UPSTATE FRESHWATER INSTITUTE

Richard Pouyat, Ph.D.
Office of Senator Moynihan
464 Russell Senate Office Building
Washington, D.C. 20510-3201

June 25, 1997

Dear Dr. Pouyat:

This submission is in response to your request for our critical review of the Onondaga Lake Total Maximum Daily Loads (TMDL) analyses (draft of 5·30·97) for ammonia and phosphorus. It is our understanding that these documents were prepared by the New York State Department of Environmental Conservation (NYSDEC).

As you know, Onondaga Lake is arguably the most polluted lake in the United States. A suite of standards intended to protect the fishing and contact recreation resources of the lake are violated on a routine basis, mostly as a result of the discharge from the Metropolitan Syracuse Waste Water Treatment Plant (METRO), operated by Onondaga County.

We have been involved in the interdisciplinary research of Onondaga Lake and the adjoining river system for many years (S.W. Effler since the mid-1970s, M.T. Auer since the mid-1980s), and have guided and executed the development and testing of the mathematical models, which now support lake management efforts. We have published our findings in numerous (more than 80) manuscripts in peer-reviewed journals and in a book. Approximately 80 scientists and engineers collaborated in the preparation of this body of work. A list of our publications relating to Onondaga Lake and adjoining systems is appended. That attachment also documents the honors accorded our group by the national and international research community in recognition of the merit and quality of our work.

A substantial portion of this research has been funded by the USEPA, though our on-going work is currently being conducted on a **pro bono** basis. The research community studying Onondaga Lake has worked hard to disseminate these findings to all interested parties; e.g., frequent meetings that have included regulators, professional reports and presentations, and publication in the peer-reviewed scientific and engineering literature.

Considering the extremely degraded condition of Onondaga Lake and the high costs of remediation options under consideration, it is essential that the best available technical information, tools and techniques be applied in conducting the TMDL analyses. Regulatory officials responsible for the development of TMDLs have an obligation to

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access and incorporate related critical research findings into the TMDL process. The TMDL analyses for Onondaga Lake submitted by NYSDEC fail to meet this obligation and, as a result, are fundamentally flawed. The analyses rely heavily on data obtained from the Onondaga County lake monitoring program (a data base with a long history of problems), systematically ignoring the wealth of federally-sponsored research findings made available to the regulatory community by our research group.

A number of the short-comings in the TMDL analyses are listed below. A more detailed development of an evaluation of the TMDLs is presented in the attached review and additional supporting material appears as numbered **Attachments**.

Technical Short-Comings of TMDL Analyses of 5·30·97

1. Ammonia
   a. failure to differentiate free ammonia from total ammonia, and to identify free ammonia as the toxic form,
   b. failure to adequately accommodate the influence of hydrologic variability,
   c. failure to quantitatively link predictions of total ammonia concentrations to free ammonia concentrations,
   d. use of an unreliable pH data base (Onondaga County monitoring program),
   e. incorrect identification of June as the critical month (instead of April) for ammonia levels in the lake, in evaluating the in-lake discharge of METRO,
   f. failure to accommodate the residual impacts of the Allied Signal waste beds, and
   g. failure to present the results of the analysis within the context of the "violation count policy" used by USEPA.

2. Phosphorus
   a. failure to accommodate the effects of differences in the bioavailability of phosphorus in the various inputs; linked short-comings include
      (1) the benefit of diversion of METRO is understated,
      (2) the benefit of non-point source controls/reductions in rural portions of the watershed is overstated,
      (3) the feasibility of reaching a 20 $\mu g \cdot L^{-1}$ total phosphorus concentration goal for the lake is understated (i.e., overly pessimistic),
   b. failure to identify the urban component of tributary loads as the appropriate focus for management reductions,
   c. incorrect focus on rural portions of the watershed for reductions in tributary loading,
   d. inadequate documentation of development of loads associated with CSOs,
   e. use of unreliable phosphorus data (Onondaga County monitoring program),

f. failure to use phosphorus loads reported in the peer-reviewed literature,
g. failure to acknowledge 40% reductions as an unreasonable goal for non-point source reductions in phosphorus loading,
h. failure to address the issue of critical (hydrologic) conditions in the analysis,
i. failure to adequately develop the rationale for important features of the TMDL calculations, and
j. failure to accommodate recent research findings on sediment release (feedback).

We welcome your continued interest in the present and future condition of Onondaga Lake and in the role of the research community in supporting a management plan grounded in the best scientific information possible. We are committed to bringing appropriate technical scrutiny to bear on the TMDL analyses and welcome the opportunity to meet with you, with others involved in the management of Onondaga Lake, and with the scientific community at large, to discuss these vital issues further.

Respectfully,

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cc: Hon. J. T. Walsh
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N. Spiegel, Esq.
C. Staszak
* S. Sage
* D. Coburn
R. Hennigan
C. Driscoll

* all attachments included

AWARDS and TESTIMONY

- **1995 North American Lake Management Society (NALMS) Award to Steven W. Effler, for Technical Excellence in Research**

  " ….. in recognition of your important contribution to research, understanding, and control of pollution in urban lakes, with particular emphasis on Onondaga Lake."

- **1995 Best Practice Oriented Paper of the Year, Water Resources Planning and Management** ***Journal of the American Society of Civil Engineers, Vol. 121 (3)***

  Validation of a Water Quality Model for Seneca River, NY".

- **Winner of the Award for Best Student Poster, at the 16th International Symposium of Lake Reservoir, and Watershed Management, North American Lake Management Society, Minneapolis, Minnesota**

  Tomasoski, K.A., M.T. Auer, M.J. Babiera, and S.W. Effler. 1996. "Determining Bioavailability of Sediment Phosphorus Using Algal Bioassays and Chemical Fractionation", Poster presented by K. A. Tomasoski.

- **Testimony: Senate Committee on the Environment and Public Works, 1989 and 1992**

  - description of the pollution problems of Onondaga Lake.

NUMBERED CONTRIBUTIONS OF THE UPSTATE FRESHWATER INSTITUTE, INC. ONONDAGA LAKE AND THE SENECA RIVER

1. Effler, S.W., Rand, M.C. and Tamayo, T. 1979. Effects of Heavy Metals and Other Pollutants on the Sediments of Onondaga Lake. *Water, Soil, and Air Pollution* 12:177-134.

2. Meyer, M. and Effler, S.W. 1980. Changes in the Zooplankton of Onondaga Lake, 1969-1978. *Environmental Pollution (Series A)* 23:131-152.

3. Effler, S.W., Field, S.D., Meyer, M.A. and Sze, P. 1981. Response of Onondaga Lake to Restoration Efforts. *Journal of Environmental Engineering Division, ASCE* 107:191-210.

4. Wilcox, D.A. and Effler, S.W. 1981. Formation of Alewife Concretions in Polluted Lake. *Environmental Pollution (Series B)* 2:203-215.

5. Field, S.D. and Effler, S.W. 1982. Photosynthesis-Light Mathematical Formulations. *Journal of Environmental Engineering Division* ASCE 108:199-203.

6. Effler, S.W., Jaran, P. and Carter, C.F. 1982. Onondaga Lake and Dissolved Oxygen in Seneca River. *Journal of Environmental Engineering Division* ASCE 109:945-951.

7. Effler, S.W., McCarthy, J.M., Simpson, K.W., Unangst, F.J.V., Schafran, G.C., Schecher, W.D., Jaran, P., Hsu, H.A. and Khalil, M.T. 1984. Chemical Stratification in the Seneca/Oswego Rivers NY. *Water, Air and Soil Pollution* 21:335-350.

8. Field, S.D. and Effler, S.W. 1983. Light-Productivity Model for Onondaga Lake, NY. *Journal of Environmental Engineering Division*, ASCE 109:830-844.

9. Wodka, M.C., Effler, S.W., Driscoll, C.T., Field, S.D., and Devan, S.D. 1983. Diffusivity - Based Flux of Phosphorus in Onondaga Lake. *Journal of Environmental Engineering Division* ASCE 109:1403-1415.

10. Devan, S.P. and Effler, S.W. 1984. The Recent History of Phosphorus Loading to Onondaga Lake, NY. *Journal of Environmental Engineering Division* ASCE 110:93-109.

11. Yin, Chenging and Johnson, D.L. 1983. Sedimentation and Particle Class Balances in Onondaga Lake, NY. *Limnology and Oceanography* 29:1193-1201.

12. Wodka, M.C., Effler, S.W. and Driscoll, C.T. 1985. Phosphorus Deposition from the Epilimnion of Onondaga Lake. *Limnology and Oceanography* 30:833-843.

13. Effler, S.W., Perkins, M.G. and Field, S.D. 1984. Onondaga Lake and the Dynamics of Chloride in the Oswego River. *Water, Air and Soil Pollution* 23:69-80.

14. Effler, S.W., Devan, S.P. and Rodgers, P. 1985. Chloride Loading to Lake Ontario from Onondaga Lake, NY. *Journal of Great Lakes Research* 11:53-58.

15. Effler, S.W., Driscoll, C.T., Wodka, M.C., Honstein, R., Devan, S.P., Jaran, P., and Edwards, T. 1985. Phosphorus Cycling in Ionically Polluted Onondaga Lake, New York. *Water, Air and Soil Pollution* 24:121-130.

16. Effler, S.W., Wodka, M.C. and Field, S.D. 1984. Scattering and Absorption of Light in Onondaga Lake. *Journal of Environmental Engineering Division* ASCE 110:1134-1145.

17. Effler, S.W. and Driscoll, C.T. 1985. Calcium Chemistry and Deposition in Ionically Polluted Onondaga Lake, NY. *Environmental Science and Technology* 19:716-720.

18. Effler, S.W., Perkins, M.G., Whitehead, K.A. and Romanowicz E.A. 1996. Ionic inputs to Onondaga Lake: Origins, character, and changes. *Lake and Reservoir Management* 12(1):15-23.

19. Effler, S.W. and Driscoll, C.T. 1985. A Chloride Budget for Onondaga Lake, NY, USA. *Water, Air and Soil Pollution* 27:29-44.

20. Effler, S.W., Schimel, K. and Millero, F.J. 1986. Salinity, Chloride and Density Relationships in Ion Enriched Onondaga Lake, NY. *Water, Air and Soil Pollution* 27:169-180.

21. Effler, S.W., Owens, E.M. and Schimel, K.A. 1985. Density Stratification in Ionically Polluted Onondaga Lake, USA. *Water, Air and Soil Pollution* 27:247-258.

22. Effler, S.W. and Owens, E.M. 1986. The Density of Inflows to Onondaga Lake, USA, 1980 and 1981. *Water, Air and Soil Pollution* 28:105-115.

23. Effler, S.W., Wodka, M.C., Driscoll, C.T., Brooks, C., Perkins, M.G. and Owens, E.M. 1986. Entrainment-Based Flux of Phosphorus in Onondaga Lake. *Journal of Environmental Engineering Division* ASCE 112:617-622.

24. Effler, S.W. and Owens, E.M. 1987. Modifications in Phosphorus Loadings to Onondaga Lake, USA, Associated with Alkali Manufacturing. *Water, Air and Soil Pollution* 32:177-182.

25. Effler, S.W. and Owens, E.M. 1996. Density Stratification in Onondaga Lake:1968-1994. *Lake and Reservoir Management* 12(1):25-33.

26. Field, S.D. and Effler, S.W. 1988. Temperature and the Productivity-Light Relationship. *Water Resources Bulletin* 24:325-328.

27. Effler, S.W., Perkins, M.G. and Brooks, C. 1986. The Oxygen Resources of the Hypolimnion of Ionically Enriched Onondaga Lake, NY, USA. *Water, Air and Soil Pollution* 29:93-108.

28. Effler, S.W. 1987. The Impact of a Chlor-Alkali Plant on Onondaga Lake and Adjoining Systems. *Water, Air and Soil Pollution* 33:85-115.

29. Garofalo, J.E. and Effler, S.W. 1987. Coating of Zooplankton with Calcium in Onondaga Lake, NY. *Environmental Science and Technology* 21:604-606.

30. Bloom, N.W. and Effler, S.W. 1990. Seasonal Variability in the Mercury Speciation of Onondaga Lake, NY. *Water, Air and Soil Pollution* 53:251-265.

31. Effler, S.W. and Perkins, M.G. 1987. Failure of Spring Turnover to Occur in Onondaga Lake, NY. USA. *Water, Air and Soil Pollution* 34:285-291.

32. Owens, E.M. and Effler, S.W. 1989. Changes in Stratification in Onondaga Lake, NY. *Water Resources Bulletin* 25:587-597.

33. Auer, M.T. and Effler, S.W. 1989. Variability in Photosynthesis: Impact on DO Models. *Journal of Environmental Engineering Division*, ASCE 115:944-963.

34. Owens, E.M., and Effler, S.W. 1996. Modeling the impacts of a proposed hypolimnetic wastewater discharge on stratification and mixing in Onondaga Lake. *Lake and Reservoir Management* 12(1):195-206.

35. Effler, S.W., Hassett, J.P., Auer, M.T. and Johnson, N. 1988. Depletion of Epilimnetic Oxygen, and Accumulation of Hydrogen Sulfide in the Hypolimnion of Onondaga Lake, NY, USA. *Water, Air and Soil Pollution* 39:59-74.

36. Johnson, D.L., Jaio, F., DeSantos, G. and Effler, S.W. 1991. Individual Particle Analysis of Suspended Materials in Onondaga Lake, NY. *Environmental Science and Technology* 25:736-744.

37. Canale, R.P. and Effler, S.W. 1989. Stochastic Phosphorus Model for Onondaga Lake. *Water Research* 23:1009-1016.

38. Perkins, M.G. and Effler, S.W. 1996. Optical Characteristics of Onondaga Lake 1968-1990. *Lake Reservoir Management* 12(1):103-113.

39. Effler, S.W., Brooks, C.M., Auer, M.T., and Doerr, S.M. 1990. Free Ammonia in a Polluted Hypereutrophic, Urban Lake. *Journal of Water Pollution Control Federation* 62:771-779.

40. Auer, M.T., Storey, M.L., Effler, S.W., and Auer, N.A. 1990. Zooplankton Impacts on Chlorophyll and Transparency in Onondaga Lake, NY. USA. *Hydrobiologia/* Dev. Hydrobiol 200/201:603-617.

41. Brooks, C.M. and Effler, S.W. 1990. The Distribution of Nitrogen Species in Polluted Onondaga Lake, NY., USA. *Water, Air, and Soil Pollution* 52:247-262.

42. Effler, S.W., Doerr, S.M., Brooks, C.M., and Rowell, C. 1990. Chloride in the Pore Water and Watercolumn of Onondaga Lake, NY., USA. *Water, Air and Soil Pollution* 51:215-326.

43. Effler, S.W. and Perkins, M.G. 1996. An Optics Model for Onondaga Lake. *Lake and Reservoir Management* 12(1):115-125.

44. Effler, S.W., Johnson, D.L., Jiao, J. and Perkins, M.G. 1992. Optical Impacts and Sources of Suspended Solids in Onondaga Creek, USA. *Water Resources Bulletin* 28:252-262.

45. Effler, S.W., Brooks, C.M., Addess, J.M., Doerr, S.M., Storey, M.L., and Wagner, B.A. 1991. Pollutant Loadings from Solvay Waste Beds to Lower Ninemile Creek, NY. *Water, Air and Soil Pollution* 55:427-444.

46. Gelda, R.R., Auer, M.T., Effler, S.W., Chapra, S.C., and Storey, M.L. 1996. Determination of Reaeration Coefficients: A Whole Lake Approach. *Journal of Environmental Engineering* ASCE 122(4):269-275.

47. Gelda, R.K. and Auer, M.T. 1996. Development and Testing of a Dissolved Oxygen Model for a hypereutrophic Lake, N.Y. *Lake and Reservoir Management* 12(1):165-179.

48. Auer, M.T., and Niehaus, S.L. 1993. Modeling Fecal Coliform Bacteria: I. Field and Laboratory Determination of Loss Kinetics. *Water Research* 27:693-701.

49. Canale, R.P., Auer, M.T., Owens, E.M., Heidtke, T.M., and Effler, S.W. 1993. Modeling Fecal Coliform Bacteria: II. Model Development and Application. *Water Research* 27:703-714.

50. Auer, M.T., Johnson, N.A., Penn, M.R. and Effler, S.W. 1992. Measurement & Verification of Rates of Sediment Phosphorus Release for a Hypereutrophic Urban Lake. *Hydrobiologia* 253:301-309.

51. Driscoll, C.T., Effler, S.W., Auer, M.T., Doerr, S.M., and Penn, M.R. 1993. Supply of Phosphorus to the Water Column of a Productive Hardwater Lake: Controlling Mechanisms and Management Considerations. *Hydrobiologia* 253:61-72.

52. Storey, M.L., Auer, M.T., Barth, A.K., and Graham, J.M. 1993. Site-specific Determination of Kinetic Coefficients for Modeling Algal Growth. *Ecological Modeling* 66:181-196.

53. Storey, M.L. and Auer, M.T. 1996. Laboratory Determination and Field Verification of a Photosynthesis/Light Response Curve for the Seneca River, New York. *Journal of Freshwater Biology* (in review).

54. Heidtke, T.M., and Auer, M.T. 1992. Partitioning Phosphorus Loads: Implications for Lake Restoration. *Journal of Water Resource Planning and Management*, ASCE 118:562-579.

55. Auer, M.T., Johnson, N.A., Penn, M.R., and Effler, S.W. 1996. Pollutant Sources, Depositional Environment, and the Surficial Sediment of Onondaga Lake, New York. *Journal of Environmental Quality* 25:46-55.

56. Auer, M.T., Doerr, S.M., and Effler, S.W. 1996. A Zero Degree of Freedom Total Phosphorus Model. *Lake and Reservoir Management* (accepted).

57. Doerr, S.M., Effler, S.W., Whitehead, K.A., Auer, M.T., Perkins, M.G., and Heidtke, T.M. 1994. Chloride Model for Polluted Onondaga Lake. *Water Research* 28:849-861.

58. Driscoll, C.T., Effler, S.W., and Doerr, S.M. 1994. Changes in Inorganic Carbon Chemistry and Deposition of Onondaga Lake, New York. *Environmental Science and Technology* 28:1211-1218.

59. Canale, R.P., Owens, E.M., Auer, M.T., and Effler, S.W. 1995. Validation of a water quality model for Seneca River, NY. *Journal of Water Resources Planning and Management*, ASCE 121:241-250.

60. Effler, S.W., Brooks, C.M., Whitehead, K., Wagner, B., Doerr, S.M., Perkins, M., Siegfried, C., Walrath, L., and Canale, R.P. 1995. Impact of Zebra Mussel Invasion on River Water Quality. *Water Environment Research* 68:205-214.

61. Effler, S.W., and Siegfried, C. 1994. Zebra Mussel (Dreissena polymorpha) Populations in the Seneca River, New York: Impact on Oxygen Resources. *Environmental Science and Technology*. 28:2216-2221.

62. Penn, M.R., Auer, M.T., Van Orman, E.L., and Korienek, J.J. 1995. Phosphorus Diagenesis in Lake Sediments: Investigations Using Fractionation Techniques. *Marine and Freshwater Research* 46:89-99.

63. Van Orman, E.L., Auer, M.T., and Penn, M.R. 1996. A Diagenesis-Based Model of Sediment Phosphorus Release. *Lake and Reservoir Management* (in review).

64. Gelda, R.K., Auer, M.T., and Effler, S.W. 1995. Determination of Sediment Oxygen Demand by Direct Measurements and by Inference from Reduced Species Accumulation. *Marine and Freshwater Research* 46:81-88.

65. Addess, J.M., and Effler, S.W. 1996. Summer methane fluxes and fall oxygen resources of Onondaga Lake, New York. *Lake and Reservoir Management* 12(1):91-101.

66. Penn, M.R. and Auer, M.T. 1996. Sediment Mediation of the Water Column Response to Reductions in External Phosphorus Loading. *Lake and Reservoir Management* (in review).

67. Connors, S.D., Auer, M.T., and Effler, S.W. 1996. Phosphorus Pools, Alkaline Phosphatase Activity, and Phosphorus Limitation in Hypereutrophic Onondaga Lake, NY. *Lake and Reservoir Management* 12(1):47-57.

68. Wang W., and Driscoll, C.T. 1996. Patterns of Total Mercury Concentration in Onondaga Lake, New York. *Environmental Science and Technology* (in press).

69. Effler, S.W., Brooks, C.M., and Whitehead, K.A. 1996. Domestic Waste Inputs of Nitrogen and Phosphorus to Onondaga Lake, and Water Quality Implications. *Lake and Reservoir Management* 12(1):127-140.

70. Doerr, S.M., Effler, S.W., and Owens, E.M. 1996. Forecasting Impacts of a Hypolimnetic Wastewater Discharge on Lake Water Quality. *Lake and Reservoir Management* 12(1):207-217.

71. Canale, R.P., Gelda R. and Effler, S.W. 1996. Development and Testing of a Nitrogen Model for Onondaga Lake, N.Y. *Lake and Reservoir Management* 12(1):151-164.

72. Doerr, S.M., Canale, R.P. and Effler, S.W. 1996. Development and testing of a total phosphorus model for Onondaga Lake, N.Y. *Lake and Reservoir Management* 12(1):141-150.

73. Penn, M.R. and Auer, M.T. 1996. The Seasonal Variability in Phosphorus Speciation and Deposition in a Calcareous Hypereutrophic Lake. *Journal of Marine Geology* (accepted).

74. Effler, S.W. and S.M. Doerr. 1996. Water Quality Model Evaluations for Scenarios of Loading Reductions and Diversion of Domestic Waste around Onondaga Lake. *Lake and Reservoir Management* 12(1):181-193.

75. Effler, S.W. and Hennigan, R. 1996. Onondaga Lake, New York: Legacy of Pollution. *Lake and Reservoir Management* 12(1):1-13.

76. Siegfried, C.A., Auer, N.A. and Effler, S.W. 1996. Changes in Zooplankton of Onondaga Lake: Causes and Implications. *Lake and Reservoir Management* 12(1):59-71.

77. Effler, S.W. (ed.) 1996. Limnological and Engineering Analysis of a Polluted Urban Lake. Prelude to Environmental Management of Onondaga Lake, New York. Springer-Verlag. New York, N.Y.

78. Effler, S.W., Doerr, S.M., and Owens, E.M. 1996. Effect of Reduced Salinity Input on River Stratification and Dissolved Oxygen. *Water, Air, and Soil Pollution* (in press).

79. Womble, R.N., Driscoll, C.T. and Effler, S.W. 1996. Calcium Carbonate Deposition in Ca^{2+} Polluted Onondaga Lake, New York, U.S.A.*. *Water Resources Research* 30(9):2139-2147.

80. Effler, S.W., Boone, S.R., Siegfried, C.A., Walrath, L. and Ashby, S.L. 1996. Mobilization of Ammonia and Phosphorus by Zebra Mussels (*Dreissena polymorpha*) in the Seneca River, New York. In F.W. D'Itre Proceedings of the 6th International Zebra Mussel and Other Aquatic Nuisance Species Conference. Ann Arbor Press (in press).

81. Brooks and Effler S.W. 1996. Dry Weight Deposition Polluted Onondaga Lake, New York. USA. *Water, Air, and Soil Pollution* (accepted).

82. Effler, S.W., C.M. Brooks, and C.T. Driscoll. 1996. Depositing Seston in a Ca^{2+} Enriched Lake: Long-term Changes in Rates and Stoichiometry. Can. J. Fish. Aquat. Sci. (in revision).

83. Whitman, T. and M.T. Auer. 1996. Modeling and Measurement of Nitrogen Diagenesis and Ammonia Release from the Sediments of a Hypereutrophic Lake. *Canadian Journal of Fisheries and Aquatic Sciences* (in review).

A Critical Review of the Ammonia and Phosphorus

TMDL Analyses for Onondaga Lake

(draft of 5·30·97): S.W. Effler

I. AMMONIA

A. Nomenclature and Free Ammonia

The nomenclature adopted in the treatment of ammonia is overly simplistic, inconsistent with that used by USEPA (1985) and in the related scientific literature (e.g., Effler et al. 1990, 1996a), and should be considered inappropriate for a TMDL analysis. It is the unionized (e.g., "free") form of ammonia (usually represented as NH_3 (e.g., Effler et al. 1990, 1996a)) that "has been demonstrated to be the principal toxic form of ammonia" (p.90, USEPA 1985). Failure to differentiate NH_3 from other forms of ammonia has not served to simplify and enhance the presentation, rather, it has made it cryptic and has "masked" a fundamental short-coming of the TMDL analysis (failure to base the analysis on simulations of in-lake concentrations of NH_3; see subsequent treatment).

"In aqueous ammonia solutions, un-ionized ammonia exists in equilibrium with the ammonium ion and the hydroxide ion. The equation expressing this equilibrium can be written as:

$$NH_{3(g)} + nH_2O_{(l)} \leftrightarrow NH_3 \cdot nH_2O_{(aq)} \leftrightarrow NH_4^+ + OH^- + (n-1)H_2O_{(l)}$$

As indicated in this equation, the dissolved ammonia molecule exists in hydrated form. The dissolved un-ionized ammonia is represented for convenience simply as NH_3. The ionized form is represented as NH_4^+. The term 'total ammonia' refers to the sum of

these; i.e., $NH_3 + NH_4^+$" (p.1, USEPA 1985). Often total ammonia is represented as T-NH_3 (e.g., Canale et al. 1996, Effler et al. 1990, 1996a). The concentration of NH_3 is calculated from the concentration of T-NH_3, pH, temperature, and (in some cases) ionic strength.

It is not valid to argue that presentation of T-NH_3 concentrations is an equivalent alternative to that of NH_3 concentrations, as NH_3 is the primary toxic specie. "Ammonia" as used in the TMDL analysis, refers to T-NH_3. Toxicity criteria set by USEPA (1985) for ammonia were based on the review of literature findings of the toxicity response to NH_3, not T-NH_3. Findings for experiments where T-NH_3 concentration were reported, but NH_3 could not be calculated, were eliminated from the data base that supported development of the toxicity criteria (USEPA 1985; e.g., see p.86). It is noteworthy that throughout USEPA's (1985) ammonia criteria document quantitative ammonia data are expressed in terms of un-ionized ammonia (NH_3); except tables of criteria concentrations on p.'s 96 and 97, where T-NH_3 listings (back-calculated from NH_3) appear **after** the NH_3 tables.

B. Simulation of T-NH_3: Failure to Adequately Accommodate the Influence of of Hydrologic Variability

The development and testing of a nitrogen (N) model for Onondaga Lake, capable of simulating T-NH_3, has been documented in the peer-reviewed literature (Canale et al. 1996). This model has been accepted by NYSDEC and other parties. Model performance has been demonstrated to be particularly good for T-NH_3 in spring (Canale et al. 1996; further demonstrated at the presentation at USEPA Region 2 offices on April

14, 1997 - subsequently this presentation is referenced as "presentation to USEPA/April 14"). The particularly good model performance in spring is largely associated with: (1) the seasonal flushing rate characteristics of the lake (Effler and Whitehead 1996), and (2) kinetic considerations (presentation to USEPA/April 14; also see letter to K Callahan of May 6, 1997). Effective application of this model represents an important step in the TMDL process. The application presented in the TMDL analysis is inadequate, and should not be considered acceptable.

Data (e.g., Effler et al. 1996a) and model (e.g., Canale et al. 1996) analyses have demonstrated the critical role tributary flow (e.g., provides dilution for the METRO discharge) plays in influencing T-NH_3 concentrations in the lake's epilimnion. For example, major variations in T-NH_3 concentrations commonly occur year-to-year (Effler et al. 1996a), and would continue to occur for METRO in-lake discharge options (Canale et al. 1996, presentation to USEPA/April 14). Higher T-NH_3 concentrations, and thus higher probability of violation of NH_3 standards, are associated with lower tributary flows (e.g., Effler et al. 1996a). Thus it is important to identify and accommodate appropriate critical tributary flow conditions in the development of TMDLs for T-NH_3 for this system. The draft TMDL analysis for 5·30·97 is inadequate in this regard.

The user-friendly software provided with the N model has the hydrology of three years "built in" to accommodate hydrologic variability in a preliminary (e.g., screening tool) way (e.g., Effler and Doerr 1996, also see Effler et al. 1996d). One option was 1987, for which the annual flow was the second lowest for the 1971-1990 (20 y) interval. The "two in twenty" (i.e., one in ten) corollary to streams/rivers is superficially attractive, but it fails to capture the critical flow characteristics for this specific parameter/lake

combination. A rigorous evaluation of the dependency of T-NH_3 predictions on tributary flow conditions should be considered essential to support the determination/ accommodation of critical flow conditions to be incorporated in the TMDL analysis, particularly in light of the estimated cost of the alternatives. The draft TMDL analysis of 5·30·97 fails to make adequate use of the available hydrologic record for the system (e.g., Effler and Whitehead 1996, presentation to EPA/April 14).

An appropriate treatment of the influences of hydrologic variability has been presented (presentation to USEPA/April 14), that takes advantage of the tributary flow record for the 1971-1995 interval, to fairly accommodate the influence of variability in (i.e., critical) flow conditions. This analysis demonstrated (presentation to USEPA/April 14) that the time scale of critical flow conditions in Onondaga Lake is on the order of months (e.g., 2 to 3), not a year. For example, for the critical time of year for NH_3 in Onondaga Lake (see subsequent sections of this review), 1987's rank is 7 (not 2 or 3) out of 25 years. The hydrologic conditions adopted in the TMDL analysis are an inappropriate representation of critical conditions.

We have incorporated the entire hydrologic record since 1971 in our most recent evaluations of related remediation alternatives (e.g., presentation to USEPA/April 14). This upgrade in the application of the Onondaga Lake N model was cited in our letter to K. Callahan of Region 2/EPA of May 6, 1997 (enclosed as **Attachment No. 1**).

> "UFI has developed an upgraded mode of application* of the Onondaga Lake Nitrogen Model to accommodate the important influence of hydrologic variability in mediating the extent of the impact of METRO's discharge on T-NH_3 concentrations in the upper waters of Onondaga Lake

- utilizes the continuous tributary hydrologic record available since 1971.

* *Note: no changes in the Nitrogen Model have been made" (P4).*

NYSDEC made no effort to communicate with UFI on this model application upgrade between the time of the presentation to EPA/April 14 and the submission (5·30·97) of the draft TMDL. Continuous simulation of T-NH_3 concentrations for the 1971-1995 hydrologic conditions for the various METRO effluent options (presentation to USEPA/April 14) has the additional advantage of being consistent with existing USEPA "count" policy for NH_3 violations (personal communication R.J. Erickson, USEPA research laboratory, Duluth, MN).

C. Failure to Quantitatively Link Predicted T-NH_3 with NH_3

A TMDL analysis for ammonia should focus on establishing T-NH_3 loads that will protect against the occurrence of potentially toxic concentrations of free ammonia (NH_3). The draft TMDL analysis is seriously flawed in that no quantitative linkage is presented between T-NH_3 and NH_3 concentrations. This requires quantitatively accommodating pH and temperature. Instead, the draft TMDL **arbitrarily** invokes a 75 to 80 percentile for epilimnetic pH values and near-maximum temperature, at a monthly time step, to specify in-lake T-NH_3 concentration standards. No justification is presented for this protocol, and why it should be considered appropriate. This analysis needs to be quantitative (e.g., reflecting a probability of violation of a NH_3 standard), and to more fully use the available data.

At the April 14 presentation to EPA, a methodology to predict NH_3 concentrations, and the corresponding status with respect to NH_3 criteria, was reviewed. This protocol provides the necessary quantitative linkage from predicted T-NH_3

concentrations (N model) to predictions of NH_3 and status with respect to NH_3 criteria. The methodology is probabilistic in nature, utilizing the distributions of pH and temperature measurements made in the upper waters of the lake over a number of years. Further, it was found to be consistent with EPA's present perspective on such analyses (R.J. Erickson, personal communication, USEPA research laboratory, Duluth MN).

The presentation in the draft TMDL concerning the development of critical conditions and development of in-lake T-NH_3 standards is incomplete. More details will need to be provided to allow full technical review, including complete data listings and specifications of all calculations.

D. pH Data, Inadequacy of the Onondaga County Monitoring Program as a Data Source

pH is a very important parameter in the free ammonia issue. The fraction of T-NH_3 that exists as NH_3 (f), and the toxicity (e.g., criteria) of NH_3, are both functions of pH (e.g., Brooks and Effler 1990, Effler et al. 1990, USEPA 1985). As acknowledged in the TMDL analysis, these dependencies are highly sensitive to pH; e.g., small changes in pH result in major differences in the NH_3 concentration associated with a specified T-NH_3 concentration. Thus it is extremely important that pH monitoring data used to support the TMDL analysis for ammonia be accurate.

Inexplicably, the NYSDEC has utilized pH data collected as part of the Onondaga County monitoring program to support the draft TMDL analysis. The County's monitoring program has a long history of data quality problems, with which NYSDEC is well aware (see subsequently listed attachments). The use of this unreliable pH data set causes estimates of the lake's assimilative capacity to be biased high, because the

County's pH values are false low (presentation to USEPA/April 14). The use of this unreliable data base in the TMDL analysis more than negates any claims of accommodation of a margin of safety (MOS, see P.12 of TMDL analysis).

The unreliable character of the County's pH data is well established, as addressed in the following documents.

1. Within the RI/FS process for the Allied Chemical site (western shore of Onondaga Lake), and by request of NYSDEC, UFI performed a critical review of pH data available for the lake. That report (Doerr, S.M. and S.W. Effler, 1994. Submitted to NYSDEC, Wolf Rd., Albany NY. **enclosed as Attachment No. 2)** concluded "this [Onondaga County] data base is clearly flawed in so many years that it calls into question the entire data set" (p.12).
2. Subsequently, the County's pH data quality problem was identified and characterized in detailed correspondence
   a. letter and attachment from S.W. Effler (UFI) to J. Fitzpatrick (HydroQual Consultants) of July 25, 1995 (enclosed as **Attachment No. 3**)
   b. letter and attachment from S.W. Effler (UFI) to J. Fitzpatrick (HydroQual Consultants) of February 27, 1996 (enclosed as **Attachment No. 4**)
   c. letter and attachments from S.W. Effler (UFI) to R.A. Mustico (NYSDEC) of April 27, 1995 (enclosed as **Attachment No. 5**)
   d. letter and attachments from S.W. Effler (UFI) to T. Larson (NYSDEC) of February 22, 1996 (enclosed as **Attachment No. 6**)

3. In a letter to Allied Signal of August 12, 1996, NYSDEC supported rejection of Onondaga County's pH data for model ($CaCO_3$) application

> "The pH data set from Onondaga County is unreliable (e.g., unrealistic interannual variations) and should not be used in it's entirety."

The parenthetic description "(the latest available)" (p.12 of draft TMDL) is inadequate justification for the selection of the unreliable County pH data to support the analysis. The parenthetic description is inaccurate. Even if it were not inaccurate, it is not justification for the use of unreliable data where alternative high quality data are available. The highest quality and most representative pH data set available for Onondaga Lake for the designated interval (1993 - 1996) is that collected by UFI. The interval of pH data should be expanded to include the post Allied closure period, for which reliable field pH measurements are available; i.e., 1991 - 1996. What is the justification for excluding the 1991 and 1992 observations? The UFI measurements were conducted under USEPA funding over the 1991-1994 interval; the same program of measurements was continued, on a **pro bono** basis, in 1995 and 1996. NYSDEC is aware of this on-going program. UFI makes more frequent pH measurements than the County, and these data have supported a number of peer-reviewed research publications in which pH is a critical parameter (e.g., Driscoll et al. 1993, 1994, Effler and Driscoll 1985, Effler et al. 1990, Brooks and Effler 1990). The short-comings of the County data set were made evident (e.g., graphically) at the presentation to EPA of April 14.

E. June Is Not the Critical Month

Perhaps the most clear manifestation of the various technical short-comings in the ammonia TMDL analysis is the mis-identification of June as the **critical month** (p. 11).

Failure to accommodate a wide enough range of tributary hydrology and the character of the problems of the County pH data may have contributed to this misrepresentation of the seasonality of critical conditions. Through a much more rigorous treatment of hydrologic variability, and simulations of NH_3, we established (presentation to EPA/April 14) that April (and secondarily May) is the critical month for NH_3 in Onondaga Lake, with respect to the proposed in-lake discharge of an upgraded METRO effluent (see item No. 8 of May 6, 1997 letter to K. Callahan; **Attachment No. 1**). The performance of the N model in simulating T-NH_3 is the best in this spring interval (see earlier section of this review).

F. Failure to Accommodate the Residual Impacts of the Allied Signal Waste Beds

Residual inputs of waste from soda ash manufacture (Cl^-, Na^+, Ca^{2+}, and T-NH_3) continue to enter Onondaga Lake from the Allied Signal site, mostly via Ninemile Creek (Effler 1996, Effler et al. 1991, Effler et al. 1996b). One of the impacts of these residual inputs is depression of pH (Effler 1996 (Chapter 5), Driscoll et al. 1994, presentation to EPA/April 14, letter of May 6, 1997 to K. Callahan). The effect was documented from observations following closure of the facility (Driscoll et al. 1994). Thus, the residual waste inputs result in an artificially high assimilative capacity for T-NH_3 waste (by depression of pH). Remediation of this residual impact of the industrial site (e.g., RI/FS process) would result in a loss of assimilative capacity for T-NH_3 waste. This has not been accommodated in the ammonia TMDL analysis.

This situation raises interesting questions with respect to regulatory policy. Does METRO have the right to use (for long range planning) the added assimilative capacity offered by residual waste impact from an adjoining industrial superfund site, where remediation efforts are underway? Technical aspects of this issue were addressed at the

presentation to EPA/April 14, and an appropriate methodology to accommodate the effect in an assimilative capacity analysis was presented.

II. PHOSPHORUS

A. Failure to Accommodate The Differences in the Bioavailability of Phosphorus in the Various Inputs

Phosphorus (P) loading is the principal regulator of primary productivity in most lakes (e.g., Hutchinson 1973, Vollenweider 1982, Wetzel 1983), including Onondaga Lake (Effler et al. 1996a). Phosphorus is received in various chemical forms in inputs. The availability of the various forms to support primary production differs greatly (e.g., DePinto et al. 1981, Young et al. 1982). Usually almost all the dissolved P load is available to support primary production (e.g., DePinto et al. 1981). However, the reactivity/availability of particulate forms of P differ greatly according to sources. The USEPA has dedicated substantial research funding to develop methodology (e.g., DePinto 1982) and apply it to apportion P loading according to sources in sensitive systems (e.g., DePinto 1981, Martin et al. 1985, Young et al. 1982, 1985). A selective listing of the scientific literature dedicated to the bioavailability issue is enclosed as **Attachment No. 7**.

The most superficial analysis of relative bioavailability of the inputs to Onondaga Lake, partitioning loads according to the dissolved and particulate fractions, indicates the METRO load has greater bioavailability than the streams, as a larger fraction of the P from this source is dissolved (Effler et al. 1995). Further, our review of the bioavailability literature (see **Attachment No. 7**) found that particulate P in domestic waste effluent is in general more available to support phytoplankton growth (e.g., primary

production) than particulate P normally found in streams. While considering relative bioavailability is not critical for effective management for many lakes, because domestic effluent contributions are usually relatively minor, the major contribution of METRO (Effler et al. 1996a) makes the issue potentially critical for Onondaga Lake. This lead to an unsolicited proposal by our research consortium (by M.T. Auer) to conduct bioavailability experiments on the various inputs, that was submitted to OLMC in early 1992. The proposed research was not funded. Some of our concerns for the implications of not having this critical information to support related management deliberations were shared with OLMC in a letter from M.T. Auer to OLMC of March 16, 1992 (**Attachment No. 8**).

We were so convinced the bioavailability issue was potentially critical to support an effective P management strategy for Onondaga Lake that we pursued this research on a **pro bono** basis. Our findings were first presented to professional peers in November 1996 at the Annual Meeting of the North American Lake Management Society in Minneapolis, MN (**see Attachment No. 9**). The paper won an award at that meeting. Subsequently, on December 6, 1996, S.W. Effler briefed the voting representatives of OLMC on the salient features of these findings and their potential significance. A detailed briefing on the bioavailability research findings, including the implications for lake management issues, and, specifically, the feasibility of reaching the specified total P (TP) goal for the lake, was made at the presentation of April 14, 1997, at EPA offices in New York City. Related salient findings were included in our summary letter of May 6, 1996; e.g., see items 2. and 3. under New Observations and Findings (**Attachment No.**

1). NYSDEC has made no effort to contact the research team concerning these findings and how best to incorporate them into the TMDL analysis for P.

METRO is the most potent source of particulate P for supporting phytoplankton growth in Onondaga Lake; the urban portion of Onondaga Creek is the next most potent. In simple terms, a kilogram of particulate P from METRO grows more algae than a kilogram of particulate P from any of the other significant sources of P to the lake. These findings are not unexpected, but are in fact consistent with observations reported for other sites (see **Attachment No. 7**).

We demonstrated the great significance the bioavailability effect on the relative potency of P loads had on P management issues for the lake, and particularly the feasibility of reaching the TP goal of 20 $\mu g \cdot L^{-1}$, at the April 14 presentation at EPA. This analysis was conducted within the context of sensitivity analyses with the existing TP model. Based on our bioavailability findings, we can endorse a model upgrade/ enhancement, to modify the existing P model framework (Doerr et al. 1996) to accommodate the partitioning of loads (e.g., dissolved P, particulate P, according to its bioavailability) and these fractions within the lake.

The TMDL analysis for P in Onondaga Lake is fatally flawed by the failure of NYSDEC to consider the relative bioavailability of P loads to the lake. This is particularly troublesome in light of the well-established literature on this topic available by the early 1980's, and the fact that NYSDEC has been informed of the bioavailability findings for the lake's inputs on three occasions. Failure to consider relative bioavailability has resulted in the following misrepresentations in the TMDL analysis

1. the benefit of diversion of METRO is understated,
2. the benefit of non-point source controls/reductions (particularly rural Onondaga Creek and Ninemile Creek) is overstated, and
3. the feasibility of reaching a 20 $\mu g \cdot L^{-1}$ TP goal for the lake is understated (i.e., overly pessimistic).

For these, and other reasons, described subsequently, the TMDL analysis for P fails to fairly represent features of the understanding of this system critical to its effective management.

B. Misconceptions/Misrepresentations of P Loads from Sources Other Than METRO

The TMDL presentation on tributary loads (LA) is seriously flawed, and demonstrates a lack of familiarity with related research findings for this system. Instead of utilizing quantitative research findings obtained specifically for this system, NYSDEC has reached inappropriate conclusions from unreferenced sources; e.g., "through **literature search** (though none cited) and **conversations** with non-point source experts, it has been concluded that ……" (p. 16, draft TMDL P analysis of 5·30·97). The failure to fully utilize the available research (mostly funded by USEPA) findings for this system is inexplicable as the information has been made available to NYSDEC in several forums over the last 10 years.

The TMDL presentation fails to identify the urban component of the tributary load as the proper primary focus for reductions in the total tributary load (LA). The TMDL presentation on dry weather overflows (e.g., leaky sewers) is unclear (p.4, paragraph 3, lines 12 and 13), and could be interpreted that these inputs (particularly

along Onondaga Creek) have been eliminated. Implementation of a BMP program has apparently reduced dry weather inputs, but substantial inputs clearly continue (e.g., Table 3.35, P. 187; Fig. 3.95, p. 188 of Effler and Whitehead (1996)). Fecal coliform concentrations from a fixed frequency monitoring program have shifted lower since execution of the BMP program. However, an average fecal coliform concentration of > 25,000 "colony forming units" $\cdot 100\ ml^{-1}$ was observed over a 10 d dry weather period in the summer of 1987 (after the BMP program; Canale et al. 1993). This, and more recent observations, indicate untreated sewage is continuing to reach Onondaga Creek and the lake. This component of the urban input would be expected to be in a more bioavailable form, than rural runoff, as borne out by the results of the bioavailability experiments (presentation to EPA/April 14). For example, TP concentrations are generally higher at the mouth of Onondaga Creek, and soluble reactive P (SRP) represents a greater fraction of TP, compared to conditions documented at the downstream boundary of the rural portion of the watershed (Effler et al. 1995).

Heidtke and Auer (1992) estimated the unit area load (UAL) for TP upstream of the City of Syracuse for Onondaga Creek to be about 40-45 $kg \cdot km^{2} \cdot y^{-1}$, compared to 335-490 $kg \cdot km^{-2} \cdot y^{-1}$ for the urban portion of the watershed, establishing that dramatic enrichment occurs within the urban reach. Effler and Whitehead (1996) expanded the analysis of the partitioning of urban and rural loads. They reported more than 60% of the TP load from Onondaga Creek emanated from the urban portion of the watershed over the October 1988 to September 1989 interval. Effler and Whitehead (1996) concluded (p. 156) the urban component of the Onondaga Creek load is the appropriate focus for reduction of inputs from this tributary. The estimated UAL for Ninemile Creek, based on

intensive monitoring (Effler et al. 1991), was 33 $kg \cdot km^{-2} \cdot y^{-1}$. The UALs for the rural portions of the lake's watershed have been described as "typical" (Effler and Whitehead 1996) of values reported in the literature (e.g., Beaulac and Reckhow 1982, Clesceri et al. 1986, Hartigan et al. 1983, Johnson et al. 1978). Execution of BMP programs for land use in rural areas may be expected to achieve a **maximum** reduction in TP loading of 10 to 25% (e.g., Johnson et al. 1978), depending on the fraction of land involved in various uses. NYSDEC presents a goal of 40% reduction in tributary (LA) loads. This appears to be an unreasonable goal. Can NYSDEC provide compelling statistics and literature citations (e.g., **"literature search",** p.16, draft TMDL P analysis of 5·30·97) that such reductions are routinely, or even infrequently, achieved elsewhere? Such an unrealistic goal for nonpoint, embedded within the TMDL analysis, postures against the feasibility of attaining the 20 $\mu g \cdot L^{-1}$ goal.

