptake of soluble reactive P (SRP) and utilization of dissolved organic P (DOP) by the lake's phytoplankton was presented. It was concluded that the high concentrations of phytoplankton biomass maintained from mid-to late summer annually were in part sustained by the DOP pool (Connor et al. 1995). Concentrations of SRP were shown to be an inadequate representation of nutrient limitation in the lake. Portions of their analysis are extended here for 1993.

Soluble reactive P (SRP) is an imperfect representation of the external P pool available for algae uptake. This analyte includes ortho-P and the reactive fraction of the dissolved organic P pool. The unreactive fraction of the DOP pool, can be made available to algae through enzymatic hydrolysis (Healy and Hendzel 1979, Gage and Gorham 1985). Enzymes cleave ortho-P groups from large organic P molecules otherwise unavailable to algae (Bentzen et al. 1992). The most well-known of these enzymes are the alkaline phosphatases, which have been the subject of many studies (e.g., Fitzgerald and Nelson 1966, Francko 1983, Hantke and Melzer 1993). Phytoplankton growth is known to be related to internal (stored) nutrient concentration (Auer and Canale 1982, Auer et al. 1986, Droop 1968). A measure of this concentration is cell quota (Q). Here Q, the P content of a unit biomass, is estimated as the ratio of particulate P (PP = TP-TDP) to C_T ($\mu gPP \cdot \mu g^{-1}$ chlorophyll). This representation of Q is imperfect to the extent that there are contributions to PP other than phytoplankton and that the cellular content of chlorophyll is subject to variation (Auer et al. 1986). The

unreactive pool of dissolved organic P (DOP; i.e., not included in SRP measurement) is estimated here as the residual, DOP = TDP-SRP.

Paired seasonal distributions of dissolved P species (2), Q, and C_T are presented for 1993 in Figure 5-7. Despite year-to-year differences in the temporal details of these distributions, associated with interannual variations in the timing and intensity of phytoplankton blooms, several of the patterns that emerged in 1993 are recurring (see Connor et al. 1995); others are unique for the 1989-1993 interval. Concentrations of DOP were initially high in spring. The spring phytoplankton bloom was diminished compared to earlier years, perhaps related to the failure of spring turnover to occur and the unusually high non-phytoplankton turbidity (i.e., reduced light availability) that prevailed during the high runoff period of April. The very high Q value in April (Figure 5-7b) was probably in part an artifact of high concentrations of PP associated with non-phytoplankton particles. Decreases to very low phytoplankton concentrations were observed in late May and late June (Figure 5-7c), which were largely responsible for the high clarity documented for those intervals (Chapter 3). The decrease in C_T in May proceeded substantial depletions in the dissolved P pool(s), though the mid-June bloom clearly drove SRP down to low levels.

Abrupt increases in SRP were observed during both clearing events, as in earlier years. These presumably reflect the reduction in phytoplankton uptake, with continued external

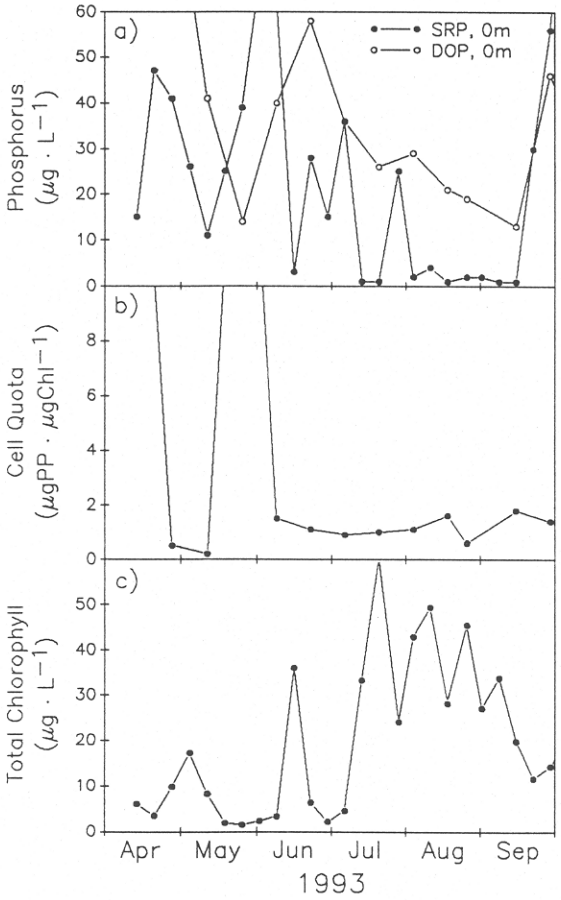


Figure 5-7. Time series for the upper waters of Onondaga Lake in 1993: a) SRP and DOP, b) cell quota (Q), and c) chlorophyll.

loading, and perhaps an elevated level of recycle within the upper waters (Auer et al. 1990). Cell quota increased dramatically during the first clearing event indicative of luxury uptake of P, as in earlier years, but was not detected by the monitoring program for the second clearing event in late June. The depletion of DOP over part of the May clearing event (Figure 5-7a) remains unexplained. Distinct blooms occurred after both clearing events, as observed in earlier years (Connor et al. 1995). Phytoplankton biomass concentrations remained relatively high from mid-to late summer. SRP concentrations remained low (mostly $< 2\ \mu g \cdot L^{-1}$) for much of this period, as did the values of Q ($< 2\ \mu gPP \cdot \mu g^{-1}$ chlorophyll), though the period of SRP depletion was shorter than in recent years (Connor et al. 1995). The DOP pool decreased over this period of depleted SRP, suggesting algal utilization to sustain the elevated levels of phytoplankton. The apparent use of DOP by the lake's phytoplankton is consistent with the findings of Connor et al. (1995), and supports their position that SRP concentration is an inadequate representation of nutrient limitation in Onondaga Lake (Connor et al 1995). Further, values of Q remain above levels (e.g., Auer et al. 1986) associated with a substantial degree of nutrient limitation.