The unrealistic goal for non-point (tributary; i.e., 40% reduction) is an outcome that attends the failure to consider the differences in bioavailability of the various sources (see section II. A. of this review). The NYSDEC compounds this error by focusing on the wrong non-point sources for reductions. At the presentation to EPA of April 14, the particulate P fraction downstream of the urban portion of Onondaga Creek was reported to be several times more potent, with respect to supporting algae growth, than inputs from Ninemile Creek and the rural portion of Onondaga Creek. The primary non-point source issues (sources) **are not** associated with agriculture and erosion in the watershed (e.g., 604 (b) and 319 projects; see p.16 of 5·30·97 draft of TMDL for P). In fact it is likely that the goal of 20 $\mu g \cdot L^{-1}$ TP could be reached by diversion and remediation of the urban tributary loading components, without reductions in the rural component (e.g.,

presentation to EPA/April 14). The particulate fractions from Ninemile Creek and rural Onondaga Creek have been demonstrated to have relatively low potency for support of algae growth (presentation to EPA/April 14), and the dissolved P concentrations from these areas are low (Effler et al. 1991, 1995, Effler and Whitehead 1996). Erosion problems are cited in the TMDL analysis as a concern for non-point loading. There appears to be a lack of recognition that a major contribution of suspended solids to the lake is the "mud boils" (Effler et al. 1992, Effler and Whitehead 1996). Much of the rural particulate P is probably associated with this material (e.g., Effler and Whitehead 1996). Despite the fact that vast quantities of this material have accumulated in upstream portions (e.g., stream banks downstream of the mud boils) of Onondaga Creek, and that portions of this material are resuspended during high flow events and transported downstream towards the lake, this material should not be attributed to the process of soil erosion.

Proper review of the research findings presented in the followings forums/sources could not have lead to the flawed focus/strategy (rural emphasis) presented by NYSDEC (p.16, TMDL analysis for P, draft of 5·30·97) for non-point control in the draft TMDL analysis of 5·30·97.

1. Effler et al. 1991; Ninemile Creek loading analysis (see references).
2. Effler et al. 1992; "mud boil" contributions to Onondaga Creek suspended solids loading (see references).
3. Heidtke and Auer 1992; partitioning of rural/urban contributions to P loading for Onondaga Creek (see references).

4. Working group meetings, 205J/OLMC, 1989-1993.
5. Effler et al. 1995; more P, and more in a dissolved form, at Onondaga Creek mouth than at downstream boundary of rural portion of watershed (see references).
6. Effler and Whitehead 1996; additional partitioning analysis of P loading for Onondaga Creek (see references).
7. Presentation to voting representatives of OLMC on December 6, 1996; relative bioavailability of inputs identified (METRO > urban Onon. Cr. > rural Onon. Cr. > Ninemile Cr.).
8. Presentation to EPA/April 14, 1997 (Region 2 offices, New York City); relative bioavailability of inputs identified and analysis of implications for feasibility of reaching TP goal of 20 $\mu g \cdot L^{-1}$ presented.
9. Salient findings reported at presentation to EPA/April 14, 1997, reviewed in letter of May 4, 1997 to K. Callahan (**Attachment No. 1**).

The treatment of CSOs as a source of P is cryptic. For example, an annual load of 13,628 lbs/year is given (p.12) for CSO discharge after capture and treatment of 62% of the annual average wet weather combined sewage. What are the data sources, assumptions, and calculation procedures on which this load estimate is based? The claimed annual CSO load after stage II is 5,337 lbs/yr (p. 14), representing a 61% reduction. The presentation remains highly cryptic here - again, what are the data sources, assumptions, and calculation procedures that supported this analysis? Regardless of the details of these estimates, important questions and concerns remain. It has been acknowledged previously that the CSO load varies from dry to wet years; a reasonable

range for prevailing conditions has been presented as 4,500 (dry year) to 10,000 $kg \cdot y^{-1}$ (wet year; Effler and Whitehead 1996, also see Smithgall et al. 1991). Why then would a single average be carried through TP model analyses that include dry and wet year cases?

C. The Long History of Quality Problems with Phosphorus Data from the Onondaga County Monitoring Program

As part of the development of the TMDL analysis, NYSDEC provides a brief, and very selective, review of P data for the system. The review is selective in that only data collected as part of Onondaga County's monitoring program are presented. This is puzzling in light of the well-documented long-term prevalence of problems in this program and the availability of high quality data supported by EPA funding. The character of the problems of the County program is reviewed on a year-by-year basis in Table 1; related technical treatment of these problems can be found in sources listed in Table 2. Despite being aware of the various short-comings in the County monitoring P data base (all documents of Table 2 addressed to NYSDEC staff, or NYSDEC staff copied, except **Attachment No. 10**), NYSDEC makes no mention of it in the TMDL analysis.

It is noteworthy that insights into the short-comings of the County monitoring program were gained under grants from USEPA, namely: (1) 205J grant administered by NYSDEC; (2) a comparative analysis of Onondaga County vs. other sources of P data for the system, conducted for NYSDEC as part of the RI/FS for the Allied site; (3) as part of the preparation of the **State of the Lake** report for OLMC. In contrast to the data quality problems of the County program, the alternate more comprehensive and reliable

Table 1: Short-comings in Onondaga County Monitoring Program for Phosphorus for Onondaga Lake and Its Inputs (see key to identify problem type).

Year	Problems (x = yes)	Onondaga Lake		Inputs	
		TP	SRP	METRO	Tributaries
1970	x	1*	2+	1	1, 2
1971	x	1	2	1	1, 2
1972	x	1	2	1	1, 2
1973	x	1	2	1	1, 2
1974	x	1	2	1	1, 2
1975	x	1	2	1	1, 2
1976	x	1	2	1	1, 2
1977	x	1	2	1	1, 2
1978	x	1	2	1	1, 2
1979	x	1	2	1	1, 2
1980	x	1	2		1, 2
1981	x	1	2		1, 2
1982	x	1	2		1, 2
1983	x	1	2		1, 2
1984	x	1	2		1, 2
1985	x	1	2		1, 2
1986	x	1	2		1, 2
1987	x	1	2		1, 2
1988	x	1	2		1, 2
1989	x	1	2		1, 2
1990	x	?**	2		?
1991	x	?	2		?
1992	?	?	?		?
1993	?	?	?		?
1994	?	?	?		?
1995	?	?	?		?
1996	?	?	?		?

key: * 1 - TIP measured instead of TP

+ 2 - detection limit problems; conc.'s tend to be false high

** ? - rigorous independent data quality analysis has not been conducted

Table 2: Documentation of Problems with the Quality of Phosphorus (P) Data from the Onondaga County Monitoring Program

Source No.	Date	Reference	Attachment No.
1	May 5, 1990	memo from S.W. Effler to attendees (Onondaga County employees) of presentation (by S.W. Effler) of April 26, 1990, reviews various County data problems, including P	**10**
2	Feb. 26, 1992	letter and attachments to R. Ott, Dept. Drainage & Sanitation, Onondaga County, documenting systematic problems with the quality (e.g., false high conc's) of tributary data	**11**
3	March 1994	"A comparative analysis of phosphorus data for Onodaga Lake, and implications", a report by Effler and Doerr, submitted to NYSDEC (Allied RI/FS)	**12**
4	April 27, 1995	letter and attachments to R.A. Mustico, NYSDEC; critical review of Allied's consultant's draft **Calcite Modeling Report** that was flawed from use of County data (including P)	**5**
5	July 25, 1995	letter from S.W. Effler to J. Fitzpatrick (HydroQual), identifying data problems of Onondaga County monitoring program to support modeling	**3**
6	Jan. 16, 1996	letter with attachment, from S.W. Effler to T. Larson (NYSDEC), analysis of Onondaga County P data problems for use in models for Allied RI/FS process	**13**
7	Jan. 24, 1996	letter from S.W. Effler to J. Fitzpatrick (HydroQual), rebuttal to Fitzpatrick response (Dec. 27, 1995) and Allied Signal response of Effler letter of July 25, 1995 (item 5 of this Table), reviews problems with County P data	**14**
8.	Feb. 22, 1996	letter and attachment from S.W. Effler to T. Larson (NYSDEC), reviews various aspects of the problems of the County monitoring data base, including P	**6**

phosphorus data collected under USEPA funding has supported a number of manuscripts in peer-reviewed scientific journals (e.g., Auer et al. 1990, 1993, Driscoll et al. 1993, Connors et al. 1996, Effler et al. 1996a, Doerr et al. 1996, Heidtke and Auer 1992, Effler and Whitehead 1996, Effler et al. 1996c). **These data have not been considered in the analysis**.

Only through detailed analyses did the character and prevalence of the P data problem from the County monitoring program emerge. This was promoted by Onondaga County's repeated reference to total inorganic P (TIP) analytical results as total P (TP). For example, the reviews of TP loading history to the lake presented by Devan and Effler (1984) and Canale and Effler (1989) must be considered qualitative, rather than quantitative, as County data were incorporated in those analyses.

As documented in referenced attachments (see Tables 1 and 2), TIP was measured in the lake and tributaries instead of TP through 1989. The TIP measure systematically omits particulate organic P (i.e., contributions of phytoplankton biomass), and thereby has little value (in the absence of paired TP data) as a water quality measure in a hypereutrophic lake. Thus the statement (p.6 of the TMDL analysis)

> "An in-lake minimum monthly mean phosphorus concentration of 0.15 $mg \cdot L^{-1}$ was reportedly observed in August 1981".

is not representative of TP concentration(s) in the lake because the P fraction measured systematically omitted particulate organic P. Further, the County monitoring program has a history of detection limit problems for P analyses (see Table 1 and **Attachments 3, 5, 6, and 10-14**) that may at times have extended to this concentration range. The much higher concentrations presented for 1968-69 (p.6) are almost certainly more accurate, but

potential influences of data problems need to be acknowledged unless assurances to the contrary can be made. The average epilimnetic concentration presented for "recent years" is potentially misleading. Presumably, "concentration" as used here refers to the concentration of TP. However, inclusion of County results for 1986, 1987, 1988, and 1989 (e.g., the loading table presented on P.6 of the TMDL analysis) is inappropriate because the reported concentrations were actually for TIP (Table 1, also see **Attachments 3, 5, 6, and 10-14**). The character of the disparity between TP and TIP measurements for the lake's epilimnion was described by Effler et al. (1996c; see Figure 5.46 of Chapter 5). The quality of the lake TP data from the County program since 1990 (e.g., Table 1) needs to be rigorously examined, particularly in light of historic short-comings in the program (see **Attachment No. 12**).

The breakdown of contributions to annual TP (presumed) loading by METRO and individual tributaries is flawed for a least three (3) reasons. First, the loads presented in the County's annual reports for METRO (at least through the 1989), were based on infrequent (e.g., $2 \cdot month^{-1}$) TIP analyses instead of the daily TP measurements made since 1980, and thus are inaccurate (see **Attachments 13 and 14**). METRO TP loads for these years were presented by Effler and Whitehead (1996). Second, tributary TP loads at least through 1989 are unreliable because of detection limit problems and TIP was measured instead of TP (**Attachment 11, 13 and 14**). In general, reported estimates of tributary TP loading from the County data base for that interval tend to be false high, thereby under-representing the relative contribution of METRO. Third, the METRO load from 1993 should not be considered representative because of the influence of construction upgrades (Effler et al. 1996a).

D. Phosphorus Model Predictions for Case 3 (Table 1, TMDL) are Too High

We have made runs with the TP model (Doerr et al. 1996) corresponding to those designated in Table 1 of the TMDL analysis. We find the predictions associated with Case 3 (METRO effluent concentrations of 0.02 $\mu g \cdot L^{-1}$) to be too high. We cannot be sure of the reasons for these differences, though it seems likely the software upgrade to accommodate reductions in sediment P release for major reductions in external P loading was not used in the analysis. Failure to adopt this upgrade would also result in overly pessimistic predictions for METRO diversion scenarios. System-specific research findings and related literature supporting this software upgrade were described in some detail in the peer-reviewed literature by Effler and Doerr (1996). We transmitted this upgrade to NYSDEC, via a memorandum to S. Eidt, on July 11, 1996. The entire memo appears below.

> "As per your phone request of July 11 (1:30 PM), 1996, please find enclosed the modified software for the Onondaga Lake total phosphorus (TP) model that reproduces the simulations presented in the manuscript "Water Quality Model Evaluations for Scenarios of Loading Reductions and Diversion of Domestic Waste Effluent Around Onondaga Lake" (Lake and Reservoir Management, volume 12, pages 181-193, by S.W. Effler and S.M. Doerr, published in March 1996).
>
> It is important to note and understand that the lower summer average TP concentrations predicted for METRO diversion options with this modified software do not represent a change in the model but rather reflect findings that have resulted in improved inputs to the same model. Specifically, the sediment phosphorus release rate ($R_{sed,8}$) for diversion options is now specified as 5 $mgP \cdot m^{-2} \cdot d^{-1}$ (see Table 1, p. 183, of the above Effler and Doerr manuscript), as per findings of Penn (1994; "The Deposition, Diagenesis and Recycle of Sedimentary Phosphorus in a Hypereutrophic Lake, Ph.D. Dissertation, Michigan Technical University).
>
> The Effler and Doerr manuscript should be relied upon as the appropriate reference for application of the Onondaga Lake water quality models to evaluate management alternatives for METRO, particularly diversion options.

This MEMO should accompany all copies of the modified software that are distributed to interested parties."

E. TMDL Summary (starting on p.10)/Model Application and Calculations

County monitoring data for the last six years were used (p.10 of draft TMDL analysis for P). Specifically, what six years, 1990-1995? The use of Onondaga County loading data, particularly with the exclusion of other data sources, is inexplicable for a number of reasons.

1. The long history of P data quality problems of the County program (see Tables 1 and 2),
2. exclusion of P loading information collected under NYSDEC and USEPA funding (1989-1994; 1995 and 1996 data sets collected **pro bono** by the same researchers),
3. exclusion of P loading information for the same years that has already been subjected to independent peer-review (Effler et al. 1991, 1996a (**Attachment No. 15**), Doerr et al. 1996), and
4. exclusion of particularly detailed loading estimates for certain years/tributaries (supported by runoff event/high frequency based sampling programs; e.g., Effler et al. 1991, 1996a, Heidtke and Auer 1992).

Were the tributary data used, or were the reported annual loading estimates used? Loading estimates should not be described as data, because they are the result of calculations. A wide range of loading calculation protocols exist; loading estimates can be very sentsitive to the specific methodology used. Do the calculated loads agree with those presented in the peer-reviewed literature (Effler et al. 1996a) for the same years?

What is the modeling rationale for development of the TMDL analysis, as outlined in the draft analysis of 5·30·97? Clearly the approach adopted differs from that used for ammonia. The ammonia analysis at least acknowledges the concept of critical (e.g., hydrologic) conditions. No mention of the concept is made in the P analysis. Why wasn't the TP model applied to a wider range of documented conditions in a effort to identify defensible critical conditions? What is the rationale for the six year averaging? The descriptor "**modeled** non-point source loading" (p.10) is used, but this is not an output of a mechanistic model; such a description should be reserved for the outcome of the application of a deterministic non-point loading model (e.g., GWLF). Instead, here it is the residual of the County six year average TP load and a METRO effluent load. The METRO load is calculated as the product of the design flow (84.2 mgd) and an invoked effluent concentration of 0.55 $mg \cdot L^{-1}$ (approximately representative of prevailing conditions). The significance/ justification of this calculated ("modeled" according to TMDL analysis, p.10) non-point load is obscure in the presentation. It should not be expected to be representative of the prevailing non-point load, as the design flow is about 20% higher than prevailing conditions (e.g., Effler et al. 1996a). This should be expected to result in under-representation (estimation) of the prevailing non-point load (calculated as the residual of the total and METRO loads).

Refences

Auer, M.T., N. Johnson, M.P. Penn and S.W. Effler. 1993. Measurement and verification of rates of sediment phosphorus release for a hypereutrophic urban lake. Hydrobiology 253: 301-309.

Auer, M.T., M.L. Storey, S.W. Effler, N.A. Auer and P. Sze. 1990. Zooplankton impacts on chlorophyll and transparency in Onondaga Lake, New York, U.S.A. Hydrobiology 200/201: 603-617.

Beaulac, M.N. and K.H. Reckhow. 1982. An examination of land-use nutrient export relationships. Water Resources Bull. 18: 1013-1024.

Brooks, C.M. and S.W. Effler. 1990. The distribution of nitrogen species in polluted Onondaga Lake, NY, U.S.A. Water Air Soil Pollut. 52:247-262.

Canale, R.P., M.T. Auer, E.M. Owens, T.M. Heidtke and S.W. Effler. 1990. Modeling fecal coliform bacteria. II. Model development and application. Water Res. 27:703-714.

Canale, R.P. and S.W. Effler. 1989. Stochastic phosphorus model for Onondaga Lake. Water Res. 23:1009-1016.

Canale, R.P., R.K. Gelda and S.W. Effler. 1996. Development and testing of a nitrogen model for Onondaga Lake. Lake Reserv. Manage. 12:151-164.

Clesceri, N.L., S.J. Curan and R.I. Sedlak. 1986. Nutrient loads to Wisconsin lakes: Part I. Nitrogen and phosphorus export coefficients. Water Resources Bull. 22:983-990.

Connors, S.D., M.T. Auer and S.W. Effler. 1996. Phosphorus pools, alkaline phosphatase activity, and phosphorus limitation in hypereutrophic Onondaga Lake. Lake Reserv. Manage. 12:47-57.

DePinto, J.V. 1982. An experimental apparatus for evaluating kinetics of available phosphorus release from aquatic particulates. Wat. Res. 16:1065-1070.

DePinto, J.V., T.C. Young and S.C. Martin. 1981. Algal-available phosphorus in suspended sediments from lower Great Lakes tributaries. J. Great Lakes Res. 7:311-325.

Devan, S.P. and S.W. Effler. 1984. History of phosphorus loading to Onondaga Lake. J. Environ. Engr. ASCE 110:93-109.

Doerr, S.M., R.P. Canale and S.W. Effler. 1996. Development and testing of a total phosphorus model for Onondaga Lake. Lake Reserv. Manage. 12:141-150.

Driscoll, C.T., S.W. Effler, M.T. Auer, S.M. Doerr and M.R. Penn. 1993. Supply of phosphorus to the water column of a productive hardwater lake: Controlling mechanisms and management considerations. Hydrobiology 253:71-72.

Driscoll, C.T., S.W. Effler and S.M. Doerr. 1994. Changes in inorganic carbon chemistry and deposition of Onondaga Lake, New York. Environ. Sci. Technol. 28:1211-1218.

Effler, S.W. (ed.) 1996. Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, New York. Springer-Verlag, NY, 832p.

Effler, S.W., C.M. Brooks, J.M. Addess, S.M. Doerr, M.L. Storey and B.A. Wagner. 1991. Pollutant loadings from Solvay waste beds to lower Ninemile Creek, New York. Water Air Soil Pollut. 55:427-444.

Effler, S.W., C.M. Brooks, M.T. Auer and S.M. Doerr. 1990. Free ammonia in a polluted hypereutrophic urban lake. Res. J. Wat. Pollut. Contr. Fed. 62:771-779.

Effler, S.W., C.M. Brooks, M.G. Perkins, S.M. Doerr, K.A. Whitehead, B.A. Wagner and C.T. Driscoll. 1995. Onondaga Lake monitoring report, 1994. Submitted to the Onondaga Lake Management Conference. Syracuse, NY.

Effler, S.W, C.M. Brooks and K.A. Whitehead. 1996a. Domestic waste inputs of nitrogen and phosphorus to Onondaga Lake, and water quality implications. Lake Reserv. Manage. 12:127-140.

Effler, S.W. and S.M. Doerr. 1996. Water quality model evaluations for scenarios of loading reductions and diversion of domestic waste effluent around Onondaga Lake. Lake Reserv. Manage. 12:181-193.

Effler, S.W. and C.T. Driscoll. 1985. Calcium chemistry and deposition in ionically polluted Onondaga Lake, NY. Environ. Sci. Technol. 19:716-720.

Effler, S.W., et al. 1996c. Chemistry (Chapter 5). In S.W. Effler (ed.). Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, New York. Springer-Verlag, NY, pp. 263-383.

Effler, et al. 1996d. Mechanistic Modeling of water quality in Onondaga Lake (Chapter 9). In S.W. Effler (ed.) Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, New York. Springer-Verlag, NY, pp. 667-788.

Effler, S.W., and D.L. Johnson, J.F. Jiao and M.G. Perkins. 1992. Optical impacts and sources of suspended solids in Onondaga Creek, U.S.A. Water Resources Bull. 28:251-262.

Effler, S.W., M.G. Perkins, K.A. Whitehead and E.A. Romanowicz. 1996b. Ionic inputs to Onondaga Lake: Origins, character and changes. Lake Reserv. Manage. 12:15-23.

Effler, S.W. and K.A. Whitehead. 1996. Tributaries and discharges (Chapter 3). In S.W. Effler (ed.). Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, New York. Springer-Verlag, NY, pp. 97-199.

Hartigan, J.P., T.F. Quasebarth and E. Southerland. 1983. Calibration of NPS model loading factors. J. Environ. Engr. ASCE 109:1259-1272.

Heidtke, T.M. and M.T. Auer. 1992. Partitioning phosphorus loads: implications for lake restoration. J. Water Resources Plan. Manage. ASCE 118:562-579.

Hutchinson, G.E. 1973. Eutrophication: the scientific background of a contemporary practical problem. Am. Sci. 61:269-279.

Johnson, M.G., J.C. Comeau, T.M. Heidtke, W. Sonzogni and B. Stahlbaum. 1978. Management information base and overview modeling. PLUARG Special Report to the International Joint Commission, Windsor, Ontario, Canada.

Martin, S.C., J.V. DePinto and T.C. Young. 1985. Biological availability of sediment phosphorus inputs to the lower Great Lakes. USEPA, Environmental Research Laboratory, Duluth, MN, EPA/600/53-84/100.

Smithgall, C., P.E. Moffa and R. Klosowski. 1991. 1990 Onondaga Creek phosphorus loading evaluations (memo). Moffa and Associates Inc., Syracuse, NY.

United States Environmental Protection Agency (USEPA). 1985. Ambient water quality criteria for ammonia - 1984. Office of Water Regulations and Standards Criteria and Standards Division, Washington, D.C.

Vollenweider, R.A. (ed.) 1982. Eutrophication of waters: Monitoring, assessment and control. Organization of Economic Cooperation and Development, Paris, France.

Wetzel, R.G. 1983. Limnology, 2nd ed. Saunders College, Philadelphia, PA.

Young, T.C., J.V. DePinto, S.E. Flint, M.S. Switzenbaum and J.K. Edzwald. 1982. Algal availability of phosphorus in municipal wastewater. J. Water Pollut. Contr. Fed. 54:1505-1516.

Young, T.C., J.V. DePinto, S.C. Martin and J.S. Bonner. 1985. Algal-available particulate phosphorus in the Great Lake basin. J. Great Lakes Res. 11:434-446.

LIST OF ATTACHMENTS

NO.	DESCRIPTION
1.	letter to K. Callahan, USEPA, May 6, 1997; from S.W. Effler and M.T. Auer.
2.	report, "A comparative analysis of pH data for Onondaga Lake", submitted to NYSDEC as part of Allied Signal RI/FS, by S.M. Doerr and S.W. Effler.
3.	letter with attachment to J. Fitzpatrick, HydroQual Inc., July 25, 1995; from S.W. Effler.
4.	letter with attachment to J. Fitzpatrick, HydroQual Inc., February 27, 1996; from S.W. Effler.
5.	letter with attachment to R. Mustico, NYSDEC, April 27, 1995; from S.W. Effler.
6.	letter with attachment to T. Larson, NYSDEC, February 22, 1996; from S.W. Effler.
7.	selective listing of literature on the bioavailability of particulate phosphorus.
8.	letter to T. Mulvey, Onondaga Lake Management Conference, March 16, 1992; from M.T. Auer.
9.	program cover and abstract for bioavailability findings for Onondaga Lake, 16th Annual International Symposium on Lake, Reservoir and Watershed Management, November 1996; abstract of findings to be presented at the 1997 Annual Meeting of the Michigan Water Environment Association.
10.	memorandum of May 5, 1990 to attendees of meeting of April 26, 1990; from S.W. Effler.
11.	letter and attachment to R. Ott, Dept. Drainage and Sanitation of Onondaga County, February 1992; from S.W. Effler.
12.	report, "A comparative analysis of phosphorus data for Onondaga Lake, and Implications", submitted to NYSDEC as part of Allied Signal RI/FS, by S.W. Effler and S.M. Doerr.
13.	letter and attachment to T. Larson, NYSDEC, January 16, 1996; from S.W. Effler.

14. letter and attachment to J. Fitzpatrick, HydroQual Inc., January 24, 1996; from S.W. Effler.

15. copy of the manuscript, "Domestic waste inputs of nitrogen and phosphorus to Onondaga Lake, and water quality implications", Vol. 12, pp. 127-140, *Lake and Reservoir Management*, by S.W. Effler, C.M. Brooks, and K.A. Whitehead.

UPSTATE FRESHWATER INSTITUTE

May 6, 1997

Ms. Kathleen Callahan, Director
Division of Environmental Planning and Protection
US EPA, Region II
24th Floor
290 Broadway
New York, N.Y. 10007-1866

Dear Ms. Callahan:

Thank you for the courtesy extended to us for our presentation of April 14, concerning Onondaga Lake and the Seneca River, and the implications of an in-lake discharge of an up-graded METRO effluent (effluent concentrations: total phosphorus (TP) = 0.12 $mg \cdot L^{-1}$; total ammonia ($T\text{-}NH_3$) = 4 $mg \cdot L^{-1}$ for October - April, = 2 $mg \cdot L^{-1}$ for May - September). You and your staff showed great patience with a rather lengthy and detailed presentation. This letter is intended to be a technical summary of the salient information presented. As you are aware, most of the material was new research findings from on-going unfunded efforts by the Upstate Freshwater Institute (UFI) and Professor Auer (Michigan Technological University).

Review Material

To place the significance of the new research in context, and to acquaint those in the audience unfamiliar with the lake and the prevailing problems, it was necessary to review certain earlier findings, as listed below. The supporting documentation for this material can be found in the more than 70 peer-reviewed manuscripts published on the lake and river by our research team, or in one of the following two volumes:

(i). "Limnological and Engineering Analysis of a Polluted Urban lake. Prelude to Environmental Management of Onondaga Lake, New York", edited by S.W. Effler, published by Springer-Verlag, New York

(ii). Volume 12, No. 1, March 1996 issue of the peer-reviewed journal *Lake and Reservoir Management*; all 18 research articles of the issue were on Onondaga Lake.

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Selective Listing of Reviewed Points

1. Onondaga Lake was an oligo-mesotrophic lake before European development of the surrounding area,

2. METRO's discharge makes an unprecedented contribution (nearly 20%) to the total inflow to Onondaga Lake, relative to wastewater effluent contributions to other lakes in the United States,

3. the METRO discharge is presently responsible for exceedances of the New York State guidance value for the summer average total phosphorus (TP) concentration in the epilimnion,

4. the METRO discharge is presently responsible for violations of New York State (NYS) water quality standards for free ammonia (NH_3), nitrite (NO_2^-), dissolved oxygen (DO) and clarity,

5. dissolved oxygen issues
   a. **dissolved oxygen in the hypolimnion,** a regional perspective for mesotrophic lakes:
      i) mesotrophic lakes with similar morphometry to Onondaga Lake (e.g., Otisco Lake and Cazenovia Lake) develop hypolimnetic anoxia by late summer. These conditions are natural and should not be considered violations, and
      ii) oxygen depletion in the hypolimnion of Onondaga Lake in summer would be akin to that observed in other mesotrophic central NY lakes of similar morphometry following diversion of METRO.

   b. **severe lake-wide oxygen depletion** presently occurs annually during fall turnover in Onondaga Lake:
      i) NYS standards are violated lake-wide as a result of the METRO discharge,
      ii) annual lake-wide depletion of this magnitude is unprecedented, on a nation-wide basis,
      iii) most fish leave the lake during this period, and
      iv) diversion of METRO (out-of-lake discharge) will eliminate the lake-wide violations of the DO standard.

6. the fish flesh of Onondaga Lake continues to be contaminated with mercury (Hg),

7. features of NH_3 chemistry, and the effects of ambient environmental conditions on NH_3 concentrations and related toxicity standards, were reviewed,

8. the character and margin of prevailing violations of the chronic NH_3 standard in Onondaga Lake were reviewed,

9. features of the Onondaga Lake nitrogen (N; includes T-NH_3) model were reviewed,

10. features of the zebra mussel invasion, as these invaders affect the water quality and waste assimilative capacity of the Seneca River were reviewed.

New Observations and Findings

1. mercury (out of the laboratory of C.T. Driscoll, Syracuse Univ.),
   a. METRO is the largest external source of methyl-mercury to Onondaga Lake,
   b. METRO is a major source of total mercury to Onondaga Lake

2. the relative potency (bioavailability) of external phosphorus loads to the lake (as "realized" load) has been assessed; METRO is the most potent source of phosphorus (urban part of Onondaga Creek next most potent),
   e.g., a pound of phosphorus from METRO grows more algae than a pound of phosphorus from any other source,

3. phosphorus and trophic state; based on sensitivity analyses with the existing total phosphorus model for Onondaga Lake,
   - eutrophic conditions would persist in Onondaga Lake with the proposed in-lake discharge, thus improvements would **not** be expected in
   a. summertime algae/phytoplankton concentrations,
   b. the occurrence of **nuisance** phytoplankton blooms,
   c. clarity,
   d. the rapid rate of oxygen depletion in the hypolimnion in summer, and lake-wide during fall turnover, and
   e. the high rates of ammonia release from sediments and sediment oxygen demand.

4. recent and anticipated changes in the USEPA free ammonia (NH_3) criteria were reviewed within the context of "relative change", since the 1984/95 criteria
   - changes may influence mid-summer standards (e.g., "softer") substantially, but effects on the months of April and May are modest (e.g., < 20%)

5. "acute" toxicity NYS standards for free ammonia are violated (probably annually) in the upper waters of the lake during algae blooms,

6. the method used by the NYS Department of Environmental Conservation (NYSDEC) to develop a site-specific total ammonia standard protective for the USEPA free ammonia criteria was described
   - the method is flawed because it is not based on quantitative predictions of free ammonia.

7. UFI has developed an upgraded mode of application* of the Onondaga Lake Nitrogen Model to accommodate the important influence of hydrologic variability in mediating the extent of the impact of METRO's discharge on T-NH_3 concentrations in the upper waters of Onondaga Lake

   - utilizes the continuous tributary hydrologic record available since 1971.

   ** Note: no changes in the Nitrogen Model have been made.*

8. April (and secondarily May) is the critical month for (free) ammonia in Onondaga Lake with respect to the proposed in-lake discharge of the METRO effluent,

   - e.g., violations most numerous and severe in April.

9. predictions of total ammonia for the critical month of April with the Onondaga Lake Nitrogen model are particularly reliable, because of seasonal flushing rate characteristics of the lake, and kinetic considerations,

10. the critical role of representative pH data in the analysis of free ammonia standard(s) for the proposed METRO discharge option was described,

11. pH data from the Onondaga County monitoring program lack the credibility to support the analysis of the METRO proposal with respect to free ammonia standard(s),

    - NYSDEC has recommended against the use of County pH data in other water quality modeling analyses because of credibility problems,
    - comparisons presented between UFI and County pH data for recent years continue to indicate the County data set is inferior.

12. application of the Onondaga Lake Nitrogen model demonstrates the proposed in-lake discharge would continue to violate a NYSDEC - type total ammonia standard an unacceptable number of times,

13. an alternate probabilistic approach for predicting free ammonia concentrations directly from the Nitrogen Model (consistent with the USEPA perspective, but widely different from the approach presently used by NYSDEC) was developed,

14. application of the probabilistic approach with the Nitrogen Model establishes the proposed in-lake discharge will result in exceedances of the USEPA's present, and forthcoming, criteria for free ammonia (including the most lenient interpretations),

15. residual impact from the Allied site depresses pH, thereby increasing the present "apparent" assimilative capacity of the lake for ammonia waste,

    i.e., remediation of the Allied site would result in reductions in the waste assimilative capacity of the lake for ammonia.

16. accommodation of the residual effect from the Allied site in the analysis indicates that even greater treatment at METRO (e.g., 3 $mg \cdot L^{-1}$ in winter and 1 $mg \cdot L^{-1}$ in summer) would result in unacceptable violations of free ammonia standards,

17. use of Onondaga County's unreliable pH data results in "false-high" assimilative capacity for ammonia in Onondaga Lake,

18. major shifts in the character of the zebra mussel invasion of the Seneca River are occurring,

19. the assumption that the zebra mussel invasion, and the coupled impacts on water quality, will persist at the levels documented for the 1993-1995 interval is inconsistent with ecological theory related to invasions of exotic species, as well as the European experience with this invader.

Our analysis presented on April 14,. 1997, concluded the proposed in-lake discharge of an up-graded METRO effluent will not meet water quality standards for Onondaga Lake. For the reasons established at the presentation, we have a high degree of confidence in the accuracy of this conclusion. The research findings summarized here will be more fully developed in related manuscripts for professional journals, now in preparation.

Respectfully,

S.W. Effler, Ph.D.
Director of Research

M.T. Auer, Ph.D.
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cc:

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A COMPARATIVE ANALYSIS OF PH DATA FOR ONONDAGA LAKE

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February 1994

Background:

The pH value is a critical water quality parameter; e.g., there are New York State (NYS) standards for pH that need to be met. The pH value of most lakes is regulated by the CO_2-HCO_3^--$CO_3^=$ buffering system. The pH value is a major regulator of biological assemblages. The value of pH plays a particularly important role in two different problems for Onondaga Lake, the excess precipitation of $CaCO_3$ associated with ionic waste discharges from the soda ash/chlor-alkali facility (Driscoll et al. 1994, Effler and Driscoll 1985), and excessively high concentrations of free ammonia (NH_3) caused by the exceedingly high loads of total ammonia received from METRO (Effler et al. 1990, Brooks and Effler 1990). Faulty pH data can lead to incorrect conclusions about the equilibrium conditions with respect to $CaCO_3$, and errors in calculated concentrations of NH_3 and the status with respect standards intended to protect against the toxicity of this species.

Measurements of pH have been made by at least three different programs for portions of the last 25 year period. The two principal programs with respect to related water quality issues are those of Onondaga County's Department of Drainage and Sanitation (D&S, since the late 1960's) and the Upstate Freshwater Institute (UFI, extends back to the late 1970's). Another program was conducted cooperatively by the NYSDEC and Onondaga County Health Department (NYSDEC/DOH). Earlier, Walker (1991) conducted a comparative analysis of data bases available for Onondaga Lake, in an effort to identify anomalous

observations. Statistical and graphical methods and limnological reasoning were applied to identify and "flag" anomalous values (Walker 1991). Walker's (1991) perspective was the adequacy of the various data sets to support the depiction of long term trends. The demands for reliable pH data to support equilibrium calculations, associated with the $CaCO_3$ precipitation and NH_3 issues, are by comparison more rigorous. Here we briefly review Walker's findings for pH and expand the comparative analysis of pH data bases.

Walker (1991) noted NYSDEC/DOH pH values in the epilimnion tended to be higher than values determined by D&S over the 1975-1990 interval, the pattern was particularly distinct over the 1984-1990 interval. Much stronger differences were noted between UFI (lab) and D&S (field) hypolimnetic data over the 1979-1981 interval. D&S values were much higher, the median difference over the 1979-1981 interval was ~0.8 units (Walker 1991). Whereas no biases were detected in comparing UFI and DOH/DEC lab pH data for the upper waters over the same period. It was noted that the very high pH values measured in the lake's hypolimnion (e.g., > 9.0) in 1980 and 1981 were inconsistent with the dominance of respiratory metabolism at those depths (Walker 1991). Based on these and other considerations Walker (1991) "flagged" the hypolimnion data of D&S for the 1979-1981 interval, describing these data as "likely in error".

Walker's (1991) analysis and UFI's on-going analysis of available data bases for the lake (Effler 1994a) have identified a number of short-comings in the overall D&S monitoring data base

(includes many parameters) for the Onondaga Lake system. Until clearly identified and recognized by users, these problems confound fair evaluations of the lake's water quality and status with respect to standards, and identification of trends. Some of the problems identified in the D&S data base to date are summarized in Table 1 below. The analysis presented here expands

TABLE: Problems with the Onondaga County Department of Drainage and Sanitation Data Base for the Onondaga Lake System

Parameter	Problem Description	Reference
dissolved oxygen (DO)	false low in epilimnion, false high in hypolimnion 1976-1981, data rejected	Walker 1991
	presence of DO near lake bottom when reduced species present, 1972-1988	Walker 1991
temperature	false high in hypolimnion, 1979-1981 data rejected	Walker 1991
pH	as described above, and expanded on herein	Walker 1991, this report
hydrogen sulfide	false low in 1972-1974 (rejected), suspicious differences noted in other years	Walker 1991
phosphorus (P)	monitored total inorganic P instead of total P until 1989	Effler and Whitehead 1994, Effler et al. 1994
soluble reactive P	false high values in upper productive waters of lake for much of summer	unpublished analysis
chloride	unreliable lake concentrations, 1979 and 1982	Doerr et al. 1994
total inorganic P for tributaries and related loads	unreliable during periods of lower concentrations, before 1989	Effler 1992, Effler and Whitehead 1994

the envelop of questionable pH data collected in the D&S monitoring program, and reviews the character of pH distributions that is consistent with limnological principles and systematic

differences in pH and laboratory pH documented for the lake.

Comparison of Laboratory and Field pH Measurements

Systematic differences in pH measurements made in situ (in the field) and the laboratory may emerge, despite proper analytical protocol, for lakes that experience significant deviations from saturated conditions with respect to the concentration of CO_2. Oversaturated samples tend to "degas" (loss of CO_2) during transport and laboratory analysis, resulting in an increase in pH for the laboratory measurement compared to the field measurement. The converse occurs for undersaturated samples. The watercolumn of Onondaga Lake has been demonstrated to be oversaturated with respect to CO_2 (Driscoll et al. 1994). Strong stratification in the degree of oversaturation develops during the summer. The lowermost waters are the most oversaturated (Driscoll et al. 1994) because of the localized production of CO_2 at the sediment-water interface. Under these conditions degassing of Onondaga Lake water samples, and thereby an upward shift in pH from paired field measurements, is expected.

Since 1991 UFI has made paired field and laboratory measurements of pH for Onondaga Lake. The relationship between these measurements is demonstrated in Figures 1-4. All depths for each of three years, 1991, 1992, and 1993 are evaluated in Figure 1(a-c). A recurring relationship emerges for all three years. Laboratory pH is higher than field pH at all but the highest pH values, consistent with the degassing mechanism. The disparity is greatest at the lowest pH values, that are measured

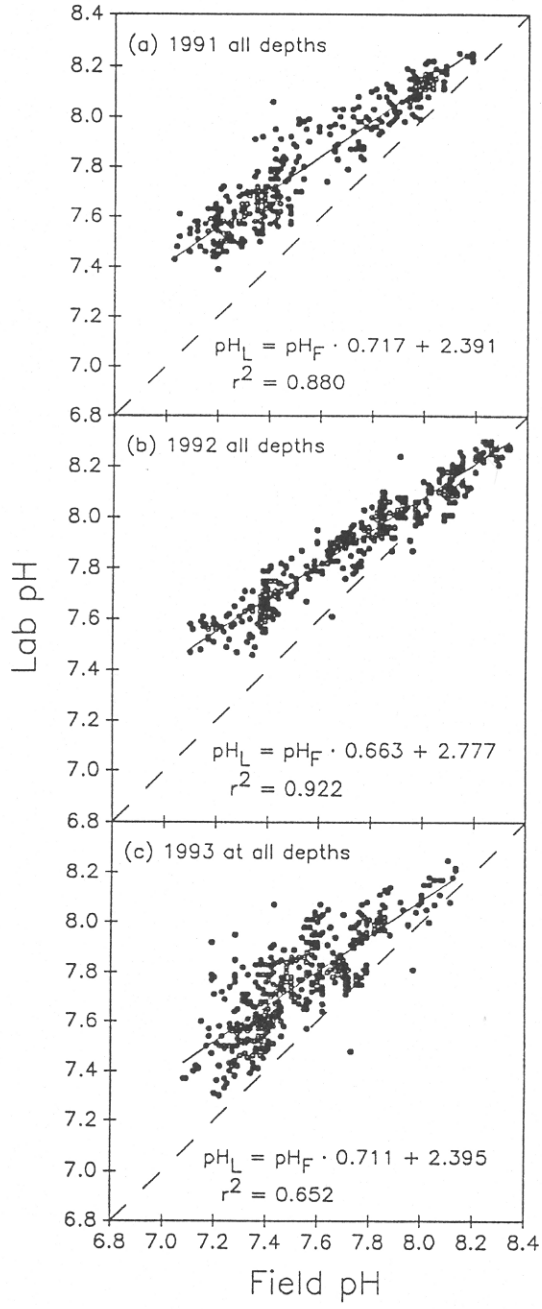


Figure 1: Evaluation of the relationship between paired UFI measurements of pH made in the laboratory and in the field (in situ) for Onondaga Lake, all depths : a) 1991, b) 1992, and c) 1993.

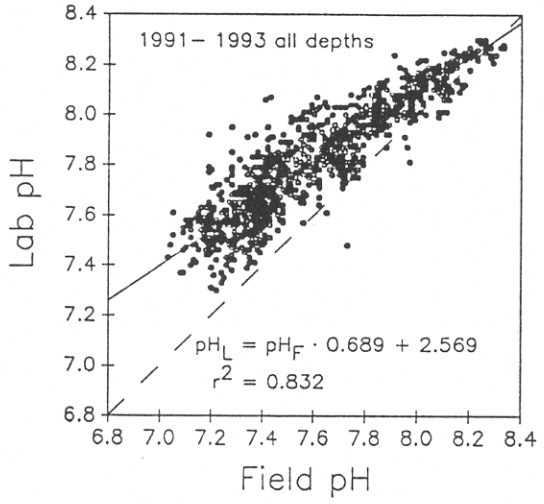


Figure 2: Evaluation of the relationship between paired UFI measurements of pH made in the laboratory and in the field (in situ) for Onondaga Lake, all depths, for the interval 1991-1993.

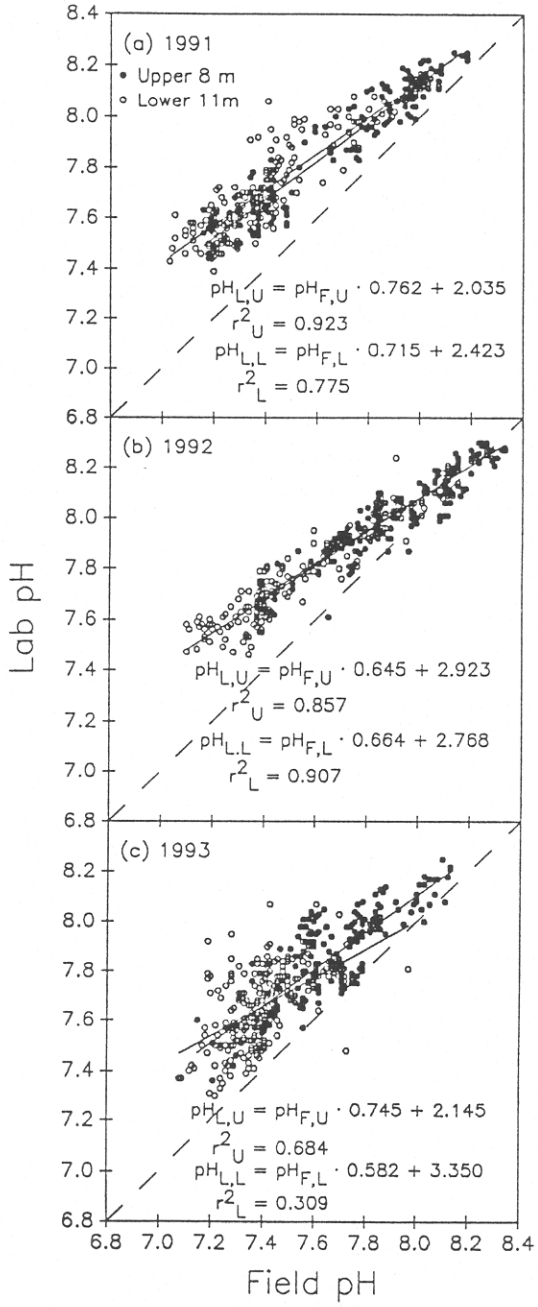


Figure 3: Evaluation of the relationship between paired UFI measurements of pH made in the laboratory and in the field (<u>in situ</u>) for Onondaga Lake, segmented for the epilimnion (upper 8m) and hypolimnion (lower 11m) : a) 1991, b) 1992, and c) 1993.