CHAPTER 6

CALCIUM CARBONATE, INORGANIC CARBON, AND pH

Background

Many hard water lakes become oversaturated with respect to the solubility of $CaCO_3$ (usually as calcite) during the productive summer period; both physiochemical (e.g., Brunskill 1969, Strong and Eadie 1978) and biochemical (e.g., photosynthesis; Effler 1984, Effler and Driscoll 1985, Effler et al. 1982) processes can contribute to the development of these conditions and the stimulation of $CaCO_3$ precipitation. Precipitation and deposition of $CaCO_3$ is a widely observed phenomenon in hard water lakes (Effler 1987b, Kelts and Hsu 1978, Jones and Bowser 1978). This results in the removal of aqueous Ca^{2+} and dissolved inorganic (DIC), and often the accumulation of $CaCO_3$ in the underlying sediments (Jones and Bowser 1978). The phenomenon has broader importance, as it may influence the cycling of other constituents such as P (Wodka et al. 1985) and dissolved organic carbon (Otsuki and Wetzel 1973), and particles that serve as nuclei for precipitation (Johnson et al. 1991). Further, water clarity has been observed to decrease greatly during periods of $CaCO_3$ precipitation in some lakes (e.g., Effler et al. 1991b, Weidemann et al. 1985) due to increases in light scattering.

The entire water column of Onondaga Lake was found to be oversaturated with respect to the solubility of calcite ($CaCO_3$) over the spring to fall interval before the closure of the facility (e.g., Effler and Driscoll 1985, Effler 1987a),

indicating a continuous tendency for the precipitation of calcite, and, once formed, no tendency for dissolution. These conditions have been described as extraordinary (Effler 1987a; particularly for the hypolimnion), and have been attributed to the very high concentrations of Ca^{2+} maintained in the lake from the ionic waste discharge of the soda ash/chlor-alkali facility (Effler and Driscoll 1985). Despite the major (60-70%) reduction in lake concentrations of Ca^{2+} brought about by the decreased loading that accompanied closure of the facility, the lake remained oversaturated with respect to calcite through 1990 (Driscoll et al. 1994). Contrary to the speculation of Yin and Johnson (1984), there is no evidence of dissolution of a significant fraction of deposited $CaCO_3$ in Onondaga Lake before or after closure. Significant shifts in the distributions of inorganic carbon and pH have occurred in response to the decrease in Ca^{2+} concentrations, that are manifestations of reduced $CaCO_3$ precipitation. The depletion of DIC and alkalinity from the epilimnion in summer has decreased, a clear indication that $CaCO_3$ precipitation/deposition was greater during the operation of the soda ash/chlor-alkali facility (Driscoll et al. 1994). This position is supported by the 3-fold reduction in the downward flux of particulate inorganic carbon (PIC) since closure, determined from analysis of sediment trap collections (Driscoll et al. 1994). The ionic waste discharge from the soda ash/chlor-alkali facility clearly increased precipitation and deposition of $CaCO_3$ in the lake (Driscoll et al. 1994), and thereby accelerated the "filling-in" of the lake (Effler 1987a).

Calcium carbonate is the single largest component of the lake's deep water (Rowell and Effler 1994) and near-shore (Auer et al. 1995b) sediments. Further, the distribution of pH values in the upper waters is narrower and values are shifted higher (Driscoll et al. 1994). These changes reflect the maintenance of higher buffering capacity and reduced H^+ production associated with $CaCO_3$ precipitation, respectively, since closure (Driscoll et al. 1994).

The Ca^{2+} discharge from the facility has altered the near shore sediments of Onondaga Lake through the formation of $CaCO_3$ - enriched deposits. A large delta of soft sediment, composed mostly of $CaCO_3$, has formed at the mouth of Ninemile Creek. Most of this $CaCO_3$ was probably formed in the creek, between the point(s) of entry of the Ca^{2+} waste from the facility's lagoons and the creek mouth. Portions of the delta were dredged in the late 1960's. Much of the near shore zone of the lake (particularly for depths < 2 m) is covered with oncolites (Madsen et al. 1992), ovoid crytalgal structures or concretions, with concentric laminations. These concretions are composed mostly of $CaCO_3$ (92%) and range in size from a few millimeters to as much as 15 cm is diameter (Dean and Eggleston 1984). Dean and Eggleston (1984) contend that the formation of oncolites in Onondaga Lake is a result of the Ca^{2+} enriched discharge of ionic waste from the soda ash/chlor-alkali facility, and that these

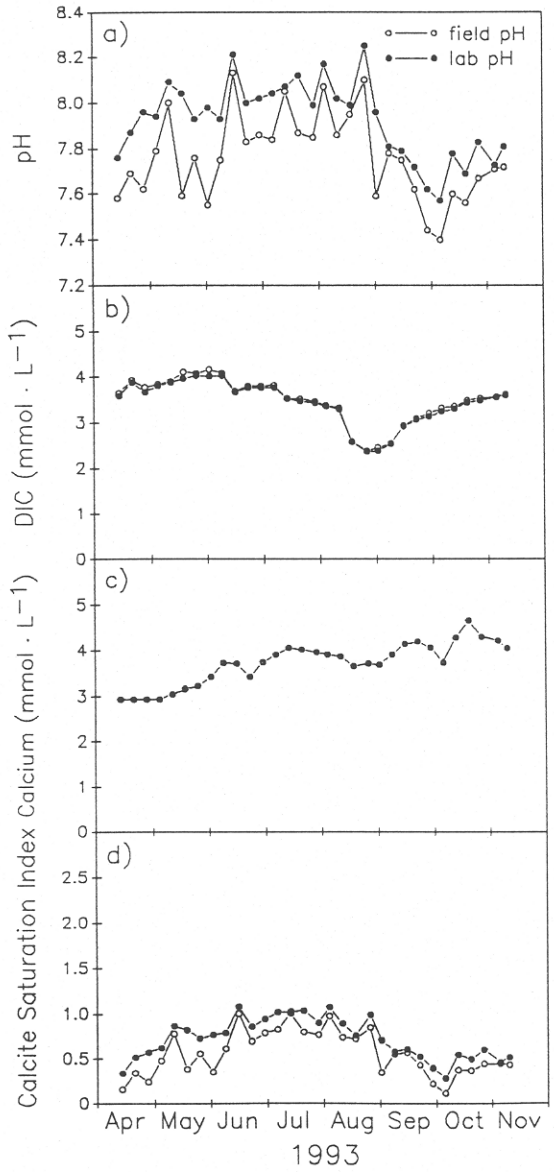


Figure 6-1. Time series for the upper waters of Onondaga Lake in 1993: a) paired field and laboratory pH values, b) dissolved inorganic carbon (DIC), c) calcium (Ca^{2+}), and d) calcite saturation index (SI) values.

clear evidence for the precipitation of $CaCO_3$ from the upper waters (Figure 6-1b). The magnitude of the DIC depletion in 1993 was approximately the same magnitude as reported by Driscoll et al. (1994) for earlier post-closure years. The temporal structure for Ca^{2+} was distinctly different (Figure 6-1c). The increasing Ca^{2+} concentrations through mid-July reflect waste inputs (mostly from Ninemile Creek) that receive less dilution from the reduced summer inflow to the lake. The increased precipitation of late summer, in contrast to the DIC signature, was manifested instead as a "leveling off" followed by a minor decrease in August.

The upper waters of the lake were oversaturated throughout the April-November interval of 1993 (Figure 6-1d), indicating a continuous tendency for precipitation of $CaCO_3$. Use of laboratory measurements lead to overestimation of the degree of oversaturation of the lake with respect to the solubility of calcite, but the effect was modest (e.g., differences is SI values in most cases ≤ 0.2). The distributions of SI (based on laboratory measurements, to maintain consistency with other populations) in the upper waters in 1993 are compared to observations for three other periods in Figure 6-2(a-d), 1) 1980 and 1981, 2) 1985, and 3) 1989. Note that despite the major reductions in Ca^{2+} concentrations since closure of the soda ash/chlor-alkali facility the equilibrium conditions with respect to the solubility of calcite have not changed substantially (Figure 6-2). This is a manifestation of an approximately compensating shift to higher pH values (Figure 6-3), though the

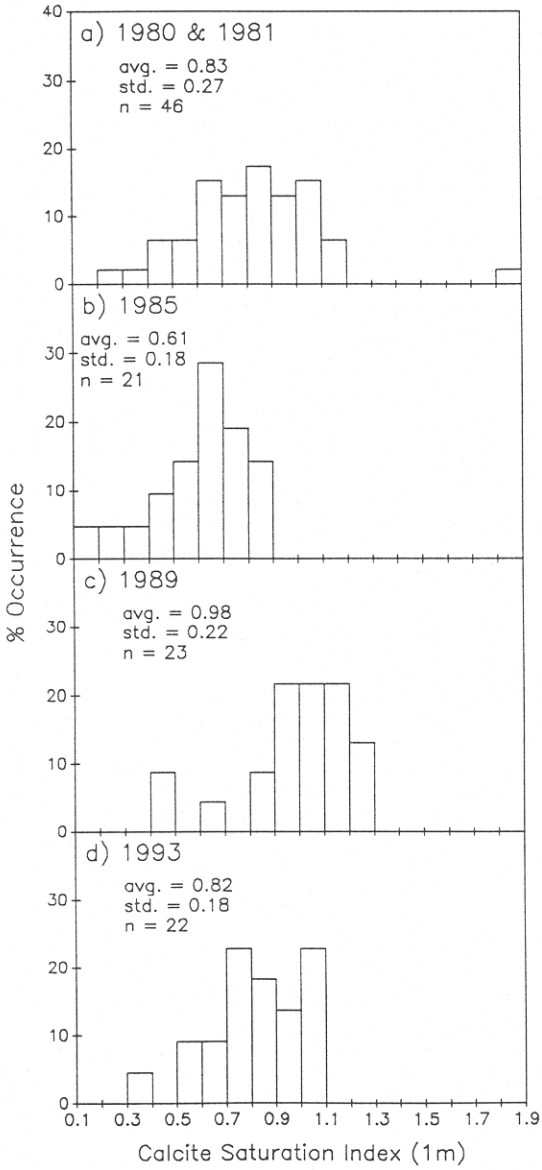


Figure 6-2. Comparison of summertime distributions of calcite saturation index (SI) values for the upper waters of Onondaga Lake for selected years: a) 1980 and 1981, b) 1985, c) 1989, and d) 1993.

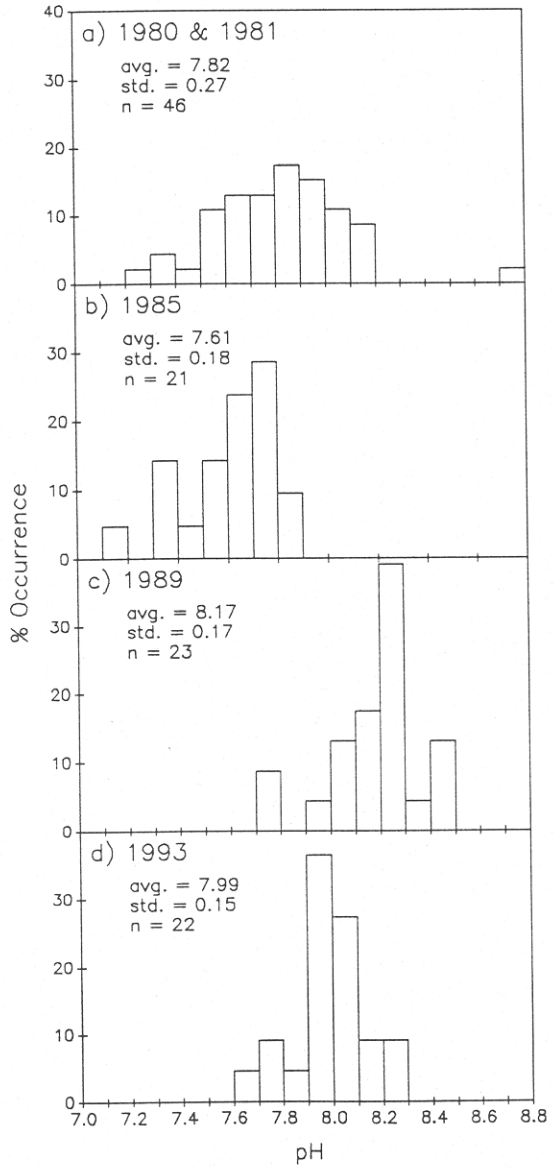


Figure 6-3. Comparison of summertime distributions of pH values for the upper waters of Onondaga Lake for selected years: a) 1980 and 1981, b) 1985, c) 1989, and d) 1993.

pH observations of 1993 were somewhat lower than those reported in 1989.