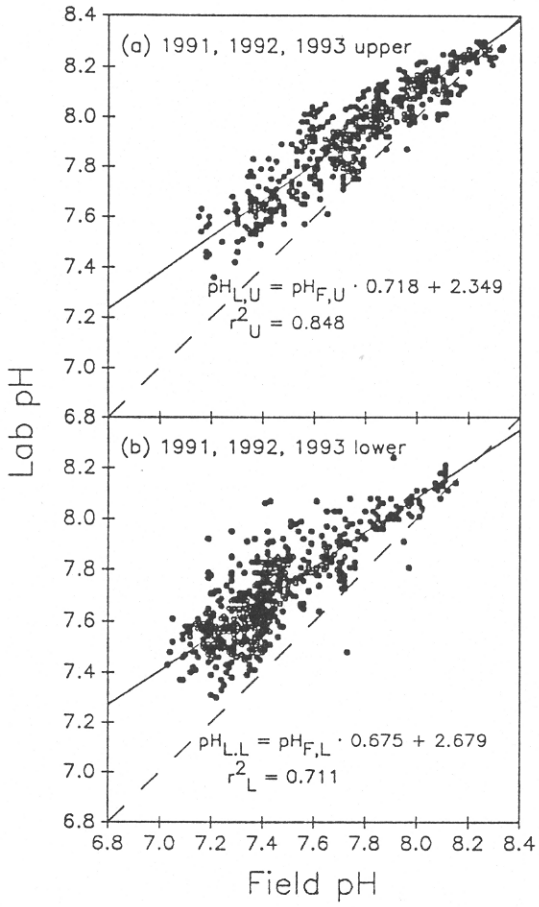


Figure 4: Evaluation of the relationship between paired UFI measurements of pH made in the laboratory and in the field (in situ) for Onondaga Lake, for the interval 1991-1993 : a) epilimnion, and b) hypolimnion.

in the deepest parts of the hypolimnion, which are most oversaturated with CO_2 (Driscoll et al. 1994). The similarity of the relationship for the three years indicates it is recurring (Figure 1(a-c)). The relationship for the combined data base (all three years) is evaluated in Figure 2. Epilimnion and hypolimnion relationships are evaluated on a year-specific basis in Figure 3(a-c), and lumped together for all three years in Figure 4(a and b). Segmenting the data in this way has little effect on the relationships (from regression). The highest pH

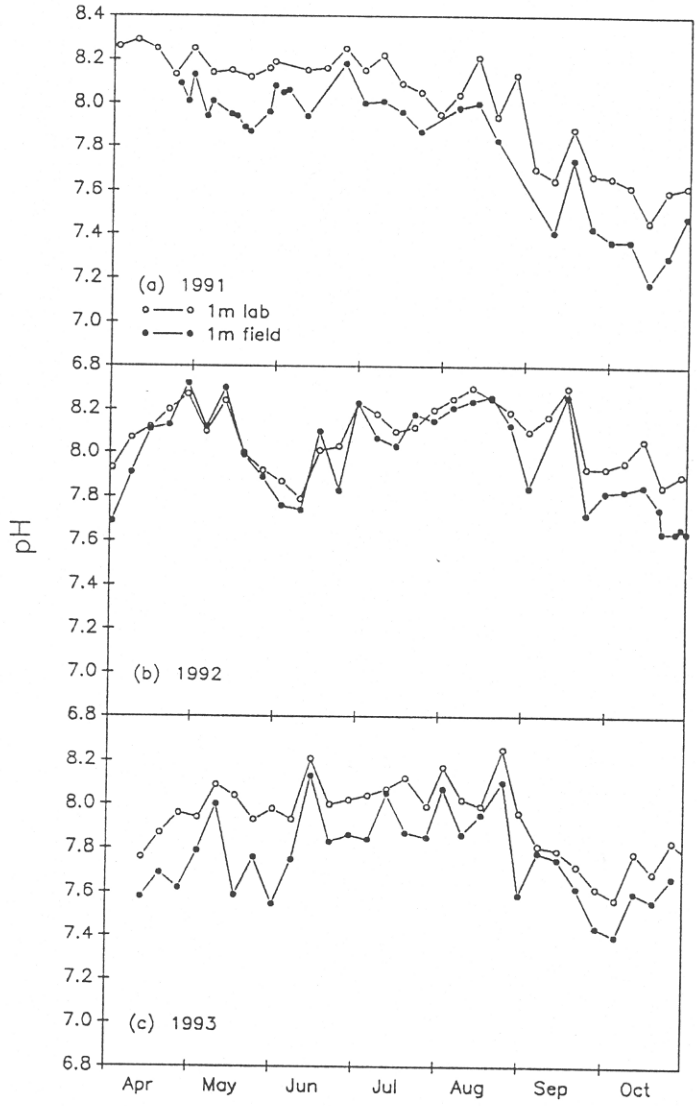


Figure 5: Comparison of temporal distributions of paired UFI measurements of pH made in the laboratory and in the field (in situ) for the surface waters of Onondaga Lake : a) 1991, b) 1992, and c) 1993.

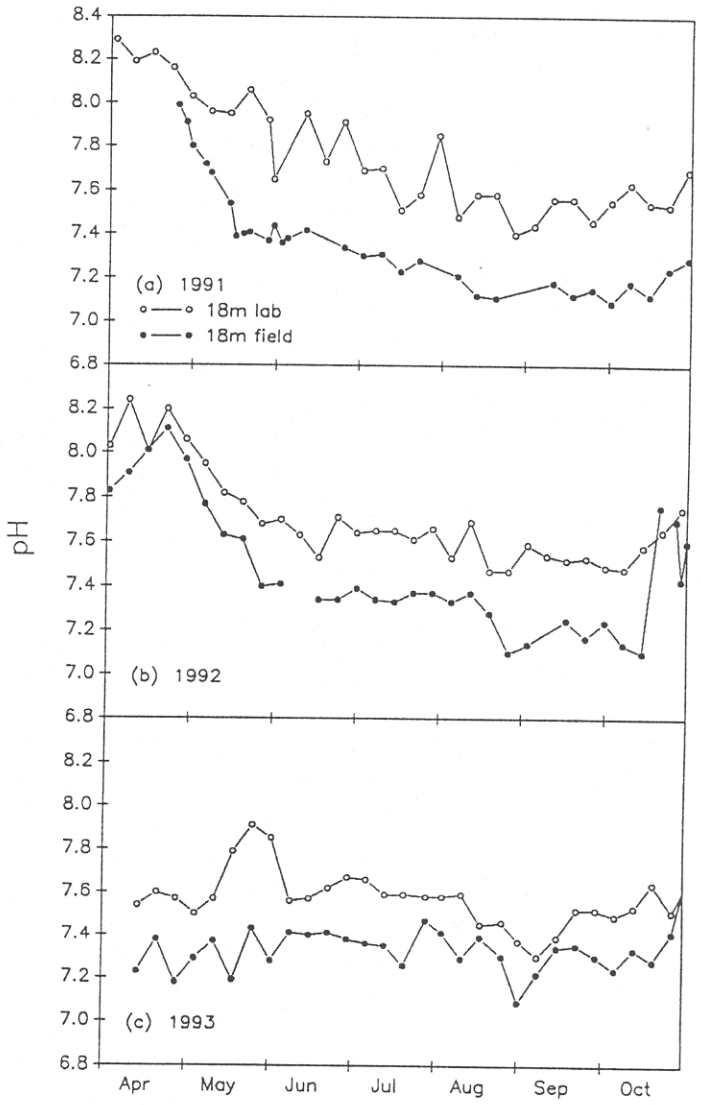
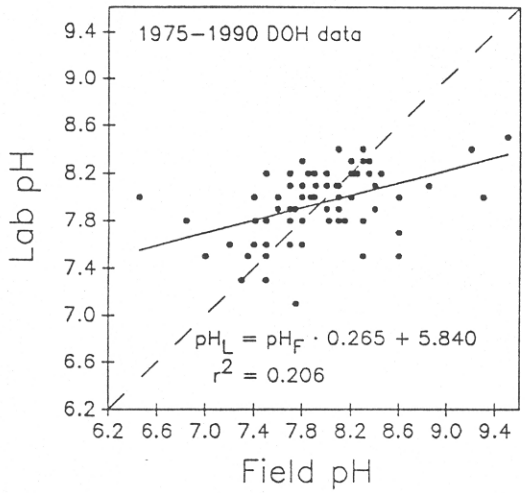


Figure 6: Comparison of temporal distributions of paired UFI measurements of pH made in the laboratory and in the field (in situ) for the near bottom (18m) waters of Onondaga Lake : 1) 1991, 2) 1992, and 3) 1993.

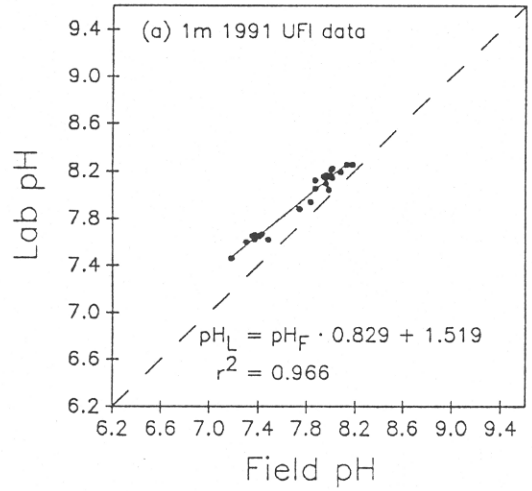
data sets. The relationship between laboratory and field pH is evaluated for the NYSDEC/DOH data base (1975-1990) in Figure 7. A strong systematic relationship does not emerge from this data base. The data base available for this type of analysis for the D&S program was small; 11 paired measurements at each of two depths (1 and 16 m) in 1991. These measurements depict an tendency for laboratory values to exceed field values, but strong relationships do not emerge from these small populations (Figure 8). However, rather strong relationships emerge from the UFI program conducted at the same depths in the same year; the same sampling days used by D&S were in this case augmented by more frequent monitoring (weekly for UFI, biweekly for D&S). Shortcomings in the NYSDEC/DOH (Figure 7) and D&S (1991; Figure 8) programs are indicated compared to the UFI program (Figure 1-4, and 9). The shortcomings of the NYSDEC/DOH program, in this instance (however, see subsequent analysis of other features and portions of the D&S data base), are more severe. The problems of the NYSDEC/DOH and D&S pH programs imply limitations in protocol or instrumentation in either, or both, the laboratory and field measurements.

Temporal Distributions of pH: Comparisons

Temporal characteristics of pH measurements made by the various groups over the period of monitoring are depicted for the surface (0 m) and near-bottom (18 m) waters in Figures 10 and 11, respectively. UFI measurements started in 1978; UFI made no measurements over the 1982-1984 interval. With the exception of the spring of 1980, pH values reported by UFI for 0 m were ≤ 8.65


1975–1990 DOH data
$pH_L = pH_F \cdot 0.265 + 5.840$
$r^2 = 0.206$
Lab pH
Field pH
9.4
9.0
8.6
8.2
7.8
7.4
7.0
6.6
6.2
6.2 6.6 7.0 7.4 7.8 8.2 8.6 9.0 9.4

[redacted]



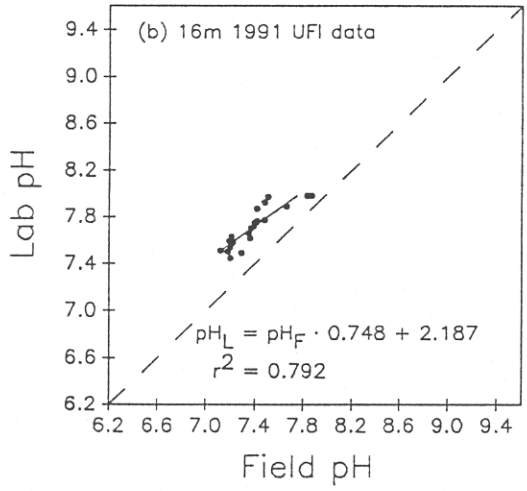


Figure 9: Evaluation of the relationship between paired UFI measurements of pH made in the laboratory and in the field (in situ) for Onondaga Lake in 1991 : a) 1m, and b) 16m.

Om – pH

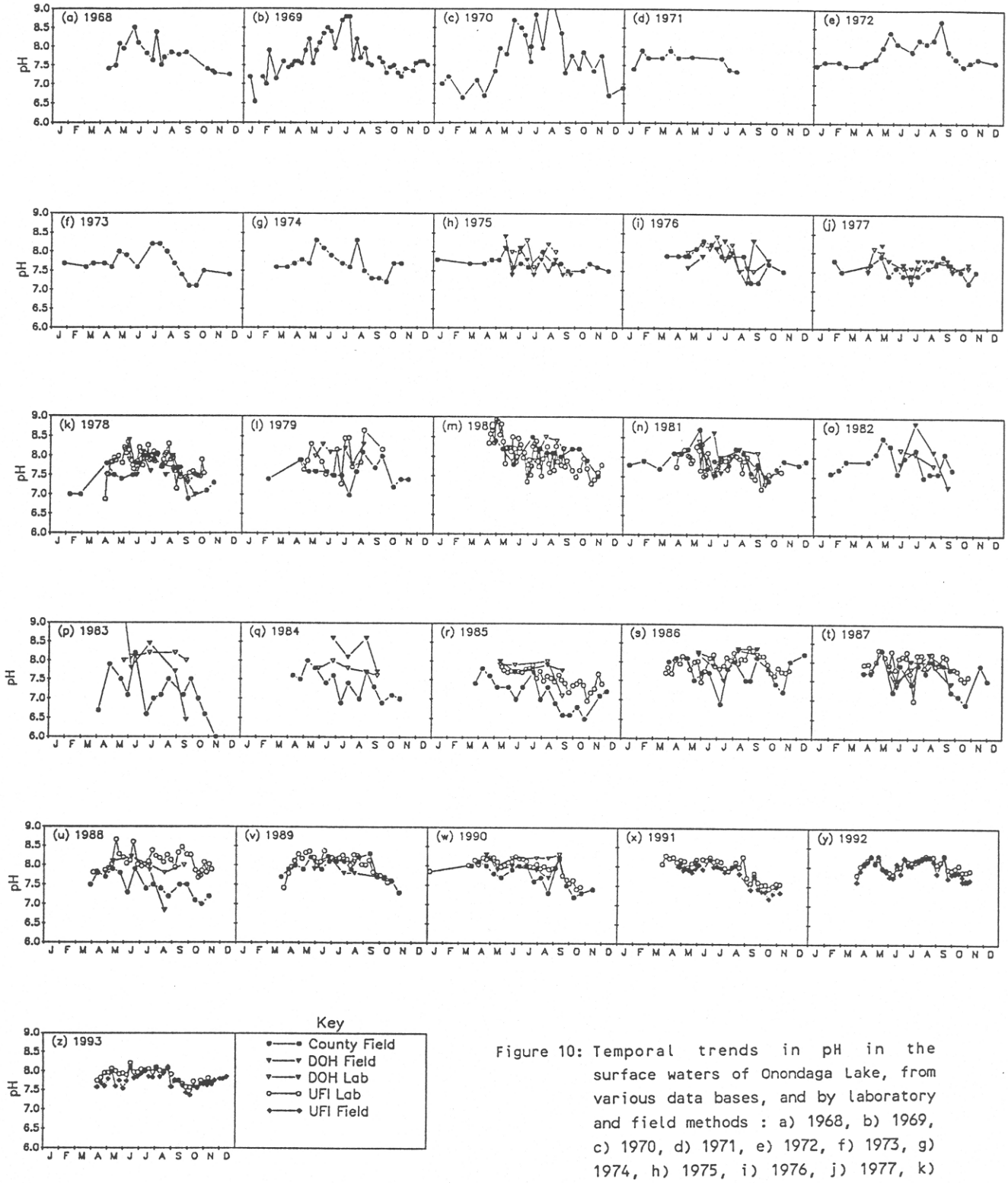


Figure 10: Temporal trends in pH in the surface waters of Onondaga Lake, from various data bases, and by laboratory and field methods : a) 1968, b) 1969, c) 1970, d) 1971, e) 1972, f) 1973, g) 1974, h) 1975, i) 1976, j) 1977, k) 1978, l) 1979, m) 1980, n) 1981, o) 1982, p) 1983, q) 1984, r) 1985, s) 1986, t) 1987, u) 1988, v) 1989, w) 1990, x) 1991, y) 1992, z) 1993.

18m – pH

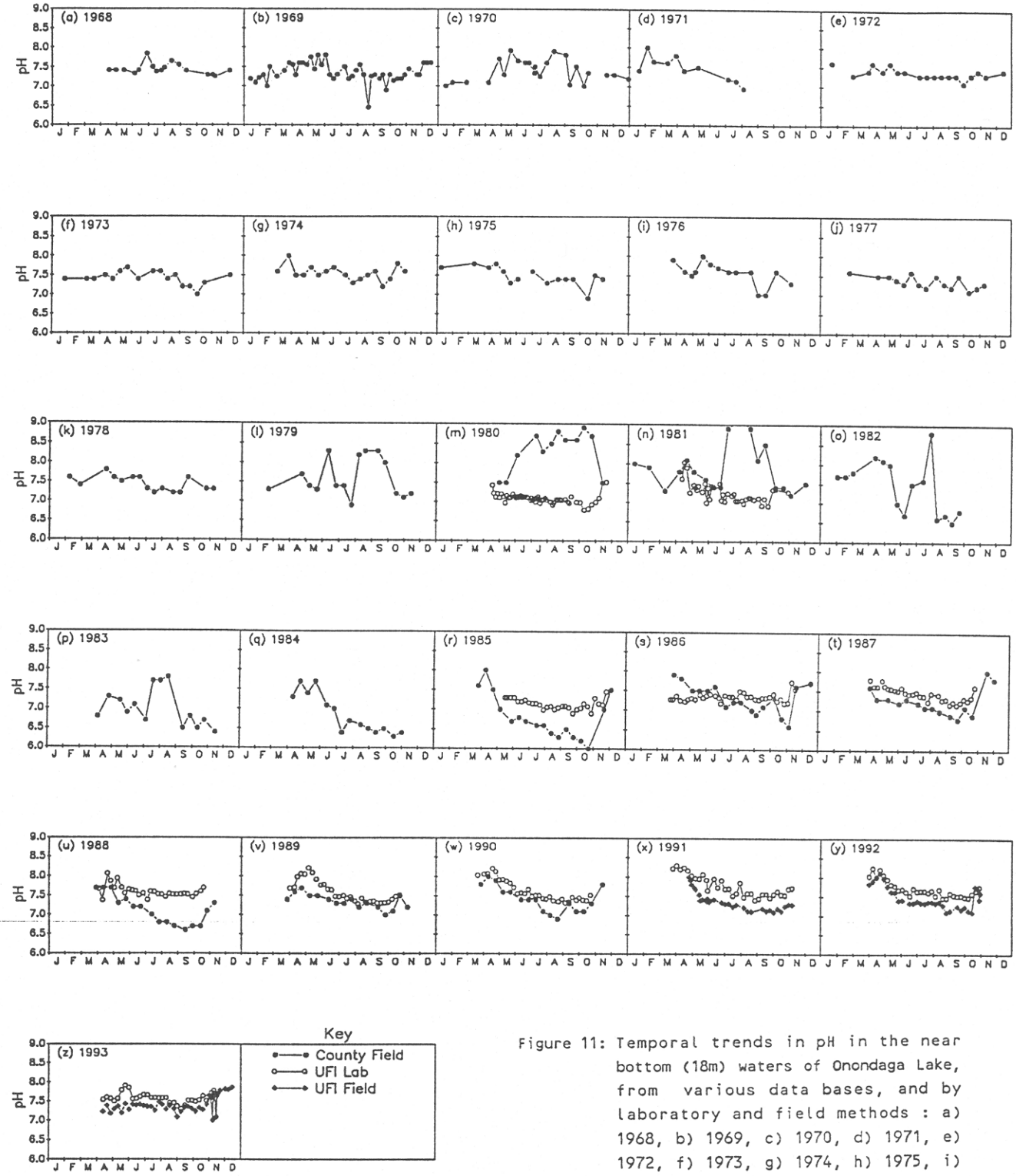


Figure 11: Temporal trends in pH in the near bottom (18m) waters of Onondaga Lake, from various data bases, and by laboratory and field methods : a) 1968, b) 1969, c) 1970, d) 1971, e) 1972, f) 1973, g) 1974, h) 1975, i) 1976, j) 1977, k) 1978, l) 1979, m) 1980, n) 1981, o) 1982, p) 1983, q) 1984, r) 1985, s) 1986, t) 1987, u) 1988, v) 1989, w) 1990, x) 1991, y) 1992, z) 1993.

(Figure 10). Higher values were reported by D&S in 1969, 1970, 1972 and 1980, and by NYSDEC/DOH in 1982 and 1983 (Figure 10). These very high values should be considered suspect for this system, which is so well buffered (e.g., Effler and Driscoll 1985, Driscoll et al. 1994). A pH value of about 7.2 represents the lower bound reported by UFI for the surface waters; this corresponds to conditions after the onset of complete fall turnover, when pH tends to be depressed (see Figure 10x). The D&S program reports lower values, several substantially lower, over the period of record (e.g., 1967, 1970, 1978, 1993, 1983-1988). The very low values reported for this program are particularly suspect for 1983 and 1985; so low that $CaCO_{3(s)}$ would be undersaturated, which is inconsistent with the precipitation and deposition of $CaCO_3$ documented over the 1985 interval (Effler 1994b). In 1985 and 1988 UFI measurements were substantially higher than those of D&S for the surface waters (Figure 10r and u), a substantial discrepancy persisted for parts of 1986 and 1987 (Figure 10s and t). By comparison, the systematic differences, described earlier, between field and laboratory measurements performed by UFI in 1991-1993 were small (Figure 10x-z).

Several anomalous features of the D&S pH data emerge from review of their data from the lower waters (Figure 11). Note that the UFI data sets depict relatively smooth temporal changes within each of the monitored years. Generally progressive decreases or near uniformity is evident in these data (Figure 11). In contrast, irregular and abrupt changes are manifested in

the D&S data base for several years; e.g., 1969, 1970, 1976, 1979-1983. This is inconsistent with observations reported by UFI for the lake, and characteristics reported for other productive lakes by other investigators (Wetzel 1983). There are no known processes (CO_2 sinks and sources) that could cause such abrupt changes in CO_2 concentrations in the near-bottom waters of a productive lake during summer stratification. The abrupt pH increases reported for the bottom waters by D&S during summer stratification (e.g., Figure 11c, l, m, n, o, p) are particularly problematic. These increases basically correspond to abrupt increases in CO_2 uptake/consumption. What mechanism could account for such pH behavior in the bottom of a hypereutrophic lake? The systematic differences in field (lower) and laboratory measurements made by UFI over the 1991-1993 interval explains some of the differences observed between UFI and D&S in 1986, 1987, and 1989, but cannot accommodate the major differences reported for 1985 and 1988 (Figure 11).

Temporal variability manifested at a longer time scale (e.g., years) is depicted for the surface and near-bottom (18 m) waters of the lake, according to the different monitoring programs, in Figures 12 and 13. A robust statistic (e.g., not greatly influenced by a limited number of errors in measurements), the median, is employed to represent the longer term variations in pH. The least variability is apparent for the UFI data base (Figures 12 and 13). The most striking difference within this data base occurred in 1985. A modest increasing trend in pH for the upper waters has been reported (Figure 12b)

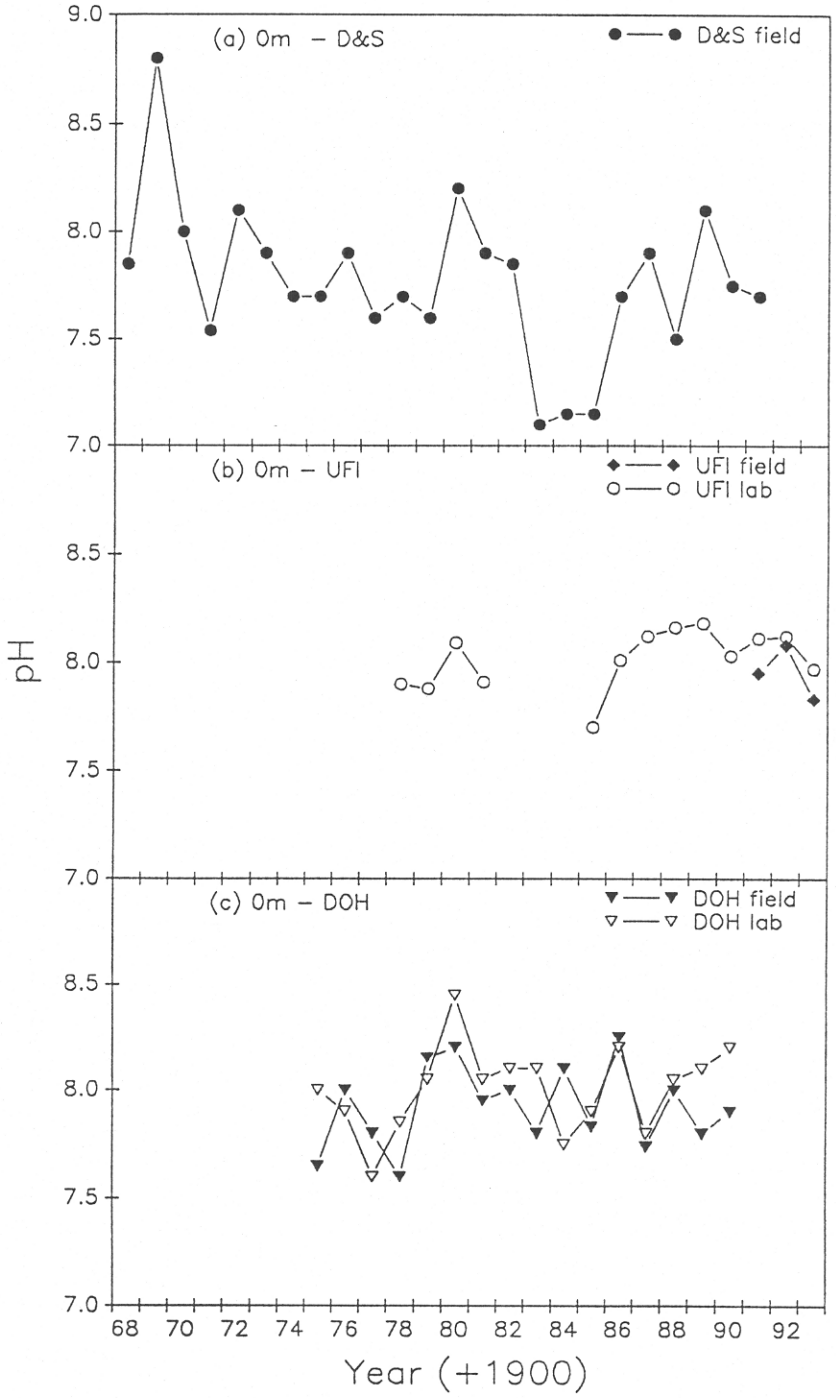


Figure 12: Long-term trends in pH in the surface waters of Onondaga Lake, according to the median observation : a) D&S, b) UFI, and c) NYSDEC/DOH.

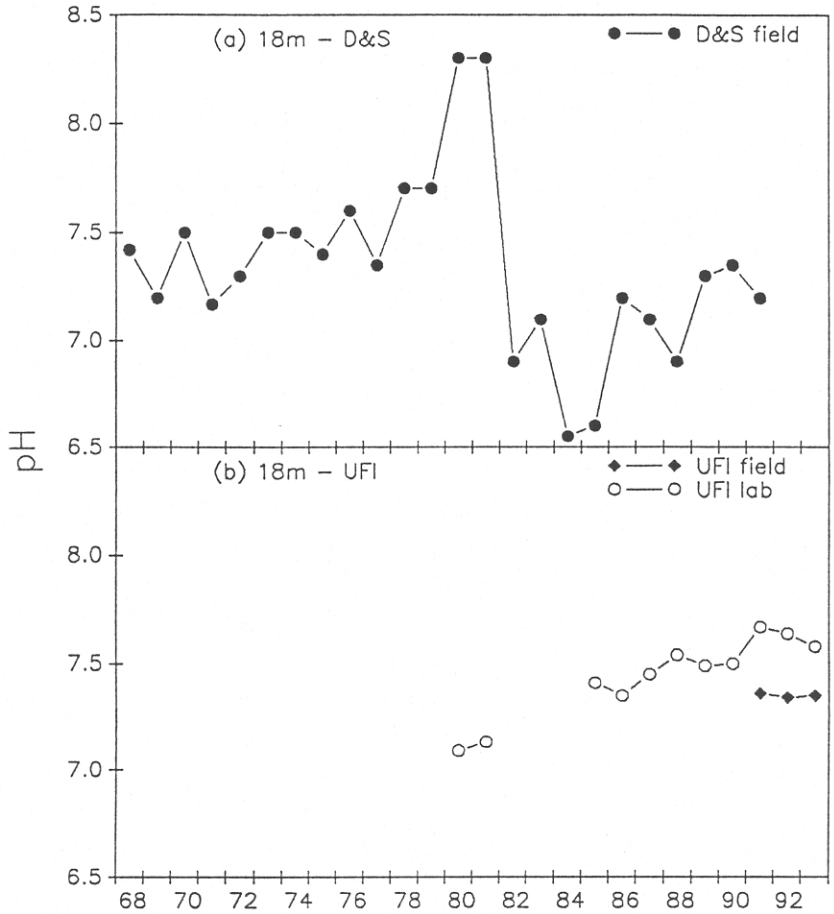


Figure 13: Long-term trends in pH in the near bottom (18m) waters of Onondaga Lake, according to the median observation : a) D&S, and b) UFI.

following closure of the soda ash/chlor-alkali plant, associated with reduced $CaCO_3$ precipitation (Driscoll et al. 1994). The increasing trend in pH in the lake's hypolimnion is consistent with the reported reduction in organic deposition in the lake (Effler 1994b).

More abrupt year-to-year changes are observed for the NYSDEC/DOH data base for the surface waters (Figure 12). This may in part reflect the rather limited sampling frequency used, combined with the substantial seasonal differences that are known to occur (e.g., Figure 5). The temporal distributions that emerge from the D&S program are by far the most "noisy" (abrupt year-to-year differences; Figure 12a and 13a). This variability is unreasonable for such a well-buffered system. What plausible scenario could explain the instability in pH manifested in the D&S data base before and after the closure of the soda ash/chlor-alkali facility (Figures 12 and 13)? This data base should be considered highly suspect as a record of the entire 1968-1991 interval. This should not be construed as an indictment of the entire D&S pH data base. Rather, great care must be exercised in the selecting those portions of the D&S data base that can be reliably used. Perhaps the best basis for selection of the portions of the D&S data base that can be used is consistency with the UFI data. Particularly suspect portions of the D&S pH data base include 1969, 1971, 1974, 1975, 1977-1985, and 1988 (Figures 12 and 13). The D&S data for 1980, 1981, 1984 and 1985 appear to be in gross error. For example, dissolution of $CaCO_3$ deposits would be expected at the

unrealistically low pH values of 1984 and 1985 (Figure 13), yet this is not supported by other chemistry measurements (particularly Ca^{2+}) made in the lake over that period.

The discrepancies between D&S and UFI pH data are revisited in Figures 14 and 15, for the surface and near-bottom waters, respectively. In this comparison the UFI laboratory data has been adjusted to corresponding estimates of field pH, according to the relationship of Figure 2. Even after this adjustment, substantial differences between the D&S and UFI data sets remain for most years. The instability of the D&S data on a yearly basis, and sometimes seasonally, does not support the veracity of these data.

Vertical Distributions

The vertical distributions pH reported by the D&S and UFI programs for two selected years, 1980 and 1991 are compared in Figures 16 and 17, respectively. Profiles are presented for the May-September interval. Dates of monitoring do not always coincide for the two programs; the closest date of monitoring was selected from the UFI data base for comparison to the more infrequent D&S measurements. UFI measurements were collected at 1 m depth intervals; D&S reported observations at 3 m intervals. The UFI profiles presented for 1980 (Figure 16) are adjusted laboratory measurements (according to relationship of Figure 2) to represent field conditions; direct field measurements are presented for 1991 (Figure 17).

Various features of the 1980 D&S profiles make them suspect. First increases with depth in the hypolimnion are inconsistent

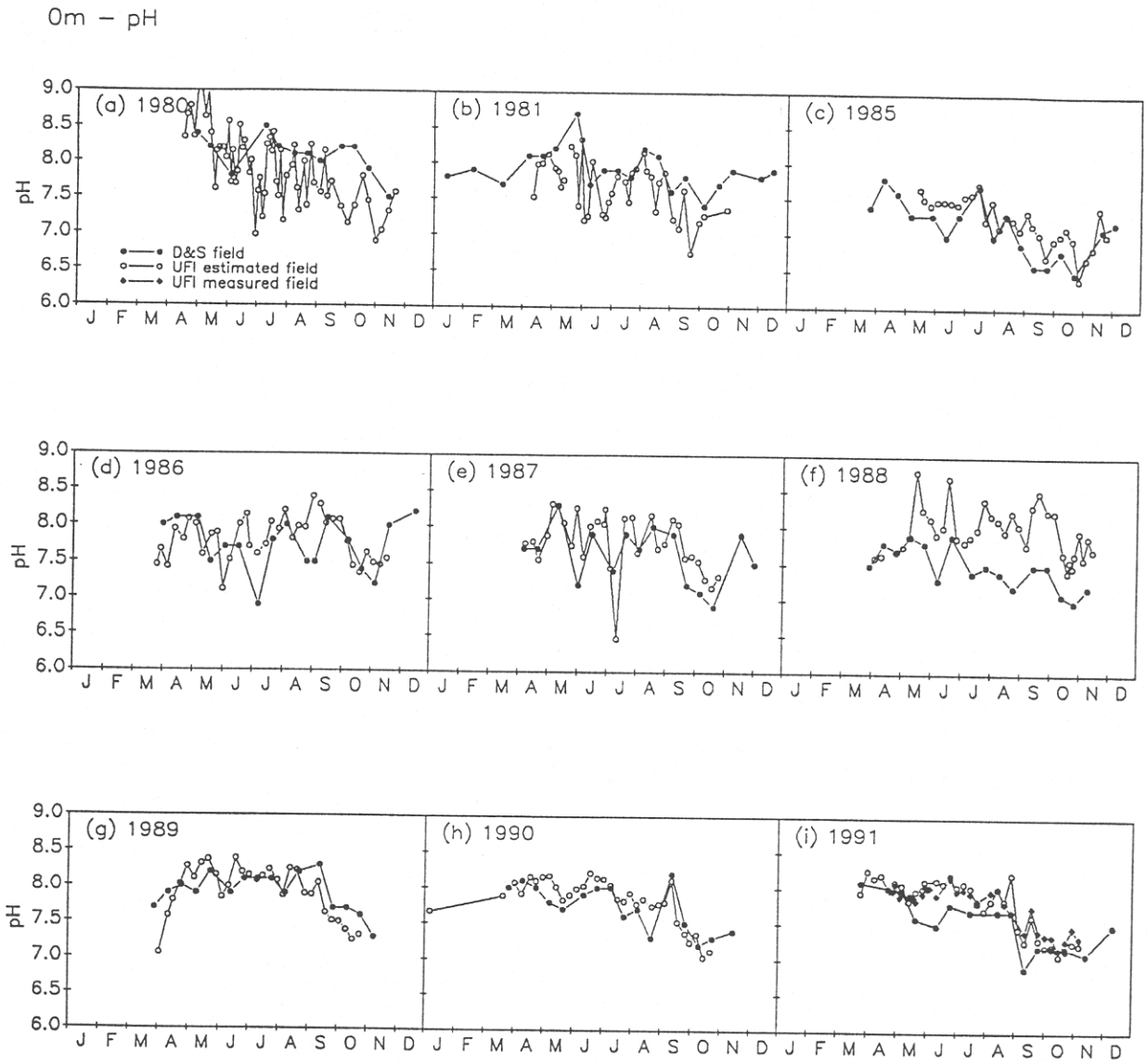


Figure 14: Comparison of temporal distributions of pH in the surface waters of Onondaga Lake for D&S and UFI data basis, with adjustments for UFI laboratory measurements (see Figure 2) : a) 1980, b) 1981, c) 1985, d) 1986, e) 1987, f) 1988, g) 1989, h) 1990, and i) 1991.

18m – pH

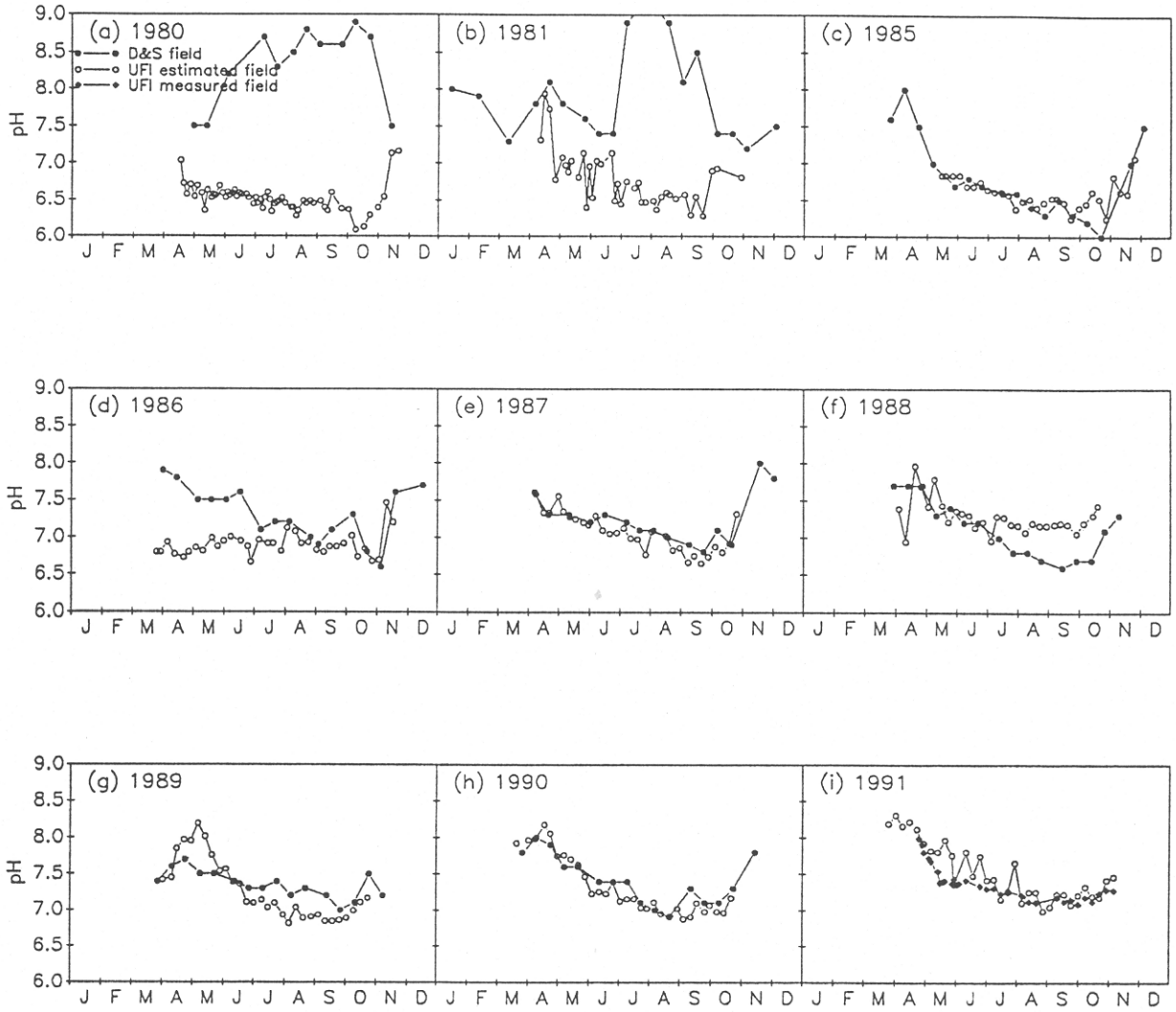


Figure 15: Comparison of temporal distributions of pH in the near bottom (18m) waters of Onondaga Lake for D&S and UFI data basis, with adjustments for UFI laboratory measurements (see Figure 2) : a) 1980, b) 1981, c) 1985, d) 1986, e) 1987, f) 1988, g) 1989, h) 1990, and i) 1991.

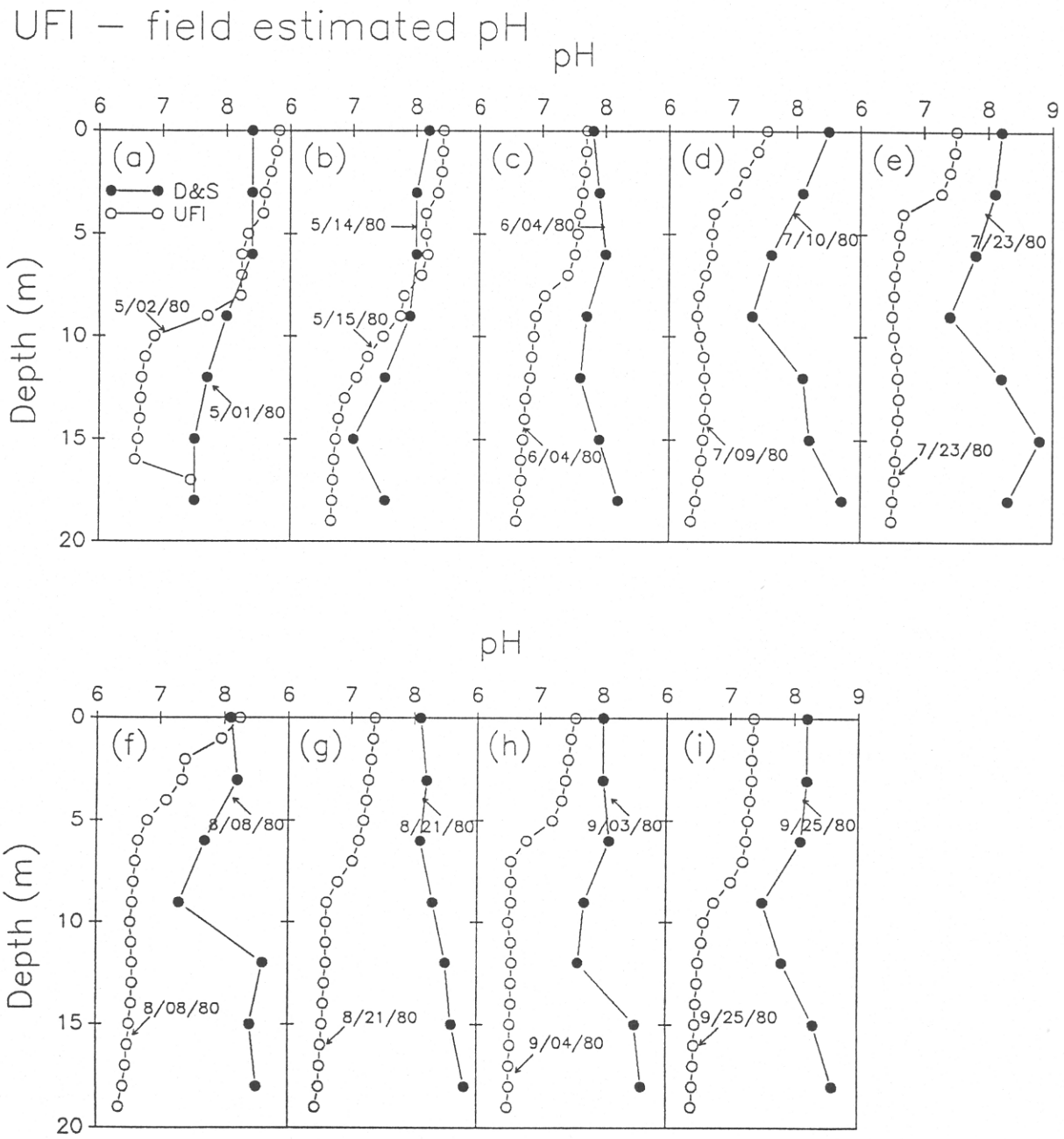


Figure 16: Comparison of pH depth profiles for Onondaga Lake for UFI and D&S data bases, 1980 : a) early May, b) mid-May, c) early June, d) early July, e) late July, f) early August, g) late August, h) early September, and i) late September.

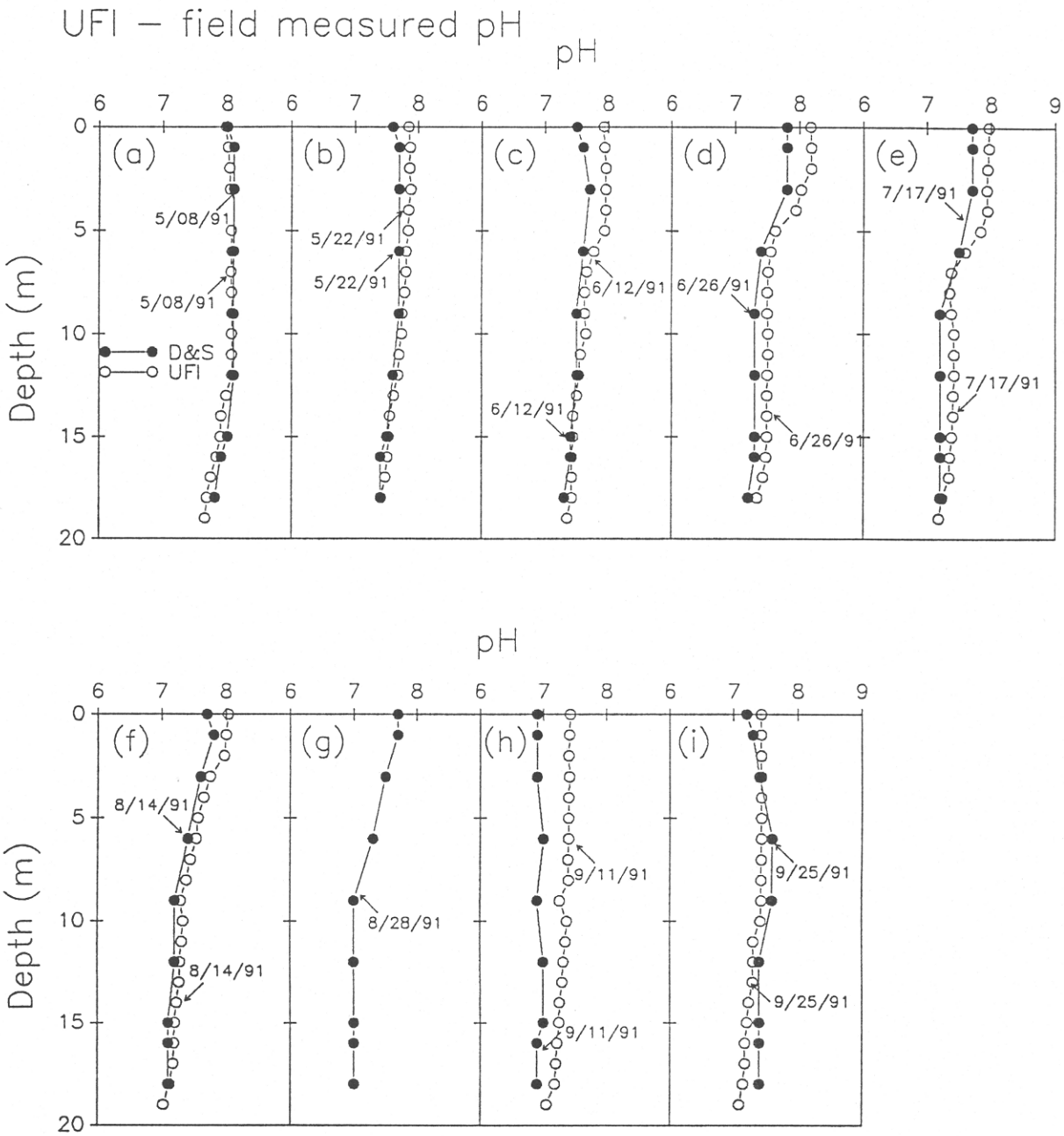


Figure 17: Comparison of pH depth profiles for Onondaga Lake for UFI and D&S data bases, 1991 : a) early May, b) late May, c) mid-June, d) late June, e) mid-July, f) mid-August, g) late August, h) early September, and i) late September.

with the UFI profiles (Figure 16) and profiles reported for other productive lakes during the stratification period (Wetzel 1983). Specifically what mechanism could explain such an increase in pH? A sink for CO_2 would have to operating at the lake bottom. This is inconsistent with the progression of the decomposition of organic matter and coupled accumulation of CO_2 observed during stratification. With the exception of the very bottom of the first profile (possibly explained by plunging Ninemile Creek inflow), the UFI data demonstrate the classic (e.g., Wetzel 1983) transformations in depth and time. Note the D&S data also demonstrates an inexplicable increase in pH in the hypolimnion for much of the monitored period.