Vertical distributions of pH (in situ), DIC, Ca^{2+}, and SI are presented for mid-April, mid-June, mid-August, and mid-October in Figure 6-4. Substantial vertical differences in pH, DIC, and SI occurred during summer stratification, associated largely with differences in metabolic activity in the strata (e.g., CO_2 production in the hypolimnion associated with decomposition processes). The stratified Ca^{2+} concentrations observed in mid-April reflect the plunging of ionic waste from the waste bed area, carried by Ninemile Creek, and subsequent failure of spring turnover (see Chapter 4). The extent of Ca^{2+} stratification diminished by mid-June due to the entry of the enriched inflow(s) into the epilimnion. The mid-depth peak of mid-August is consistent with the distribution observed at that time for Cl (Chapter 4), another ionic waste constituent with the same origins (Effler and Whitehead 1995). The vertical structure of SI generally tracks that of pH. The upper waters were substantially more oversaturated with respect to the solubility of calcite than the lower waters during summer stratification. As observed in other years before (Effler and Driscoll 1985) and after (Driscoll et al. 1994) closure of the soda ash/chlor-alkali facility, essentially the entire water column remained oversaturated over the spring to fall interval of 1993. Thus there was no tendency for redissolution of deposited $CaCO_3$. This is supported by the absence of distinct increases of Ca^{2+} concentrations in the lake's hypolimnion during the summer.

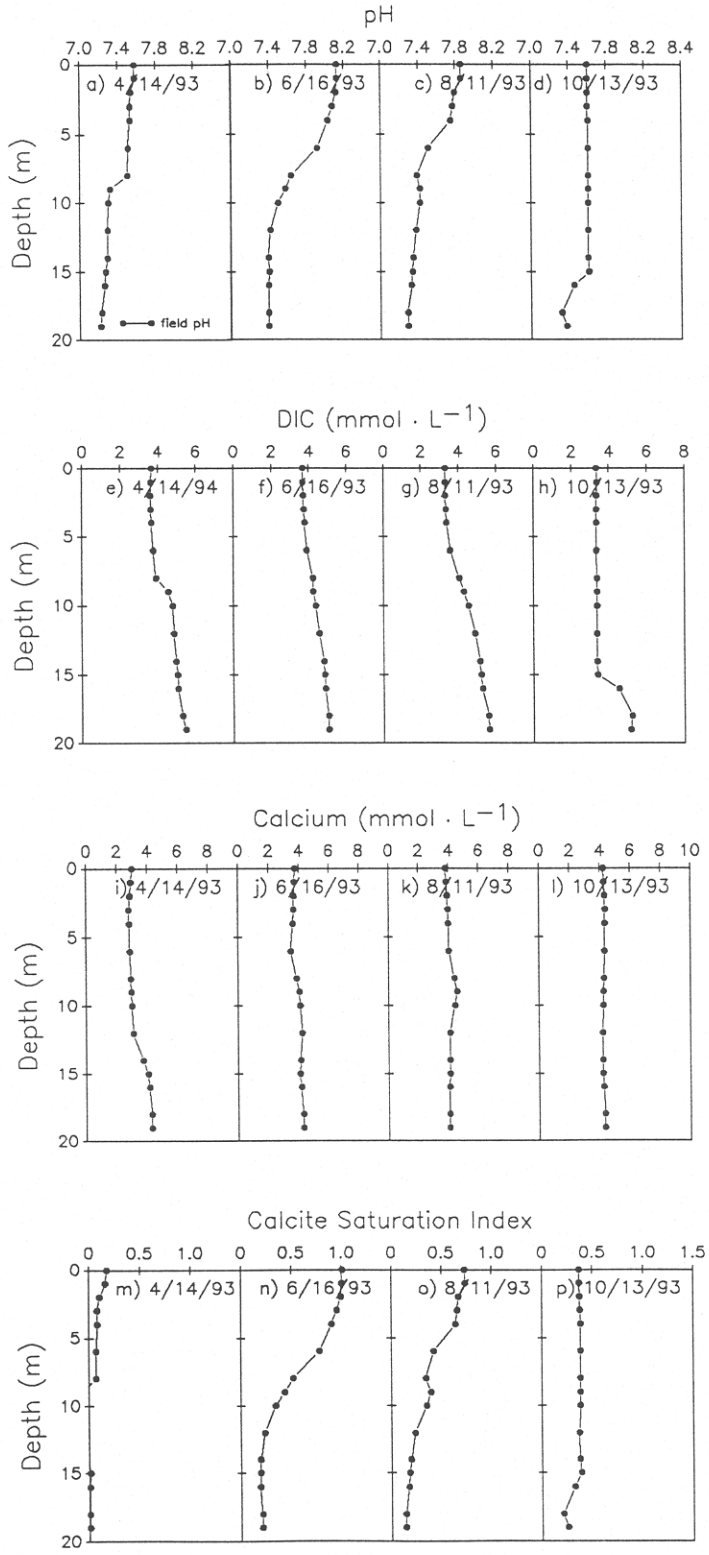


Figure 6-4. Profiles for selected dates in Onondaga Lake in 1993: a)-d) pH, e)-h) dissolved inorganic carbon (DIC), i)-l) calcium (Ca^{2+}), and m)-p) calcite saturation index (SI) values.

CHAPTER 7

OPTICS

Background

The behavior of light in water has important ecological and water quality implications. High clarity, low turbidity, absence of muddy appearance, and blue color, are nearly ubiquitous desires of lake users. As light passes down through water irradiance diminishes and its spectral quality changes as a result of absorption. Light is absorbed in water by four components; water itself, dissolved yellow substances (gelbstoff), phytoplankton, and tripton. The spectral character of absorption by these materials is generally widely different (Kirk 1983). Scattering is caused almost entirely by particles. Scattering increases light attenuation by increasing the pathlength that photons must traverse, thereby increasing the likelihood of the photons being absorbed. Particle scattering varies little with wavelength in the photosynthetically active radiation (PAR; 400-700 nm) interval compared to absorption (Kirk 1983, Phillips and Kirk 1984). The relative absorption/ scattering characteristics of different particle types (e.g., phytoplankton, $CaCO_3$, clays) are widely disparate (e.g., Bricaud et al. 1983, Kirk 1985, Weidemann et al. 1985). Substantial differences in composition and concentration of light attenuating substances occur between lakes and within individual lakes with time, causing major differences in the intensity of light absorption and light scattering. These are manifested as differences in a number of measurable optical properties that

describe light penetration, the angular distribution of irradiance, and the spectral quality of irradiance (Kirk 1983).

Recently, Effler and Perkins (1995) have documented the optical properties of Onondaga Lake for the late 1960's to 1990 period. Further, they provided a detailed analysis for the 1987-1990 interval that included measurements of attenuating components, light penetration (as measured by Secchi disc transparency, SD, and the vertical attenuation coefficient for downward irradiance, K_d), the angular distribution of irradiance, and the spectral character of attenuation $K_{d(\lambda)}$, and estimates of the absorption (a) and scattering (b) coefficients, and their components. Strong dynamics in phytoplankton biomass and major runoff events were found to cause wide and abrupt variations in a and b, and thereby SD, K_d, and $K_{d(\lambda)}$. A model for predicting K_d and SD from concentrations of attenuating substances, that is consistent with optical theory and utilized system-specific relationships that quantify contributions to a and b, was developed, tested, and applied. It was demonstrated that the primary components responsible for low SD and high K_d in the lake were phytoplankton and tripton (other than $CaCO_3$). Gelbstoff and $CaCO_3$ were relatively unimportant.

The improvements in the clarity of the lake since closure of the soda ash/chlor-alkali facility, attributed largely to increased zooplankton grazing, were documented in Chapter 3. Other changes in optical properties over the same period included reduced K_d and decreases in a and b. These changes were largely associated with reductions in phytoplankton biomass (e.g., C_T),

$CaCO_3$ particles, and perhaps other forms of tripton (Effler and Perkins 1995). Despite the improvements, the optical aesthetic features of the lake are still often degraded, irregularly failing to meet the 1.2 m clarity standard for a bathing beach. Here we document the dynamics of concentrations of light attenuating materials and light penetration (SD and K_d) in the lake in 1993.

Attenuating components measured in the 1993 monitoring program include C_T (a measure of phytoplankton biomass), turbidity (T, NTU), $CaCO_3$ turbidity (T_c, NTU), and gelbstoff (humic substances, as measured by the absorption of filtered water at a wavelength of 440 nm; $\underline{a}_{y(440)}$). While T_c and gelbstoff are relatively minor attenuating components on a seasonal basis, T_c is irregularly important over short periods, and gelbstoff concentrations limit the spectral quality of the lake under high clarity conditions (Effler and Perkins 1995). The value of K_d is calculated according to the Beer-Lambert law

$$E_{d(z)} = E_{d(o)} e^{-Kd \cdot z} \qquad (1)$$

in which $E_{d(o)}$, $E_{d(z)}$ = downward irradiance just below the surface and at depth(z) ($\mu E \cdot m^{-2} \cdot s^{-1}$). Operationally, the value of K_d is determined as the slope of the regression of the natural logarithm of E_d on z, usually in the depth region of the 10% ($Z_{0.1}$) light level. The quantum underwater light sensor used, and thus K_d, is sensitive to the photosynthetically active radiation wavelength interval (PAR; 400-700nm); which is also appropriate for general aesthetic concerns as it coincides with the human vision waveband.

Attenuating Components: 1993

The temporal distributions of the monitored light attenuating components over the April-September interval of 1993 are presented in Figure 7-1. Pronounced variations were observed for all these attenuating materials. Gelbstoff levels were higher in spring (Figure 7-1a), probably associated with the very high spring runoff (Chapter 2), were lowest in mid-summer, and increased somewhat in early fall. The average $\underline{a}_{y(440)}$ value for the monitoring period of 1993 was 0.747, the second highest observed over the seven year interval of 1987-1993 (Effler and Perkins 1995), and well within the range of values reported as typical of productive waters (Davies-Colley and Vant 1987). Gelbstoff is known to have both autochthonous and allochthonous sources (Bricaud et al. 1981, Davies-Colley and Vant 1987). Effler and Perkins (1995) concluded that terrigenous inputs regulated gelbstoff levels in Onondaga Lake. The uncoupled distributions of $\underline{a}_{y(440)}$ (Figure 7-1a) and C_T (Figure 7-1c) in 1993 continues to support this position.

Turbidity in a lake or reservoir is caused by a heterogeneous population of suspended particles, which may include clay, silt, finely divided organic and inorganic matter, phytoplankton, and other microscopic organisms. In general, this population of particles is a composite of sediment received as tributary inputs, resuspended lake deposits, and particles produced within the water column of the lake (e.g., phytoplankton and $CaCO_3$ particles). The temporal distributions of T and T_C at a depth of $z_{0.1}$ at the south deep station are presented for the

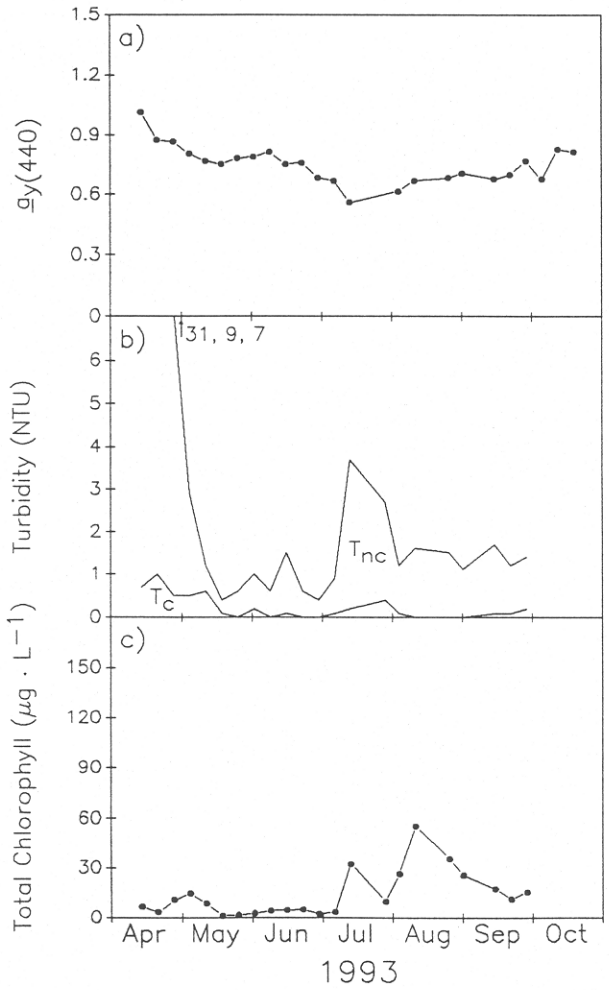


Figure 7-1. Time series of light attenuating materials in the upper waters of, Onondaga Lake in 1993: a) gelbstoff ($a_{y(440)}$), b) turbidity (T) and calcite turbidity (T_c), and c) chlorophyll (C_T).