Results for the two programs are much more comparable for 1991 (Figure 17). No anomalous increases with depth in lower layers are observed (Figure 17). Differences between the epilimnion and hypolimnion are minimal for the D&S data set. A temporal disparity emerges in late summer and early fall, however. The D&S measurements became distinctly lower in early September (Figure 17h), yet become somewhat higher than the UFI observations by late September. This increase in the D&S values, particularly in the lower layers, is unlikely during this period, as the lake was still stratified, and thus CO_2 was probably still accumulating. The less abrupt temporal change over that same period depicted by the UFI data (Figure 17) is more likely.

The Flawed D&S pH Data Base

Several problems in the D&S pH data base have been identified here. There are inconsistencies with well established

limnological paradigms manifested in a number of years of the D&S pH data base. Particularly problematic is the temporal instability manifested throughout this data base (1968-1991), on both short- and long-term scales. These variations for this well buffered system are inexplicable, as they are uncoupled from the dynamics of recognized forcing conditions. By comparison, the UFI data base (covering a shorter interval) is much more temporally stable and is consistent with well established limnological paradigms. Both short- and long-term trends in the UFI pH data base are consistent with the documented dynamics of forcing conditions for the lake (e.g., Driscoll et al. 1994, Effler and Driscoll 1985, Effler et al. 1990, Brooks and Effler 1990). These trends and related analyses have been independently supported by the peer-reviewed process associated with professional publications.

There is no reason to believe all the D&S pH is incorrect. However, this data base is clearly flawed in so many years that it calls into question the entire data set. How does the data user decide which subset of the D&S pH data is reliable? The D&S pH data base does not appear to be a legitimate alternative to the UFI data base over the period of the UFI program. Earlier (< 1978) D&S data are also highly suspect. Comparative analysis of laboratory and field pH measurements made by these two programs in 1991 continues to support the UFI program.

Hydroqual (PTI's consultant) is presently conducting a "calcite" modeling analysis of Onondaga Lake for the 1985-1990 interval that is utilizing D&S data, including pH. This

selection could result in a fundamentally flawed analysis, that could affect important related conclusions on the $CaCO_3$ problem. Specifically, much of the D&S pH data for 1985 and 1988 is almost certainly incorrect.

Comments on Letter of J.J. Fitzpatrick to Mr. T.J. Larsen (NYSDEC): these augment my earlier comments on this letter submitted on December 6, 1993

Re: data sets used to calibrate $CaCO_3$ deposition model for Onondaga Lake

This letter focuses on the inconsistencies in pH data for the lake. Data for the Allied intake are used in the analysis; the reasons for use of these data instead of routine water column data is never made clear. Central to the presentation/analysis included in the letter is the use of their chemical equilibrium model (RCHEM) as a diagnostic tool to calculate pH values corresponding to $CaCO_3$ equilibrium conditions.

It is important to note that disequilibrium commonly prevails with respect to $CaCO_3$ (calcite) in hardwater lakes (see reviews in Effler and Driscoll 1985, and Effler 1987). Equilibrium calculations for Onondaga Lake (using MINEQL) presented by our team in the peer-reviewed literature (Driscoll et al. 1994, Effler and Driscoll 1985) indicate oversaturated conditions prevailed in the lake over the 1985-1990 interval, at least over the spring-fall interval, and particularly in the upper waters. Under these conditions measured pH values exceed values that would result from calculations that invoke equilibrium. This is important in reviewing their modeling

analyses (e.g., center panels of Figures 1 and 2). Thus I find the use of the description "consistent" on P.2 (**P**3) somewhat confusing, as it's used when model calculations approximately **match** observations. Instead consistency should refer to the condition of calculated pH values being **lower** than observed, as that is the prevailing condition in Onondaga Lake and many other hardwater lakes (perhaps as in Figure 1 of the letter for 1989 and 1990).

I was surprised to see the calculations were performed at a "constant" temperature (25°C), as the seasonality in temperature can be rather easily accommodated in most chemical equilibrium models. The indicated sensitivity analysis with a reduced solubility constant seems to be ill-conceived. Seeking a "match" in observed and calculated pH values in later years (inconsistent with observations, as indicated above) and demonstrating a worsening in the match for the earlier years misses the salient point - there is a fundamental problem in the D&S pH data base with respect to inexplicable temporal instability. Presuming the equilibrium calculations are correct (we have not independently checked these), numerous false low pH observations are included in the D&S data base, particularly in 1985, and in portions of 1986, 1987, and 1988 (their Figure 1). In contrast, UFI has reported relatively stable (modest increasing trend) pH conditions over the same period, and relatively stable and continuously oversaturated conditions with respect to the solubility of calcite ($CaCO_3$; Driscoll et al. 1994). The undersaturated conditions calculated for portions of 1985

(Figures 1 and 2 of letter) are inconsistent with the $CaCO_3$ deposition observed throughout the summer (Effler 1994b).

The issue raised about comparison of field and laboratory measurements of pH was addressed earlier in this document. While the issue is of interest, these systematic differences cannot account for the instability problem demonstrated for the D&S data base. The analysis of their Figure 3 (letter) in fact demonstrates the NYSDEC/DOH data set is unreliable, as a consistent relationship should be observed between these paired measurements (see our Figures 1-4). We believe the analysis presented earlier in this document establishes that the D&S pH base is unreliable, particularly for use over rather extended periods of time, as is the case for the Hydroqual analysis (1985-1990).

Other components of Hydroqual's chemical equilibrium/calcium carbonate model include measurements of TIC, alkalinity, Ca, and temperature. UFI has no systematic data base for TIC or Ca, however, we support use of the D&S Ca data for that purpose (e.g., Driscoll et al. 1994). Contrary to the indications of the letter, UFI has a complete alkalinity data base for the 1985-1990 interval, as documented by Driscoll et al. (1994). These distributions are compared for the surface waters of the lake for the 1987-1991 in Figure 18; they are quite similar. We support the use of the UFI data because of the more complete temporal and vertical coverage and the detailed analysis these data have already been subjected to (Driscoll et al. 1994). We have not analyzed the D&S temperature data base for the 1985-1990

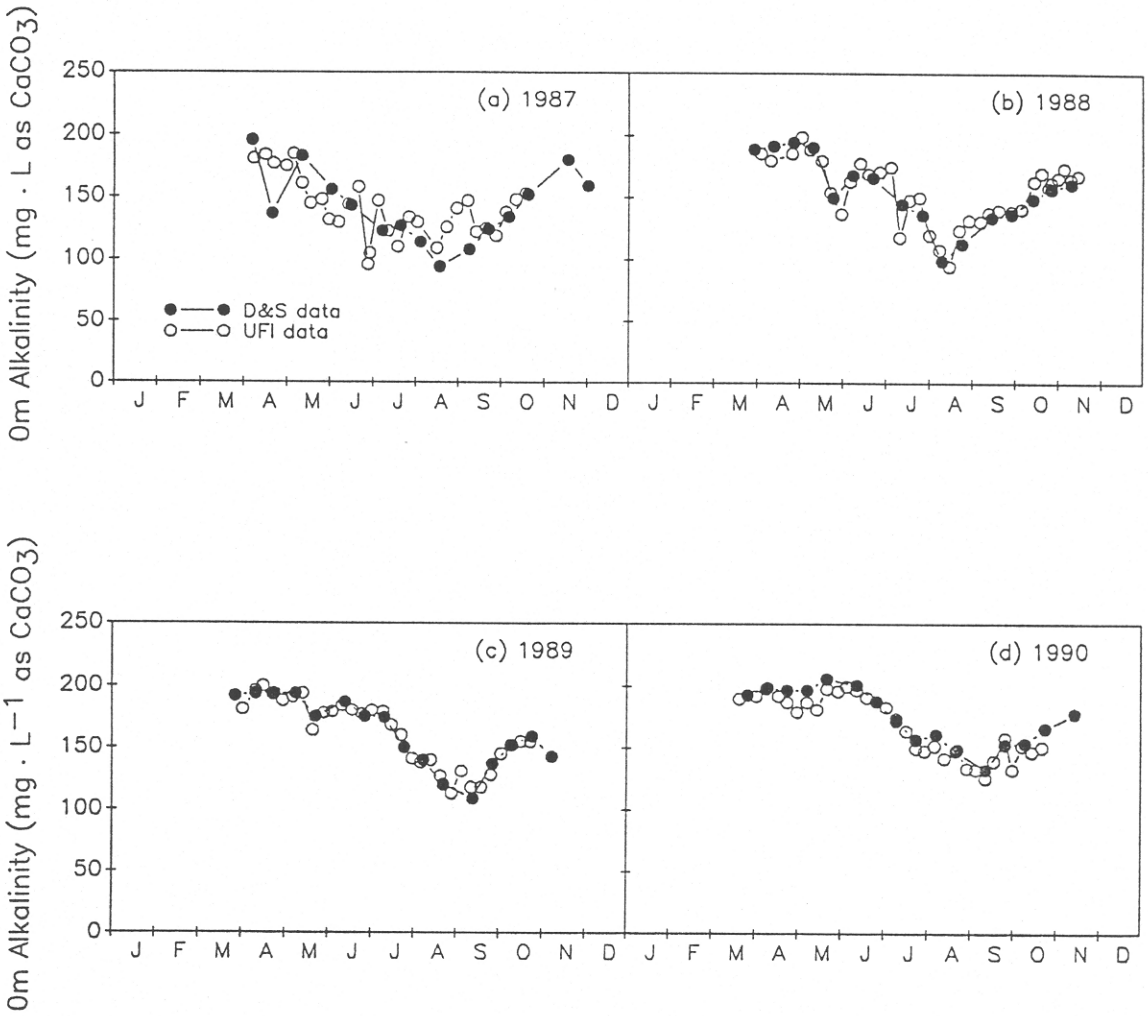


Figure 18: Comparison of temporal distributions of alkalinity in the surface waters of Onondaga Lake from D&S and UFI data bases : a) 1987, b) 1988, c) 1989, and d) 1990.

interval; recall they have had problems historically with this basic parameter (Table 1).

References

Brooks, C.M., and Effler, S.W. 1990. The distribution of nitrogen species in polluted Onondaga Lake, N.Y., U.S.A. Water, Air, Soil Pollut. **52:** 247-262.

Doerr, S.M., Effler, S.W., Whitehead, K.A., Auer, M.T., Perkins, M.G., and Heidtke, T.M. 1994. Chloride model for polluted Onondaga Lake. Water Res. (in press).

Driscoll, C.T., Effler, S.W., and Doerr, S.M. 1994. Changes in inorganic carbon chemistry and deposition of $CaCO_3$ in Onondaga Lake. Environ. Sci. Technol. (in press).

Effler, S.W. 1987. The importance of whiting as a component of raw water turbidity. J. Amer. Water Works Assoc. **79:** 80-82.

Effler, S.W. 1992. Unsolicited report, submitted to R. Ott, concerning the Onondaga County data base for total inorganic phosphorus for Onondaga Creek. February 26, 1992.

Effler, S.W. (editor) 1994a. The State of Onondaga Lake. Report submitted to the Onondaga Lake Management Conference, Syracuse, NY.

Effler, S.W. 1994b. Deposition. Section 8.1. of Chapter 8, Sediments. In: S.W. Effler (editor), The State of Onondaga Lake. Report submitted to the Onondaga Lake Management Conference, Syracuse, NY.

Effler, S.W., Brooks, C.M., Auer, M.T., and Doerr, S.M. 1990. Free ammonia and toxicity criteria in a polluted urban lake. Res. J. Water Pollut. Contr. Fed. **62:** 771-779.

Effler, S.W., and Driscoll, C.T. 1985. Calcium chemistry and deposition in ionically enriched Onondaga Lake, New York. Environ. Sci. Technol. **19:** 716-720.

Effler, S.W., Driscoll, C.T., Doerr, S.M., Auer, M.T., and Wagner, B.A. 1994. Phosphorus. Section 5.5. of Chapter 5, Chemistry. In: S.W. Effler (editor), The State of Onondaga Lake. Report submitted to the Onondaga Lake Management Conference, Syracuse, NY.

Effler, S.W., and Whitehead, K.A. 1994. Tributaries and Discharges, Chapter 3. In: S.W. Effler (editor), The State of Onondaga Lake. Report submitted to the Onondaga Lake Management Conference, Syracuse, NY.

Walker, W.W. 1991. Compilation and Review of Onondaga Lake Water Quality Data. Report submitted to Onondaga County Department of Drainage and Sanitation. Syracuse, NY.

UPSTATE
FRESHWATER
INSTITUTE

July 25, 1995

Dr. James Fitzpatrick
HydroQual, Inc.
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Mahwah, N.J. 07430

Dear Dr. Fitzpatrick:

Review of HydroQual's Modeling Analysis for Onondaga Lake, Deep-Water Discharge of METRO: No. 1, Problems with Supporting Data from Onondaga County's Monitoring Program

I recently obtained a copy of HydoQual's modeling analysis, and support documentation, for the County's proposal to discharge the METRO effluent to the lower layers of Onondaga Lake. My review of the documentation is on-going. I have been involved with the study of Onondaga Lake since the mid-1970's, under the auspices of UFI since 1980. This experience and familiarity with the system (e.g., the various research and monitoring programs) places me in a potentially unique position to review features of the HydroQual analysis. From time-to-time I will be writing to you to share my thoughts concerning various features of the analysis; e.g., supporting data base for the lake, adequacy of representation of lake processes, model framework, modeling protocol, etc. This first letter will focus on limitations in the data base adopted by HydroQual in the modeling effort, in particular the data quality problems that pervade Onondaga County's lake and tributary monitoring program.

Background

I had for some time been concerned about errors and short-comings in Onondaga County's monitoring data (from an on-going program conducted by the Department of Drainage and Sanitation), and in particular the potential for problems if these data were used as a basis to evaluate the status of the lake, identify trends since the start of the program in 1970, or to support testing of mechanistic models. A preliminary analysis in 1988 by UFI found substantial problems in the Drainage and Sanitation data base, e.g., errors in dissolved oxygen, pH, and phosphorus measurements in a number of years. That same year we

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approached Onondaga County with our concerns. In an effort to resolve such problems with data bases for the lake, Onondaga County supported a study, that was conducted under the direction of Dr. William W. Walker. UFI cooperated in this study by providing a portion of our lake data; supporting components of this effort are described by Walker (1991; see p.3). The goal was to compile all the Onondaga Lake data and subject the data to quality analyses. The results of Walker's analysis are summarized in a report submitted to Onondaga County in 1991, "Compilation and Review of Onondaga Lake Water Quality Data".

Dependence of the HydroQual Analysis on Drainage and Sanitation Data

HydroQual's modeling analyses rely quite heavily on data from Drainage and Sanitation monitoring program. This is a fundamental flaw in these analyses. HydroQual justifies the use of these data by indicating they all come from the "unified database" of Walker (1991). This is misleading in at least two respects. First only a subset (selected parameters) of the compiled lake data was subjected to any quality analysis. For example, no quality analysis was conducted on tributary data. Thus what is the credibility of external loads, so critical to the credibility of dynamic mechanistic model predictions. Further, no quality analysis was conducted on lake calcium (Ca) and total inorganic carbon (TIC) data, key parameters for HydroQual's calcium carbonate ($CaCO_3$) analysis conducted on behalf of Allied. Secondly, the rigor of Walker's (1991) data quality analysis is inconsistent with the applications HydroQual has made of this data set. The scrutiny received by the parameters addressed by Walker (1991) was from the perspective of the adequacy of the various data sets to support depiction of long-term trends, not for support of sophisticated mechanistic models such as those used by HydroQual. Walker (1991) used statistical and graphical methods and limnological reasoning in evaluating data. I believe it is fair to say that there had to be compelling reasons for Walker (1991) to "flag" measurements as likely in errors. Much larger portions of the County data base (particularly the earlier years) than flagged by Walker (1991) should be considered questionable, and therefore inappropriate to support model testing.

Selected Features of the Problems of the Drainage and Sanitation Data Base

Adoption of Onondaga County data, particularly for the earlier years of the program, simply because it has been compiled and not "flagged" by Walker (1991) as likely in error, should not be considered appropriate. Consider the pervasiveness and character of the data problems already established for a number of parameters in the Onondaga County data base. Selected features of the data problems are reviewed here.

1. <u>temperature</u> - perhaps the most basic field measurement. Drainage and Sanitation measured false high temperatures in the lakes hypolimnion for at least three consecutive years (1971-1981; Walker, 1991), despite the fact that the measurements clearly deviated from earlier observations.

2. <u>dissolved</u> <u>oxygen</u> (DO) - one of the most fundamental and important of the water quality parameters for Onondaga Lake. **Drainage and Sanitation collected highly erroneous DO data from the lake for six (6) consecutive years (1976-1981; Walker 1991).** Measured DO values in the epilimnion were routinely false low, unrealistically indicating substantial undersaturation with respect to equilibrium concentrations. Measured DO values in the hypolimnion were false high, routinely indicating the presence of oxygen despite the presence of reduced species such as hydrogen sulfide (H_2S; a clear inconsistency). Walker (1991) reported that Drainage and Sanitation's DO measurements were false high in portions of the hypolimnion in a number of other years, again when H_2S was observed to be present. Clearly oversight of the program in that era was inadequate.

   Epilimnetic DO values reported by Onondaga County in the early 1970's were lower than reported in recent years. Measurements from other groups are not available for the early 1970's. Thus, according to the protocol of the quality analysis conducted by Walker (1991), there was no basis to question these data. However, based on the clearly manifested pervasive problems Drainage and Sanitation had with this parameter in subsequent years, there is no compelling justification to accept the early 1970's DO data as representative. The more appropriate assumption is that those data are suspect.

   Reliance on the County's early 1970s DO data as a measure of model performance (Figure 2-8 of HydroQual (2) 1995; particularly for epilimnion) is inappropriate, and not defensible in light of the documented problems Drainage and Sanitation had in measuring this parameter. Further, HydroQual should make clear the origins of the data adopted in each year, for each parameter presented in their reports, as there are distinct differences in data quality.

3. <u>pH</u> - particularly critical parameter in HydroQual's analysis of the $CaCO_3$ precipitation issue of Onondaga Lake (conducted on behalf of Allied).

   HydroQual's acceptance of Walker's (1991) quality analysis for this parameter for their application in the $CaCO_3$ model analysis is particularly inappropriate. The pH value is critical in <u>estimating</u> $CaCO_3$ concentrations

and simulating the kinetics of $CaCO_3$ formation according to HydroQual's $CaCO_3$ model. The pH data should be subjected to a substantially more rigorous quality analysis for such an application.

In fact Walker (1991) identified suspect Drainage and Sanitation pH data. Drainage and Sanitation field pH data were higher than UFI laboratory pH measurements in the 1979-1981 interval, but became lower in the later portion of the record. Walker (1991) considered the County's pH data from the hypolimnion suspect between 1979 and 1981. On a number of occasions Drainage and Sanitation reported higher pH values in the hypolimnion than the epilimnion. Such extraordinary measurements have never been explained by Drainage and Sanitation; these are probably errors.

HydroQual chose not to utilize field pH data reported by UFI because of potential degasing effects on the measurements. This <u>systematic</u> short-coming was readily remediated by UFI. Unfortunately, there appear to be pervasive problems in the Drainage and Sanitation pH data that are not easily remedied. For example, consider the interannual variation in pH conditions in the surface and near-bottom waters of the lake in the Drainage and Sanitation data base compared to UFI observations (Figure 1 and 2, respectively). The highly variable conditions indicated by the Drainage and Sanitation data are unreasonable, particularly for such a well-buffered system. What plausible scenarios, limnological/water chemistry phenomena, could explain the instability manifested in the Drainage and Sanitation data? The very low bottom water pH values of 1984 and 1985 should have resulted in dissolution of sedimentary $CaCO_3$, yet there are no indications this occurred. Particularly suspect portions of the Drainage and Sanitation data base include 1969, 1971, 1974, 1975, 1977-1985, and 1988. The County data for 1980, 1981, 1984 and 1985 appear to be in gross error. The fact that Drainage and Sanitation data are the only available in some years (i.e., <u>B</u>est <u>A</u>vailable <u>D</u>ata) does not justify the incorporation of these questionable data in HydroQual's modeling analysis.

Why should the Drainage and Sanitation data base for pH be considered reliable, in light of the major problems the same program had with DO measurements, (arguably field DO measurements are considered more routine/less difficult than pH measurements)? Indeed, the inconsistent instabilities manifested in the Drainage and Sanitation data (particularly in the absence of sound limnological explanations) argue against use of these data.

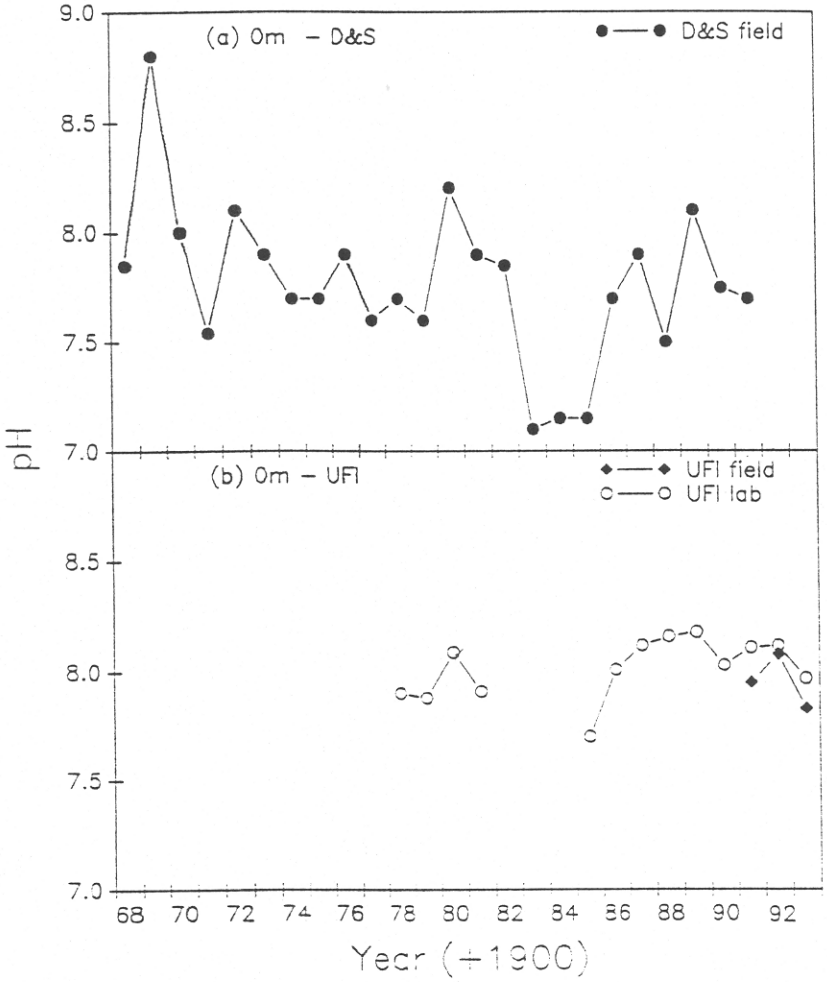

Figure 1. Long-term trends in pH in the surface waters of Onondaga Lake, according to the median observation: a) D&S, and b) UFI.

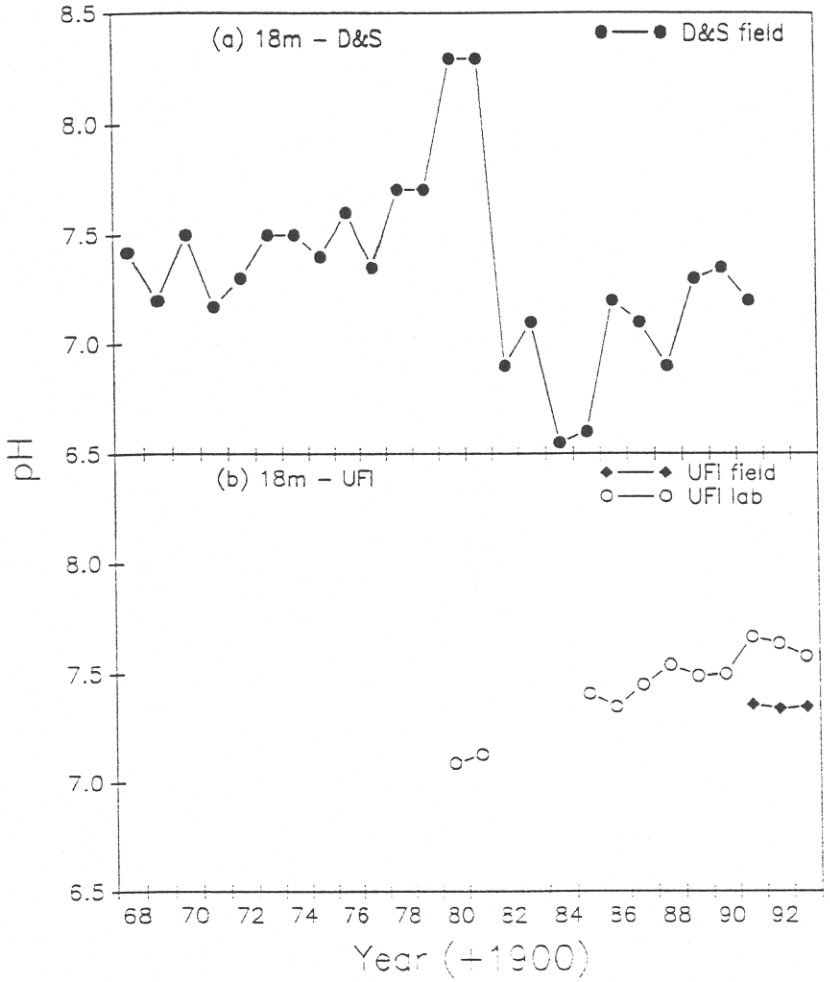

Figure 2. Long-term trends in pH in the near bottom (18m) waters of Onondaga Lake, according to the median observation: a) D&S, and b) UFI.

chlorophyll a from phaeopigments. Lorenzen's (1967) method has been found to be fundamentally flawed for application to Onondaga Lake, apparently associated with the unreliable partitioning of chlorophyll a and phaeophytin (Auer et al. 1994). The method produces false high estimates of phaeopigments and false low values for chlorophyll a. The sum of the concentrations of chlorophyll a and phaeophytin provided by the Lorenzen (1967) method provides a better estimate of the concentration of phytoplankton pigments.

8. Calcium (Ca) - an important constituent influencing $CaCO_3$ formation in Onondaga Lake. Lake concentrations reported by Drainage and Sanitation for 1970 and 1971 and adopted by HydroQual in their $CaCO_3$ analysis are almost certainly false high. Recall Walker (1991) provided no quality review of lake Ca data in his analysis. Several factors support the position that the Ca data for 1970 and 1971 are unreliable. More detailed review would probably identify other questionable years of Ca data from the Drainage and Sanitation program.

Charge balance calculations based on annual average concentrations reported by Onondaga County (1971, 1972) depict substantial surpluses of cations in both 1970 and 1971, consistent with false high concentrations of a major cation such as Ca^{2+}.

Further, the distinctly higher Ca concentrations in 1970 and 1971 relative to Cl (salinity) concentrations is inconsistent with the known uniformity of the ratios of Cl, Ca, and sodium (Na) maintained in Allied's soda ash waste. Only changes in the manufacturing process or product recovery (e.g., $CaCl_2$) could explain such a disparity. This would need to be fully documented by the facility's production records, that should be available to HydroQual as a consultant to Allied.

There are well established problems with this suite (Ca, Na, and Cl) of measurements in Drainage and Sanitation's monitoring program. For example, 41% of the paired observations of major ions in Ninemile Creek for the 1981-1989 interval were rejected in an analysis of the interrelationships in the concentrations of the various ions, for failure to meet the QA/QC criterion of charge balance within 10% (Effler and Whitehead 1994). Of the three major ions, Cl^-, Na^+, and Ca^{2+}, Cl^- should be considered the most reliable. Simple titration procedures were available at that time for Cl^-, and the Cl^- data hold up reasonably well in supporting a long-term Cl^- model for the lake (Doerr et al. 1994). The concentrations of Na^+ and Ca^{2+} were determined by atomic absorption spectrometry, a more challenging procedure for commercial laboratories at that time.

4. H_2S - Walker (1991) rejected values reported by Onondaga County over the 1972-1974 interval, and indicated other values were suspicious.

5. chloride (Cl) - unreliable lake concentrations were reported by the County for 1979 and 1982 (Doerr et al. 1994).

6. Phosphorus (P) - a key material in considering the water quality problems related to cultural eutrophication. Drainage and Sanitation failed to measure the most fundamental phosphorus specie related to cultural eutrophication, total phosphorus (TP), for about 20 years. Instead they measured total inorganic phosphorus (TIP) that systematically omits organic forms of P (e.g., phytoplankton). Thus TIP is a poor estimator of TP for the upper waters of the lake.

   Drainage and Sanitation has had, and continues to have detection limit problems with the measurement of soluble reactive P (SRP). Drainage and Sanitation measurements have routinely been false high during periods of SRP depletion, which leads to mis-interpretations concerning P availability to the lake's phytoplankton.

   The accuracy of P loads to Onondaga Lake based on Drainage and Sanitation data is severely compromised by short-comings in that program. Tributary loads, particularly before 1990 are inaccurate (e.g., false high). For example, in an unsolicited report to R. Ott of Drainage and Sanitation in 1992 I indicated the loads from Onondaga Creek were false high, apparently associated with inappropriate laboratory protocol. Loading estimates for TP for the tributaries (< 1989) and METRO (< 1980) from the Drainage and Sanitation data base are based on TIP measurements and empirical expressions developed by Effler and Whitehead (1994) between TP and TIP concentrations. We emphasized the limitations in these expressions for support of loading estimates, which HydroQual (1995(2); p. 1-35) largely repeated. Loads generated for before 1980 (when TP daily monitoring of the METRO effluent commenced) should be considered highly uncertain and inappropriate to support model testing. Estimates of TP loading from METRO, the major source, were based on infrequent (e.g., biweekly) measurements of TIP. There are no compelling reasons to accept the empirical expressions for METRO, based on 1989/1990 paired measurements, as accurate for the period before 1980, particularly in light of the changes in treatment over the same interval.

7. Chlorophyll a - determined by Drainage and Sanitation according to the spectrophotometric procedures of Lorenzen (1967). The method claims to separate

9. Total Inorganic Carbon (TIC) - is an important constituent in HydroQual's analysis of $CaCO_3$, conducted on behalf of Allied. Drainage and Sanitation's TIC data base for both the lake and the inputs should be considered suspect until it is subjected to detailed quality assurance analysis, for a number of reasons.

   a. First, this parameter received no quality analysis by Walker (1991). Thus the analytical method(s), responsible laboratories, quality assurance procedures are not documented.

   b. Secondly, TIC was not a priority parameter throughout Drainage and Sanitation's program. For example, substantially less lake measurements were made compared to the principal parameters since the early 1980s. No TIC lake measurements were included in Walker's (1991) compilation for 1968-1971, 1975, 1981, and 1982.

   c. Uncoupled distributions of loading and lake concentrations for alkalinity and TIC are manifested in Drainage and Sanitation's data base. Such distributions would need explanation to support the use of these data in detailed mechanistic models.

Implications of Data Limitations on Modeling Period

The model(s) should be rigorously tested for a period much shorter than the duration of the Drainage and Sanitation monitoring program. The chosen shorter period should be from recent years for which there is greater reliability in the lake and loading data. This would allow clear differentiation in short-comings of model performance from the effects of unreliable data. Extension to a longer period should be considered only after model credibility is clearly established for the shorter period, and after data credibility is established for the longer period.

What is the point of extending the period of model testing to 21 years before model credibility has been clearly established for a shorter period? A subtle effect of the extension is to make the short-comings in model performance within individual years less apparent. Twenty-one years of data and simulations is at first glance impressive, simply for the long duration, but it obscures the details of model performance. The modeled interval, together with the long interval of data averaging (one month, or one year), gives a false impression of model success, that is brought into question only after careful review of the plots. Model performance in fact appears to be poor for several parameters within a number of individual years. Unfortunately, it is presently difficult, if not impossible, to differentiate the influences of model performance from that of unreliable

monitoring data.

Potential Implications of Limitations/Errors in the Drainage and Sanitation Data Base for Assessing the Responsibility of Allied for Excessive Calcium Carbonate ($CaCO_3$) Deposition in Onondaga Lake

Onondaga County has long voiced its concern that Allied pay its fair share for the clean-up of Onondaga Lake. As you are aware, a potential area of responsibility for Allied identified by the NYSDEC is the excessive precipitation and deposition of $CaCO_3$ in the lake that has been attributed to Allied's waste discharge (particularly of Ca^{2+}). As indicated by HydroQual, "Much of the work described in this report (to Onondaga County, for the deep-water discharge analysis) was originally performed as part of a remedial and feasibility study (RI/FS)" prepared for Allied. However, HydroQual has failed to indicate to the County that their RI/FS analysis minimizes the responsibility of the Allied waste for fostering $CaCO_3$ precipitation and deposition in the lake, and that the analysis relies critically on questionable Drainage and Sanitation data (pH, TIC and Ca, etc.). The veracity of these and other data needs to be clearly established before model credibility can be established and related management decisions made.

Please feel free to contact me with any questions you may have concerning my comments (315-466-1309).

Respectfully,

Steven W. Effler, Ph.D.
Director of Research

cc: N.G. Kaul, NYSDEC
D. Palm, NYSDEC
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References

Auer, M.T., S.W. Effler, M.L. Storey, S. Connors, and P. Sze. 1994. Phytoplankton, Biology (Chapter 6). In S.W. Effler (ed.) The State of Onondaga Lake. Submitted to the Onondaga Lake Management Conference.

Doerr, S.M., S.W. Effler, K.A. Whitehead, M.T. Auer, M.G. Perkins and T.M. Heidtke. 1994. Chloride model for polluted Onondaga Lake. Water Res. **28:** 849-861.

Effler, S.W. and K.A. Whitehead. 1994. Tributaries and Discharges (Chapter 3). In S.W.Effler (ed.) The State of Onondaga Lake. Submitted to the Onondaga Lake Management Conference, Syracuse, NY.

HydroQual(2). 1995. Application of the Onondaga Lake Eutrophication Model in the Evaluation of METRO Treatment Alternatives and Wasteload Allocation. Submitted to Onondaga County, Syracuse, NY.

Walker, W.W. 1991. Compilation and Review of Onondaga Lake Water Quality Data. Submitted to Onondaga County, Syracuse, NY.

UPSTATE FRESHWATER INSTITUTE

February 27, 1996

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Communication No. 5 to HydroQual Concerning Onondaga Lake: Comments on HydroQual Responses to UFI Statements (Communication No. 1) Concerning Problems with Onondaga County DO, pH, and TIC and Calcium Data

This letter is the fifth concerning HydroQual's modeling analysis of Onondaga Lake. In this communicaiton we address unsettled issues related to the limitations of Onondaga County's (D&S) dissolved oxygen (DO), pH, total inorganic carbon (TIC), and calcium (Ca) data to support model testing. For the record, we reiterate (see letter of October 2, 1995) UFI's reasons for participating in this dialogue: "1) our past work on Onondaga Lake, 2) the implications if the models are used as the basis of management action, 3) the ongoing controversy about scientific analysis and studies on the Lake, 4) the conflicting interests of Onondaga County and Allied-Signal in these matters, and 5) our commitment to the rehabilitation of Onondaga Lake based on unimpeachable scientific analysis".

Thank you for taking the time to consider our comments concerning these data. We continue to have great concern regarding the quality of the D&S data adopted by HydroQual for the water quality/calcite model(s). However, we believe that a reasonably "quality-assured" data set could be developed to support the steady-state model for some segment of the 1970-1990 period presently being addressed by HydroQual. Further, it is our position that this effort would be best served by conducting modest investigations of error in the measurement of pH, and the partitioning of alkalinity, Ca, and TIC between the dissolved and particulate phases in the lake (e.g., 1996). The later effort would support the rather elegant theoretical framework developed by HydroQual for the calcite model.

Reasonably detailed comments concerning D&S data quality problems, and related HydroQual responses, for DO, pH, Ca and TIC appear in the attachment. Some of the more salient features follow.

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1. DO - We continue to take issue with HydroQual's use of certain portions of the County data base, though these problems are secondary compared to the more fundamental D&S data problems identified for eutrophication modeling in communication No. 4.

2 pH

a. The potential effect of diurnal variations in influencing the D&S and UFI pH data bases is minor. UFI monitoring data have been shown to be generally representative of daily average conditions.

b Limited "internal consistency" analyses depict unrealistic interannual variations in carbon dioxide concentrations if D&S pH data are adopted.

c Onondaga Lake is a relatively well buffered system. In the absence of this buffering even greater diurnal and seasonal variation would be observed.

d. It remains that the interannual variations in pH reported by D&S are unrealistic and inconsistent with other limnological data over the same period.

e The fact that the D&S pH data were collected in the field is inadequate justification to adopt these data for model testing.

3 Calcium and TIC

a The adoption of D&S calcium and TIC data, in the absence of quality assurance analyses, is inexplicable and inconsistent with HydroQual's stated concern with quality analysis of pH methods.

b. Charge balance calculations are a fundamental quality assurance procedure that should be conducted before adopting any calcium data.

c Limited "internal consistency" analyses suggest that D&S TIC data for the upper waters of the lake are false low in at least two years, supporting the position that D&S's TIC data base should be considered suspect until it is subjected to detailed quality assurance analysis.

I am sure that we all agree that it is to everyone's advantage to make absolutely sure that all scientific work on Onondaga Lake stands up to rigorous scrutiny. We have undertaken this correspondence in that spirit.

Please feel free to contact us with any questions you may have concerning the contents of this communication (315-466-1309).

Sincerely,

S.W. Effler, Ph.D.
Director of Research

and

C.T. Driscoll, Ph.D.
Professor,
Department of Civil and
Environmental Engineering
Syracuse University

cc: Mr. Walter Shepard, Allied Signal, Inc.
Mr. Gary Bigham, PTI Environmental Services
Mr. Timothy Larson, NYSDEC
Mr. Ronald Sloan, NYSDEC
Mr. N.G. Kaul, NYSDEC
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Mr. David Coburn, Onondaga County
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Mr. Joseph Mastriano, D&S, Onondaga County
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Dr. Elizabeth Moran, Stearns & Wheler
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Dr. William W. Walker
Dr. Emmet M. Owens, Syracuse University
Mr. Donald Hughes

ATTACHMENT - DETAILED COMMENTS

Dissolved Oxygen

extent of the limitations of dissolved oxygen (DO) data collected by D&S is not acknowledged in HydroQual's response to the UFI letter of July 25, 1995 Walker (1991 reported negative bias for the epilimnion and positive bias for the hypolimnion for the 1976-1981 period, as indicated in UFI's letter of July 25 1995. HydroQual indicates its agreement with the assessment for the hypolimnion data ("We agree with Dr. Walker's assessment of the hypolimnetic data . " p.4 HydroQual response of December 27 1995, to UFI letter of July 25, 1995), but does not comment on the epilimnetic data HydroQual indicates Walker (1991 flagged the 1978-1981 DO data as suspect, but Walker (1991 actually rejected all D&S lake data over the 1976-1981 interval HydroQual only excluded the D&S DO data from 1977 through 1981 in their calibration analysis. We see no justification for using the 1976 data, in light of Walker's (1991) recommendation. As noted by HydroQual (response of December 27, 1995) and Walker (1991), other less severe short-comings have been identified for other years. Moreover we see no justification for HydroQual's deletion of the high DO observation ~ 20 $mg \cdot L^{-1}$ of August 1970 as UFI has measured such high concentrations during severe phytoplankton blooms.

HydroQual's argument that lower epilimnetic concentrations before 1976 (and before the upgrade of METRO, secondary and P removal) are consistent with the higher METRO BOD loading during that period is not defensible. HydroQual's position is supported

only if the oxygen demand associated with higher BOD discharge is accurately quantified within the context of the other source and sink processes in the lake. The lake DO model of Gelda and Auer (1996) indicates that the BOD sink for DO in the epilimnion is insignificant for the period after 1988. We don't discount that the oxgyen sinks were larger before the METRO upgrade, but that can hardly be considered a compelling argument for the reported lower epilimnetic DO concentrations. We expect this effect would be difficult to resolve from field data, particularly in light of the magnitude and frequency of variations in other DO source/sink (e.g., phytoplankton) processes relative to the sampling frequency of the D&S program.

HydroQual has taken exception with what they call our methodology for dismissing the data collected by D&S for a specific water quality parameter by identifying a problem in the data for a few specific years and then suggesting that the entire 21 year record is therefore questionable or invalid". (p.1 HydroQual's response of December 27, 1995 to UFI's letter of July 25, 1995 We strongly believe that as a user of D&S's data HydroQual must accept some level of responsibility for the veracity of this information set. HydroQual is using D&S data to evaluate issues that have not been a focus of attention by D&S personnel (e.g., Ca, TIC, pH). Many measurements in the data set have not been rigorously evaluated for applications that HydroQual are conducting. It is essential that (to the extent possible the problems of assessing the behavior and performance of complex models not be compounded by issues of data quality.

six consecutive years (1976-1981 the D&S's DO data are not usable, more minor problems persisted in most of the other years. The magnitude of these deficiencies legitimately raises questions about the acceptability of earlier DO data to support model testing. Under such circumstances, compelling data/arguments are required to (not reject) adopt the D&S 1970s DO data as a basis evaluating the performance of the eutrophication model. The absence of contrary DO data before 1976, the alluded to (but not well quantified) BOD loading/in-lake DO relationship, and the use of the Winkler titration method (collection of representative samples can be difficult where disequilibrium is common or prevails), are far from compelling arguments to accept these DO data as a basis to evaluate model performance

pH

HydroQual indicates in its December 27, 1995 response (p.6), to the UFI letter of July 25, 1995, that "pH data, together with calcium, alkalinity and TIC data, were used to back-estimate solid phase calcium carbonate for calibration purposes. If there serious errors in the pH data, then the back-estimated calcite concentrations would also be error" How could such an error be detected in the absence of watercolumn measurements of solid phase $CaCO_3$ measurements? We presume the answer is calibration to downward flux rates of $CaCO_3$.

We believe that pH is one of the two most important measurements in the assessment of the impact of ionic waste discharged by AlliedSignal to Onondaga Lake (the direct measurement of $CaCO_3$ deposition being the other; Womble et al

1996). As a result, it is critical that HydroQual: 1 fully understand the uncertainty and limitations of pH measurements and, 2 quantify the effects of uncertainty in pH on model calculations We believe that model calculations of the distribution of alkalinity and inorganic carbon between dissolved and particulate phases, and subsequent predictions of calcite deposition are very sensitive to pH HydroQual should quantify model uncertainty to pH and assess this uncertainty within the context of limitations in pH measurements for the lake

HydroQual's justification for not rejecting the D&S pH data for the epilimnion for the interval 1979-1981 is weak Hypolimnetic pH data were identified as suspect for that interval by Walker (1991). Thus selected observations from profiles collected by D&S during this interval were considered acceptable by HydroQual, but observations from the hypolimnion made on the same profiles with the same pH meter were rejected by HydroQual HydroQual indicates the UFI data were not considered because of the lack of QA/QC information, but Walker (1991) reviewed sampling, analytical and quality assurance protocols including UFI program) in his analysis If HydroQual was unsatisfied with those descriptions, the original investigators could have been approached to obtain this information

We noted what continues to be a systematic discrepancy in the adjusted pH values by UFI and measurements by D&S for profiles plotted by HydroQual (see Figures 11 and 12 - in letter from HydroQual dated December 27, 1995). This discrepancy should be evaluated

a. Effect of Diurnal Variations

A change of focus is noted in the discussion of pH in the letters of AlliedSignal (November 15, 1995) and HydroQual (December 27, 1995), related to the potential effects of natural diurnal variations on pH records for the lake. This issue is a major point of emphasis in the AlliedSignal letter (~ 2 pages), but essentially not addressed in the HydroQual letter. thrust of the AlliedSignal letter on this issue appears to be that this process may explain systematic differences (e.g., extended periods) in two different (e.g., D&S and UFI) data sets for the lake. Results from other lakes are referred to "Times series studies of other lakes show that the daily cycle of photosynthesis and respiration can change the pH by 2 units on a diurnal basis" p.5, AlliedSignal letter of November 15, 1995), but no citation(s) are presented Indeed, diurnal variations in pH are widely reported in the literature (e.g., Crumpton and Isenhart 1988, Talling 1974, Verdium 1960). "The magnitude of the diurnal variations in pH are expected to be greatest on days of peak photosynthetic rate and minimum surface turbulence e.g., clear calm day during a phytoplankton bloom). (p.5-59, "State of Lake"

UFI has published the approximate time of pH sampling in it's monitoring of Onondaga Lake (e.g., Brooks and Effler 1990 State of Lake" ; about ~ 1000 hr (± 1 hr AlliedSignal (letter of November 15, 1995) gives no indication of this consideration or the sampling time adopted by D&S. We are surprised of omission, since it is critical to an evaluation of this issue,

and since HydroQual is a consultant to both Onondaga County and Allied Signal. You should find that D&S monitoring is conducted at approximately the same time of day as the sampling by UFI. A systematic discrepancy, that might be expected if samples were collected by the two programs at very different times of day, is not a factor in the comparison of the D&S and UFI data. Thus the observed extraordinary interannual variations in the D&S pH data base for the upper waters for the 1968-1991 period (Figures 1 cannot be attributed to "diurnal effects" because an approximately uniform time of day for lake monitoring has been used.

UFI has indicated that the time of day of its monitoring would cause only slight bias in reflecting daily average pH "State of the Lake", p.5-59; from daily average H^+ concentration). Recently collected (unpublished) pH data, based on hourly measurements made over several weeks, support this observation (Figure 2). Measurements were made in situ with a Hydrolab SONDE (operated and calibrated according to the manufacturer), for the April to late June and early October to early December intervals of 1994. The amplitudes of the pH variations at a depth of 1 m were substantially less than the 2 pH unit upper bound described in the AlliedSignal letter of November 14, 1995 and were attenuated at a depth of 4 m (Figure 3). Significant diurnal variations are limited to the upper mixed layer. Thus diurnal effects/time of day of monitoring cannot explain the large interannual variations in pH indicated by the County data base for lower layers of the lake (Figure 4)

b. Internal Consistency, pH/Alkalinity/TIC (DIC) Data

existing measurements of pH, alkalinity and TIC should have been evaluated for internal consistency, using mass law and mass balance equations (e.g., Stumm and Morgan 1996). For example, if pH and alkalinity are known, concentrations of CO_2 and DIC can be calculated (e.g., Driscoll et al. 1994). To illustrate this approach we present here an analysis of internal consistency for the upper waters of the lake for three selected years, 1980, 1988, and 1989. No claim is made that these cases are representative of the entire D&S/UFI data bases. Rather, we believe these analyses provide valuable insight, and must be conducted on all data sets to ensure that an internally consistent, quality assured data set is available to evaluate the performance of the calcite model. Our analysis assumes that alkalinity is in a strictly dissolved form. This assumption is probably imperfect, however, the potential contribution from $CaCO_3$ particles is in general small For example, PIC was < 5% of DIC in the upper waters of the lake in 1989 (unpublished data UFI).

Seasonal patterns of alkalinity, pH, inorganic carbon (TIC DIC and CO_2 (% saturation) for the D&S and UFI data bases are compared in Figures 5, 6, 7, and 8. The trends in alkalinity for the two data sets match well (Figure 5 suggesting these data are of generally high quality. The agreement in pH values differs substantially between the three years (Figure 6; also see Figure 1). In 1980 pH values measured by D&S tended to be somewhat higher than the UFI laboratory measurements, and distinctly

higher than the UFI data after adjusting laboratory measurements field conditions (Figure 6a) The D&S pH values were markedly lower than UFI's laboratory measurements in 1988, and remained much lower than the adjusted values for that year (Figure 6b). In contrast to the other two years, the D&S and UFI pH trends agreed reasonably well for 1989 (Figure 6c

Clear inconsistencies in the D&S TIC data emerge from this analysis for 1980 (Figure 7a) and 1988 (Figure 7b) In particular, D&S TIC data were substantially less than DIC concentrations calculated from either the UFI or D&S data on a number of occasions in these two years (also see Figure 9a and b). These differences cannot be explained by the potential contribution of the modest quantities of $CaCO_3$ to the alkalinity measurements. This suggest that the D&S TIC data are false low at least these occasions. Perhaps degasing of CO_2 contributed, or perhaps there are inaccuracies/limitations in the unspecified sampling procedures, holding time, and analytical procedures. In contrast, the internal consistency indicated for 1989 data sets indicates these data may be acceptable to support model testing. Differences in the calculated DIC values the two data sets are an outcome of the differences in pH (Figure 6).

Calculated concentrations of CO_2 (from pH and alkalinity) in upper waters of Onondaga Lake depict conditions of oversaturation with respect to atmospheric values for almost the entire monitoring period of all three years, based on both the D&S and UFI (adjusted pH values used) data bases (Figure 8). The

average percent saturation values calculated for the May-September interval for each of the three years from the data bases are presented in Table 1. Wide variations emerge

TABLE 1: Average percent CO_2 saturation for the May-September interval, UFI and D&S data bases, upper waters of Onondaga Lake

Year	% CO_2 saturation D&S	UFI+
1980	196	921
1988	1618	443
1989	552	493

+ adjusted field pH values, according to $pH_{lab} = 0.718 \cdot pH_{field} + 2.349$

between these years (Figure 8, Table 1), according to the data base, driven largely by differences in pH conditions. differences between 1980 and 1988, based on D&S data (a factor of about 8), are probably unrealistic. What phenomena could explain changes of this magnitude? Similarly, what phenomena could explain the reduction by a factor of more than 3 from 1988 to 1989, indicated by the D&S data (Table 1)? These interannual variations are inconsistent with indicators of CO_2 metabolism for the lake (e.g., primary production; "State of Onondaga Lake", measurements of organic and inorganic carbon deposition in sediment traps; Womble 1995 (M.S. Thesis) Note that interannual variations indicated for the UFI data (Table 1 are smaller, and that the D&S and UFI tend to converge for 1989.

We restricted our preliminary analysis of internal consistency in measurements of alkalinity, pH and TIC to upper waters of Onondaga Lake. The analysis should be extended

to the lower waters. Unfortunately, the lower water additional problems Elevated concentrations of sulfide in the lower waters may oxidize in sample bottles following collection This phenomenon will result in the production of strong acids resulting in an error in measured values of alkalinity This problem may eventually preclude use of the hypolimnetic data in the analysis of changes in calcite deposition. In any event analysis should be conducted in the lower waters to investigate if the data set is suitable for use in this assessment.

HydroQual made an effort to emphasize the similarity of the D&S and UFI data sets in their Figures 17 and 18. The scaling of the plots and the numerous years included tend to mask the differences. As demonstrated above, substantial differences prevailed in pH and inorganic carbon concentrations in some of the years. Further, HydroQual has presented the calculated DIC results of Driscoll et al. (1994) as TIC. If HydroQual calculated DIC/TIC from D&S pH and alkalinities, the above inconsistencies would have been recognized

HydroQual has implied that the differences reported for pH in the lake surface waters by D&S and Driscoll et al. 1994 over the 1980-1990 interval (HydroQual's Figure 17 are attributable to the difference between field and laboratory methods This is a misrepresentation, as the differences are greater than can be explained by these methods. Further, the strong interannual variations in pH (HydroQual's Figure 17 of December 27, response; also see Figures 1 and 2 of UFI letter of July 25 1995), and the long-term trend in pH, based on D&S data remain

unexplained

c. pH Buffering

has indicated that, Onondaga Lake is a relatively well-buffered system (e.g., Driscoll et al. 1994, "State of Onondaga Lake" 1994). We see nothing in HydroQual's presentation that argues against that position. In fact HydroQual seems to agree, e.g., "The high alkalinity of the water in Onondaga Lake (2.2 to 3.9 meq/L) indicates that it is more strongly buffered than many lakes" (p.8, HydroQual letter of December 27, 1995 to UFI). Further, UFI does not disagree that the extremely high productivity conditions in the lake can (and do) result in substantial seasonal (e.g., Effler et al 1990, Effler and Driscoll 1985) and diurnal (Figures 2 and 3 variations in pH Additionally, the detailed temporal structure of pH can vary year-to-year associated with interannual variations in the timing of phytoplankton blooms (e.g., "State of Lake" 1994 However "average" (or median) pH values tend to remain relatively uniform (e.g., compared to the unrealistic interannual variations indicated in the pH data of D&S (Figure 1) year-to-year in this relatively well buffered system. It remains that the interannual variations in pH reported by D&S (Figure 1 are unrealistic and inconsistent with the relatively well-buffered character of this lake. Further, the structure indicated in the D&S data (Figure 1 is inconsistent with indicators of primary production over the same period "State of Lake" 1994)

d. Calcite Equilibrium Conditions

AlliedSignal's comments concerning the inconsistency of D&S

pH data with calcite equilibrium conditions (p.13 of November 1995 letter) fail to address the real issue. UFI and co-workers have found the upper waters of the lake to be oversaturated with respect to the solubility of calcite throughout the spring to fall interval of all monitored years before and after closure of the AlliedSignal (e.g., Driscoll et al. 1994, Effler and Driscoll 1985, "State of Lake" 1994). The results of equilibrium condition calculations with D&S data differ greatly Undersaturated conditions are indicated for at least 1983, 1984 1995, and 1986 (see Driscoll et al. 1994 for description of calculations), and for rather extended periods for the first 3 of these years. As indicated by Doerr and Effler (1994), these undersaturated conditions are inconsistent with the deposition of $CaCO_3$ documented throughout the spring to fall interval of "State of Lake" 1994, Womble et al. 1996). The pH/undersaturated calcite equilibrium conditions associated with the D&S data base become even more incongruent when considered within the context of deposition results (Womble et al. 1996 equilibrium conditions that prevail in other years (e.g., before and after the 1983-1986 interval). Similar (e.g., oversaturated) calcite equilibrium conditions are calculated for UFI and data sets for the upper waters for 1980 and 1981 because values were similar. The average rates of downward flux of $CaCO_3$ in the lake were very similar in 1980, 1981, and 1985 (Womble et al. 1996). The undersaturated conditions, driven by uncertain D&S pH values, remain highly inconsistent for 1985. low pH values in the other 3 years are likely in error, based on

considerations of calcite equilibrium conditions.

Calcium and TIC

HydroQual's acceptance of the D&S calcium and TIC data related responses (letter of December 27, 1995), appears inconsistent with the position established elsewhere in their response concerning pH, and also expressed in the AlliedSignal letter of November 14, 1995. Both HydroQual and AlliedSignal expressed great concern about the omission of descriptions of sampling and analytical protocols for pH. These procedures were not repeated in the analysis of Doerr and Effler (1994), as they appeared in Walker's (1991) analysis. The unfortunate omission in Walker (1991 was the UFI protocol for calibration of the HYDROLAB for field measurements (according to the manufacturer). Yet HydroQual has not expressed similar concern for the lack of quality analysis of the calcium and TIC data, though HydroQual considers these parameters to be primary (p.6, HydroQual letter of December 27 Can HydroQual/AlliedSignal provide QA/QC information for the D&S measurements of calcium and TIC e.g., method, instrumentation, identity of laboratory, sample handling, performance characteristics.

Other inconsistencies appear, or are implied, in the HydroQual response. HydroQual has expressed great concern over implications of degasing of CO_2 for pH measurements, yet no discussion has been provided on the influence of this same phenomenon on TIC measurements. Frankly, we're somewhat concerned with HydroQual's lack of understanding of this critical analysis; e.g., on p.15, paragraph 4, lines 4 and 5, HydroQual

indicates the D&S TIC measurements were made in the field "The D&S pH and TIC data are as measured in the field, " The D&S TIC analyses were laboratory measurements. Total inorganic carbon is in general a laboratory measurement. The inconsistencies in the D&S data base for DIC/TIC identified in the examples evaluated earlier in the pH section establish the need for a careful QA/QC analysis of the entire D&S TIC data base. These example analyses of data consistency support UFI's earlier statement related to this parameter, "Drainage and Sanitation's TIC data base for both the lake and the inputs should be considered suspect until it is subjected to detailed quality assurance analysis, (item No. 9, UFI letter of July 25, 1995 to HydroQual). Contrary to HydroQual's statement (p.15 paragraph 3, last sentence), the D&S data should be accepted only as an outcome of a rigorous evaluation of the internal consistency of pH, alkalinity and TIC data. Based on the inconsistencies identified earlier, that draw into question the D&S TIC data, HydroQual's position on the TIC data ("It seems reasonable to conclude, in the absence of any opposing data, TIC data for earlier years are reasonable p.16, HydroQual letter to UFI of December 27, 1995) is not supported

The near match of calcium concentrations presented in Driscoll et al. (1994) and by HydroQual (top panel, Figure 17 HydroQual response of December 27, 1995) for the 1980-1990 period is not a basis to accept earlier D&S data, particularly when change balance was violated in certain of the earlier years.

Years for which change balance cannot be demonstrated should not be accepted, unless there is compelling evidence that it is not associated with calcium measurements Ion ratios may also valuable for a quality assurance analysis (e.g., Effler Whitehead 1994)

HydroQual did not respond to issues raised by UFI concerning the D&S Ca data base, based on charge balance calculations. Such calculations are routinely used in QA analyses of major ion data. There is an established history of problems with the D&S major ion data with respect to charge balance (e.g., Effler Whitehead 1994) Has HydroQual conducted such analyses on lake and tributary data sets? These are an essential component in the development of an acceptable data set for model testing.

References

Brooks, C.M., and Effler, S.W. 1990. The distribution of nitrogen species in polluted Onondaga Lake, N.Y., U.S.A. Water Air Soil Pollut. **52:** 247-262.

Crumpton, W.G., and Isenhart, T.M. 1988. Diurnal patterns of ammonia and unionized ammonia in streams receiving secondary treatment effluent. Bull. Environ. Contam. Toxicol. **40:** 539-544.

Doerr, S.M., and Effler, S.W. 1994. A comparative analysis of pH data for Onondaga Lake. Report submitted to NYSDEC, Albany, NY.

Driscoll, C.T., Effler, S.W., and Doerr, S.M. 1994. Changes in inorganic carbon chemistry and deposition of Onondaga Lake, New York. Environ. Sci. Technol. **28:** 1211-1218.

Effler, S.W., Brooks, C.M., Auer, M.T., and Doerr, S.M. 1990. Free ammonia in a polluted hypereutrophic, urban lake. Res. J. Water Pollut. Contr. Fed. **62L** 771-779.

Effler, S.W., and Driscoll, C.T. 1985. Calcium chemistry and deposition in ionically polluted Onondaga Lake, NY. Environ. Sci. Technol. **19:** 716-720.

Effler, S.W., and Whitehead, K.A. 1994. Tributaries and discharges (Chapter 3). State of Onondaga Lake, S.W. Effler (ed.), submitted to the Onondaga Lake Management Conference, Syracuse, NY.

Gelda, R.K., and Auer, M.T. 1996. Development and testing of a dissolved oxygen model for a hypereutrophic lake. Lake Reservoir Manage. (in press)

Stumm, W., and Morgan, J.J. 1996. Aquatic Chemistry (3rd Ed.) John Wiley & Sons, New York.

Talling, J.F. 1974. Measurements on non-isolated communities: In standing waters. In R.A. Vollenweider (ed.), A Manual on Methods for Measuring Primary Production in Aquatic Environments, IBP Handbook No. 12, Blackwell Scientific, London.

Verduin, J. 1960. Phytoplankton communities in Western Lake Erie and the CO_2 and O_2 changes associated with them. Limnol. Oceanogr. **5:** 372-380.

Walker, W.W. 1991. Compilation and review of Onondaga Lake water quality data. Report submitted to Onondaga County, Syracuse, NY.

Figure Captions

Figure 2. Evaluation of the relationship between the daily average pH and the pH at 0930 hr within the upper waters of Onondaga Lake.

Figure 3. Percent occurrence of the amplitude of pH variation within individual days in the upper waters of Onondaga Lake: a) depth of 1 m, for 72 days, and b) depth of 4 m, for 58 days.

Figure 4. Long-term trends in pH in the near bottom (18m) waters of Onondaga Lake, according to the median observation: a) D&S, and b) UFI.

Figure 5. Comparison of temporal distributions of UFI and Onondaga County (D&S) alkalinity data for upper waters of Onondaga Lake: a) 1980, b) 1988, and c) 1989.

Figure 6. Comparison of temporal distributions of UFI and Onondaga County (D&S) pH data for upper waters of Onondaga Lake: a) 1980, b) 1988, and c) 1989. UFI adjust data based on analysis of Doerr and Effler (1994).

Figure 7. Comparison of the temporal distributions of UFI and Onondaga County estimates of DIC and County measurements of TIC for upper waters of Onondaga Lake: a) 1980, b) 1988, and c) 1989.

Figure 8. Comparison of the temporal distributions of percent saturation for CO_2, based UFI and Onondaga County programs, for the upper waters of Onondaga Lake: a) 1980, b) 1988, and c) 1989.

Figure 9. Distributions of the ratio TIC/DIC for D&S data from the surface waters of Onondaga Lake: a) 1980, b) 1988, c) 1989. DIC is calculated from paired pH and alkalinity data.

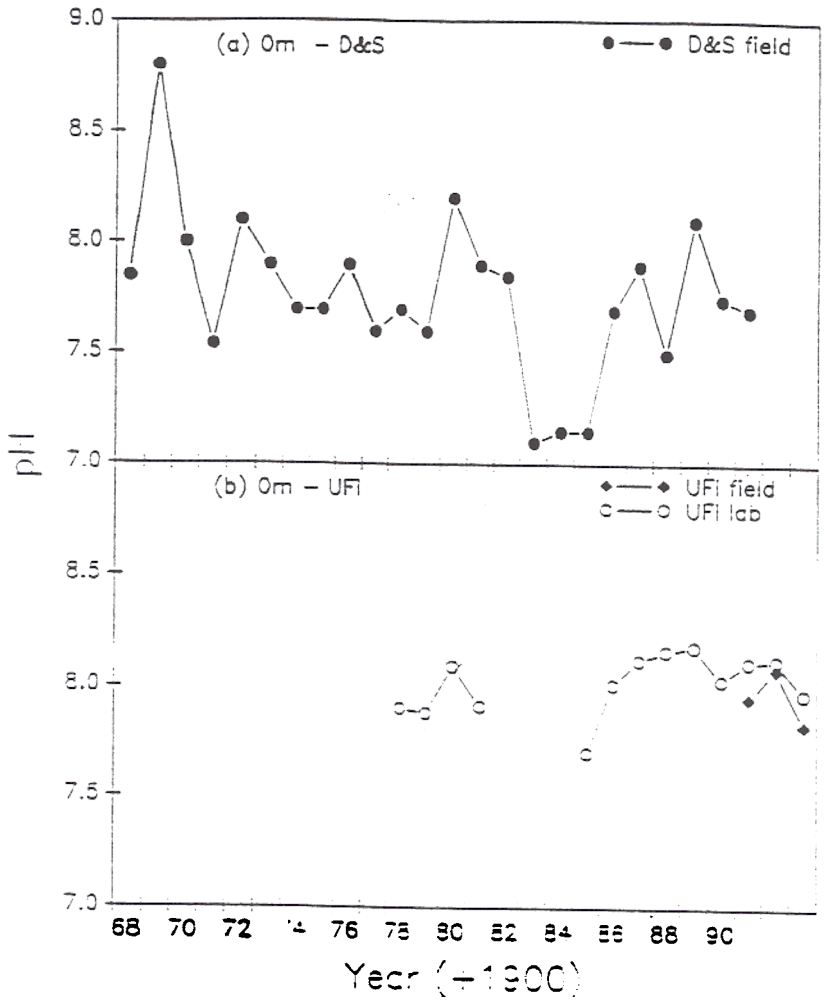
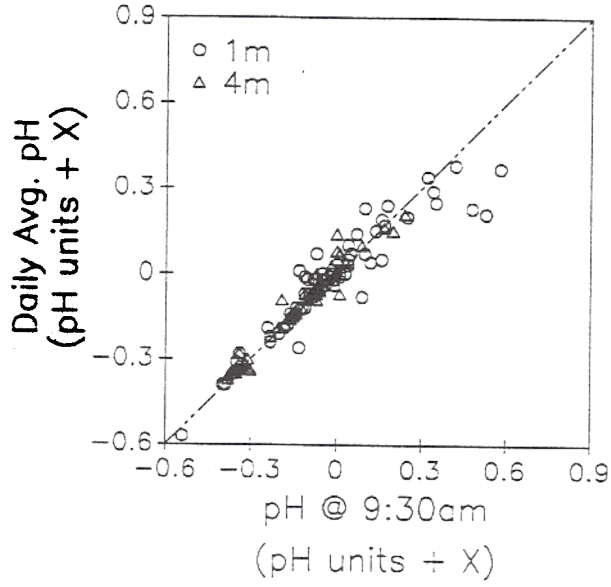


Figure 1. Long-term trends in pH in the surface waters of Onondaga Lake, according to the median observation: a) D&S, and b) UFI.



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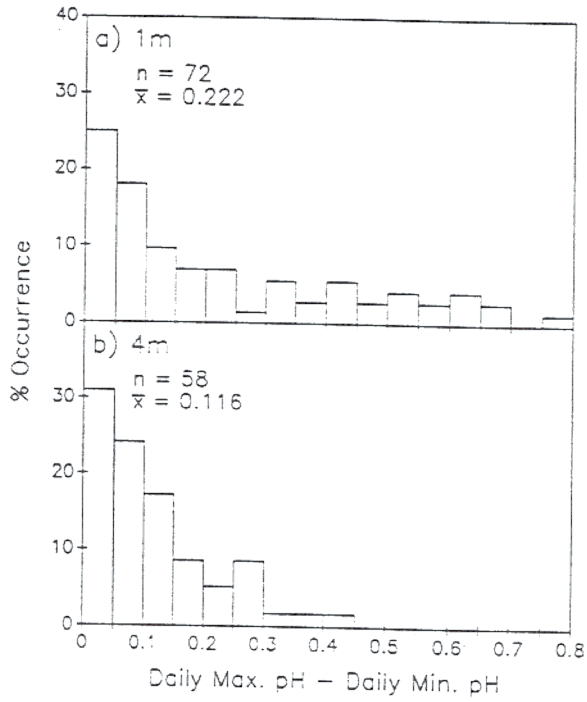

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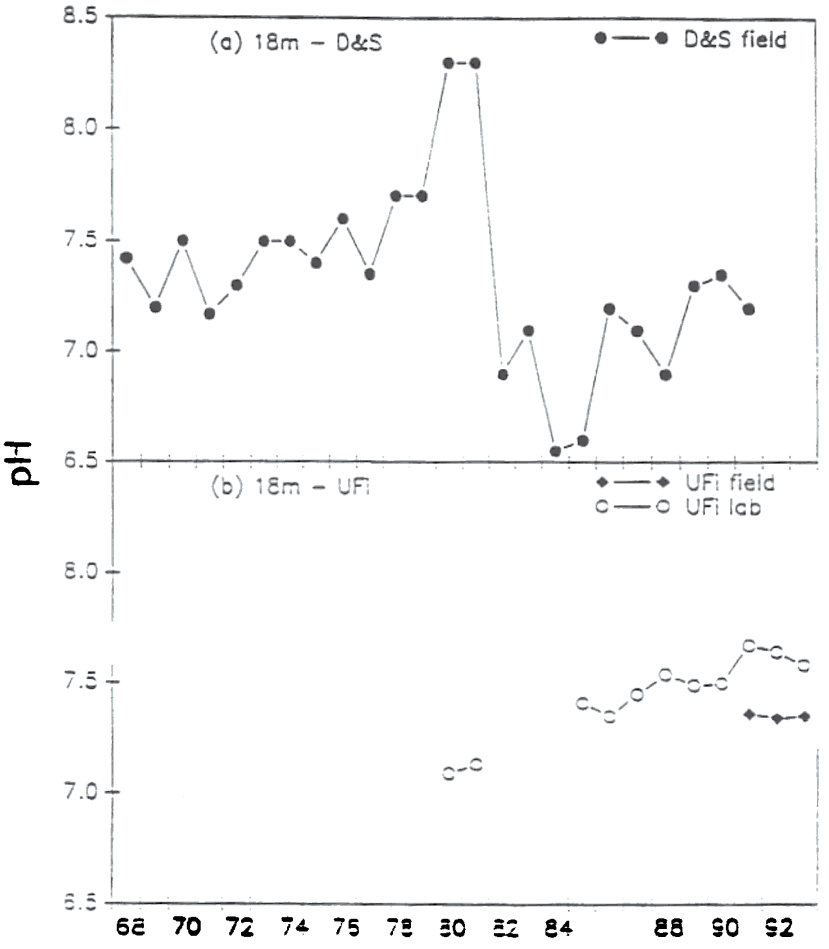

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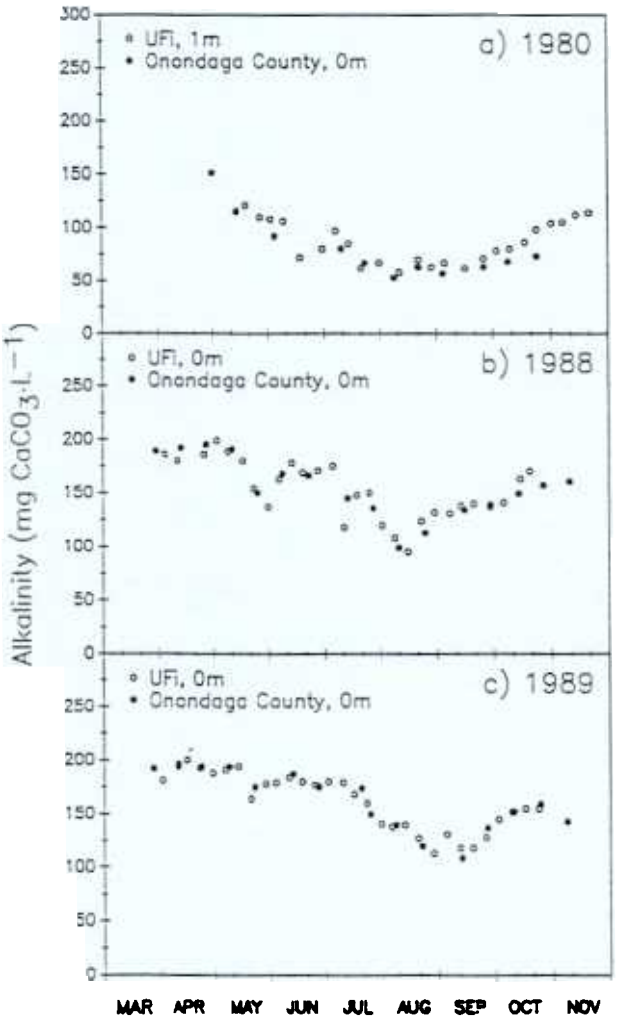

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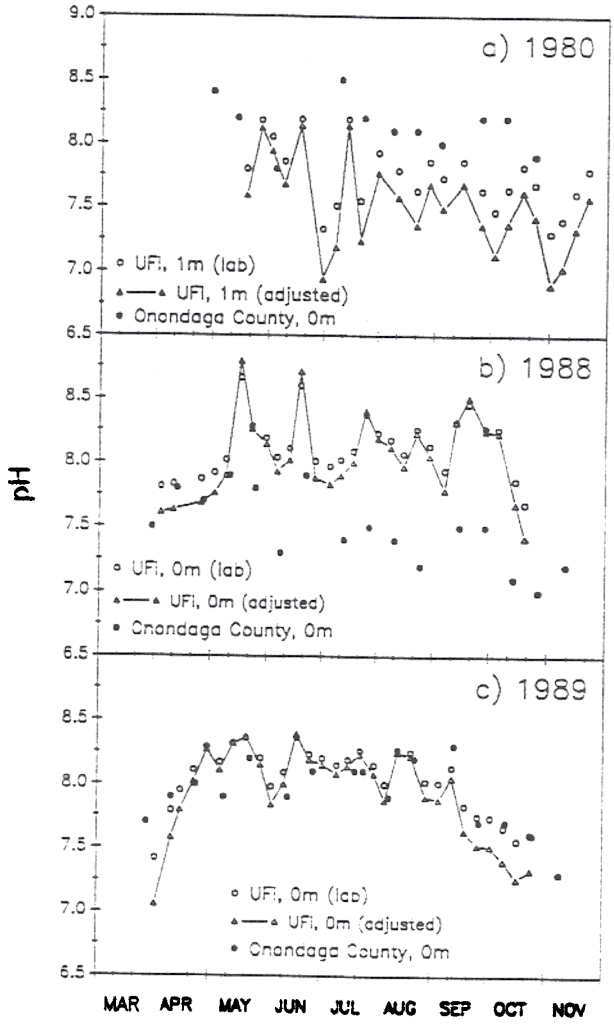

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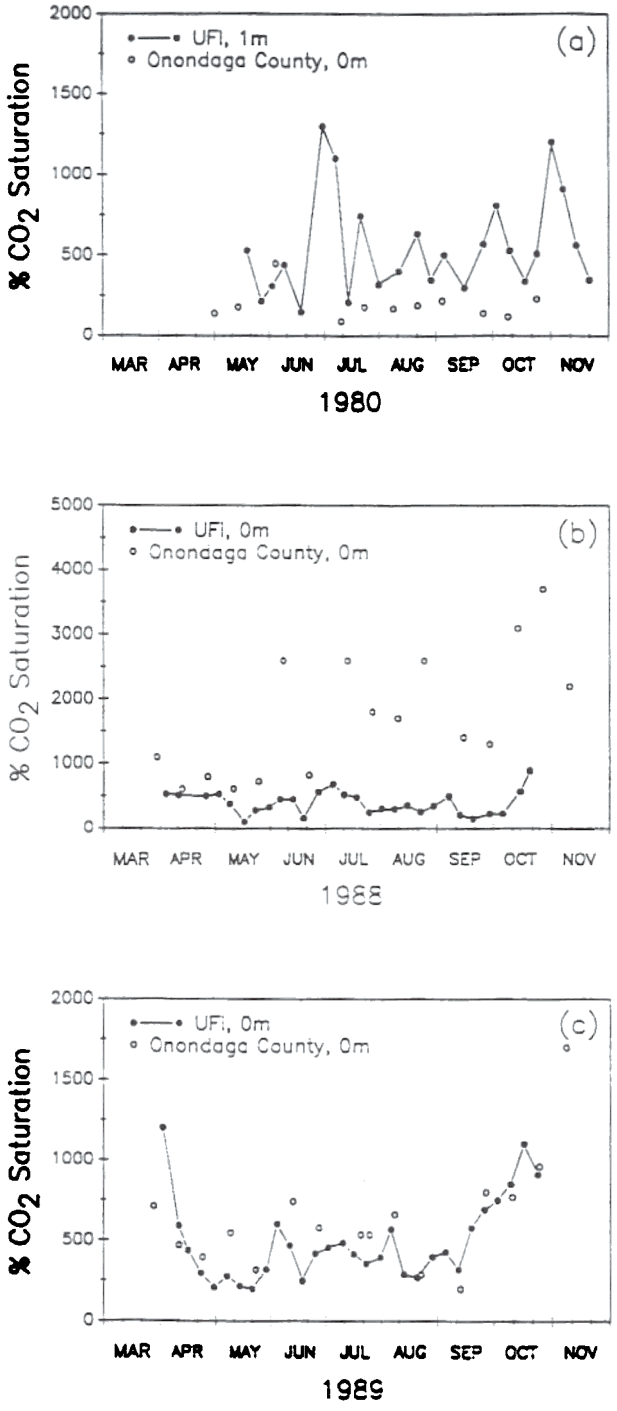

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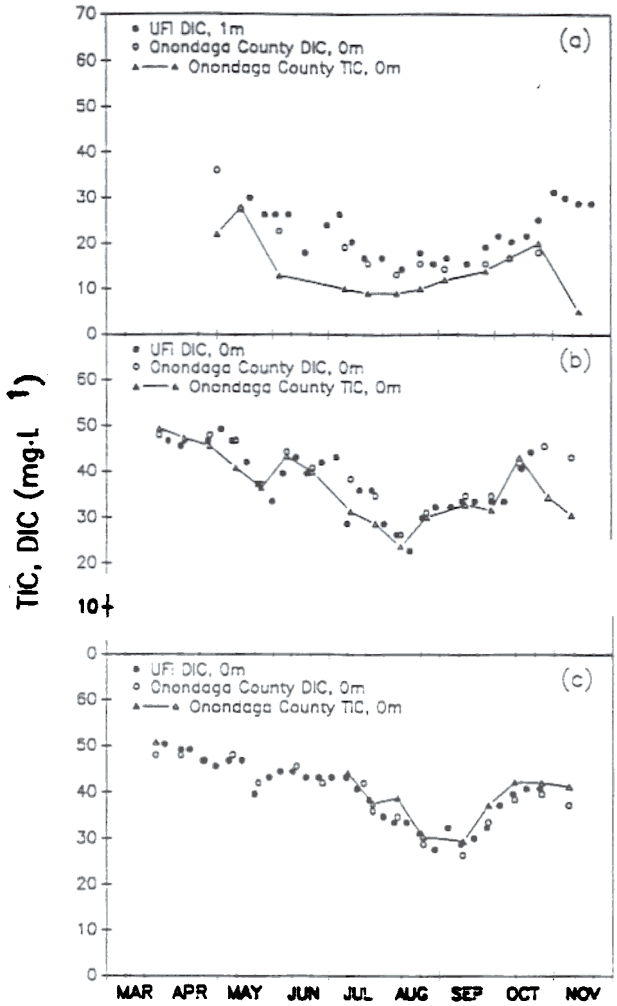

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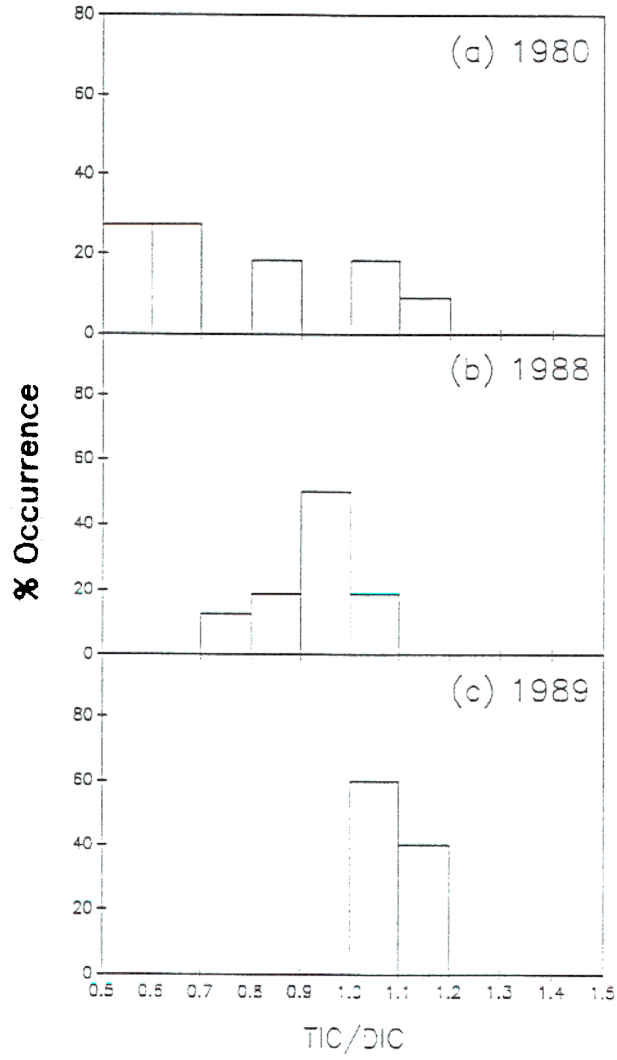

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UPSTATE
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April 27, 1995

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Dear Mr. Mustico:

I have reviewed major portions of the report of HydroQual and PTI (1994), entitled "Onondaga Lake RI/FS: Calcite Modeling Report". I am disappointed in this effort. The calcite models are far from the reliable management tools desired by the NYSDEC and promised by the consultants to address the issue and support the RI/FS process. I have from the outset cautioned and recommended against the adoption of overly complex frameworks (models) for this issue. I recommended against the inclusion of the phytoplankton, sediment, and 3-dimensional hydrodynamic submodels. The short-comings in the reviewed report identified in this cover letter and described in the attached review support my original position. Further, the modeling analysis is moving in a direction from the earlier reports that should concern the NYSDEC. It's important that you understand that I have not reviewed the entire document in detail. In particular, my review of the phytoplankton and sediment submodels is incomplete. My review of the steady-state and dynamic calcite models continues. However, I believe it is important to document my analysis of the portions reviewed now because of the character and magnitude of the problems encountered to date. Further, copies of the model code, or at least executable versions that allow changes in many of the model inputs, are required.

Data Bases: Short-comings in the Onondaga County (D&S) Data Base

The analysis by HydroQual and PTI (1994) relies entirely on historic data. The acceptability of data used in the analysis relies entirely on a evaluation of data bases for the lake conducted by Walker (1991). Certain important parameters taken from the Walker (1991) compilation have not been subjected to any quality assurance analysis. Walker (1991) used various approaches in evaluating the acceptability of the available data, including statistical and graphical methods and limnological

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reasoning. However, this effort was directed at only a subset (selected parameters) of the overall data base. Importantly, acceptability in Walker's (1991) work was viewed from the perspective of adequacy for supporting long-term trend analysis. In no way was Walker's (1991) analysis an evaluation of the acceptability of data to support testing of mechanistic (in some cases, dynamic) modeling. Data should meet substantially more stringent criteria of acceptability to support the models proposed by HydroQual and PTI (1994). Substantial portions of the D&S data base (the longest term program) have either been rejected or drawn into question by Walker (1991), and subsequently by myself. The D&S data problems are of a magnitude and nature that draw the entire data base into question. Based on a rather comprehensive comparative analysis, we concluded the D&S pH data base was unreliable. These data are crucial to the HydroQual and PTI (1994) analysis, in its present form. Other data important to their historic analysis, particularly the D&S TIC data, need to be subjected to detailed scrutiny. It is time that the NYSDEC takes a position on the acceptability of the D&S data base to support the model analysis. The credibility of model frameworks cannot be established when the data to which predictions are being compared are in question. The situation is yet more acute here in that a primary parameter being modeled, the concentration of $CaCO_{3(s)}$, is calculated from data in question. HydroQual and PTI (1994) need to assume a responsible position in screening the data for this analysis; deferring to the Walker (1991) report should not be considered acceptable.

Extension of the Modeling Period

Earlier progress reports on the calcite model(s) focused on a shorter period of time (1985-1989). The models have not yet been successfully applied to this shorter period. What is the point of extending the period of application to 21 years (about 4x the original period of testing) especially before calibration/verification has been established for the shorter period. One major effect of the extension is to make the short-comings of model performance less apparent. Twenty-one years of data and simulations is at first glance impressive, simply for the long duration, but it obscures model performance. This together with the long interval of data averaging (one month) gives a false impression of model success, that is brought into question only after careful review of the plots. Model performance is in fact quite often poor within individual years. Model testing should focus first on a shorter period, extending from before to after closure of the soda ash/chlor-alkali facility. Extension to a longer period should be considered only after model credibility is established for the shorter period, and after data credibility is established for the longer period. The problem of the extension to the 21 year period is compounded by the severe data quality problems of the older D&S data. Basically this facilitates the polluter arriving at alternate explanations and influences responsible for their impacts.

What Happened to Integrating the Field and Modeling Programs?

A modeling approach of "lets not let too many measurements interfere with the modeling process" emerges from my review of the document. HydroQual has been involved in water quality modeling for a long time. Certainly their earliest and simplest conceptual models for calcite included formation of $CaCO_3$ in the water column followed by deposition. Why were related studies not conducted as part of PTI's field year? These studies would be far from complex and costly; for example particulate inorganic carbon (PIC) measurements are straightforward, as are PIC analyses of sediment trap collections. Such measurements for a single year to support model calibration, and reduce the degrees of freedom of the model, should have been conducted.

Calculated concentrations of $CaCO_{3(s)}$, determined by the procedure outlined in the HydroQual and PTI (1994) report, is not an acceptable basis to test model performance. It is essential that the calculation procedure first be tested comprehensively for an entire field season. The partitioning of dissolved and particulate components of Alk, TIC, and Ca, is an interesting and potentially valuable approach. But, it remains purely speculative until it has been verified for this system.

Failure to Utilize the Available Literature for the Lake

The value of the $CaCO_{3(s)}$ settling velocity (w_s) adopted in the HydroQual and PTI (1994) report, 0.1 $m \cdot d^{-1}$, apparently is the outcome of calibration. There is no justification given for the selected value; e.g., no comparison to literature values. Further, there is no justification for not using the system-specific value reported in available documentation for the lake, which differs greatly from 0.1 $m \cdot d^{-1}$. Why has the available literature on Onondaga Lake with respect to watercolumn $CaCO_{3(s)}$ concentrations not been utilized. How much would the performance of the models deteriorate if the modeling process were constrained by the actual available measurements?

Major errors have been made by HydroQual and PTI (1995) concerning the hydrodynamics of dense inflows to the lake. These have important implications with respect to external loading for the dynamic models, and undoubtedly explain a number of the features of poor model performance. Inexplicably these errors were made despite substantial treatment of this topic for Onondaga Lake in the peer-reviewed literature. HydroQual and PTI (1994) have failed to adequately review the literature available on this lake.

Summary

I have prepared additional, more specific, comments that are attached to this letter, and several of our own analyses of their presentation. These are attached to this letter.

Where are we with respect to the $CaCO_3$ analysis after so many years? Unquestionably, some creative theoretical approaches to the issue have been advanced. However, there are no tangible findings from this work. None of the three models proposed has any substantial level of credibility for the stated goals, and thus they have no practical management utility at this time. I do believe the steady-state, and perhaps the dynamic (non-eutrophication), model frameworks have potential utility, <u>if constrained by a reasonable set of measurements and process studies</u>. However, the signs that emerge in this report are not promising in that regard. For example:

1. basic monitoring and process studies have not been conducted to support rigorous model testing,

2. available literature has not been consulted to develop calibration data sets and selected model coefficients,

3. fundamental lake processes, described in the literature, have not been understood and appropriately accommodated,

4. a compromised data set (Onondaga County D&S) for the lake has been embraced, despite the inclusion of clearly questionable measurements, without any indications of further scrutiny by the consultant, and

5. expansion of the modeling period to 21 years, before there are any clear indications of the establishment of model credibility for a shorter period.

It is hard for this reviewer not to consider the possibility that these short-comings individually and together serve the polluter on the $CaCO_3$ issue. Without question, embracing the County data set for the entire 21 year period is an error and serves Allied.

I continue to recommend against the incorporation of the eutrophication, sediment, and hydrodynamic submodels. This level of complexity is unwarranted at this time. The proposed "simple" steady-state model has major problems. Making the analysis more complex with these submodels is not going to improve the probability of developing a credible management tool. The NYSDEC needs to direct the effort to an appropriate data set and a simple framework, and the clear demonstration of model credibility for a 4-5 year period.

Sincerely

S.W. Effler
Director of Research

cc: T. Larsen
J. Bloomfield

This portion of the review is keyed to sub-headings used in the HydroQual and PTI (1994) report

1.4. Sources and Loading of Major Chemicals to Onondaga Lake

Data described in this section were not subject to any quality assurance analyses. Presumably, D&S tributary/ discharge data suffer from the same kinds of problems documented for the lake data in the subsequent sections

The accuracy of loads of phosphorus to Onondaga Lake based on D&S data is severely compromised by the short-comings in that monitoring program. Tributary loads are inaccurate (see Attachment III), and the METRO load before 1980 is inaccurate. Also see the description of the short-comings in the lake phosphorus monitoring program described in Appendix II.

HydroQual's eutrophication model partitions nutrients and carbon into a number of different forms of these constituents. Most of these parameters are not routinely included in eutrophication-related monitoring programs. This requires partitioning of external loads according to these same fractions. Much of this appears to be rather arbitrarily specificed. For example

1. " the remaining phosphorus forms (RDOP, LPOP, and RPOP) were equally apportioned as the difference between total phosphorus and TIP" (P. 1-21),
2. " while estimates of total organic nitrogen (TON) (or TKN-NH_3 were apportioned between LDON, RDON, LPON, and RPON equally" (P. 1-24),

3. "From METRO effluent, POC is equally distributed between the refractory and labile organic carbon pools; DOC is split ...., assigning 36 percent to refractory pool and 64 perfect to the labile pool distribution for refractory and labile organic pools is 80 and 20 percent, respectively" (P. 1-28)

What are the implications of these arbitrary specifications? For example, low sensitive are critical projections to these selections. For how many systems have these various fractions been measured? How much supporting literature is there for these selections?

1.5. Water Chemistry of Onondaga Lake

HydroQual and PTI (1994 apparently misunderstand status of the compiled database prepared by Walker (1991). This has resulted in a mis-representation concerning extent to which the data incorporated in the analysis have been subjected to scrutiny. Indeed the data adopted had compiled by Walker (1991). However, all these data were not subjected to quality analyses.

"Although the compiled data set includes all water quality components reportedly monitored by each agency, validation, screening, and analytical efforts are focused on nutrients and related water quality components measured at lake stations" (P.1, Walker, 1991).

Importantly, two constituents key to the calcite analysis, Ca and TIC, were compiled, but received no quality assurance analysis in Walker (1991 work. Meaning, no documentation of

analytical procedures, entity responsible for analyses changes over the period of record, and performance in quality assurance testing, is presented in the Walker (1991 report for these analytes.

Adoption of the compiled data for the calcite model analysis, because there is no documentation questioning these data (e.g., Ca and TIC), should not be acceptable, in light of the pervasive data problems already established for a number of other parameters in the D&S data base. A number of the data quality problems identified in the D&S data base are identified in Table 1. Why should the Ca and TIC data be embraced as accurate, in light of the difficulty this same program had with fundamental measurements (Table 1)?

Furthermore, the scrutiny received by the parameters addressed by Walker (1991 was from the perspective of the adequacy of the various data sets to support depiction of long-term trends, not for support of sophisticated mechanistic models. Walker 1991 used various approaches in evaluating the acceptability of the available data, including statistical and graphical methods and limnological reasoning. Data should meet substantially more stringent criteria of acceptability to support the models proposed by HydroQual and PTI (1994). For example, Walker (1991 "flagged" various of the D&S pH measurements as likely in error. However, a more detailed and rigorous analysis (Doerr and Effler 1994) draw the entire D&S data base into question

TABLE 1: Problems with the Onondaga County Department of Drainage and Sanitation Data Base for the Onondaga Lake System

Parameter	Problem Description	Reference
dissolved oxygen (DO)	false low in epilimnion, false high in hypolimnion 1976-1981, data rejected	Walker 1991
	presence of DO near lake bottom when reduced species present, 1972-1988	Walker 1991
temperature	false high in hypolimnion, 1979-1981 data rejected	Walker 1991
pH	unexplained long-term instabilities; faulty data identified for various yrs	Walker 1991, Doerr and Effler 1994
hydrogen sulfide	false low in 1972-1974 (rejected), suspicious differences noted in other years	Walker 1991
phosphorus (P)	monitored total inorganic P instead of total P until 1989	Effler and Whitehead 1994, Effler 1995, this report
soluble reactive P	false high values in upper productive waters of lake for much of summer	this report
chloride	unreliable lake concentrations, 1979 and 1982	Doerr et al. 1994
total inorganic P for tributaries and related loads	unreliable during periods of lower concentrations, before 1989	Effler and Whitehead 1995

1.5.1.1. Chloride/Salinity

a. This section has severe problems. Salinity (S; usually expressed in parts per thousand (ppt, or °/..)) is concentration of dissolved solids (weight/weight; or weight/unit volume). In most fresh waters at can be estimated as the summation of the concentrations of four major cations, Ca^{2+} Mg^{2+} Na^{+}, and K^{+}, and three major anions, HCO_3^-, SO_4^{2-}, and Cl^- (Wetzel 1983). Indeed,

concentration has been found to be good surrogate measure of S in Onondaga Lake (Effler 1995, Effler et al., 1986a). The linear S Cl^- relationships developed by Effler et al. (1986), and subsequently revised by Effler 1995, applies only for the ionic composition that prevailed in Onondaga Lake before closure of the soda ash/chlor-alkali facility. The two pre-closure expressions (Effler 1995, Effler et al., 1986a) yield nearly equivalent estimates for annual S levels before closure

The statement (p.1-36), "The marked decrease in lake salinity concentrations that occurs between 1985 and 1990 is due to the reduction in chloride loading ....", is incorrect. The attendant reductions in Ca^{2+} and Na^+ also contributed importantly to the observed reduction in lake S (Effler 1995).