April through October interval in Figure 7-1b. The extremely high turbidities in April and May were the result of runoff/flooding from a late winter snowstorm (137 cm of snow in March) and high rainfall (16.6 cm) in April. A second major peak in T occurred in July, that was also coupled to high runoff (3.9 cm rainfall in 24h). Seasonal minima in T (0.4 - 0.6 NTU) occurred during mid- May and late June. Over 99% of the variation in T was explained by variations in the non-calcite components of T (T_{nc}). The comparatively modest peaks in T_c coincided with peaks in T that followed runoff events. This supports the position that the sudden influx of terrigenous particles to the lake following major runoff events (Effler et al. 1992) triggers $CaCO_3$ precipitation events by providing heteronuclei (Johnson et al. 1991). The average value of T_c for the monitoring period was 0.2 NTU; the range was 0 to 1.0 NTU. The average contribution of T_c to T was 9%. The annual average T_c over the 1985-1991 period ranged from 0.2 to 0.8 NTU; the range of the average contribution of T_c was 6-22% (Effler and Perkins 1995). It should be noted that other central New York lakes experience much greater levels and contributions of T_c to T on a regular basis (Effler and Perkins 1994).

The temporal distribution of C_T in 1993 was described and discussed in the framework of P availability in Chapter 5. Note the low values of C_T coincide with generally low T values over the mid-May through June interval (Figure 7-1c). The relatively low C_T concentrations during the major spring peak in T supports the position that non-phytoplankton particles, probably of

terrigenous origin, were responsible for most of this turbidity. The role phytoplankton biomass played in regulating the non-calcite fraction of turbidity (T_{nc}), after the major runoff of April, is evaluated in Figure 7-2. Generally higher T_{nc} levels were observed for higher C_T concentrations. However, the relationship is not particularly strong; approximately 27% of the variability in T_{nc} was explained by variations in C_T (Figure 7-2). Sources of variability in the relationship include: variations in non-algal turbidity, algal speciation, and chlorophyll content of the phytoplankton (Effler and Perkins 1995).

Measures of Light Penetration

The Secchi disc (SD) record since 1968, and the temporal distribution of SD measurements in 1993, have been described in Chapter 3. This distribution appears again for reference here (Figure 7-3a) with the other measure of light penetration, K_d (Figure 7-3b). The inflections in SD and K_d generally tracked each other; e.g., as SD increased K_d decreased. The variations in K_d appear to have been regulated largely by changes in T from April through July and C_T from July through October. The maximum K_d (4.09 m^{-1}) and minimum SD (0.25 m) occurred during the high runoff period of April; the minimum K_d (0.37 m^{-1}) and maximum SD (7.5 m) values were observed during the mid-May clearing event. Summary statistics for K_d for the 1985-1993 period are presented in Table 7-1. The mean and median values of K_d are consistent with values measured in other years since closure of the soda ash/chlor-alkali facility, but distinctly

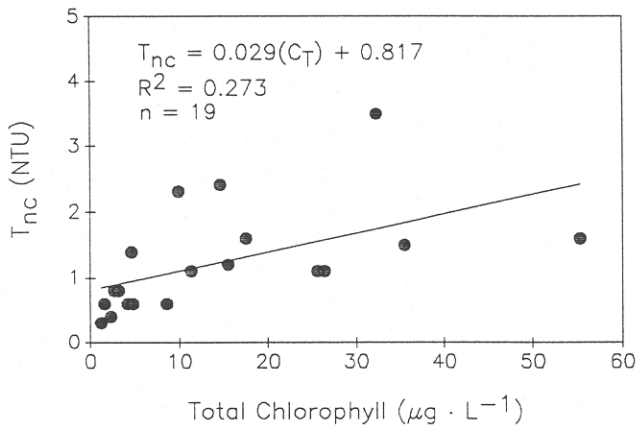


Figure 7-2. Evaluation of the relationship between non-calcite turbidity ($T_{nc} = T-T_c$) and the concentration of chlorophyll for the upper waters of Onondaga Lake in 1993.

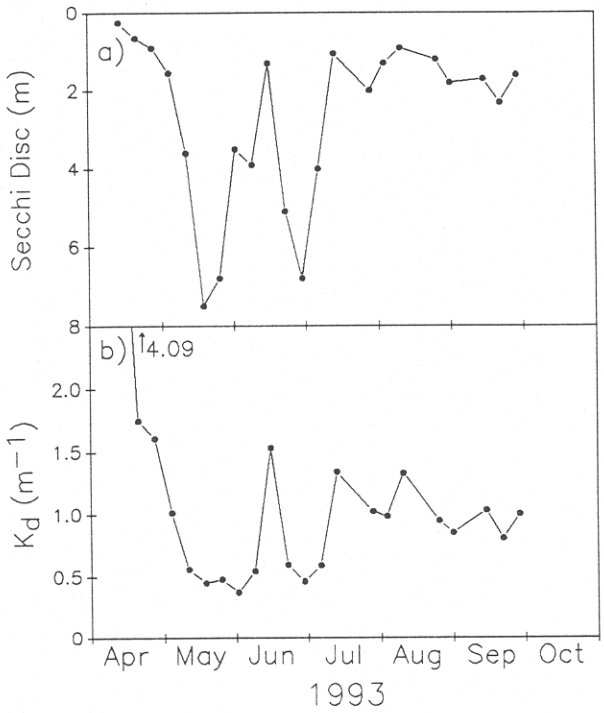


Figure 7-3. Time series of measures of light penetration in Onondaga Lake in 1993: a) Secchi disc transparency, and b) attenuation coefficient for downwelling irradiance (K_d).

Table 7-1: Summary Statistics for K_d in Onondaga Lake, 1985-1993.

Year	$\bar{x}$ (m)	median	Range, K_d(m)	n
1993	1.06	0.95	0.37-4.09	22
1992	1.09	1.15	0.47-1.53	26
1991	1.16	1.21	0.45-2.26	16
1990	1.14	0.95	0.51-2.12	14
1989	1.01	0.98	0.50-1.87	17
1988	1.09	1.09	0.48-2.74	19
1987	1.41	1.18	0.42-5.17	36
1986	1.80	1.72	0.93-3.76	23
1985	1.67	1.56	1.06-2.55	20

lower than values reported from before closure. This improvement in light penetration, as described for the SD data base (Chapter 3), is largely attributable to reductions in light attenuating particles (Effler and Perkins 1995) associated with increased zooplankton grazing (Seigfried et al. 1995).

The relationship between K_d and SD had not been quantitatively strong (e.g., temporally varying $K_d \cdot SD$ product) before 1993 (Effler and Perkins 1995); this continued in 1993. Substantial variability in the $K_d \cdot SD$ product with time for a single system, and between systems, has been observed (Effler 1985). This should not be misconstrued as indicative of limitations in data sets of these parameters, rather, it is a manifestation of the different responses of the SD and K_d measurements to the underwater light field. For example, variations in the relationship between these measures, parametrized by $K_d \cdot SD$, are largely a manifestation of temporal changes in the relative contributions of a and b to attenuation, and only secondarily to the inherent loss of sensitivity of SD at very high levels of attenuation.

It has often been assumed that K_d is regulated by the quantity of phytoplankton biomass present. This interplay has most often been quantified by a linear empirical expression of the form (e.g., Field and Effler 1983, Jewson 1977, Megard et al. 1979).

$$K_d = (K_c \cdot C_T) + K_w \qquad (2)$$

in which K_c and K_w = constants determined from the linear regression of K_d on C_T (units of $m^2 \cdot mg^{-1}$ chlorophyll and m^{-1}, respectively). The coefficient K_w has been described as representing the spectral average attenuation coefficient for water and its non-phytoplankton components. A corollary expression to represent the SD-C_T relationship, takes the form

$$SD^{-1} = (K_c' \cdot C_T) + K_w' \qquad (3)$$

in which the constants K_c' and K_w' are determined in the manner described above for K_c and K_w. While these empirical relationships are less flexible and precise than the mechanistic expressions developed by Effler and Perkins (1995), they represent a valuable framework to investigate the dependence of these measures of light penetration on the concentration of phytoplankton pigments. The relationships are evaluated in Figure 7-4(a and b). The very low light penetration observations of April associated with elevated concentrations of non-phytoplankton particles (tripton) have been eliminated from the populations for these analyses. In both cases the populations were better represented by a segmented (2) analysis. The values of K_c (= 0.012 $m^2 \cdot mg^{-1}$ chlorophyll) and K_w (= 0.655 m^{-1}) determined for the lower C_T concentration range of the 1993 data

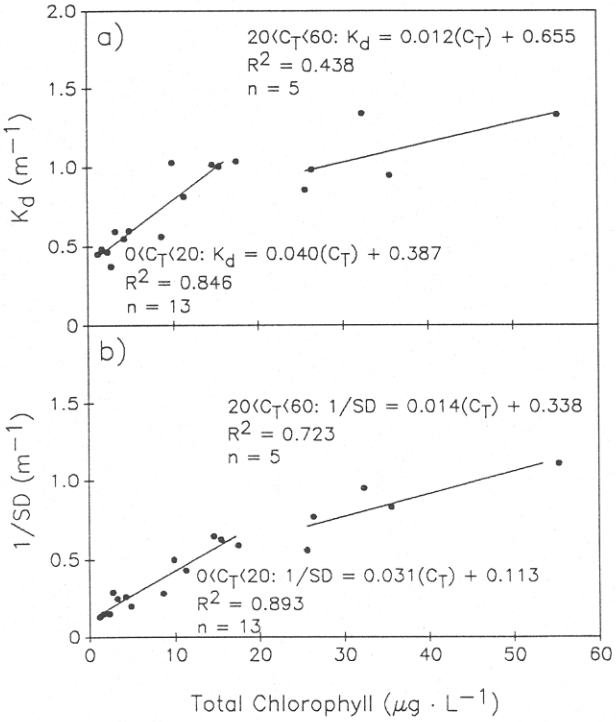


Figure 7-4. Evaluation of the relationship between measures of light penetration and the concentration of chlorophyll (C_T) for Onondaga Lake in 1993: a) attenuation coefficient for downwelling irradiance (K_d), and b) Secchi disc transparency.

set compare favorably to values determined previously for the 1987-1990 data set (K_c = 0.013 $m^2 \cdot mg^{-1}$ chlorophyll, K_w = 0.65 m^{-1}; Effler and Perkins 1995). In both cases, the two part curve fit of the data sets avoids unrealisticaly low estimates of light penetration at low C_T concentrations. These analyses indicate phytoplankton was an important regulator of light penetration in Onondaga Lake in 1993.

The relationship between T and K_d in 1993 was also evaluated (Figure 7-5). Despite the rather strong deviation from theory, a significant relationship is evident as observed over the 1987-1990 interval (Effler and Perkins 1995). Changes in T explained 60% of the variability in K_d observed in 1993.

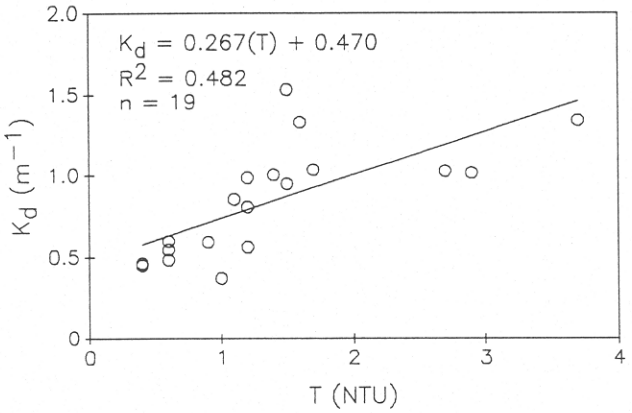


Figure 7-5. Evaluation of the relationship between the attenuation coefficient for downwelling irradiance (K_d) and turbidity (T) in Onondaga Lake in 1993.