The concentration of Cl^- continued to be a good surrogate measure of S after the closure. However, the relationship necessarily changed (see Effler 1995) as a result of the systematic shift in the ionic composition of the lake that accompanied the reduction in ionic waste (Cl^- Na^+, and Ca^{2+} loading from soda ash production. The failure to recognize the systematic shift inherent in adopting the Effler et al. (1986a) expression for the post-closure period has resulted in a substantial underestimation of the S of the lake for that period (HydroQual and PTI 1994 An appropriate estimate for the vertically and annually averaged S for Onondaga Lake for 1990 is 1.1 °/.. (Effler 1995),

instead of 0.6 ‰ (HydroQual and PTI 1994). The HydroQual and PTI (1994) estimates of S for the post-closure period are also inconsistent with ionic data reported in the open literature. For example, the Cl^- concentration(s) reported by Doerr et al. 1994) and the Ca^{2+} concentration(s) reported by Driscoll et al. (1994) for 1990 together equal about 0.6 ‰ (the value reported by HydroQual and PTI (1994) without considering the rather substantial contributions of Na^+, HCO_3^- and SO_4^{2-}

The accurate representation of Onondaga Lake's S following closure of the facility has important implications with respect to assessing the impact of continuing residual ionic waste loading from soda ash production (e.g., Doerr et al. 1994). Perhaps more importantly, it is critical with regards to the continuing deleterious impact ionic waste inputs to the lake have on the oxygen resources of the Seneca River (Canale et al. 1995, Effler 1995).

b. Was a clear <u>operational</u> definition for epilimnion and hypolimnion given; in other words, what assumption(s) about demarcating depth was made? The details of volume-weighing should be given. The issue is non-trivial for many important water quality constituents because of the strong vertical stratification manifested seasonally

c. There appears to be a blanket acceptance of the Onondaga County data base associated with the earlier analysis of Walker (1991), that is manifested here for Cl^- (S), and throughout the analysis of HydroQual and PTI (1994)

NYSDEC embraced this position? Should not the contractors have some responsibility to provide some QA/QC for data incorporated in their analysis?

d. Consider several features of HydoQual and PTI's (1994) presentation of the Cl^-(S) data in Figure 1-15. It's quite easy to become overwhelmed with the amount of data (e.g., 21 years). Certainly the vertical scaling could be reduced to better depict structure in the data. The Cl test is generally considered to be an easy one in this concentration range. However, the evidence is strong that even some of this data base for the lake is unreliable. Doerr et al (1994) found the lake Cl^- data to be particularly suspect in 1979 and 1982; e.g., unrealistic abrupt changes in lake concentrations in both years. Limited Cl^- data from an alternate source (Walker 1991 differ greatly in a number of instances. Further, the statistic plotted (monthly average) hide a number of "short-comings"

1.5.1.2. Calcium

The first sentence in this section seems inappropriate. I know of no evidence for dissolution of $CaCO_3$ in Onondaga Lake. The concentrations presented for 1970 and 1971 in Figure 1-16 are problematic; they are almost certainly false high. The time course of the ratio Ca^{2+}/S for the 1970-1990 interval, developed from HydoQual and PTI's (1994 Figures 1-14 and 1-16, is presented here as Figure 1. Note the much higher values for the ratio in 1970 and 1971. What is the explanation for these conspicuous differences. Several

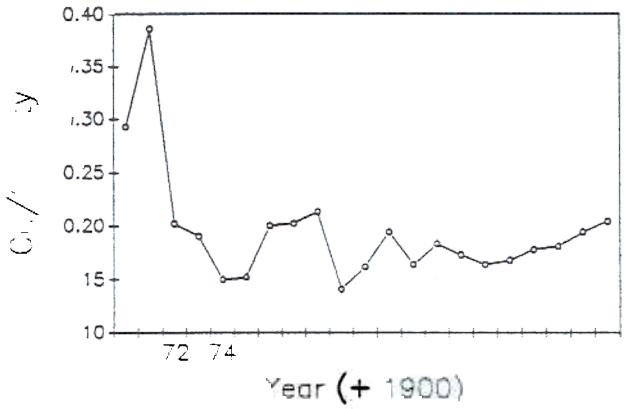

Figure 1

considerations support the position that the most logical explanation is <u>bad</u> Ca^{2+} data.

1) Recall that the relative contributions of Cl^-, Ca^{2+} and Na^+ to the ionic waste from this facility's soda ash manufacturing process were described as uniform by the USEPA (1974).
2) Charge balance calculations based on annual average concentrations reported by Onondaga County (1971, 1972) for those two years depict substantial surpluses of cations in both years
3) There are well established problems with this suite of measurements in the County's monitoring program. For example, 41% of the paired observations of major ions in Ninemile Creek for the 1981-1985 and 1986-1989 intervals were rejected in an analysis of the interrelationships in the concentrations of the various ions, for failure to meet the QA/QC criterion of charge balance within 10% (Effler and Whitehead 1995). Of the three major ions, Cl^-, Na^+, and Ca^{2+}, Cl^- data should be considered the most reliable. Simple titration procedures were available at that time. The concentrations of Na^+ and Ca^{2+} were determined by atomic absorption spectrometry, a more challenging procedure for commercial laboratories at that time.
4) Ion ratio data from the waste beds (Effler and Harnet 1995) and Ninemile Creek (Effler and Whitehead 1995) support the position that the ratio of Ca^{2+}/Cl was

uniform.

This represents a case in which the arguments to support inclusion of the 1970 and 1971 Ca^{2+} lake data in the analysis need to clearly outweigh the evidence indicating these data are questionable. The observation that the Ca^{2+} loads derived from tributary concentrations reported by the same monitoring program were high is not compelling support to retain the 1990 and 1971 lake data in the analysis. Presumably analytical problems with Ca^{2+} for lake samples would also be manifested for tributary samples. The conspicuous change implied by the Ca^{2+}/S ratios for 1970 and 1971 (Figure 1) could only be justified by a dramatic shift in manufacturing and/or waste production from the facility. No such evidence was presented by HydroQual and PTI (1994 Even if this was the case, it could not explain the major surplus in cations manifested in the data sets for those two years

1.5.1.5. pH

A summary presentation of annual pH values based on vertical and temporal averaging of H^+ concentrations as presented in Figure 1-22 of the HydroQual and PTI (1994) report has little value. Further, it confounds identification of the various flawed features of the D & S pH data set. An analysis of pH data bases for Onondaga Lake was prepared by Doerr and Effler (1994), and is attached here as Appendix I. The D&S data base for pH was found to be highly suspect; inconsistencies with well established limnological paradigms were manifested in a number of years. Particularly

problematic is the temporal instability manifested throughout this data base, on both short- and long-term scales.

1.5.2.1. Chlorophyll a

The D&S chlorophyll a data base is derived from spectrophotometric measurements made according to the method of Lorenzen (1967). This method claims to separate chlorophyll a from phaeopigments. In a comparison of methods, Auer et al. (1995) indicated the Lorenzen (1967 measurement of chlorophyll a was flawed for application to Onondaga Lake, apparently associated with the unreliable partitioning of chlorophyll a and phaeophytin. The Lorenzen (1967) method appears to produce false high estimates of phaeopigments and false low estimates of chlorophyll a. High pressure liquid chromatography (HPLC) measurements indicated that phaeopigments were essentially absent from the water column of Onondaga Lake in 1990, yet the Lorenzen (1967) method determined the average phaeophytin concentration to be 6 $\mu g \cdot L^{-1}$ Auer et al. (1995) indicated the sum of the concentrations of chlorophyll a and phaeophytin provided by the Lorenzen 1967 method is a better estimate of the concentration of phytoplankton pigments.

The language, "there is a strong seasonal cycle in chlorophyll a", is somewhat misleading. There are strong variations annually within the spring-fall interval. In fact there are substantial variations in the seasonal distributions amongst the years. The D&S monitoring program is inadequate with respect to sampling frequency to

faithfully depict the important features of the seasonal structure in this important parameter. The "scaling" of plots of Figure 1-24 (PTI and HydroQual 1994) is unfortunate, as the accommodation of the range(s) for several observations masks the seasonal structures. Recent analyses (Connors et al. 1995) indicate at least weekly monitoring is necessary to resolve important features of the dynamics of phytoplankton biomass in the lake

1.5.2.2. Dissolved Oxygen

The Onondaga County (D&S) data base for DO has severe problems, as described in part by Walker (1991). It is important to depict the extent and character of those short-comings, as it is symptomatic of problems manifested in the D&S data base for a number of parameters.

Walker (1981) recommended the rejection of six years of DO data from the D&S data base; epilimnetic values were false low and hypolimnetic values were false high, over 1976-1981 period. DO values substantially above zero continued to be recorded for the hypolimnion and accepted by the D&S program, despite the measurement of H_2S at the same depths. Apparently, UFI data available for 1978-1981 were adopted in Figure 1-25 (HydroQual and PTI 1994). continued use of D&S 1976 data by PTI and HydroQual (1994) is inexplicable (see Figure 1-25). The continuously undersaturated conditions in the epilimnion indicated for 1976-1981 period in the D&S data set should have been identified by County monitoring staff as unreasonable within

first year. False high DO values continued to be collected for the lake's hypolimnion by D&S over the 1972-1988 period. Given the prevalence of such fundamental problems for a number of years, why should earlier measurements by the same program be accepted as reliable? It is irresponsible to claim (P. 1-51 an improvement in the epilimnetic oxygen resources of the lake based on the early measurements. Further, it is inappropriate to qualitatively draw the conclusion that such a hypothetical improvement is attributable to improved treatment at METRO. It has been demonstrated that certain features of the oxygen resources of the hypolimnion have improved (Effler 1995). These improvements are largely a result of the amelioration the salinity stratification problem, caused by the soda ash facility's ionic waste, associated with the closure of facility.

Why should the D&S data base for field pH (arguably a more difficult measurement to do correctly) be considered reliable, in light of the major problems the same program had with DO measurements? Indeed, the prevailing inconsistencies identified for the D&S pH data base (e.g., unexplained year-to-year instability appear to reflect the same kind of problems.

1.5.2.3. Phosphorus

There are a number of fundamental flaws in the D&S monitoring program for P species. These short-comings have been delineated in an analysis by Effler and Doerr (1994);

portions of the analysis are attached here as Appendix II.

Even superficial review of Figure 1-26 indicates highly suspect interannual variations in the hypolimnion accumulation of PO_4. What is the possible explanation for such unusual variations?

2. Steady-State Calcite Model

2.2.2. Estimating the Equilibrium Concentration of Calcite

HydroQual and PTI (1994) attribute the scatter in their Figure 2-2B solely to contributions of particulate TIC Alk to Alk_T and TIC_T. The possibility that unreliable measurements (particularly for pH and TIC_T) contributed to the deviations from theory is not acknowledged. Most of scatter is probably the result of bad data. The deviations to the left of the line are particularly suspect; how significant can non-carbonate alkalinity be?

Equation 2-12 is critical. While it appears to have a sound theoretical basis, there is no independent validation. In other words, it must be demonstrated that equation 2-12 accurately estimates the concentration of $CaCO_{3(s)}$. The concentration of $CaCO_{3(s)}$ is the primary parameter modeled Yet there is no independent measurement of concentration. It is calculated from Alk_T, TIC_T and pH (see equations 2-8 and 2-12). The D&S pH data base is known to be compromised (Doerr and Effler 1994) and the credibility of the TIC_T data base has not been addressed. Why then should we have confidence in the calculated concentrations of $CaCO_{3(s)}$, and the model calibration effort that attempts to match these concentrations? Even if there were no questions concerning the credibility of the D&S data base, equation 2-12 needs to be verified for Onondaga Lake.

The nature of the calculated distribution of $CaCO_{3(s)}$ concentration (Figure 2-3E) raises questions

regarding the veracity of calculations and the supporting data. Negative concentrations were calculated for 1972, 1973, 1974, 1989, and 1990. They acknowledge (P. 2-11) these are due to inaccuracies in measurements and/or model assumptions. That represents approximately 25% of the 21 year data base. Each of the 5 years should not be considered equal. The first three years were before closure of the soda ash facility, when precipitation and deposition of $CaCO_3$ were undoubtedly greater. Analysis of sediment trap collections clearly indicates deposition of $CaCO_3$ throughout the spring-fall intervals of 1989 and 1990 (Effler 1995). Why should the positive values calculated for the other years be trusted as accurate? Simply because they are not negative? To imply that the positive values form some kind of "fairly regular pattern" (P. 2-11) is misleading. The "pattern" is strictly an outcome of a theoretical calculation that has not been independently tested for this system, nor has successful testing for any other lakes with significant $CaCO_{3(s)}$ concentrations been demonstrated. What structure there is in the calculated $CaCO_{3(s)}$ distribution could be largely the outcome of the bad D&S pH data base. The partitioning of Ca, TIC, and Alk presented (according to total and dissolved fractions) is also the outcome of calculations, which also has not been tested, and is compromised by the unreliable D&S data base. To justify the lack of correlation between Ca and calculated $CaCO_{3(s)}$ to a yet-to-be discussed theoretical analysis (P. 2-11) is inappropriate.

Calculated concentrations of $CaCO_{3(s)}$, determined by the procedure outlined in the HydroQual and PTI (1994) report, is not an acceptable basis to test model performance. Why were related field studies not conducted to verify the calculation procedure. The methods seem rather straightforward. Available data sets were not utilized to test the calculation procedure - why?

2.6. Application to Onondaga Lake

2.6.1. Comparison to Model Calculation

Coefficient values for the steady-state model are specified in Table 2-10. No justification for the values specified is given. Apparently they are the outcome of model calibration. Are no literature values available? The value selected (or calibrated to) for w_s is particularly troublesome. System-specific experiments using sediment traps could have easily been conducted. Further, what is the justification for not using the system-specific value reported for the lake? This value differs greatly from the 0.1 $m \cdot d^{-1}$ adopted. How much would the performance of the models deteriorate if the modeling process were constrained by the actual available measurements?

The TIC loads presented by HydroQual and PTI (1994) are highly questionable for several reasons.

1. the lack of any quality assurance on D&S TIC data; particularly in light of the known problems with other more rudimentary measurements,
2. unexplained trends in TIC loading (Figure 1-7), and

3. questionable adjustments made to TIC loads (P.'s 2-32 and 2-36).

The third issue deserves some comment. Two in-lake transformations are identified on P.'s 2-32 and 2-36, oxidation of organic C to TIC (a source), and uptake of inorganic C (a sink). These in-lake processes, contrary to the their presentation ("As a consequence of these processes, there is some uncertainty about the actual loading". (P. 2-36, HydroQual and PTI 1995) do not cause uncertainty in TIC loading. What I believe they mean is, these processes are a concern within the context of the conceptual model embraced for the steady-state model, because they have "lumped" these processes within the external loads. Of yet greater concern is the rather arbitrary manner in which these issues were addressed. For example, the loss due to primary production was ignored. What is the justification for this assumption? A second assumption is the addition of the labile TOC in the TIC load, to yield their adjusted TIC load. This is what I would describe as a "compound assumption", e.g., embedded within this assumption is the assumption of how much of the tributary and METRO TOC loads is labile (see P. 1-28).

The plots of Figure 2-9 do not represent a rigorous testing of the model's credibility, rather it represents an outcome of a "curve fitting" process. There is very little in the way of constraints to their calibration procedure; e.g., measurements of the primary state variable, $CaCO_{3(s)}$,

or rate processes such as settling velocity. The extent of fit for pH is poor, and is masked by the scaling selected for the plot. To claim the predicted trend for pH is correct is a "stretch". The stated sensitivity of pH predictions to Alk_d and TIC_d (P. 2-36) is cause for great concern, as these parameters are themselves calculated from pH (equations 2-8 through 2-12).

What tests are there for model performance that can be considered reliable? The concentration of $CaCO_{3(s)}$ is determined from pH measurements from a data base that is of questionable credibility. The calcium carbonate flux plot compares the predicted flux with what is described as the "estimated long-term average" in Figure 2-9E. No justification or citation is given for the presented band. The details of the development of this "long-term average" need to be fully documented. The implication of the presented band is that no systematic change in the downward flux of $CaCO_{3(s)}$ has occurred in the lake over the 1963-1992 period. That is incorrect (see Effler 1995).

2.6.2. Estimating the Historical Loadings

and

2.6.3. Modeling the 21 - Year Period

<u>The calculation of TIC loads by difference for years preceding 1983 should be considered a purely speculative exercise</u>. Confidence in such "difference" type estimates is reserved for those cases in which all the other values (pool size, sink, sources) are <u>known</u> with a high degree of

certainty. Can the circumstances of this modeling effort be described as approaching this constraint? The resulting estimates of TIC (Table 2-7) vary by a factor of 4 over the 1970-1982 period. Can the modelers provide any justifications/explanations for this behavior? What phenomena or activities in the lake's watershed could be responsible for such wide variations in the ratio of the Alk_T/TIC_T loading rates over a 13 year interval (Table 2-7) Under such widely varying (and strictly hypothetical TIC loading rates (Table 2-7) how can the interpolation/ extrapolation procedure for years in which there are no lake TIC measurements (1970, 1971, 1975, 1981, and 1982; see footnote of Table 2-8) be justified to support loading estimates? Figure 2-11 is far from compelling support for the speculative loading estimates.

Subsequently in the report the speculative estimates of TIC loading for the 1970-1982 interval are presented as if they have been transformed to documented observations; "The alkalinity loading to the lake remained approximately constant throughout the 21 year period, whereas the TIC_{xs} loading changed substantially" (P. 2-41). To embrace these loads and the associated 21 year analysis, and discuss them as findings of the analysis (P. 2-43) is inappropriate.

2.6.4. Causes of the Fluctuations in Calcite

The history of loading presented, as described earlier, is almost certainly incorrect. In particular, the major decline in Ca concentration over the 1970-1974 interval

(Figure 1-16) is an artifact of false high concentrations reported (e.g., 1970 and 1971

3.3.1. Assignment of Point Source and Tributary Inputs to Appropriate Horizontal Layers

and

3.3.2. Calibration of Vertical Mixing from Temperature/ Salinity Data

HydroQual and PTI (1994 acknowledge density differences between the inflows tributaries and METRO) Onondaga Lake, and correctly reference Effler and Owens (1986). Changes brought about by the closure of the soda ash/chlor-alkali facility have also been documented by Owens and Effler (1995a). Indeed, the inflows made dense by the ionic waste from soda ash production, tended to enter the lake as a plunging underflow (Effler 1987, Effler and Owens 1986). Though the tendency has been substantially reduced as a result of the closure of the facility, it has not been eliminated because of the continued release of residual ionic waste from soda ash production (Effler et al. 1991, Effler and Owens 1995, Owens and Effler 1995a). However, PTI HydroQual (1994) have failed to recognize that the density of a dense inflow is reduced upon entry into the lake basin as a result of near field mixing. This phenomenon has important implications with respect to the seasonality of salinity stratification in the lake and the effective depth of entry (i.e., loading) of enriched inflows. The extent of near field mixing depends on characteristics of the inflow and the

receiving lake, including the rate of inflow, geometry of the inflow zone, the density difference between the inflow the upper waters of the lake, and the magnitude of ambient lake turbulence (e.g., Owens and Effler 1995a, 1995b). "routing" protocol for external loads to lake layers employed by HydroQual and PTI (1994), based on direct comparison of inflow density and lake layer density, is a major error, that has important implications and explains several of the manifested short-comings in the performance of the dynamic models.

It should be noted that PTI and HydroQual's (1994) description of changes in density differences between inflows and the lake are only approximately correct. For example, following closure of the soda ash/chlor-alkali facility, during periods when METRO receives ionic waste from a lagoon adjoining the waste beds, METRO continues to be more dense than the surface waters of the lake (Effler et al. 1995)

HydroQual and PTI's (1994) stated problem with understanding and accommodating the origins of S stratification under the ice (P.3-27 is inexplicable. There is a previously stated understanding of the tendency for plunging of the inflows enriched with ionic waste. Why wouldn't the underflow phenomenon be operational under the ice? In fact, the minimal ambient lake turbulence inherent to the ice-cover period should be expected to promote development of S stratification. Furthermore, the magnitude of the thermal component of density stratification during the

ice-cover is small compared to that during summer stratification, a period during which PTI and HydroQual (1994) have (incorrectly "routed" ionic waste-enriched input to the lake's hypolimnion. The stated confusion on this issue appears even more inexplicable in light of the reference to the development of S stratification under the ice in previously published research on the lake (e.g., Effler et al. 1986b, Effler and Perkins 1987, Owens and Effler 1995a).

The development of the under-the-ice S stratification that resulted from the underflow phenomenon in the lake was identified by Owens and Effler (1995a) and Effler and Owens (1995), and certainly was implicit in the earlier presentations of Effler and Perkins 1987 and Effler et al. 1986b). Earlier modeling efforts by Owens and Effler (1985, 1989 referred to the winter S stratification phenomenon, but did not model its development. More recently Owens and Effler (1995b) have presented continuous model simulations of temperature and S stratification for the 1987-1992 period. Salinity stratification was predicted annually under the ice, associated with the continuing (but decreased) ionic enrichment of Ninemile Creek. This predicted continuing S stratification under the ice is supported by measurements

There have been two different stratification cases for Onondaga lake in recent years. In the first case S stratification established under the ice (e.g., 1980 (Effler and Perkins 1987 was not broken up during the spring mixing

period (i.e., no spring turnover). Effler and Perkins (1987) reported that the lake failed to turnover (or turnover was extremely brief) in the spring of several years before closure of the soda ash/chlor-alkali facility. In other years before closure turnover was observed. The occurrence of these two cases was largely mediated by year-specific meteorological conditions (Owens and Effler 1989, 1995a). Conditions that favored the failure of spring turnover included an extended period of ice-cover, low wind and high air temperatures in spring. In years that spring turnover occurred before closure (e.g., 1981 (Owens and Effler 1989, 1995a) , S stratification was re-established during spring as a result of the plunging of the ionically enriched inflow(s) to the lake's bottom layers. This is consistent with the propensity of an underflow to plunge to the bottom of a receiving basin under conditions of minimum water column stability. The magnitude of S stratification manifested in late spring in years that experienced spring turnover was in general less than encountered in years that turnover did not occur.

The most important point is that once density stratification was established in spring the S stratification component decreased progressively thereafter during the summer stratification period (Effler and Owens 1995, Effler et al. 1986, Owens and Effler 1989, 1995a). "This occurred because, following entrainment-based dilution of the ionic inflow, the inflow could not penetrate the well-developed

thermocline of the lake" (p.588, Owens and Effler 1989). Careful review of vertical profiles during summer stratification yields clear evidence of the entry of S-enriched water above the thermocline (e.g., Effler and Owens 1995, Owens and Effler 1995a). The nearly constant S of the lower layers during stratification and the progressive increase in the S of the upper layers over the same period (Effler and Owens 1995, Effler et al. 1986, Owens and Effler 1989, Owens and Effler 1995a) established that the high S inflows enter the upper layers (e.g., epilimnion), not the hypolimnion. Thus the routing of dense inflows to the hypolimnion during summer stratification period, for both before and after closure of the facility, adopted by HydroQual and PTI (1994), is incorrect

The implications of the error in simulating S in the lake are illustrated for 1980 in Figure 2; this plot was extracted from Figure 3-10 of the PTI and HydroQual (1994) report. While the annual average lake-wide concentration may be approximately correct, the predicted seasonal structure is completely wrong:

1. the predicted stratification is near minimal in April instead of the observed seasonal maximum,
2. the predicted epilimnion concentrations remain nearly uniform through summer instead of increasing progressively as observed, and
3. the predicted hypolimnion concentrations increase progressively through summer, instead of remaining

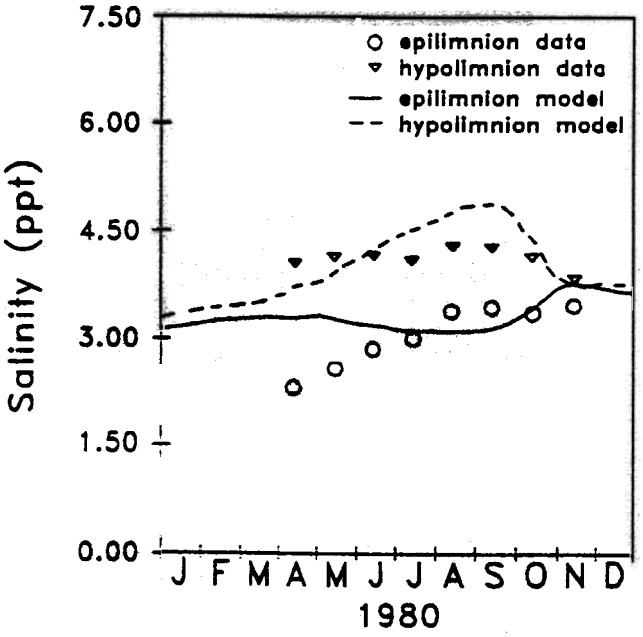
7.50
6.00
4.50
3.00
1.50
0.00
Salinity (ppt)
epilimnion data
hypolimnion data
epilimnion model
hypolimnion model
J F M A M J J A S O N D
1980

Figure 2

nearly uniform

HydroQual and PTI's (1994 presentation within a 21 year record, and their monthly averaging procedure, tends to mask these short-comings.

Claims made by PTI and HydroQual 1994) concerning success of the dynamic calcite model in simulating S, are, at the very least, inappropriate. The long-term trend in S was not simulated accurately (as indicated earlier). The S of the lake following closure is underpredicted. The long-term trend in Cl^- concentration (from which S is calculated) be captured (as claimed on P. 3-23), but this could be accomplished by a much simpler framework; e.g., completely-mixed annual or seasonal (e.g., Doerr et al. 1994) models. Further, the long-term trend may only be simulated to the extent to which loadings have been manipulated as calibration variables. Their treatment of the development of loads is cryptic and inadequate. The claim that the model "reproduces to some degree, the summer salinity stratification, " (P. 3-23 is misleading and incorrect. This qualified claim of success becomes stronger by p.3-27, and therefore a greater misrepresentation

.the model performed well with respect to the observed salinity (or chemical stratification in the summer months of most years". As established earlier, this claim is incorrect.

There are a number of important implications of HydroQual and PTI's (1994) misconceptions concerning plunging

inflows and their adopted related protocol for routing external loads to various lake layers. The dynamic models are, as a result, severely in error. The fact that a number of parameters are simulated with some accuracy, despite there fundamental problems, provides a fine example of the danger(s) inherent in adopting an overly complex modeling framework. There are plenty of "knobs" to turn in the calibration process in such models to compensate for fundamental conceptual errors. In other words, the existing calibration is as good as it is for the wrong reasons. In their present form these models have little or no management value.

What are some of the specific implications of these errors? Several notable examples are given below.

1. the previously documented failure to simulate the seasonality in S stratification (Fig.'s 3-10 and 3-11),
2. a corollary is the failure to simulate the seasonality in Ca^{2+}, a major component of the calcite precipitation issue. Instead of loading Ca^{2+} to the epilimnion in summer it is routed to the hypolimnion.
3. Consider the implications for nutrients loaded from METRO during the 1981-1985 interval. During this period the majority of external loads of TP and T-NH_3 received by the lake (from METRO) is incorrectly routed to the hypolimnion. Interestingly, predictions of the seasonality of TP and T-NH_3 for the 1981-1985 interval are not presented. These should be requested.

4. Incorrect loading of oxygenated water to the hypolimnion implies the existing DO calibration for that layer is an artifact of an artificially high oxygen sink in the model.
5. Vertical mixing coefficients are of course also wrong as a result of adjustments made in an effort to compensate for the fundamental error made with respect to the routing of ionically enriched (i.e., dense) inflows. Note the related statement, "Vertical mixing coefficients were adjusted by compromising between reproducing the observed salinity and reproducing other water quality variables such as temperate, dissolved oxygen, and nutrients" (p. 3-23; HydroQual and PTI 1994)

On the Need to Accommodate the Cooling Water Operation in Simulation of Lake Water Quality.

The soda ash/chlor-alkali facility used Onondaga Lake as a source of cooling water. Both shallow (e.g., about 3m within epilimnion) and a deep (within the hypolimnion) intakes were used. The deeper intakes were of course preferred during summer because of the lower water temperature. There were, I believe, other seasonal constraints on this operation. I believe the facility chlorinated the intake water. The chlorine demand increased during summer for the hypolimnion option, because of the accumulation of reduced species (e.g., H_2S). I believe the NYSDEC placed some additional constraints on the process.

The heating and discharge of the spent cooling water to the lake's epilimnion resulted in the net transfer of hypolimnetic water and associated chemical constituents, to the lake's epilimnion (Effler and Owens 1987, Owens and Effler 1995) i.e., an artificial form of internal cycling (Effler and Owens 1987).

This process is not accommodated in HydroQual and PTI's (1994) dynamic models, nor is it's exclusion justified. In light of the strong stratification manifested during the summer in the lake for a number of important constituents (e.g., Cl^-, Ca^{2+} TP, SRP, T-NH_3) during the operation of the cooling water process, and the substantial withdrawal rates, these internal loads need to be addressed in detail. Effler and Owens (1987) indicated that this internal load of phosphorus may have exceeded the METRO load at times. To be adequately accommodated the depth, configuration and operation of the intakes must be documented. To date this information has not been forthcoming; I requested this information on behalf of the State at a previous Albany meeting. Recollections, approximations, and second-hand information should not be accepted concerning this matter. Only after careful consideration of these date could the omission of this operation from the dynamic modeling effort be justified. HydroQual and PTI 1994) have failed to consider the issue.

The "net" loading concept proposed for the East Flume (p. 1-10) may be adequate to support the steady-state

analysis, but it is not appropriate for the dynamic models without a comprehensive analysis of the potential significance of the artificial internal load(s) inherent in the cooling water operation.

References

Auer, M.T., S.W. Effler, M.L. Storey, S. Connors and P. Sze. 1995. Phytoplankton, Biology (Chapter 6). In S.W. Effler (ed.) Onondaga Lake: Lessons in limnology and engineering analysis. Springer-Verlag, NY. (in press).

Connors, S.D., M.T.Auer and S.W. Effler. 1995. Phosphorus pools, alkaline phosphatase activity, and phosphorus limitation in hypereutrophic Onondaga Lake, NY. Lake Reservoir Manag. (in review).

Doerr, S.M., S.W. Effler, K.A. Whitehead, M.T. Auer, M.G. Perkins and T.M. Heidtke. 1994. Chloride model for polluted Onondaga Lake. Wat. Res. 28: 849-861.

Doerr, S.M., and S.W. Effler. 1994. A comparative analysis of pH data for Onondaga Lake. Submitted to New York State Department of Environmental Conservation, Albany, NY.

Driscoll, C.T., S.W. Effler and S.M. Doerr. 1994. Changes in inorganic carbon chemistry and deposition of Onondaga Lake, New York. Environ. Sci. Tech. 28: 1211-1218.

Effler, S.W. 1987. The impact of a chlor-alkali plant on Onondaga Lake and adjoining systems. Water, Air, Soil Pollut. 33: 85-115.

Effler, S.W. (ed.) 1995. Onondaga Lake: Lessons in Limnology and Engineering Analysis. Springer-Verlag, NY. (in press).

Effler, S.W., C.M. Brooks, J.M. Addess, S.M. Doerr, M.L. Storey and B.A. Wagner. 1991. Pollutant loadings from Solvay waste beds to lower Ninemile Creek, New York. Water Air Soil Pollut. 55: 427-444.

Effler, S.W. and G. Harnett. 1995. Background (Chapter 1). In S.W. Effler (ed.), Onondaga Lake: Lessons in Limnology and Engineering Analysis. Springer-Verlag, NY. (in press).

Effler, S.W., E.M. Owens. 1986. The density of inflows to Onondaga Lake, USA, 1980 and 1981. Water, Air, Soil Poll. 28: 105-115.

Effler, S.W., E.M. Owens and K.A. Schimel. 1986b. Density stratification in ionically enriched Onondaga Lake, USA. Water, Air, Soil Poll. 27: 247-258.

Effler, S.W. and E.M. Owens. 1987. Modifications in phosphorus loading to Onondaga Lake, USA, associated with alkali manufacturing. Water Air Soil Pollut. 32: 177-182.

Effler, S.W. and E.M. Owens. 1995. Density stratification in Onondaga Lake: 1968-1994. Lake Reservoir Manag. (in review).

Effler, S.W. and M.G. Perkins. 1987. Failure of spring turnover in Onondaga Lake, NY (USA). Water, Air, Soil Poll. 34: 285-291.

Effler, S.W., M.G. Perkins, K.A. Whitehead and E.A. Romanowicz. 1995. Ionic inputs to Onondaga Lake: Origins, character, changes and selected implications. Lake Reservoir Manag. (in review).

Effler, S.W., K. Schimel and F.J. Millero. 1986a. Salinity, chloride, and density relationships in ion-enriched Onondaga Lake, NY. Water, Air and Soil Poll. 27: 169-180.

Effler, S.W. and K.A. Whitehead. 1995. Tributaries and discharges (Chapter 3). In S.W. Effler (ed.) Onondaga Lake: Lessons in limnology and engineering analysis. Springer-Verlag, NY. (in press).

HydroQual and PTI. 1994. Onondaga Lake RI/FS: Calcite Modeling Report. Prepared for Allied Signal Inc., Solvay, NY.

Lorenzen, C.T. 1967. Determination of chlorophyll and phaeopigments: spectrophotometric equations. Limnol. Oceanogr. 12: 343-346.

Owens, E.M. and S.W. Effler. 1995a. Hydrodynamics and transport (Chapter 4). In S.W. Effler (ed.), Onondaga Lake: Lessons in limnology and engineering analysis. Springer-Verlag, NY. (in press).

Owens, E.M. and S.W. Effler. 1995b. Forecasting impacts of a hypolimnetic wastewater discharge on lake stratification and mixing. Lake Reservoir Manag. (in review).

Walker, W.W. 1991. Compilation and review of Onondaga Lake water quality data. Submitted to Onondaga County Department of Drainage and Sanitation. Syracuse, NY.

Wetzel, R.G. 1983. Limnology. Saunders College Publishing. Philadelphia, PA

UPSTATE
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February 22, 1996

Mr. T. Larson
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Dear Mr Larson

This letter presents recommendations concerning the completion of the calcite analysis. Our analysis presented here, is based on: 1) a rather extensive set of reviews we have prepared, as part of the RI/FS process, 2) responses from AlliedSignal and HydroQual, and 3) recent research findings (that have been accepted for publication; refer to Table 1 for a listing of this material). Also attached you will find UFI's detailed comments on responses prepared by AlliedSignal's consultants concerning the limitations of Drainage and Sanitation (Onondaga County) data bases for dissolved oxygen, pH, total organic carbon (TIC) and calcium (Ca).

The Issues and Measurements Versus Model Simulations

The major issues of concern are: 1) what impact did the AlliedSignal operation (specifically, its ionic waste discharge) have on the precipitation/deposition of calcium carbonate (calcite) in Onondaga Lake (?), and 2) what impact does the residual ionic waste loading from this site (e.g., ~ 30% of the continuing total calcium loading to the lake (Effler et al. 1996)) continue to have on calcite deposition? The first issue has been definatively quantified by Womble et al. (1996; see Table 1), based on analysis of sediment trap collections over a 10 year period extending from pre- to post-closure of the facility. **The Womble et al. (1996) analysis is the primary representation of the AlliedSignal impact on calcite deposition during the operation of the facility compared to post-closure** (includes residual impacts) **conditions**. It also represents the primary basis for testing water quality models that are designed to simulate calcite deposition. The modeling process should not be allowed to be turned "inside-out", e.g., model simulations should **never** become the primary basis to quantify the change in deposition that has been associated with the closure of the

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TABLE 1: Correspondence and manuscripts related to calcite RI/FS issue.

Item No.	Description
1	letter to R. Mustico (NYSDEC) from UFI of **April 27, 1995**: Review of HydroQual's "Onondaga Lake RI/FS: Calcite Modeling Report", with attachments
2.*	letter to HydroQual from UFI of **July 25, 1995**: Review of HydroQual's Modeling Analysis for Onondaga Lake, Deep-Water Discharge of METRO: No. 1, Problems with Supporting Data from Onondaga County's Monitoring Program
3.*	letter to HydroQual from UFI of **October 2, 1995**: Review and Evaluation of HydroQual's Modeling Analysis of the Deep-Water Discharge Management Option for METRO, Hydrodynamic Evaluation of the METRO Outfall Relocation in Onondaga Lake (with enclosure)
4.	letter to Richard A. Mustico (NYSDEC) from Walter O. Shepard (Allied Signal) of **November 14, 1995**: Summary of Comments (PTI, CDR, and HydroQual) on Review of UFI Reports (Phosphorus, and pH, and short-comings of Onondaga County data)
5.	letter from HydroQual to UFI of **December 27, 1995**: Responses to Items 2 and 3, above
6.	letter to T. Larson (NYSDEC) from UFI of **January 16, 1996**: Summary of the status of testing of HydroQual eutrophication/calcite model testing from the perspective of the limitations of the Onondaga County monitoring program
	letter to HydroQual from UFI of **January 24, 1996** (Communication No. 3): Comments on HydroQual's Responses (and Allied Signals; Items 4 and 5, above) to UFI's Evaluation of HydroQual's of METRO Outfall ...., and Additional Analyses of Related Topics (with enclosure)
8.	letter to HydroQual from UFI of **January 24, 1996** (Communication No. 4): Review of HydroQual's Phosphorus Loading Estimates and Associated Protocols, and Comments on HydroQual (and Allied Signal; Items 4 and 5 above) Responses Concerning UFI's Analysis of the Phosphorus Data Base of Onondaga County (with enclosure)
9	letter to T. Larson (NYSDEC) from UFI of **January 29, 1996**: Summary of status of transport framework of HydroQual dynamic calcite models, and expansion of review of Onondaga County data base for lake.
10.*	letter to HydroQual from UFI of **February 23, 1996** (Communication No. 5): Comments on HydroQual Responses (and Allied Signal; Items 4 and 5 above) concerning DO, pH, TIC and calcium
11.	Womble, R.N., Driscoll, C.T., and Effler, S.W. 1996. Calcium carbonate deposition in Ca^{2+} polluted Onondaga Lake, New York, U.S.A. Water Research (in press)
12.	Effler, S.W., Perkins, M.G., Whitehead, K.A., and Romanowicz, E.A. 1996. Ionic inputs to Onondaga Lake: origins, character, and changes. Lake and Reservoir Management (in press)

prepartion of these letters was not funded within the RI/FS

facility. However, a credible water quality model is necessary to evaluate the impact of residual loading of ionic waste on future deposition of calcite in the lake. For example, a "linear-type" extension of the observed impact from closure (Womble et al. 1996) to a scenario of elimination of the residual ionic waste loading - is almost certainly open to legitimate scientific challenge.

The HydroQual Calcite Models

HydroQual has developed a highly innovative approach for the calculation and simulation of calcium carbonate (solid phase; $CaCO_{3(s)}$) precipitation in Onondaga Lake. They are to be commended for these efforts. Three different mechanistic models have been developed by HydroQual to address the issue, representing a wide range in model complexity. These include a simple steady-state completely-mixed framework, a dynamic (seasonal) model that includes stratification/hydrodynamics, and the most complex, a dynamic coupled eutrophication (including sediments) calcite precipitation model. From a management perspective, the rule of thumb is - the simplest model that provides the necessary simulation capability, with credibility, is the appropriate choice. Model credibility must be demonstrated to establish management utility. Accurate data and representative process information are important to both drive and test (i.e., establish credibility) any mechanistic model. These areas are the limitations of the calcite modeling effort by HydroQual. The more complex the model the greater the demands (e.g., number of parameters for which accurate measurements are necessary, processes that need to be quantified, etc.) for supporting data and process studies.

The dynamic models unfortunately misrepresent fundamental transport processes in the lake (letters to R. Mustico from UFI of April 27, 1995, and to T. Larson from UFI of January 29, 1996). For example, an inappropriate large fraction of the Ninemile Creek inflow, and the METRO discharge for the 1981-1985 interval, is routed to the hypolimnion of the lake throughout the year. The important seasonality of plunging of the dense inflows is not represented. Outflow from the hypolimnion is incorrectly assumed. These errors are inexplicable, as the unusual transport characteristics of this lake had been well documented in the peer-reviewed literature before the initiation of the RI/FS process. Further, the errors are clearly inconsistent with monitoring data collected for the system.

The role of AlliedSignal cooling water operation in cycling various important constituents within the lake has not been explicitly incorporated in HydroQual's dynamic models (see letter to T. Larson from UFI of January 16, 1996). The use of the lake's hypolimnion as a source of cooling water by AlliedSignal resulted in the net transfer of water to the epilimnion. This may have had important water quality implications during the facility's operation. It seems unlikely that AlliedSignal's

consultants will modify the existing model frameworks to comprehensively accommodate the cooling water operation.

Limitations of the Onondaga County Data Base

Onondaga County (D&S) data have been utilized to support much of HydroQual's modeling efforts. From the outset, UFI has been concerned with the use of D&S data to support the testing of the HydroQual models (e.g., letter to R. Mustico of April 27, 1995, Table 1). We have voiced these concerns within the RI/FS process, and independently with HydroQual as part of its public domain work for the County (see items of Table 1). Walker (1991) identified numerous problems within D&S's data base, from the perspective of long-term trend analysis. UFI has identified a number of additional data quality problems, within the context of the use of these data for the mechanistic modeling applications of HydroQual. For example, a eutrophication model (i.e., the most complex calcite model) can not be rigorously tested for Onondaga Lake for the 1970-1990 period because of the lack of appropriate and reliable phosphorus concentration data for the lake and its inputs for much of that interval (see letter to T. Larson from UFI of Janaury 16, 1996, Table 1). Other data quality problems have emerged in UFI's review (letters to R. Mustico April 27, 1995, T. Larson January 16 and January 29, 1995, and attachment to this letter).

In the letter of January 29, 1996 to you, UFI reported "inconsistencies" in data originally reported by D&S versus data incorporated in the Walker data base. UFI recommended, that unless this situation can be completely resolved/explained, D&S data other than from a "primary source" should not be used to support model testing.

The primary parameters necessary to support the simple steady-state completely-mixed model are pH, alkalinity, total inorganic carbon (TIC), and calcium (Ca). There appears to be few concerns with the alkalinity data for the upper waters, as the measurements from the two programs track each other (particularly within the lake's upper layers). It is fair to assume these data are accurate and representative of conditions that have occurred in the lake. However, we have concerns over the accuracy of the other measurements (pH, TIC, Ca), (see attachment to this letter). Based on preliminary analyses for the upper waters we are optimistic that a reasonably "quality-assured" data set can be developed to support the steady-state model for some portion of the 1970-1990 period presently being addressed by HydroQual. Related recommendations are presented subsequently.

We are comfortable with positions we have previously taken with regards to data quality problems, and related implications for model testing, as described in the documents of Table 1. We would welcome additional independent external review of these technical issues if it were deemed necessary by NYSDEC.

Recommendations

a **Model Selection**

The only reasonable choice of the three HydroQual models is the simple steady-state completely-mixed model. Fundamental short- comings eliminate the other two, including: 1) errors in representation of transport, 2) failure to explicitly accommodate the effects of cooling water recycle, and 3) lack of adequate data to rigorously test the eutrophication model (the most complex of the three models). The steady-state completely-mixed model does not suffer from any of these short-comings. It is important that you understand that the dynamic models, particularly the most complex model that incorporates eutrophication, may have additional short-comings not yet identified, as our review to data has largely focused on the quality of supporting data and the transport framework(s).

b. **Period of Model Testing**

The lack of tributary TIC data limits the model testing period to after 1982. Deposition data for calcium carbonate exist for 1980, 1981, 1985-1992 to support calibration. But the absence of trap data for the 1982-1984 interval should not be considered a major problem, as the available data support the position that the downward flux (e.g., on a summer average basis) was rather uniform before closure of the AlliedSignal facility. An additional constraint on the years included in model testing is the availability of quality data. A related recommendation follows.

c. **Development of Quality-Assured Data Set**

It is critical that a "quality-assured" data set of pH, calcium, alkalinity, and inorganic carbon be developed to support testing of the simple steady-state completely-mixed calcite model. The data set should include internally consistent measurements of pH, alkalinity and inorganic carbon concentrations. Development of this data set will require a year-by-year evaluation of water chemistry values, including examination of sampling and analytical procedures. UFI has initiated this process, on a limited basis (e.g., surface waters for three selected years), in its most recent communication to HydroQual, using chemical equilibrium calculations. Calcium data should be evaluated for consistency, based on the rather uniform ratios that are manufactured with other major ions (e.g., chloride) in this system, and within the context of charge balance calculations. Ideally, the development of a quality assured data set for these parameters would be conducted involving personnel from UFI and D&S, who were involved with these monitoring programs. It is important to note that the model cannot be credibly applied (from which reliable conclusions can be drawn) without quality-assured data, for the case of hindcasting, or a defensible/consistent array of parameter values

for scenario forecasting.

d. **Field/Laboratory Studies**

A limited field/laboratory study program (e.g., 1996) would greatly enhance the credibility/management value of the calcite model. The associated costs would be relatively minor. Three components are recommended.

1. An investigation of error in the measurement of pH in Onondaga Lake - the study should include closed-cell measurements of pH, as well as traditional field and laboratory measurements using procedures previously followed by UFI and D&S.

2. partitioning dissolved and particulate concentrations of alkalinity, inorganic carbon, and calcium - which will support testing of theoretical calculations presently made within the calcite model.

3 analysis of sediment trap collections for calcium carbonate - that together with watercolumn concentrations, will support independent determination of the settling velocity of calcium carbonate, an important model coefficient.

Please feel free to contact me with any questions you may have concerning the contents of this letter, and for more specifics related to the recommendations.