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APPENDIX 1. - Miscellaneous Analyses

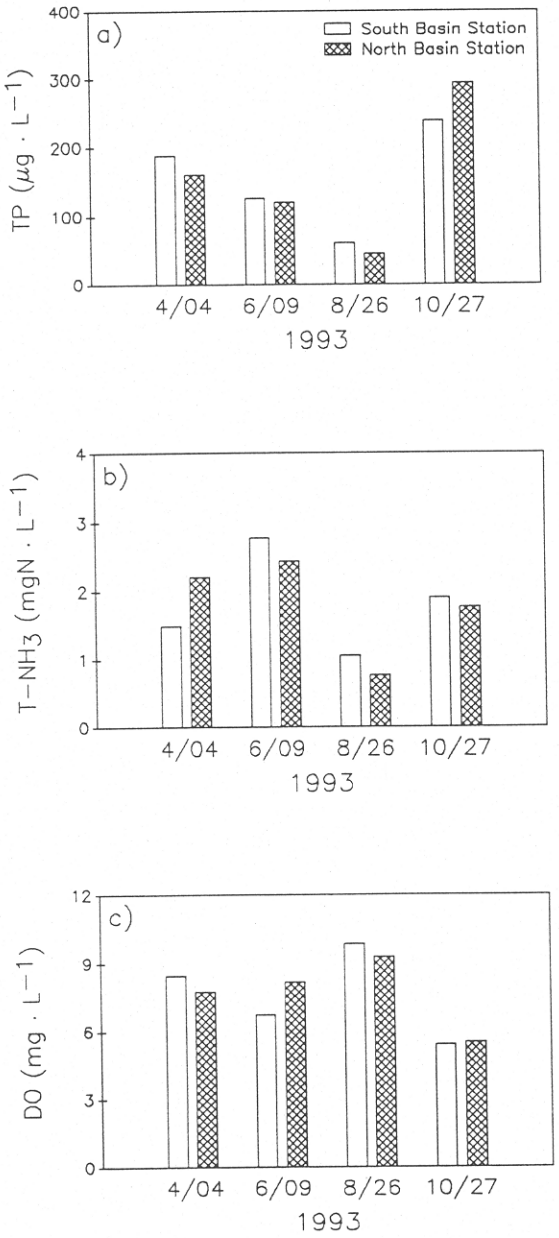

Figure A-1. Comparison of selected water quality conditions in the upper waters (0-5m) of Onondaga Lake at the South basin and North basin stations.

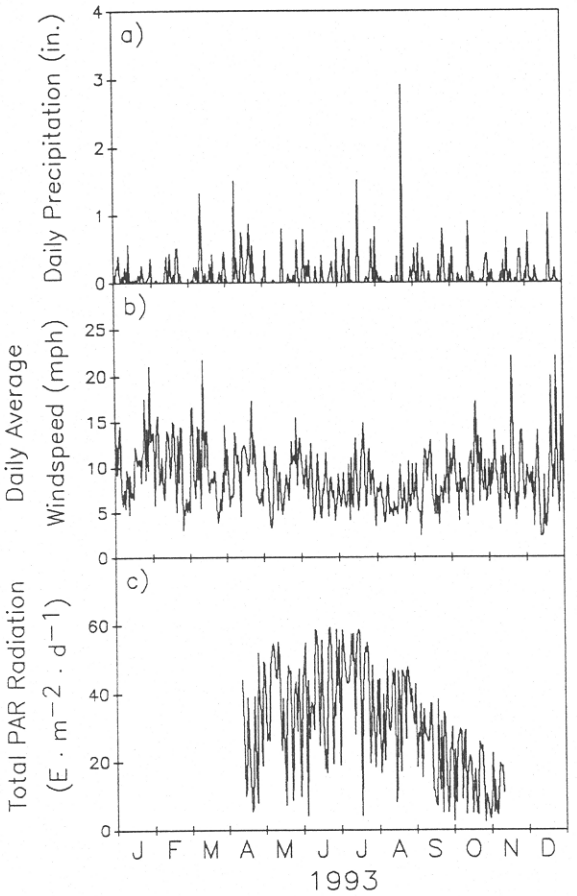

Figure A-2. Local meteorological conditions for 1993; as daily time series: a) percipitation, b) daily average wind speed, and c) daily PAR radiation.

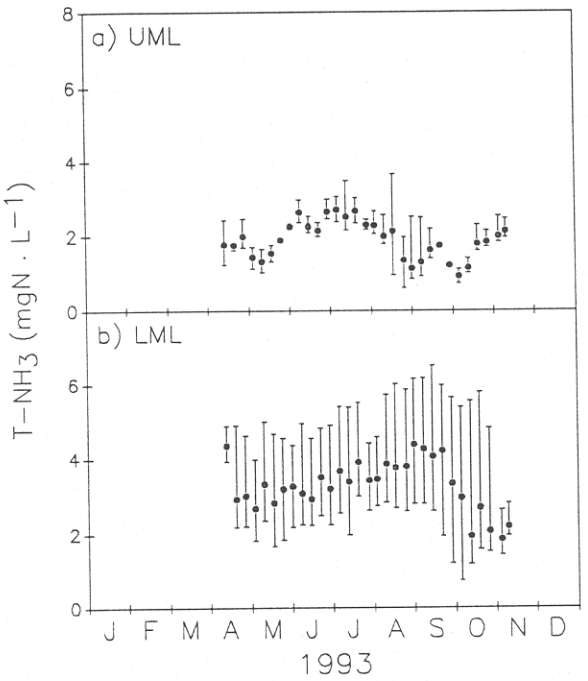

Figure A-3. Time series of volume-weighted concentrations of total ammonia ($T\text{-}NH_3$) in two layers in Onondaga Lake, 1993: a) upper mixed layer (UML), and b) lower mixed layer (LML). Bars denote range of concentrations.

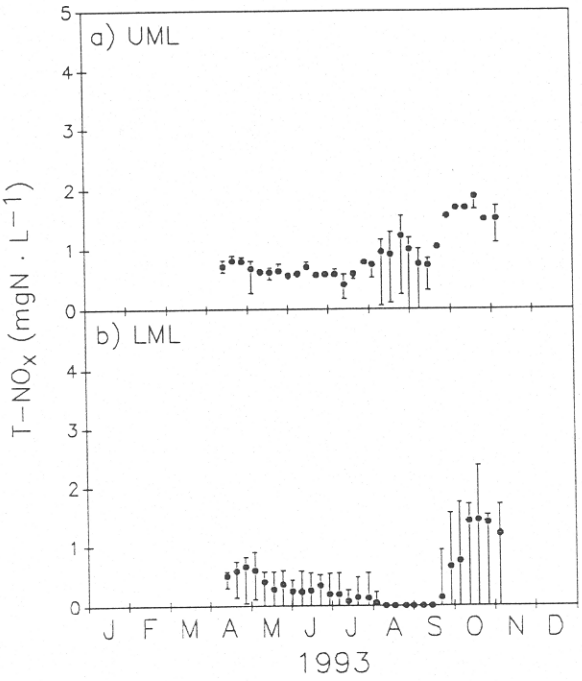

Figure A-4. Time series of volume-weighted concentrations of nitrate (NO_3^-) in two layers in Onondaga Lake, 1993: a0 upper mixed layer (UML), and b) lower mixed layer (LML). Bars denote range of concentrations.