Sincerely,

S.W. Effler, Ph.D.
Director of Research

and

C.T. Driscoll, Ph.D.
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cc: J. Bloomfield
J. Davis
E. Garvey

ATTACHMENT - DETAILED COMMENTS

Dissolved Oxygen

The extent of the limitations of dissolved oxygen (DO) data collected by D&S is not acknowledged in HydroQual's response to the UFI letter of July 25, 1995. Walker (1991 reported negative bias for the epilimnion and positive bias for the hypolimnion for the 1976-1981 period, as indicated in UFI's letter of July 25, 1995. HydroQual indicates its agreement with the assessment for the hypolimnion data "We agree with Dr. Walker's assessment of the hypolimnetic data ..." p.4 HydroQual response of December 27, 1995, to UFI letter of July 25, 1995), but does not comment on the epilimnetic data. HydroQual indicates Walker (1991) flagged the 1978-1981 DO data as suspect, but Walker (1991 actually rejected all D&S lake data over the 1976-1981 interval HydroQual only excluded the D&S DO data from 1977 through 1981 in their calibration analysis. We see no justification for using the 1976 data, in light of Walker's (1991) recommendation. As noted by HydroQual (response of December 27, 1995) and Walker (1991), other less severe short-comings have been identified for other years. Moreover we see no justification for HydroQual's deletion of the high DO observation (~ 20 $mg \cdot L^{-1}$ of August 1970, as UFI has measured such high concentrations during severe phytoplankton blooms

HydroQual's argument that lower epilimnetic concentrations before 1976 (and before the upgrade of METRO, secondary and P removal are consistent with the higher METRO BOD loading during that period is not defensible. HydroQual's position is supported

only if the oxygen demand associated with higher BOD discharge is accurately quantified within the context of the other source and sink processes in the lake. The lake DO model of Gelda and (1996) indicates that the BOD sink for DO in the epilimnion is insignificant for the period after 1988. We don't discount the oxgyen sinks were larger before the METRO upgrade, but can hardly be considered a compelling argument for the reported lower epilimnetic DO concentrations. We expect this effect would be difficult to resolve from field data, particularly in light of the magnitude and frequency of variations in other DO source/sink (e.g., phytoplankton) processes relative to the sampling frequency of the D&S program

HydroQual has taken exception with what they call "methodology for dismissing the data collected by D&S for a specific water quality parameter by identifying a problem in the data for a few specific years and then suggesting that the entire 21 year record is therefore questionable or invalid". (p.1 HydroQual's response of December 27, 1995 to UFI's letter of 25, 1995) We strongly believe that as a user of D&S's data HydroQual must accept some level of responsibility for the veracity of this information set. HydroQual is using D&S dat evaluate issues that have not been a focus of attention by D&S personnel (e.g., Ca, TIC, pH). Many measurements in the data set have not been rigorously evaluated for applications that HydroQual are conducting. It is essential that (to the extent possible) the problems of assessing the behavior and performance of complex models not be compounded by issues of data quality

six consecutive years (1976-1981 the D&S's DO data are not usable, more minor problems persisted in most of the other years The magnitude of these deficiencies legitimately raises questions about the acceptability of earlier DO data to support model testing. Under such circumstances, compelling data/arguments are required to (not reject adopt the D&S 1970s DO data as a basis evaluating the performance of the eutrophication model The absence of contrary DO data before 1976, the alluded to (but not quantified) BOD loading/in-lake DO relationship, and the use of the Winkler titration method (collection of representative samples can be difficult where disequilibrium is common or prevails), are far from compelling arguments to accept these DO data as a basis to evaluate model performance

pH

HydroQual indicates in its December 27, 1995 response (p.6) to the UFI letter of July 25, 1995, that "pH data, together with calcium, alkalinity and TIC data, were used to back-estimate solid phase calcium carbonate for calibration purposes. If there serious errors in the pH data, then the back-estimated calcite concentrations would also be error" How could such an error be detected in the absence of watercolumn measurements of solid phase $CaCO_3$ measurements? We presume the answer is calibration to downward flux rates of $CaCO_3$

We believe that pH is one of the two most important measurements in the assessment of the impact of ionic waste discharged by AlliedSignal to Onondaga Lake the direct measurement of $CaCO_3$ deposition being the other; Womble et al

1996). As a result, it is critical that HydroQual: 1 fully understand the uncertainty and limitations of pH measurements and, 2) quantify the effects of uncertainty in pH on model calculations. We believe that model calculations of the distribution of alkalinity and inorganic carbon between dissolved and particulate phases, and subsequent predictions of calcite deposition are very sensitive to pH. HydroQual should quantify model uncertainty to pH and assess this uncertainty within the context of limitations in pH measurements for the lake

HydroQual's justification for not rejecting the D&S pH data for the epilimnion for the interval 1979-1981 is weak Hypolimnetic pH data were identified as suspect for that interval by Walker (1991). Thus selected observations from profiles collected by D&S during this interval were considered acceptable by HydroQual, but observations from the hypolimnion made on the same profiles with the same pH meter were rejected by HydroQual HydroQual indicates the UFI data were not considered because of the lack of QA/QC information, but Walker (1991 reviewed sampling, analytical and quality assurance protocols including UFI program) in his analysis. If HydroQual was unsatisfied with those descriptions, the original investigators could have been approached to obtain this information.

We noted what continues to be a systematic discrepancy in the adjusted pH values by UFI and measurements by D&S for profiles plotted by HydroQual (see Figures 11 and 12 - in letter from HydroQual dated December 27, 1995) This discrepancy should be evaluated

a. Effect of Diurnal Variations

A change of focus is noted in the discussion of pH in letters of AlliedSignal (November 15, 1995) and HydroQual (December 27, 1995), related to the potential effects of natural diurnal variations on pH records for the lake. This issue is a major point of emphasis in the AlliedSignal letter ~ 2 pages), but essentially not addressed in the HydroQual letter thrust of the AlliedSignal letter on this issue appears to be that this process may explain systematic differences (e.g., extended periods) in two different (e.g., D&S and UFI) data sets for the lake. Results from other lakes are referred to ("Times series studies of other lakes show that the daily cycle of photosynthesis and respiration can change the pH by 2 units on a diurnal basis" p.5, AlliedSignal letter of November 15, 1995), but no citation(s) are presented Indeed, diurnal variations in pH are widely reported in the literature (e.g Crumpton Isenhart 1988, Talling 1974, Verdium 1960). "The magnitude of the diurnal variations in pH are expected to be greatest on days of peak photosynthetic rate and minimum surface turbulence e.g clear calm day during a phytoplankton bloom) (p.5-59, State of Lake"

UFI has published the approximate time of pH sampling in it's monitoring of Onondaga Lake (e.g., Brooks and Effler 1990, "State of Lake"); about ~ 1000 hr ± 1 hr AlliedSignal (letter of November 15, 1995) gives no indication of this consideration, or the sampling time adopted by D&S. We are surprised of omission, since it is critical to an evaluation of this issue,

and since HydroQual is a consultant to both Onondaga County and Allied Signal. You should find that D&S monitoring is conducted at approximately the same time of day as the sampling by UFI. A systematic discrepancy, that might be expected if samples were collected by the two programs at very different times of day, is not a factor in the comparison of the D&S and UFI data. Thus the observed extraordinary interannual variations in the D&S pH data base for the upper waters for the 1968-1991 period (Figures 1 cannot be attributed to "diurnal effects" because an approximately uniform time of day for lake monitoring has been used

UFI has indicated that the time of day of its monitoring would cause only slight bias in reflecting daily average pH ("State of the Lake", p.5-59; from daily average H^+ concentration). Recently collected (unpublished) pH data, based on hourly measurements made over several weeks, support this observation (Figure 2). Measurements were made in situ with a Hydrolab SONDE (operated and calibrated according to the manufacturer for the April to late June and early October to early December intervals of 1994. The amplitudes of the pH variations at a depth of 1 m were substantially less than the 2 pH unit upper bound described in the AlliedSignal letter of November 14, 1995 and were attenuated at a depth of 4 m (Figure 3 Significant diurnal variations are limited to the upper mixed layer. Thus diurnal effects/time of day of monitoring cannot explain the large interannual variations in pH indicated by the County data base for lower layers of the lake (Figure 4).

b. Internal Consistency, pH/Alkalinity/TIC (DIC) Data

The existing measurements of pH, alkalinity and TIC should have been evaluated for internal consistency, using mass law mass balance equations (e.g., Stumm and Morgan 1996) For example, if pH and alkalinity are known, concentrations of and DIC can be calculated (e.g. Driscoll et al. 1994 To illustrate this approach we present here an analysis of internal consistency for the upper waters of the lake for three selected years, 1980, 1988, and 1989. No claim is made that these cases are representative of the entire D&S/UFI data bases. Rather, we believe these analyses provide valuable insight, and must be conducted on all data sets to ensure that an internally consistent quality assured data set is available to evaluate the performance of the calcite model Our analysis assumes alkalinity is in a strictly dissolved form. This assumption is probably imperfect, however, the potential contribution from $CaCO_3$ particles is in general small. For example, PIC was < 5% of DIC in the upper waters of the lake in 1989 (unpublished data, UFI).

Seasonal patterns of alkalinity, pH, inorganic carbon (TIC, DIC) and CO_2 % saturation) for the D&S and UFI data bases are compared in Figures 5, 6, 7, and 8. The trends in alkalinity the two data sets match well (Figure 5), suggesting these data are of generally high quality. The agreement in pH values differs substantially between the three years (Figure 6; also see Figure 1 In 1980 pH values measured by D&S tended to be somewhat higher than the UFI laboratory measurements, and distinctly

higher than the UFI data after adjusting laboratory measurements for field conditions (Figure 6a). The D&S pH values were markedly lower than UFI's laboratory measurements in 1988, and remained much lower than the adjusted values for that year (Figure 6b). In contrast to the other two years, the D&S and UFI pH trends agreed reasonably well for 1989 (Figure 6c).

Clear inconsistencies in the D&S TIC data emerge from this analysis for 1980 (Figure 7a) and 1988 (Figure 7b). In particular, D&S TIC data were substantially less than DIC concentrations calculated from either the UFI or D&S data on a number of occasions in these two years (also see Figure 9a and b). These differences cannot be explained by the **potential** contribution of the modest quantities of $CaCO_3$ to the alkalinity measurements. This suggest that the D&S TIC data are false low for at least these occasions. Perhaps degasing of CO_2 contributed, or perhaps there are inaccuracies/limitations in the unspecified sampling procedures, holding time, and analytical procedures. In contrast, the internal consistency indicated for the 1989 data sets indicates these data may be acceptable to support model testing. Differences in the calculated DIC values for the two data sets are an outcome of the differences in pH (Figure 6).

Calculated concentrations of CO_2 (from pH and alkalinity) in the upper waters of Onondaga Lake depict conditions of oversaturation with respect to atmospheric values for almost the entire monitoring period of all three years, based on both the D&S and UFI (adjusted pH values used) data bases (Figure 8). The

average percent saturation values calculated for May-September interval for each of the three years from the two data bases are presented in Table 1. Wide variations emerge

TABLE 1: Average percent CO_2 saturation for the May-September interval, UFI and D&S data bases, upper waters of Onondaga Lake

Year	% CO_2 saturation D&S	UFI+
1980	196	921
1988	1618	443
1989	552	493

+ adjusted field pH values, according to $pH_{lab} = 0.718 \cdot pH_{field} + 2.349$

between these years (Figure 8, Table 1), according to the data base, driven largely by differences in pH conditions differences between 1980 and 1988, based on D&S data (a factor of about 8 , are probably unrealistic What phenomena could explain changes of this magnitude? Similarly, what phenomena could explain the reduction by a factor of more than 3 from 1988 to 1989, indicated by the D&S data Table 1)? These interannual variations are inconsistent with indicators of CO_2 metabolism for the lake (e.g., primary production; "State of Onondaga Lake", measurements of organic and inorganic carbon deposition in sediment traps; Womble 1995 (M.S. Thesis)) Note that interannual variations indicated for the UFI data Table 1 are smaller, and that the D&S and UFI tend to converge for 1989.

We restricted our preliminary analysis of internal consistency in measurements of alkalinity, pH and TIC to the upper waters of Onondaga Lake. The analysis should be extended

to the lower waters. Unfortunately, the lower water have additional problems. Elevated concentrations of sulfide in lower waters may oxidize in sample bottles following collection This phenomenon will result in the production of strong acids resulting in an error in measured values of alkalinity. This problem may eventually preclude use of the hypolimnetic data in the analysis of changes in calcite deposition. In any event analysis should be conducted in the lower waters to investigate if the data set is suitable for use in this assessment

HydroQual made an effort to emphasize the similarity of D&S and UFI data sets in their Figures 17 and 18. The scaling of the plots and the numerous years included tend to mask the differences. As demonstrated above, substantial differences prevailed in pH and inorganic carbon concentrations in some of the years. Further, HydroQual has presented the calculated DIC results of Driscoll et al. (1994) as TIC. If HydroQual calculated DIC/TIC from D&S pH and alkalinities, the above inconsistencies would have been recognized

HydroQual has implied that the differences reported for in the lake surface waters by D&S and Driscoll et al. 1994 over the 1980-1990 interval (HydroQual's Figure 17 are attributable to the difference between field and laboratory methods. This is a misrepresentation, as the differences are greater than can be explained by these methods. Further, the strong interannual variations in pH (HydroQual's Figure 17 of December 27, 1995 response; also see Figures 1 and 2 of UFI letter of July 25, 1995), and the long-term trend in pH, based on D&S data remain

unexplained.

c. pH Buffering

UFI has indicated that, Onondaga Lake is a relatively well-buffered system (e.g., Driscoll et al. 1994, "State of Onondaga Lake" 1994 We see nothing in HydroQual's presentation that argues against that position. In fact HydroQual seems to agree, e.g., "The high alkalinity of the water in Onondaga Lake 2.2 to 3.9 meq/L) indicates that it is more strongly buffered than many lakes". (p.8, HydroQual letter of December 27, 1995 to UFI). Further, UFI does not disagree that the extremely high productivity conditions in the lake can (and do) result in substantial seasonal (e.g., Effler et al. 1990, Effler and Driscoll 1985) and diurnal (Figures 2 and 3 variations in pH Additionally, the detailed temporal structure of pH can vary year-to-year associated with interannual variations in the timing of phytoplankton blooms (e.g., "State of Lake" 1994). However, "average" (or median) pH values tend to remain relatively uniform (e.g., compared to the unrealistic interannual variations indicated in the pH data of D&S (Figure 1 year-to-year in this relatively well buffered system. It remains that the interannual variations in pH reported by D&S (Figure 1 are unrealistic and inconsistent with the relatively well-buffered character of this lake. Further, the structure indicated in the D&S data (Figure 1 is inconsistent with indicators of primary production over the same period "State of Lake" 1994).

d. Calcite Equilibrium Conditions

AlliedSignal's comments concerning the inconsistency of D&S

pH data with calcite equilibrium conditions (p.13 of November 1995 letter) fail to address the real issue. UFI and co-workers have found the upper waters of the lake to be oversaturated with respect to the solubility of calcite throughout the spring to fall interval of all monitored years before and after closure of the AlliedSignal (e.g., Driscoll et al. 1994, Effler and Driscoll 1985, "State of Lake" 1994) The results of equilibrium condition calculations with D&S data differ greatly Undersaturated conditions are indicated for at least 1983, 1984, 1995, and 1986 (see Driscoll et al. 1994 for description of calculations), and for rather extended periods for the first 3 of these years As indicated by Doerr and Effler (1994), these undersaturated conditions are inconsistent with the deposition of $CaCO_3$ documented throughout the spring to fall interval of 1985 ("State of Lake" 1994, Womble et al 1996). The pH/undersaturated calcite equilibrium conditions associated with the D&S data base become even more incongruent when considered within the context of deposition results (Womble et al. 1996 and equilibrium conditions that prevail in other years (e.g., before and after the 1983-1986 interval). Similar (e.g., oversaturated) calcite equilibrium conditions are calculated for UFI and data sets for the upper waters for 1980 and 1981 because pH values were similar. The average rates of downward flux of $CaCO_3$ in the lake were very similar in 1980, 1981, and 1985 (Womble et al. 1996) The undersaturated conditions, driven by uncertain D&S pH values, remain highly inconsistent for 1985. The low pH values in the other 3 years are likely in error, based on

considerations of calcite equilibrium conditions.

Calcium and

HydroQual's acceptance of the D&S calcium and TIC data, and related responses (letter of December 27 1995), appears inconsistent with the position established elsewhere in their response concerning pH, and also expressed in the AlliedSignal letter of November 14, 1995. Both HydroQual and AlliedSignal expressed great concern about the omission of descriptions of sampling and analytical protocols for pH. These procedures were not repeated in the analysis of Doerr and Effler (1994), as they appeared in Walker's 1991 analysis. The unfortunate omission in Walker 1991 was the UFI protocol for calibration of the HYDROLAB for field measurements (according to the manufacturer Yet HydroQual has not expressed similar concern for the lack of quality analysis of the calcium and TIC data, though HydroQual considers these parameters to be primary (p.6, HydroQual letter of December 27) Can HydroQual/AlliedSignal provide QA/QC information for the D&S measurements of calcium and TIC e.g., method, instrumentation, identity of laboratory, sample handling, performance characteristics

Other inconsistencies appear, or are implied, in the HydroQual response. HydroQual has expressed great concern over the implications of degasing of CO_2 for pH measurements, yet no discussion has been provided on the influence of this same phenomenon on TIC measurements Frankly, we're somewhat concerned with HydroQual's lack of understanding of this critical analysis; e.g., on p.15, paragraph 4, lines 4 and 5, HydroQual

indicates the D&S TIC measurements were made in the field "The D&S pH and TIC data are as measured in the field, "). The D&S TIC analyses were laboratory measurements. Total inorganic carbon is in general a laboratory measurement. The inconsistencies in the D&S data base for DIC/TIC identified in the examples evaluated earlier in the pH section establish the need for a careful QA/QC analysis of the entire D&S TIC data base. These example analyses of data consistency support UFI's earlier statement related to this parameter, "Drainage and Sanitation's TIC data base for both the lake and the inputs should be considered suspect until it is subjected to detailed quality assurance analysis, item No. 9, UFI letter of July 25, 1995 to HydroQual). Contrary to HydroQual's statement (p.15 paragraph 3, last sentence), the D&S data should be accepted only as an outcome of a rigorous evaluation of the internal consistency of pH, alkalinity and TIC data. Based on the inconsistencies identified earlier, that draw into question the D&S TIC data, HydroQual's position on the TIC data "It seems reasonable to conclude, in the absence of any opposing data, TIC data for earlier years are reasonable p.16, HydroQual letter to UFI of December 27, 1995) is not supported.

The near match of calcium concentrations presented in Driscoll et al. (1994) and by HydroQual (top panel, Figure 17, HydroQual response of December 27, 1995) for the 1980-1990 period is not a basis to accept earlier D&S data, particularly when change balance was violated in certain of the earlier years.

Years for which change balance cannot be demonstrated should not be accepted, unless there is compelling evidence that it is not associated with calcium measurements Ion ratios may also be valuable for a quality assurance analysis (e.g., Effler Whitehead 1994)

HydroQual did not respond to issues raised by UFI concerning the D&S Ca data base, based on charge balance calculations. calculations are routinely used in QA analyses of major ion data. There is an established history of problems with the D&S major ion data with respect to charge balance (e.g., Effler Whitehead 1994 Has HydroQual conducted such analyses on lake and tributary data sets? These are an essential component in the development of an acceptable data set for model testing.

References

Brooks, C.M., and Effler, S.W. 1990. The distribution of nitrogen species in polluted Onondaga Lake, N.Y., U.S.A. Water Air Soil Pollut. **52:** 247-262.

Crumpton, W.G., and Isenhart, T.M. 1988. Diurnal patterns of ammonia and unionized ammonia in streams receiving secondary treatment effluent. Bull. Environ. Contam. Toxicol. **40:** 539-544.

Doerr, S.M., and Effler, S.W. 1994. A comparative analysis of pH data for Onondaga Lake. Report submitted to NYSDEC, Albany, NY.

Driscoll, C.T., Effler, S.W., and Doerr, S.M. 1994. Changes in inorganic carbon chemistry and deposition of Onondaga Lake, New York. Environ. Sci. Technol. **28:** 1211-1218.

Effler, S.W., Brooks, C.M., Auer, M.T., and Doerr, S.M. 1990. Free ammonia in a polluted hypereutrophic, urban lake. Res. J. Water Pollut. Contr. Fed. **62L** 771-779.

Effler, S.W., and Driscoll, C.T. 1985. Calcium chemistry and deposition in ionically polluted Onondaga Lake, NY. Environ. Sci. Technol. **19:** 716-720.

Effler, S.W., and Whitehead, K.A. 1994. Tributaries and discharges (Chapter 3). State of Onondaga Lake, S.W. Effler (ed.), submitted to the Onondaga Lake Management Conference, Syracuse, NY.

Gelda, R.K., and Auer, M.T. 1996. Development and testing of a dissolved oxygen model for a hypereutrophic lake. Lake Reservoir Manage. (in press)

Stumm, W., and Morgan, J.J. 1996. Aquatic Chemistry (3rd Ed. John Wiley & Sons, New York.

Talling, J.F. 1974. Measurements on non-isolated communities: In standing waters. In R.A. Vollenweider (ed.), A Manual on Methods for Measuring Primary Production in Aquatic Environments, IBP Handbook No. 12, Blackwell Scientific, London.

Verduin, J. 1960. Phytoplankton communities in Western Lake Erie and the CO_2 and O_2 changes associated with them. Limnol. Oceanogr. **5:** 372-380.

Walker, W.W. 1991. Compilation and review of Onondaga Lake water quality data. Report submitted to Onondaga County, Syracuse, NY.

Figure Captions

Figure 2. Evaluation of the relationship between the daily average pH and the pH at 0930 hr within the upper waters of Onondaga Lake.

Figure 3. Percent occurrence of the amplitude of pH variation within individual days in the upper waters of Onondaga Lake: a) depth of 1 m, for 72 days, and b) depth of 4 m, for 58 days.

Figure 4. Long-term trends in pH in the near bottom (18m) waters of Onondaga Lake, according to the median observation: a) D&S, and b) UFI.

Figure 5. Comparison of temporal distributions of UFI and Onondaga County (D&S) alkalinity data for upper waters of Onondaga Lake: a) 1980, b) 1988, and c) 1989.

Figure 6. Comparison of temporal distributions of UFI and Onondaga County (D&S) pH data for upper waters of Onondaga Lake: a) 1980, b) 1988, and c) 1989. UFI adjust data based on analysis of Doerr and Effler (1994).

Figure 7 Comparison of the temporal distributions of UFI and Onondaga County estimates of DIC and County measurements of TIC for upper waters of Onondaga Lake: a) 1980, b) 1988, and c) 1989.

Figure 8. Comparison of the temporal distributions of percent saturation for CO_2, based UFI and Onondaga County programs, for the upper waters of Onondaga Lake: a) 1980, b) 1988, and c) 1989.

Figure 9. Distributions of the ratio TIC/DIC for D&S data from the surface waters of Onondaga Lake: a) 1980, b) 1988, c) 1989. DIC is calculated from paired pH and alkalinity data.

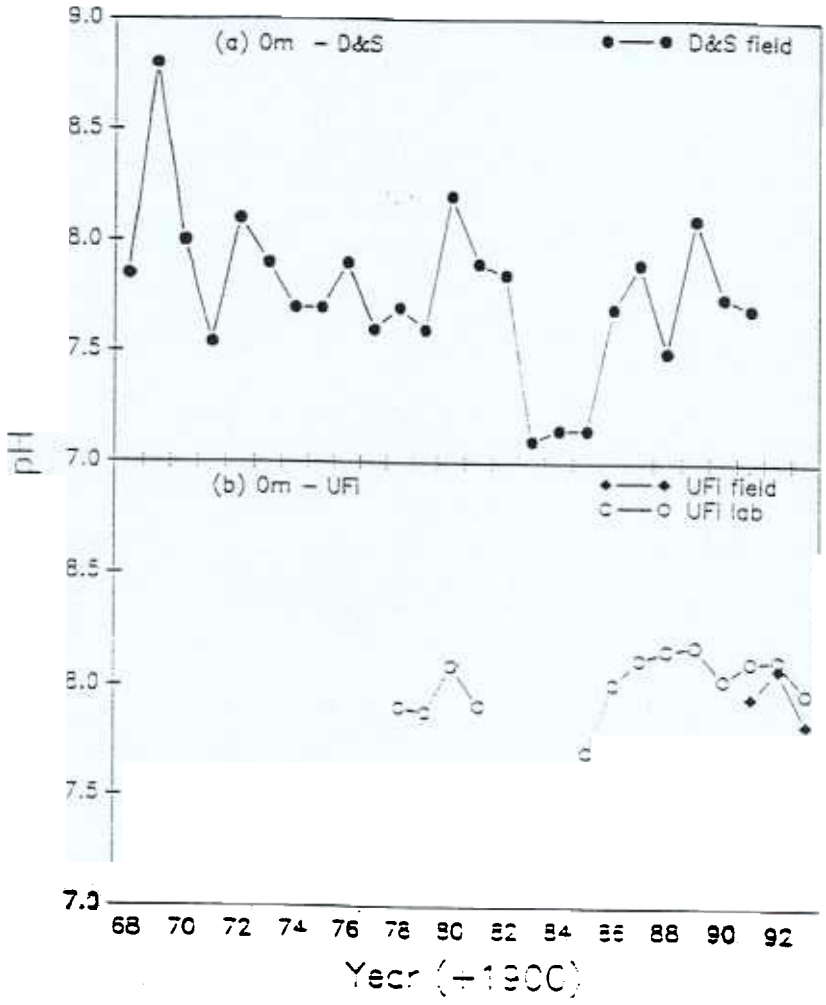
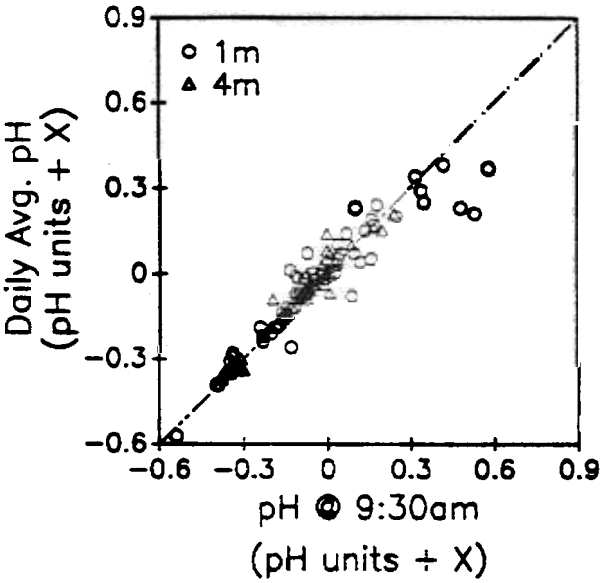


Figure 1. Long-term trends in pH in the surface waters of Onondaga Lake, according to the median observation: a) D&S, and b) UFI.



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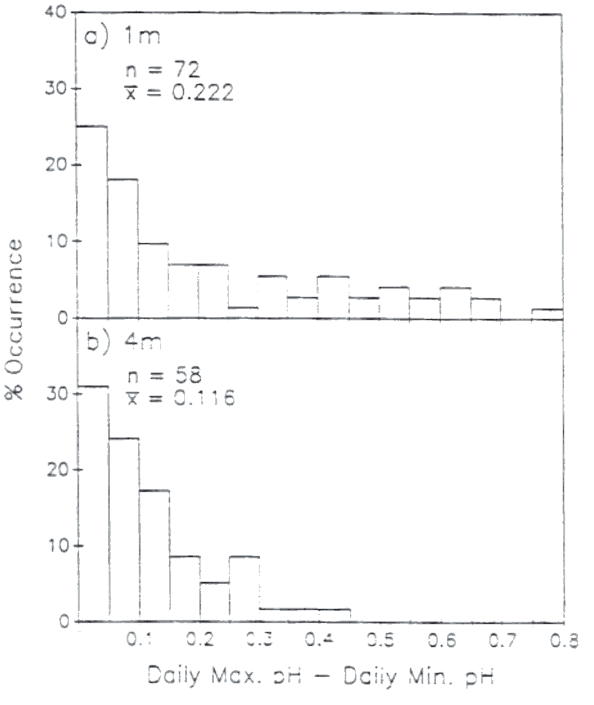

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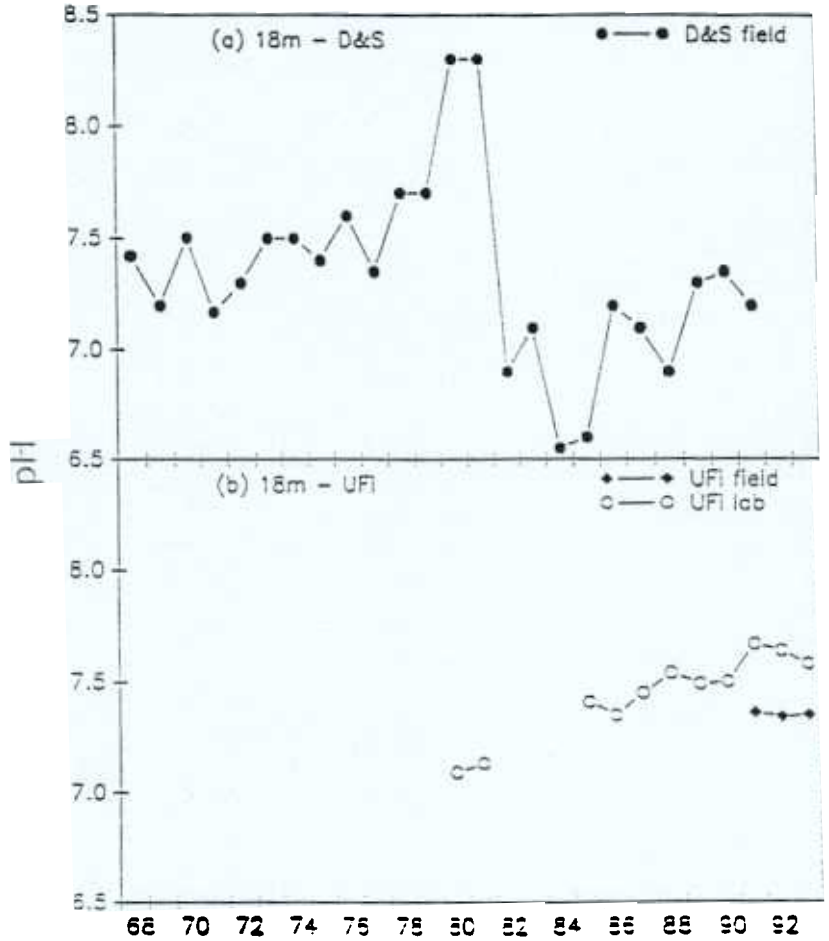

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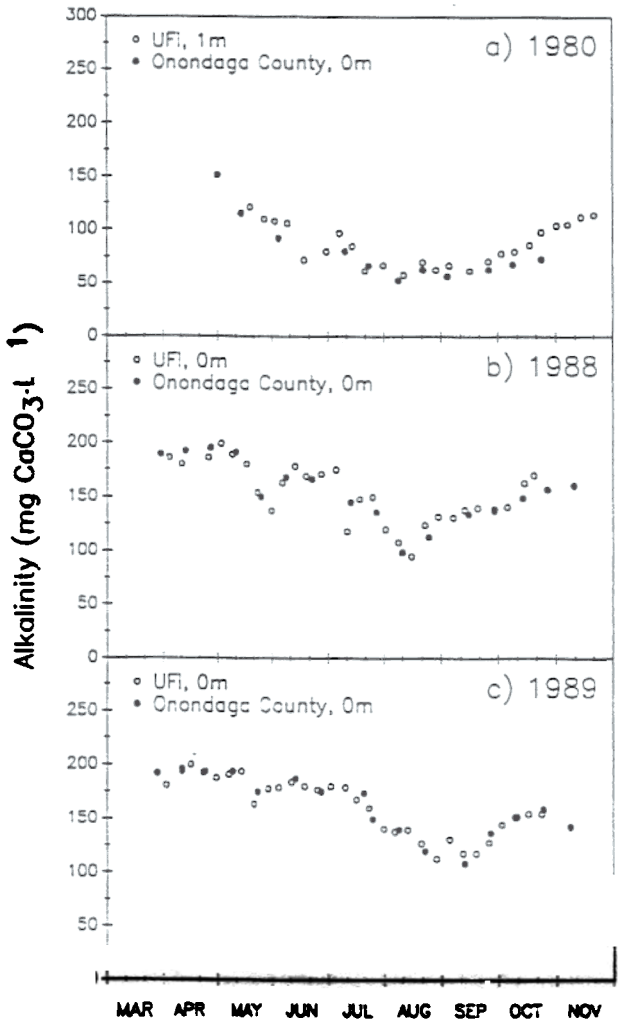
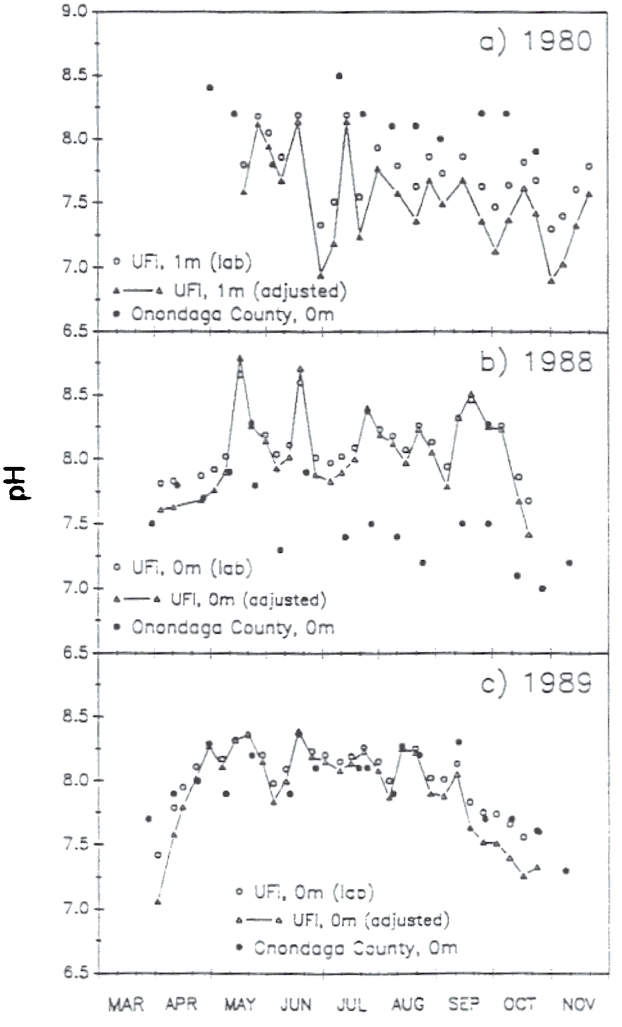


Figure 5 Comparison of temporal distributions of UFI and Onondaga County (D&S) alkalinity data for upper waters of Onondaga Lake: a) 1980, b) 1988, and c) 1989.



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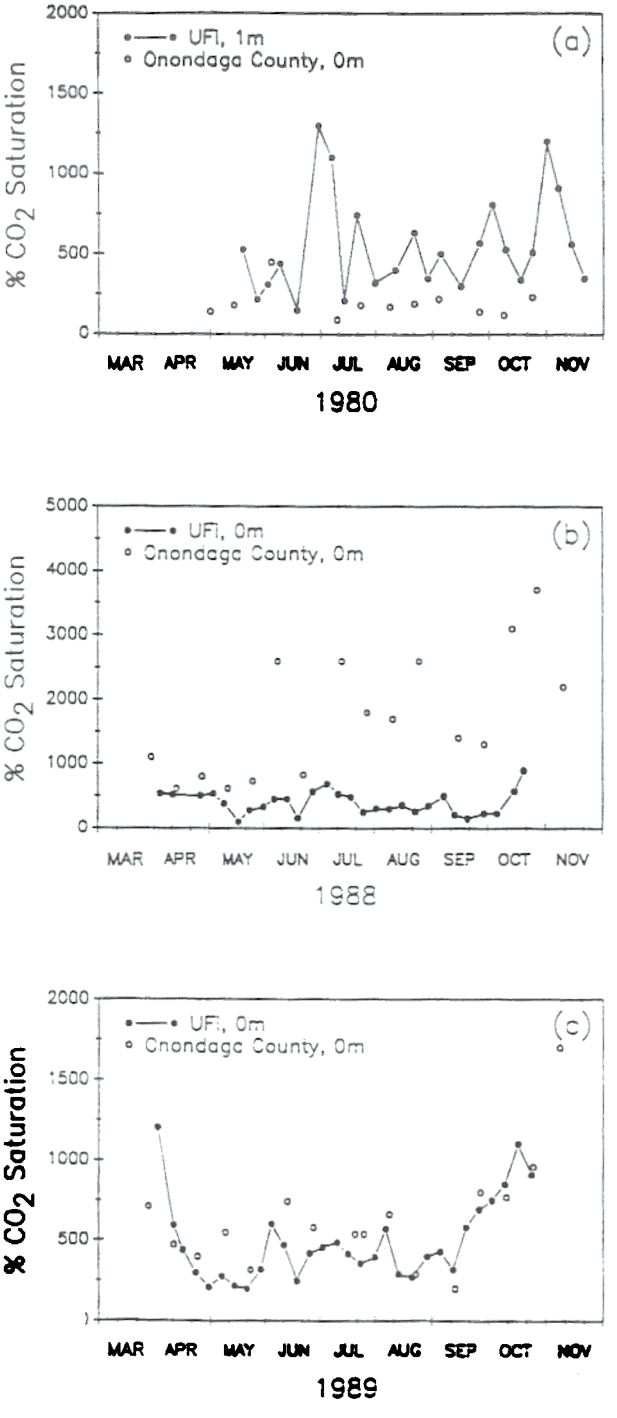

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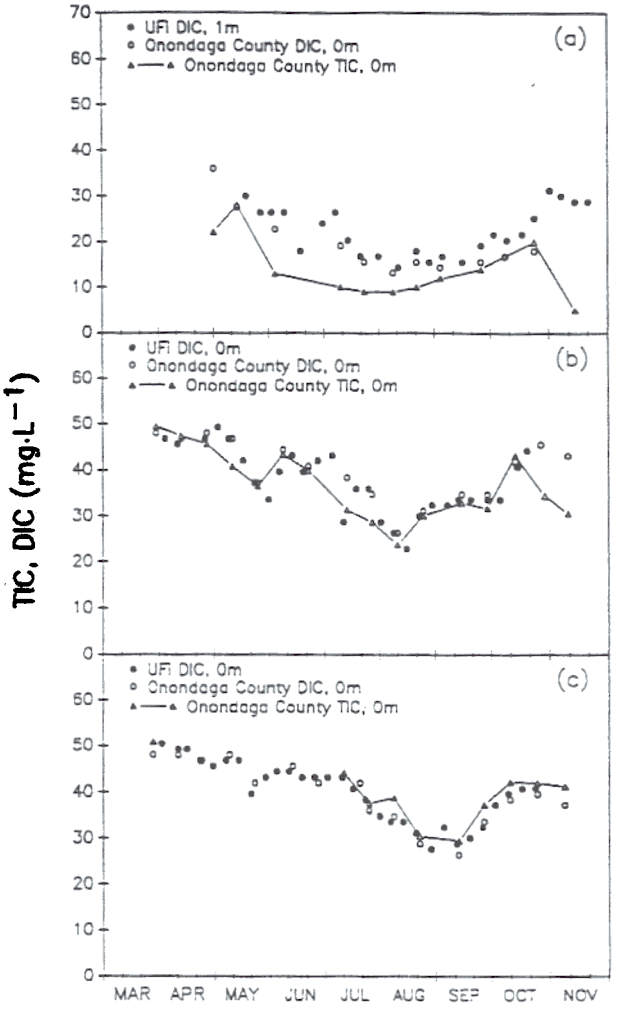

Figure 8. Comparison of the temporal distributions of percent saturation for CO_2, based UFI and Onondaga County programs, for the upper waters of Onondaga Lake: a) 1980, b) 1988, and c) 1989.

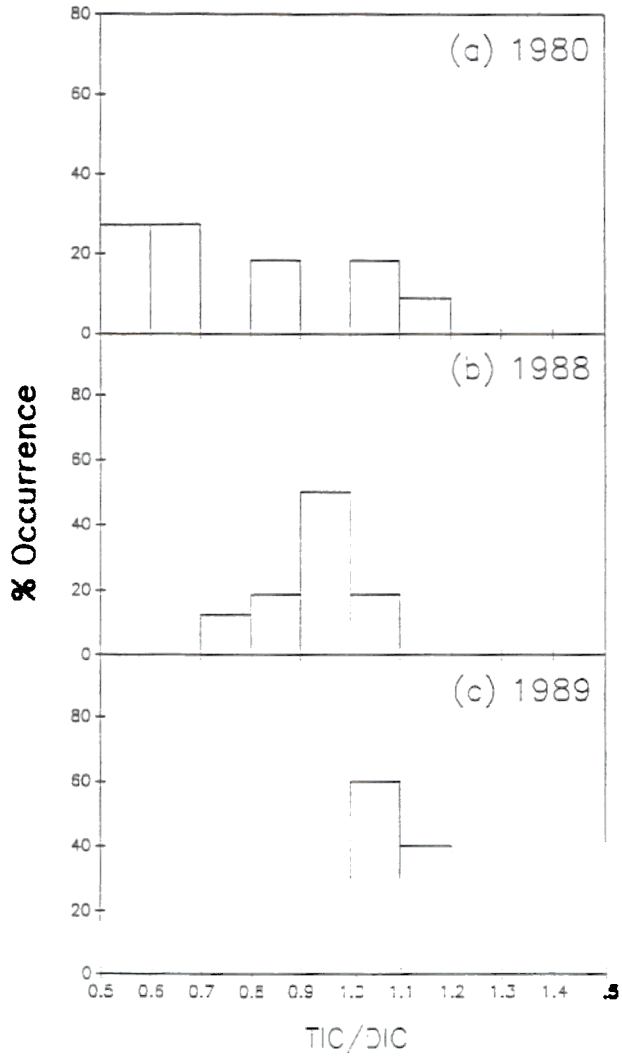

Figure 9. Distributions of the ratio TIC/DIC for D&S data from the surface waters of Onondaga Lake: a) 1980, b) 1988, c) 1989. DIC is calculated from paired pH and alkalinity data.

Bioavailability References

Bradford, M.E. and R.H. Peters. 1987. The relationship between chemically analyzed phosphorus fractions and bioavailable phosphorus. *Limnology and Oceanography* **32(5)**: 1124-1137.

Cowen, W.F. and G.F. Lee. 1976. Phosphorus availability in particulate materials transported by urban runoff. *Journal WPCF*. **48(3)**:580-591.

DePinto, J.V., 1982. An experimental apparatus for evaluating kinetics of available phosphorus release from aquatic particulates. *Water Res.* **16**:1065-1070.

DePinto, J.V., J.K. Edwald, M.S. Switzenbaum, and T.C. Young. 1980. Phosphorus removal in lower Great Lakes municipal treatment plants. EPA-600/2-8-117. WERL-Cincinnati.

DePinto, J.V., T.C. Young, and S.C. Martin. 1981. Algal-available phosphorus in suspended sediments from lower Great Lakes tributaries. *J. Great Lakes Res.* **7(3)**:311-325.

Dorich, R.A., D.W. Nelson, and L.E. Sommers. 1984. Algal availability of phosphorus in suspended stream sediments of varying particle size. *J. Environ. Qual.* **13(1)**:82-86.

Dorich, R.A., D.W. Nelson, and L.E. Sommers. 1985. Estimating algal available phosphorus in suspended sediments by chemical extraction. *J. Environ. Qual.* **14(3)**:400-404.

Ekholm, P., Markku Y-H., and P. Kylmälä. 1991. Availability of phosphorus in suspended sediments estimated by chemical extraction and bioassay. *Verh. Internat. Verein. Limnol.* **24**:2994-2998.

Furumai, H., and Ohgaki, S. 1982. Fractional composition of phosphorus forms in sediments related to release. *Water Science and Technology* **14**:215-226.

Hegemann, D. A., A. H. Johnson and J. D. Keenan. 1983. Determination of algal-available phosphorus on soil and sediment: a review and analysis. J. Environ. Qual. 12: 12 - 16.

Hieltjes, A.H.M. and L. Lijklema. 1980. Fractionation of inorganic phosphates in calcareous sediments. *J. Environ. Qual.* **9(3)**:405-407.

Logan, T.J., T.O. Oloya, and S.M. Yaksich. 1979. Phosphate characteristics and bioavailability of suspended sediments from streams draining into Lake Erie. *J. Great Lakes Res.* **5(2)**:112-123.

Martin, S.C., J.V. DePinto, and T.C. Young. 1985. Biological availability of sediment phosphorus inputs to the lower Great Lakes. US EPA, Environmental Research Laboratory, Duluth, MN, EPA/600/S3-84/100.

Pettersson, K., B. Boström, and O-S. Jacobsen. 1988. Phosphorus in sediments-speciation and analysis. *Hydrobiologia.* **170**:91-101.

Psenner, R., and Puckson, R. 1988. Phosphorus fractionation: advantages and limits of the method for the study of sediment P origins and interactions. *Archiv fur Hydrobiologie Beiheft Ergebnisse der Limnologie* **30**:43-59.

Sagher, A. 1976. Availability of soil runoff phosphorus to algae. Ph.D. Dissertation, University of Wisconsin-Madison. 176 pp.

Salisbury, D.K., J.V. DePinto and T.C. Young. 1984. Impact of algal-available phosphorus on Lake Erie water quality: mathematical modeling. Project Summary, USEPA-600 S3-84-027.

Williams, J.D.H., H. Shear, and R.L. Thomas. 1980. Availability to *Scenedesmus quadricauda* of different forms of phosphorus in sedimentary materials from the Great Lakes. *Limnology Oceanography* **25(1)**:1-11.

Williams, J.D.H., J-M Jaquet, and R.L. Thomas. 1976. Forms of phosphorus in the surficial sediments of Lake Erie. *J. Fish. Res. Board Can.* **33**:413-429.

Young, T.C., J.V. DePinto, S.C. Martin, and J.S. Bonner. 1985. Algal-available particulate phosphorus in the Great Lakes Basin. *J. Great Lakes Res.* **11(4)**:434-446.

Young, T.C., J.V. DePinto, S.E. Flint, M.S. Switzenbaum, and J.K. Edzwald. 1982. Algal availability of phosphorus in municipal wastewater. *Journal WPCF.* **54(11)**:1505-1516.

16 March 1992

Mr. T. Mulvey, Director
Onondaga Lake Management Conference
P.O. Box 7136
Syracuse, New York 13261

Dear Mr. Mulvey:

By this letter, I wish to formally comment on the significance of your decision to eliminate research related to the significance of nonpoint sources of phosphorus to water quality conditions in Onondaga Lake from the 1992 OLMC program. Specifically, we proposed to:

1) Assess the bioavailability of phosphorus in Onondaga Creek originating from urban and rural sources.

Rationale: loading assessments conducted by UFI (Heidtke and Auer, 1992) have shown that 64% of the phosphorus discharged to Onondaga Lake from Onondaga Creek originates from urban sources. Given that the urban area accounts for only 19_% of the total watershed, these sources represent a particularly rich target for phosphorus control.

It is well documented (DePinto et al., 1981; Young et al., 1981) that phosphorus originating from sewage-related sources is immediately available for algal growth and that phosphorus associated with terrigenous inputs is much less available. A true picture of the relative significance of urban and rural sources of phosphorus to Onondaga Lake must include analysis of their bioavailability. I am concerned that the Management Conference's ability to identify cost-effective remediation alternatives for Onondaga Creek will be compromised without this information.

2) Examine the lake response to intermittent, storm-related discharges of phosphorus from Onondaga Creek.

Rationale: by virtue of its position as the single largest source of phosphorus to Onondaga Lake, METRO has been identified as the primary target for phosphorus management actions. Model simulations have shown that elimination of the METRO discharge will permit the target trophic state to be approached. Some degree of additional treatment, e.g. tributary phosphorus management, will be required to meet trophic state objectives.

It is known that short-term, intermittent phosphorus discharges can provide the resources required to support algal populations for periods of days to weeks (Auer and Canale, 1982). The proposed research, biochemical monitoring of phosphorus limitation, would have served to identify the importance of this phenomenon to algal dynamics in Onondaga Lake. I am concerned that, without this information, the Management Conference will be ill suited to address the need for control of storm-related discharges of bioavailable phosphorus originating from urban sources.

These points are not of a trivial nature. I believe that information on phosphorus bioavailability will support the Management Conference's ability to make credible and valid decisions regarding the relative costs and benefits associated with urban and rural source phosphorus management on Onondaga Creek. More importantly, the potential for un-remediated phosphorus inputs to stifle the lake's response to diversion must be assessed.

Professionally, I feel that it is vital that the Management Conference be aware of technical uncertainties which may bear upon its ability to make defensible decisions regarding the future of Onondaga Lake.

Sincerely,

Martin T. Auer, Ph.D.
Research Associate

References

Auer, M.T. and R.P. Canale. 1982. Ecological studies and mathematical modeling of Cladophora in Lake Huron. 2. Phosphorus uptake kinetics. Journal of Great Lakes Research, **8**: 84-92.

DePinto, J.V., Young, T.C. and S.C. Martin. 1981. Algal-available phosphorus in suspended sediments from lower Great Lakes tributaries. Journal of Great Lakes Research, **7**: 311-325.

Heidtke, T.M. and M.T. Auer. In Press. Partitioning phosphorus loads: Implications for lake restoration. Journal of Water Resources Planning and Management.

Young, T.C., DePinto, J.V., Flint, S.E., Switzenbaum, M.S., and Edzwald, J.K. 1981. Algal availability of phosphorus in municipal wastewaters. Journal of the Water Pollution Control Federation, **54**: 1505-1516.

16 March 1992

Mr. T. Mulvey, Director
Onondaga Lake Management Conference
P.O. Box 7136
Syracuse, New York 13261

Dear Mr. Mulvey:

By this letter, I wish to formally comment on the significance of your decision to eliminate research related to algal growth in the Seneca River from the 1992 OLMC program. My concerns develop as follows:

> research conducted in 1990 and 1991 (Storey et al., 1992a; diurnal monitoring) has shown that algal respiration is an important oxygen sink for the Seneca River;
>
> a reduction in the amount of algae loaded to the river is seen as a key benefit of the phosphorus management strategies proposed for Onondaga Lake;
>
> if an effluent diversion option is selected, phosphorus discharged to the river could stimulate algal growth, eliminating any benefits accrued through trophic state reduction in the lake;
>
> historically, a portion of the METRO phosphorus discharge to Onondaga Lake has been retained in the lake sediments; following diversion, all of the phosphorus load would be received by the river ... available to support algal growth in the Baldwinsville - Phoenix reach, as well as downriver.

From what we have learned to date, it seems valid to conclude that the diversion option is seriously flawed if it serves to stimulate algal growth in the Seneca River. The results of preliminary algal bioassays conducted on the river (Storey et al., 1991b) were inconclusive. Simulation of algal growth has not been made part of the Seneca River dissolved oxygen model work plan. Thus water quality managers will have no way to assess the significance of phosphorus stimulation of algal growth in the river as it impacts the feasibility or desirability of diversion as an alternative phosphorus management strategy for Onondaga Lake.

I have discussed these points with Dr. Effler and Dr. Canale and they share my concerns. Professionally, I feel that it is vital that the Management Conference be aware of technical uncertainties which may bear upon its ability to make defensible decisions regarding the future of Onondaga Lake.

Sincerely,

Martin T. Auer, Ph.D.
Research Associate

References

Storey, M.S., Auer, M.T., and Rijkeboer, M. 1991. Nutrient bioassay conducted on the Seneca River. Internal Memo, Upstate Freshwater Institute, Syracuse, New York.

Storey, M.S., Auer, M.T., and Rijkeboer, M. 1992. Laboratory determination and field verification of a photosynthesis-light curve for the Seneca River, New York. In Review, Journal of Freshwater Ecology.

NORTH AMERICAN LAKE MANAGEMENT SOCIETY

16TH ANNUAL INTERNATIONAL SYMPOSIUM ON LAKE, RESERVOIR AND WATERSHED MANAGEMENT

FINAL PROGRAM

MINNEAPOLIS/ST PAUL, MN
NOVEMBER 13-16, 1996

Poster Session:

Hydrochemical Regime and Water Quality in Novosibirsk Reservoir and Its Principal Tributaries in Siberia, Russia

S.Ya. Tarasenko[1] and I.E. Varlamova[2], *[1]The Institute for Water and Environmental Problems (IWEP), Siberian Branch of Russian Academy of Sciences, 630090, Novosibirsk, 90, Morskoy prospect, 2. Phone: 7 3832 356005; Fax: 7 383 2 356005, E-mail: iwep@iwep.nsk.su; [2]The Exploitation Board of the Novosibirsk Reservoir 630055, Novosibirsk, Geroev Truda str., 19, Phone: 7 383 2 323186.*

Novosibirsk reservoir and principal tributaries: rivers Berd, Karakan, Miltush, Orda, and Aleus, are important sources of drinking and irrigation water and provide important fisheries. Researches show, that reservoir water has moderate mineralization (250-350 mg/l), the tributaries are more mineralized. Specific electrical conductivity of reservoir water is about 120-310 msm/s and tributaries is about 351-570 msm/sm, Eh-0.45-0.50 mv, pH- 8.0-8.5, hardness of water is moderate at 1.6-2.8 mg-eq/l. The oxygen regime is satisfactory. The water in the reservoir and tributaries has moderate pollution levels with respect to organic substances and biogeneous elements. Tendency of an increase of two- to five-fold of biogeneous element content during the past 35-40 years has occurred. This demonstrates eutrophication of reservoir water. As a whole, reservoir water has moderate pollution (II class), and the tributaries' water is in the III-IV class of quality. Proposals for improvement of reservoir and tributary ecology are formulated.

Friday: 08:30-10:00

Management Implications of Plankton Dynamics in Oligotrophic Versus Eutrophic Systems

Kent W. Thornton, *FTN Associates, Ltd., 3 Innwood Cir., STE 220, Little Rock, AR 72211; Phone: 501-225-7779; Fax: 501-225-6738; E-mail: ftn@intellinet.com.*

Water quality problems are usually associated with eutrophication and eutrophic lakes and reservoirs. Management alternatives and strategies, therefore, have been developed to address problems in eutrophic systems. However, taste and odor (T&O), filter clogging and DBP formation problems associated with phytoplankton also can occur in oligotrophic drinking water systems. Understanding the differences in plankton dynamics in oligotrophic versus eutrophic systems has significant implications for selecting and implementing appropriate management practices.

A comparative review of plankton dynamics was conducted as part of a study on an oligotrophic northeastern drinking water reservoir that was experiencing T&O problems. Differences in nutrient cycling (e.g., O-tight coupling; E-decoupled), nutrient supply (e.g., O-seasonal renewal; E-continuous supply), chlorophyll and biomass patterns, plankton loss mechanisms, organism size (e.g., O-small; E-large), forcing functions (e.g., O-biotic/abiotic; E-physical) and predictability of responses (e.g., O-low; E-high) were identified between oligotrophic (O) and eutrophic (E) systems. These differences in plankton dynamics have significant implications for implementing both watershed and in-lake management practices. Traditional management approaches to reduce plankton in eutrophic systems (e.g., hypolimnetic aeration, nutrient reduction, diversion) might not be effective in oligotrophic systems. This presentation will focus on those management practices that are applicable for oligotrophic drinking water reservoirs.

Poster Session:

Determining Bioavailability of Sediment Phosphorous Using Algal Bioassays and Chemical Fractionation

Katherine A. Tomasoski[1], Mary J. Babiera[1], Martin T. Auer[2] and Steven W. Effler[1], *[1]Department of Civil and Environmental Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, MI, 49931; Phone: 906-487-3294; Fax: 906-487-3292; E-mail: katomaso@mtu.edu or mjbabier@mtu.edu or mtauer@mtu.edu; [2]Upstate Freshwater Institute, P.O. Box 506, Syracuse, NY, 13214; Phone: 315-466-1309; Fax: 315-466-8289.*

The biological availability of the particulate-P fraction discharged from tributaries and point sources displays significant intersystem variability. Quantification of the bioavailability of the phosphorus loaded to lakes is required in the application of the water quality models which guide lake management. An algal bioassay and a chemical fractionation technique are used to examine the bio-availability of particulate-P loaded to Cannonsville Reservoir (NY) and Onodage Lake (NY). The bioassay applies a dual chamber diffusion technique with the test organism *Selenastrum capricornutum*. The chemical fractionation partitions P into loosely-sorbed, extractable biogenic, Fe/Al, Ca-mineral, and residual phases. Fractionation measurements at the start and conclusion of bioassays are used to identify the P-fractions contributing to bioavailability. Correlations between assay and fractionation results are applied to develop a protocol for defining the bioavailability of P loads to lakes. The results are examined within the context of a water quality model to track the fate of bioavailable P in lake and reservoir systems. Results from assays and fractionations of tributary and bottom sediment samples are compared to identify in-lake transformations in P-bioavailability.

Bioavailability and the Management of Phosphorus Loads to Lakes

Katherine A. Tomasoski and Martin T. Auer, Department of Civil and Environmental Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931, Phone: (906) 487-2799, Fax: (906) 487-3292, email: mtauer@mtu.edu

Phosphorus loads to lakes are managed to reduce or avoid acceleration of the eutrophication process. Best management practices (BMPs) applied in the reduction of nonpoint source loads and effluent guidelines developed to control point source inputs are traditionally based on the total phosphorus (TP) content of the water. It is well known, however, that the availability of phosphorus to support algal growth varies both within and between the soluble and particulate fractions which comprise the TP analyte. A fair and credible plan for management of point and nonpoint P sources must acknowledge the true impact of these inputs on the eutrophication process, i.e. their bioavailability.

Here we report on the application of algal bioassays and chemical fractionation techniques in identifying and partitioning the bioavailable phosphorus load to a hypereutrophic, urban system: Onondaga Lake. Located in metropolitan Syracuse, New York, Onondaga Lake receives the discharge from an 80 MGD wastewater treatment plant, urban runoff including discharges from leaky sewers and combined sewer overflows, and agricultural runoff. The phosphorus load to the system greatly exceeds that considered acceptable from the perspective of trophic state management. The selection of cost-effective remediation alternatives can be facilitated by quantifying the bioavailability of the various phosphorus inputs.

Water samples were collected from the Metropolitan Syracuse Treatment Plant (the lake's major point source), Nine Mile Creek (a major rural nonpoint source) and two sites on Onondaga Creek (representing rural and urban nonpoint contributions). Algal bioassays (*Selenastrum capricornutum*) and chemical fractionation techniques were used to quantify the fraction of particulate P in each sample which was bioavailable. The rate at which particulate P became bioavailable was determined through algal bioassays as well. The analyses were conducted under wet- and dry-weather conditions to evaluate the impact of storm runoff on bioavailability.

Bioavailability of the particulate P fraction, as determined by algal bioassays, varied from a low of 22% (rural nonpoint runoff) to a high of 58% (wastewater treatment plant discharge). The contribution of the various operationally defined chemical P fractions to bioavailability varied among sources, indicating that chemical extraction is not an appropriate substitute for bioassays in evaluating P bioavailability. The first order rate constant for P-bioavailability ranged from 0.1 d^{-1} for the tributaries to 0.3 d^{-1} for the wastewater treatment plant. With a half-life of 2-7 days, some bioavailable particulate-P is thus lost from the water column to sedimentation before it is solubilized. No significant difference was noted in the bioavailability of wet- versus dry-weather samples.

Bioavailability results were used to develop an accounting of P inputs to Onondaga Lake. It was determined that the wastewater treatment plant and urban discharges (leaky sewers and combined sewer overflows) contribute over 80% of the lake's bioavailable-P load. This stands in marked contrast to recent TP-based estimates of 47% from urban and point sources and suggests that the Metropolitan Syracuse Treatment Plant and associated urban infrastructure is an appropriate focus for phosphorus management efforts in support of lake restoration.

Abstract submitted to the 1997 Annual Meeting of the Michigan Water Environment Association.

May 5, 1990

MEMO:

REVIEW OF PRESENTATION OF APRIL 26, 1990

LOCATION: 14TH Floor Conference Room, Civic Center
TOPIC: COMPARISON OF DATA BASES FOR ONONDAGA LAKE
FROM: S. W. EFFLER
ATTENDEES: S. W. Effler, J. Barry, R. Hennigan, Mastrianno, R. Ott, J. Karanik, J. Albanese

BACKGROUND:

This memo is intended to document the salient features of the above presentation. An effort has been made to retain the original order of the presentation. Salient features of the figures are listed below. The various screens of the presentation are attached.

PRESENTATION:

SCREEN NO. 1

"mixed signals" and the potential negative side effects identified as motivation for presentation

SCREEN NO. 2

examples of bad outcomes from bad or incomplete technical information presented

SCREEN NO. 3

first "mixed signal" to be discussed is identified
free ammonia issue for Onondaga Lake developed

SCREEN NO 4

UFI results
emphasis given to top figure, since upper waters most critical from water quality perspective
lower dashed line is the chronic toxicity criterion
upper dashed line is the acute toxicity criterion
chronic criterion exceeded by wide margin routinely; acute exceeded on occasion (3)

SCREEN NO. 5

comparison of free ammonia determinations from UFI and County data bases for surface waters, 1988 and 1989
vastly different results; UFI findings substantially higher than county's, particularly in 1988
these differences have important implications with respect to management alternatives for the lake

several of the following screens present an evaluation of the cause(s) of the differences

SCREEN NO. 6

comparison of total ammonia concentrations from UFI and County, 1988, surface waters
significant differences, but not nearly enough to cause differences determined for free ammonia

SCREEN NO. 7

comparison of pH data from surface waters of lake from three sources (UFI, NYSDEC, Onondaga County)
distributions of observations from UFI and NYSDEC quite similar
County pH data low by comparison

SCREEN NO. 8

sensitivity analysis of influence of modest changes in pH on free ammonia, for a vertical profile
indicated small errors in pH (± 0.2 pH units) cause major errors in free ammonia

SCREEN NO. 9

comparison of <u>median</u> pH values from UFI and County
County values systematically lower since 1983; particularly unrealistic for 1983 - 1985 and 1988 (similar differences between NYSDEC and County observed, but not presented here).
thus the problem appears to be false low pH values measured by the County

SCREEN NO. 10

reduction in loading necessary at METRO (preliminary estimate, <u>not final model</u> prediction) to avoid exceeding USEPA chronic free ammonia criterion for non-salmonids; based on UFI free ammonia data for 1988
this analysis would change significantly if it were based on County data; much less reduction in TKN loading would be necessary

SCREEN NO. 11

a page from D & S's most recent consultant report was presented
S. Effler state that in light of the differences shown in SCREEN NO. 5, it was difficult to reconcile the <u>implication</u> of similarity between the data sets (see paragraph 4, P.21)

SCREEN NO. 12

conceptual diagram to show the central role of phosphorus in regulating phytoplankton concentrations, transparency and the oxygen resources of the lake

SCREEN NO. 13

review of nature of limitation of phytoplankton growth by soluble reactive phosphorus (SRP); typical values of K_p presented
at high concentrations (e.g., > 3 to 10 $\mu g \cdot L^{-1}$) phosphorus is not limiting to phytoplankton growth

SCREEN NO. 14

comparison of UFI and County SRP data for 1987; they match only at the very high concentrations common to fall turnover
further, the much lower concentrations measured by UFI were consistent with observed phytoplankton biomass and transparency conditions
a detection limit problem is indicated for the County data (i.e., can't measure the low concentration that actually prevailed for much of the time)
thus the County data cannot be used to keep apprised of the status of limitation of algae growth with respect to this key nutrient

SCREEN NO. 15

example profiles of reduced oxygen-demanding species
illustrates the accumulation of these forms that occurs annually
this causes lake-wide oxygen depletions during the fall mixing period

SCREEN NO. 16

comparison of dissolved oxygen concentrations measured in the upper waters of the lake by UFI and the County during the fall mixing period of 1978
NYSDEC surface water standard is 4 $mg \cdot L^{-1}$
County program fails to detect a contravention

SCREEN NO. 17

similar comparison as in previous screen but for 1988
increased frequency of measurements by county but fails to capture maximum impact (minimum oxygen concentration)
other years referred to, mixed success in County program in capturing the oxygen sag

the "sag" (oxygen depletion) phenomenon is largely a manifestation of the METRO discharge; an effort should be made to accurately measure it, just as a facility on a stream is required to document the "sag" downstream

SCREEN NO. 18

comparison of UFI and County data in 1978; dissolved oxygen profiles (measurements with depth)
major differences; no oxygen below 10 m according to UFI; oxygen present in significant concentrations top to bottom according to County
this comparison representative of the respective data bases for most of the summer
hydrogen sulfide odor quite noticeable for lower water throughout much of summer period; presence of hydrogen sulfide inconsistent with presence of oxygen (i.e., County data seems questionable)

SCREEN NO. 19

plot on left presents a similar comparison of oxygen concentrations for 1980; basically same outcome
hydrogen sulfide profile from the same day measured by UFI; the indicated presence of large quantities of hydrogen sulfide is inconsistent with the County's measurements
the apparent short-comings in the County's data, indicated here, persist throughout the year
further, it appears that these problems in the oxygen data persist throughout a number of years; comparisons with UFI data from 1978 - 1981 support this position; additional questionable data outside of this period

SCREEN NO. 20

this is the County's data sheet from the date of previous plot indicating that hydrogen sulfide was detected by monitoring personnel during the sampling of the lower waters

SCREEN NO. 21

shows the accumulation of hydrogen sulfide in the lower waters (hypolimnion) during the summer of three years measured by the UFI program
dramatic reduction (improvement) in hydrogen sulfide in 1989, that was manifested as reduced oxygen depletion in the lake during fall turnover compared to earlier years
it is unfortunate that the County chose not to monitor this critical parameter (despite recommendations) until after the major change(s)

SCREEN NO. 22

tabular data of total mercury concentrations from selected lake tributaries and the lake outlet for a single sampling in November of 1989
concentrations approximately an order of magnitude less than reported by County
character of County data indicates they are at their detection limits, yet not reported as less than or equal to in monitoring reports
County presentation of data, including loading of mercury could be highly misleading with respect to the lake's mercury problem; particularly since METRO may be a relatively large source of this material
it was also indicated that the County had the same problems for mercury data from the lake

SCREEN NO. 23

1. The County's monitoring program almost certainly presently understates the impact of METRO on the lake's problems of free ammonia and dissolved oxygen. It probably understates the relative role of METRO in mercury loading to the lake, and thereby may understate the role of METRO in the lake's mercury problem.

   I am sure that this is not the intention of the County's effort. However, it is not a wise position for the County to place itself in.

2. Several important features of the data from Onondaga County's program conflict with those being obtained by UFI as part of their effort to develop water quality models for the lake. These "mixed signals" are dangerous for the modeling, and related water quality management, efforts, and not in the best interests of Onondaga County or the lake. These "mixed signals" could negatively affect the efforts of the management conference.

4. Further, the continued lack of agreement in key aspects of the data could result in the call for more detailed studies (e.g., far in excess of basic monitoring), that could greatly delay the ability to make important management decisions.

5. At some point it will be necessary to conduct a "diagnostic study" of the lake, that will require an analysis of the entire data base (County, UFI and DEC data bases). It is essential to analyze the County data base to remove all clearly identifiable errors and to more clearly reflect detection limit problems where they exist.

February 26, 1992

Mr. Randy Ott, P.E.
Department of Drainage and Sanitation
Onondaga County
650 Hiawatha Blvd. - West
Syracuse, N.Y. 13204

Dear Randy:

Please find enclosed a draft section of the Tributary (No. 4) Chapter of the State of the Lake Report, that I am submitting to you as an unsolicited report. The reason for this is that it documents my review of the Onondaga Creek TIP data base, and, I believe, gives compelling justification for not considering this data base in the rural/urban partitioning of the TP load for this tributary. Liz Moran has reviewed the salient features of the analysis. I believe we are in agreement concerning the basic limitations of this data base to support the analysis of partitioning for the creek. Comments made by J. Bloomfield at the recent Water Quality working group meeting indicate he also agrees with this finding. The analysis of the Onondaga Creek TIP data base has been eliminated from the State of the Lake Report; thus the four figures numbered I through IV, and related text, will not appear.

Yours truly,

S.W. Effler

S.W. Effler, Ph.D.

cc: L. Moran
J. Mastrianno
Files

3.2.6.2.5. Onondaga Creek

3.2.6.2.5.1. Background

Onondaga Creek has drawn special attention with regards to TP concentrations and loading for two reasons: 1) it has been demonstrated to be the second largest source of external TP loading (Heidtke and Auer 1992), and 2) the strong differences in land uses and TP loading e.g., on a "unit area load" UAL) basis) within the watershed of the creek. Recall that though most of the watershed is rural - 80%), the stream passes through the City of Syracuse just before entering Onondaga Lake. The rural portion of the creek receives runoff from agricultural and wooded lands and a high sediment load from the "mud boils" (Effler et al. 1992). Recall further that large quantities of "mud boil" deposits are scoured from portions of the creek below these discharges during high flow events (see earlier sections of this chapter; Effler et al. 1992). The urban portion of the stream receives surface runoff, combined sewer overflows and probably inputs from leaking sewers.

Selected features of various monitoring programs conducted on the creek are presented in Table 18. The Dorwin Avenue site was added to the County's monitoring program in 1983. Though this program is limited in the frequency of monitoring (e.g., it was not intended to support the development of seasonal water quality models), it's longevity makes it potentially valuable. Approximately 185 paired measurements of phosphorus were made at Spencer Street and Dorwin Avenue as part of that program over the 1983-1989 interval; recall TIP was measured instead of TP through

TABLE 18: Onondaga Creek Monitoring Programs for TP

Program	Period	Site(s)	Frequency	Description/Source
	since 1990	Spencer St/ Dorwin	biweekly	long-term Onondaga County program (Onondaga County 1990, 1991).
2	summer 1987	Spencer St.	$\geq 1 \cdot day^{-1}$	support of TP model development (Heidtke 1989)
3	April 1988 - Oct. 1989	Spencer St./ Dorwin Ave.	$1\text{-}2 \cdot day^{-1}$	support for partitioning of rural/ urban contributions (Heidtke and Auer 1992)
	summer 1990	Spencer St./ Dorwin Ave.	$\geq 24 \cdot day^{-1}$, irregularly	rural/urban contributions for storm events (Heidtke 1991, Smithgall et al. 1991)
5	1990 and 1991	Spencer St.	11 times in 1990	NYSDEC (Rotating Intensive Basin Survey: RIBS)

1989. The creek was monitored approximately daily at Spencer Street for TP during dry weather periods in the June-early September interval of 1987 to support testing of a mechanistic TP model for the lake. More frequent monitoring was conducted during two intense storms. Subsequent efforts have focused on partitioning the rural and urban components of the creek load, and on more fully resolving wet weather contributions. The creek was monitored regularly at both Spencer Street and Dorwin Avenue, usually at a frequency of twice per day, over the period April 1988 - October 1989 (program 3, Table 18 Samples were collected with an automatic sampler, except during the winter, when samples were collected manually. The concentration of TP was measured on 692 samples from the Dorwin Avenue site over this

interval; 674 samples were analyzed from Spencer Street. Additionally, six storm events were monitored in detail (≥ 1 sample/hr) at the two sites in the spring/summer interval of 1989 and 1990, using automatic sampling equipment. Features of this monitoring program are described in Table 19. A single event received modest coverage in 1989. Approximately 430 samples were collected and analyzed for TP from the two stations for these events. More exact start and stop times for the events are presented elsewhere (Heidtke 1991).

TABLE 19 Description of Event Sampling

Event	No. of Observations Dorwin	Spencer	Sampling Interval
1	80	78	May 10-12, 1990
2	123	126	May 15-19, 1990
3	101	99	June 8-11, 1990
4	39	47	June 18-19, 1990
5	69	67	July 20-22, 1990
6	21	15	Sept 14-15, 1989

3.2.6.2.5.2. Intensive 1988/1989 and Long-Term Programs

The sharply contrasting time series of TP concentrations observed for Dorwin Avenue and Spencer street during the intensive April 1988 - October 1989 program are presented in Figure 45a and b (note the different scaling used to resolve the distributions The concentrations at Spencer Street greatly exceeded those at Dorwin Avenue for most of the study period; the differences were particularly great in August and September of 1988. Daily average flows at the two sites over the same period

are presented in Figure 45c. Relatively large inputs are implied for the urban portion of the watershed by the magnitude of the concentration differences as the differences in flow for the two sites were small by comparison. Smithgall (1989) indicated that a major break in the sewer system was at least partially responsible for the extremely high TP concentrations observed at Spencer Street in August and September of 1988. The relationships between TP concentration and flow at the two sites are evaluated in a log-log format in Figure 46a and b. Data available for the summer of 1987 (program 2; Table 17 have also been included for Spencer Street (Figure 46b), as they extend the observations for low flow conditions. No strong functionality between TP concentration and flow emerged for either site. Higher variability in TP concentrations with flow was indicated for Spencer Street than Dorwin Avenue. Note, however, that most of the highest concentrations observed at Dorwin Avenue occurred at some of the highest flows (Figure 46a)

The distributions of TP concentrations measured at the two Onondaga Creek stations during the April 1988 - October 1989 (1988/1989 program are presented in an alternate format in Figure 47. The distributions for these stations were strikingly different. None of the observations at Dorwin Avenue exceeded 0.8 $mg \cdot L^{-1}$; 98% of the concentrations were less than 0.2 $mg \cdot L^{-1}$ and 90% were less than 0.1 $mg \cdot L^{-1}$ Figure 47a). The distribution of TP at Spencer Street is illustrated for the entire 1988/1989 data set (Figure 47b) and the last 12 month interval (October 1, 1988 through September 30, 1989; Figure 47c) This time

segmentation isolates the period believed to be influenced by a break in the sewer system (Smithgall 1989). The distributions of concentrations at Spencer Street for both the entire population and the 12 month segment were skewed to substantially higher values; e.g., more than 50% of the observations were greater than 0.1 $mg \cdot L^{-1}$ (Figure 47b and c). Six percent of the observations for the entire Spencer Street population were greater than 1 $mg \cdot L^{-1}$, and thus fall outside of the bounds of the figure. The distributions of the sub-sets within the most common concentration interval for both sites, 0.0 - 0.1 $mg \cdot L^{-1}$, have been further resolved as insets of Figure 47 (a-c) Twenty-five percent of all the observations at Dorwin Avenue fell within the narrow range of 0.02 - 0.03 $mg \cdot L^{-1}$, and more than 70% were within the range 0.00 - 0.05 $mg \cdot L^{-1}$ Figure 47a, inset). Analytical protocol is critical at these low concentrations, e.g., use of a path length of at least 5 cm for spectrophotometric measurements is recommended for accurate and precise determinations (APHA 1989). Only about 15% of all the observations at Spencer Street were within the 0 - 0.05 $mg \cdot L^{-1}$ interval Figure 47b, inset). Elimination of the first six months of TP measurements at Spencer Street caused the distribution of concentrations to be shifted to somewhat lower concentrations (Figure 47c); e.g., 45% of the observations exceeded 0.1 $mg \cdot L^{-1}$ and less than 2% exceeded 1 $mg \cdot L^{-1}$ The mean concentrations of TP over the entire program were 0.05 $mg \cdot L^{-1}$ at Dorwin Avenue and 0.28 $mg \cdot L^{-1}$ at Spencer Street. The mean concentration at Spencer Street for the 12 month segment was 0.15 $mg \cdot L^{-1}$

The flow conditions under which the grab samples were collected for this program were generally representative of flow conditions over the monitoring period. The mean instantaneous flow rate corresponding to concentration measurements at Dorwin Avenue was 2.83 $m^3 \cdot s^{-1}$; individual values ranged from 0.51 to 20.70 $m^3 \cdot s^{-1}$. A mean annual flow of 2.55 $m^3 \cdot s^{-1}$ was reported by USGS for 1988; a mean flow of 3.74 $m^3 \cdot s^{-1}$ was reported for the 1989 water year. The daily minimum and maximum reported for the 1989 water year were 0.57 and 19.82 $m^3 \cdot s^{-1}$ The mean instantaneous flow rate corresponding to measured concentrations at Spencer Street was 4.28 $m^3 \cdot s^{-1}$ with a range of 1.05 to 20.10 $m^3 \cdot s^{-1}$ These values closely resemble published USGS flow values for the 1989 water year mean 4.50 $m^3 \cdot s^{-1}$, daily minimum 1.08 $m^3 \cdot s^{-1}$,and daily maximum (18.83 m^3 s^{-1} flows. The average flows encountered during the April 1988 to October 1989 interval, and for the 12 month segment, are compared to conditions documented for the corresponding intervals included in the longer term flow monitoring data base in Table 20. Average flows

TABLE 20: Comparison of Flow(s) During the 1988/1989 Program (No. 4) to Documented Long-term Conditions

Statistics	Dorwin Avenue	Spencer Street
average flow ($m^3 \cdot s^{-1}$)		
*1988/1989	3.22	4.03
**1968(71)-1989	3.65	4.93
rank		
entire program	8th of 21	5th of 18
12 month segment	9th of 23	7th of 20

* April 1988 through October 1989
** since 1968 for Dorwin Ave.; since 1971 for Spencer Street

at both stations during the 1988/1989 program were less than the longer term means. Flows over the entire intensive study period rank eighth highest of the last twenty-one intervals for Dorwin Avenue, and fifth of the last eighteen for Spencer Street.

A replicate sampling and TP analysis program was conducted over the April-December interval of 1989 at both stations, as part of the intensive 1988/1989 effort (program 3, Table 18), to evaluate the representativeness of the results of single grab samples. On approximately 40 occasions three separate grab samples were collected at each site. The three samples were collected as three separate "grabs" from different portions of the stream cross-section, within about 5 minutes of each other. The precision of the TP results was high for both sites. Less than 25% of the triplicates from Dorwin Avenue had a relative error greater than 10%; only 3% had a relative error greater than 15%. Less than 25% of the triplicates from Spencer Street had a relative error greater than 10%; only 10% had a relative error greater than 15%. The relative error was observed to exceed 5% at Dorwin Avenue only when the TP concentration was greater than 0.05 $mg \cdot L^{-1}$ In contrast, relative errors in excess of 10% were observed at Spencer Street only at concentrations less than 0.05 $mg \cdot L^{-1}$ The representativeness of grab samples for TP at the Onondaga Creek monitoring sites has been further tested by the NYDEC by conducting their RIBS monitoring program, which utilizes a USGS method to obtain a flow-composited sample across a stream cross-section, simultaneously with the collection of grab samples. Results from grab samples were supported as

representative, based on the nearly equivalent values obtained with the two sampling methods on five different occasions in 1990 at Spencer Street (over a range of concentrations of 0.05 to 0.43 $mg \cdot L^{-1}$), and on three occasions at both sites in 1991.

The distributions of TIP established for the two stations by the long-term County monitoring program (program 1; Table 18) are presented in Figure Ia and b; again insets for the distributions in the 0.0 0.1 $mg \cdot L^{-1}$ interval are included. These distributions differ in important ways from those presented for TP in Figure 47. Concentrations of TIP reported for Dorwin Avenue in the long-term program have been higher than those observed for TP in the intensive program of 1988/1989. Nearly 25% of the observations in the long-term program exceeded 0.1 $mg \cdot L^{-1}$, compared to only 10% for the 1988/1989 program. Slightly more than 50% of the TIP observations in the long-term program fell in the 0.0 - 0.05 $mg \cdot L^{-1}$ range, compared to more than 70% of the TP measurements for the 1988/1989 effort. This disparity is made more severe by the fact that TIP is by definition a fraction of (i.e., ≤) TP (Figure 39). Measurements made on the same days in 1988 and 1989 for the two different programs are compared in Figure IIa. Such a comparison has inherent limitations; because the samples for the two programs were usually not collected at the same time. However, the analysis serves to illustrate the propensity for higher concentrations in the long-term program also prevailed during the intensive 1989/1990 program; in 20 of 28 cases TIP was distinctly higher than the TP measured on the same day. These incongruities are probably related to

limitations in the County's analytical protocol; that prevailed through 1989; e.g., use of a 1 cm path length for absorbance measurements. Standard Methods APHA 1989) recommends a path length of at least 5 cm in the concentration range of 0.01 to 0.25 $mg \cdot L^{-1}$ A path length of 10 cm was used routinely in the 1988/1989 intensive program. Note that no incongruities in paired measurements of TIP and TP were observed in 1990 and 1991 (Figure 39d), after analytical changes were made, that included increases in path length. Total phosphorus loading estimates for Dorwin Avenue based on the long-term County program through 1989 would almost certainly be unreliable, and probably false high, apparently as a result of analytical short-comings

A shift to higher TIP concentrations downstream at Spencer Street compared to Dorwin Avenue is indicated for the long-term program (Figure Ia and b), but the divergence between the two sites is much less for this program than reported for TP in the intensive 1988/1989 study. This is only in part due to the inclusion of false high TIP values for Dorwin Avenue in the long-term program (Figure Ia versus Figure 47a); TIP concentrations at Spencer Street were substantially lower than TP values reported for the 1988/1989 program Figure Ib versus Figure 47b). For example, only about 25% of the TIP observations at Spencer Street exceeded 0.1 $mg \cdot L^{-1}$ compared to more than 55% of the TP measurements exceeding this concentration in the 1988/1989 program. Analytical protocol continues to be a concern at lower concentrations, which represent a significant fraction of the observations. However, a more important short-coming with

regards to the support of a TP budget for the creek emerges from comparison of results from this program with TP measurements made in 1987, 1988, and 1989 (Figure Ib). Note the character of the disparity in the data bases for Spencer Street strongly contrasts that depicted earlier for Dorwin Avenue (Figure IIa) The concentration of TP tended to exceed TIP, and by a large amount in about a third of the observations, indicating a major contribution by forms of P not detected by the TIP analysis (probably mostly organic P Recall that the earlier presentation of paired TP and TIP concentrations for Spencer Street for 1990 and 1991 (Figure 39c indicated the significant, and occasionally major, contribution of organic P as operationally specified by paired TP and TIP analyses).

The distribution of the contribution of organic P to TP at Spencer Street is presented for two different intervals, 1987-1989 (based on same day measurements) and 1990-1991, in Figure IIIa and b, respectively. The distribution for Dorwin Avenue for 1990-1991 is presented in Figure IIIc. Apparently organic P often represented a significant, and sometimes dominant, fraction of TP at Spencer Street over the 1987-1989 interval. It appears that more recently (1990-1991 organic P has frequently been a significant component of TP, but rarely a dominant component. Organic P represented relatively less of the TP at Dorwin Avenue compared to Spencer Street over the 1990-1991 interval. The increase in organic P downstream may be associated with the input of sewage from the urban area. The relationship between the percent contribution of organic P and the concentration of TP is

evaluated in Figure IV. Recall that the 1990-1991 data are based on paired observations of TIP and TP, and thus are more reliable than the values presented for 1987-1989, based on "same day" measurements. No relationship emerges for the 1990-1991 data set, however, the very high TP concentrations reported for the earlier years appear to have been mostly organic P. Greater sewage inputs in the earlier period may explain these differences (e.g., Smithgall 1989). The fraction of organic P at Spencer Street did not appear to be a function of stream flow in either interval.

The distributions of the most recent measurements (1990-1991) of TP at Dorwin Avenue and Spencer Street (Figure 48a and b), despite the rather small population sizes, support the observations for the intensive 1988/1989 program at Dorwin Avenue, but indicate a potential shift to lower concentrations at Spencer Street from those that prevailed during the last 12 months of the intensive program. Subsequently presented analyses indicate that more intensive sampling would be necessary to substantiate this position. Perhaps a decrease at Spencer Street has occurred as a result of reduced sewage inputs (e.g., repair of sewer break(s)). The occurrence of significant year-to-year variations in urban inputs of organic P would seriously compromise any effort to recreate TP concentrations (and thereby loads) at Spencer Street from the TIP data base, by subsequent collection (since 1990) of paired observations of TIP and TP (e.g., Figure 39c).

3.2.6.2.5.3. Events

Time series plots of instantaneous flows, measured concentrations and calculated loads are presented for Dorwin Avenue and Spencer Street for three of the six monitored events (No.'s 2,4 and 5; Table 19) in Figures 49, 50 and 51 (a-c). The hydrographs have appeared earlier in this chapter. Plots for all six events appear elsewhere (Heidtke 1991). The mid-May event (No.2; Figure 49) was the largest monitored in 1990. Substantial increases in TP concentration were observed at both stations with the increase in flow. Concentrations at Dorwin Avenue were greater than at Spencer Street for much of the event. However, at mid-day of May 17 concentrations at Spencer Street were greater, probably as a result of a CSO event (Smithgall et al. 1991). Note that concentrations generally decreased through May 18, despite the continued elevated flows. Recall that the mid-June (No. 4) event was modest in comparison, with rainfall intensity that varied substantially across the basin (Smithgall et al. 1991). The time series of TP concentrations at Spencer Street tracked very closely the hydrograph for that site (Figure 50a and b). A modest delayed increase in TP was observed at Dorwin Avenue. The mid-July event included two rainfall events, that are particularly well resolved in the hydrograph for Spencer Street (Figure 51a). The time series of TP concentrations at both sites (Figure 51b) again tracked the respective hydrographs closely.

A mean concentration was determined for each event by integrating the "loadograph" (the time series of instantaneous

instantaneous peak flows than the others; the peak instantaneous flows were approximately 24.6 and 27.8 $m^3 \cdot s^{-1}$ for events 2 and 6, respectively. None of the other events exceeded 20 $m^3 \cdot s^{-1}$, and only one exceeded 15.5 m^3 s^{-1} The mean flow for these two events ranged from more than 2 to 6 times that of the other events (Table 21

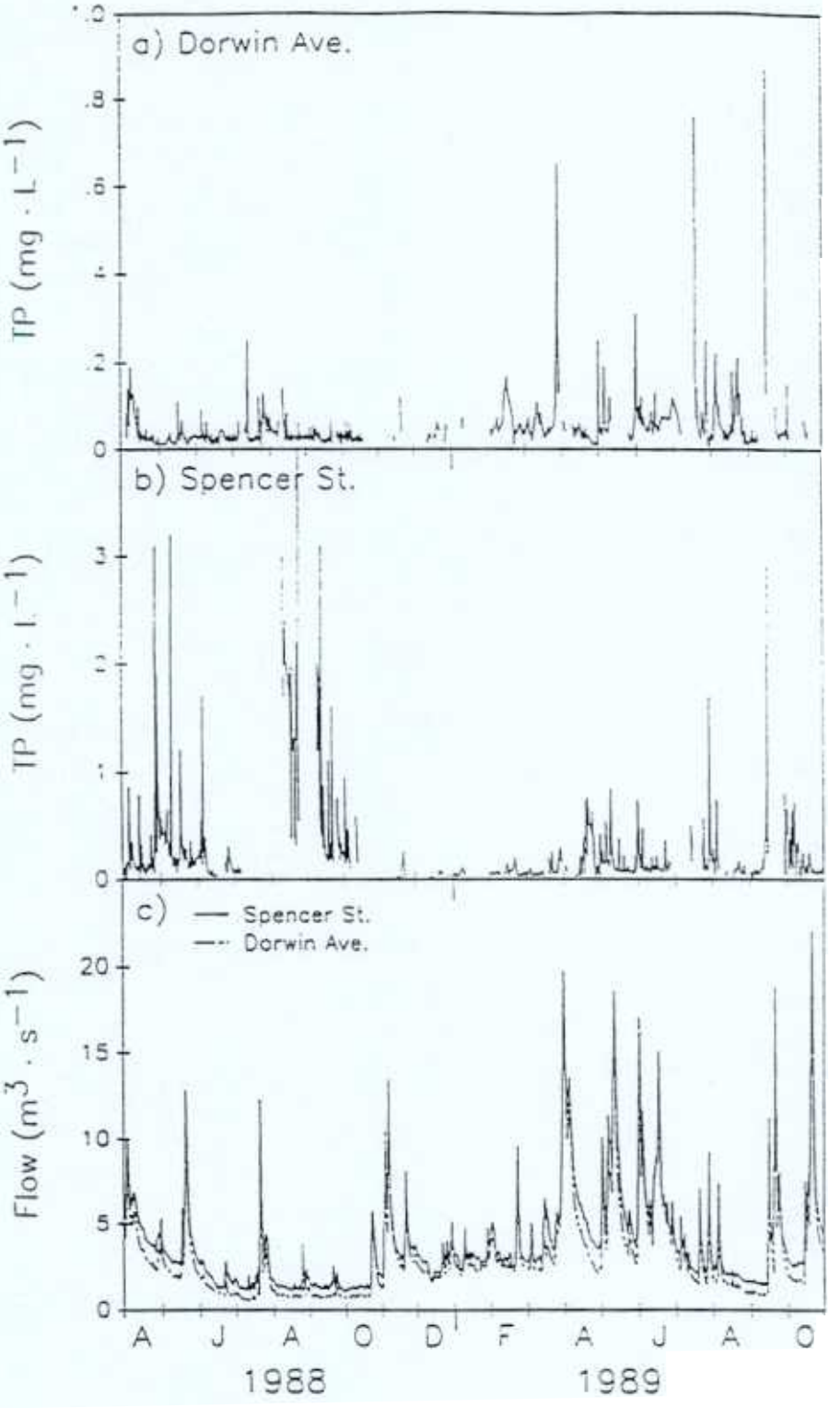

Figure 45. Time series for Onondaga Creek for the April 1988 - October 1989: a) instantaneous concentrations of TP at Dorwin Avenue, b) instantaneous concentrations of TP at Spencer Street, and c) daily average flow at Dorwin Avenue and Spencer Street.

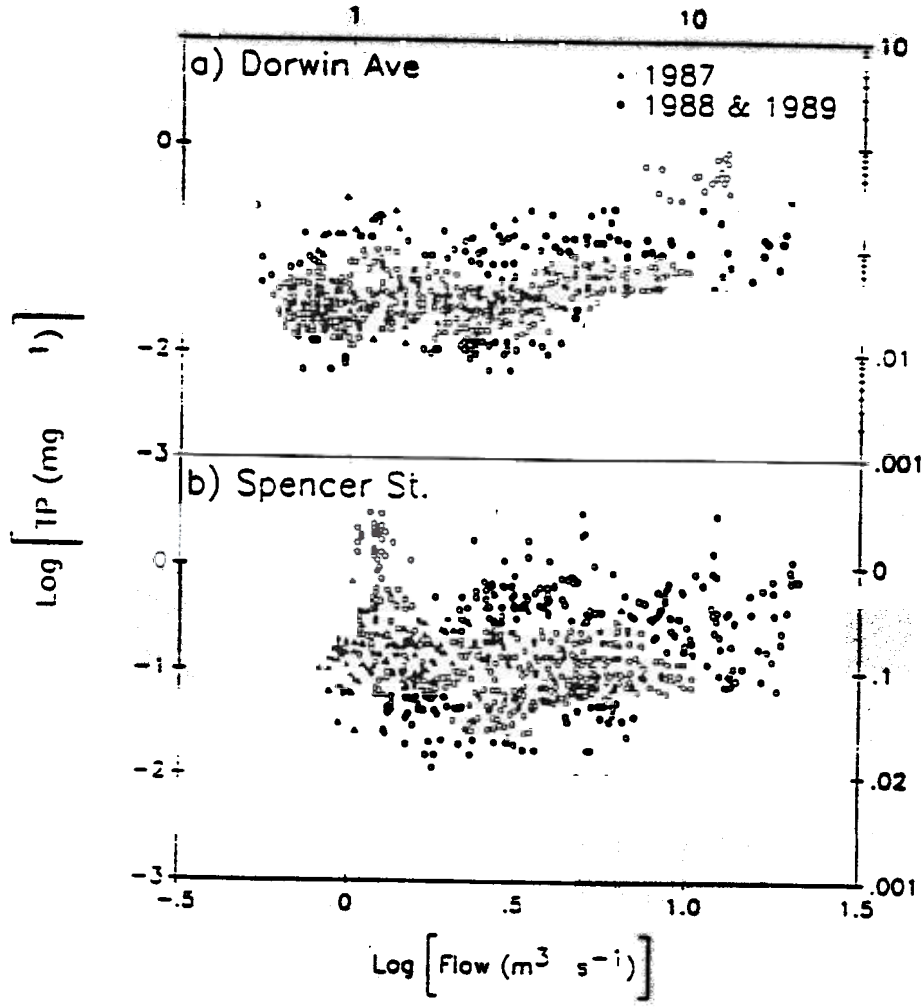

Figure 46. Evaluation of the relationships between TP concentration and flow in Onondaga Creek: a) Dorwin Avenue, and b) Spencer Street.

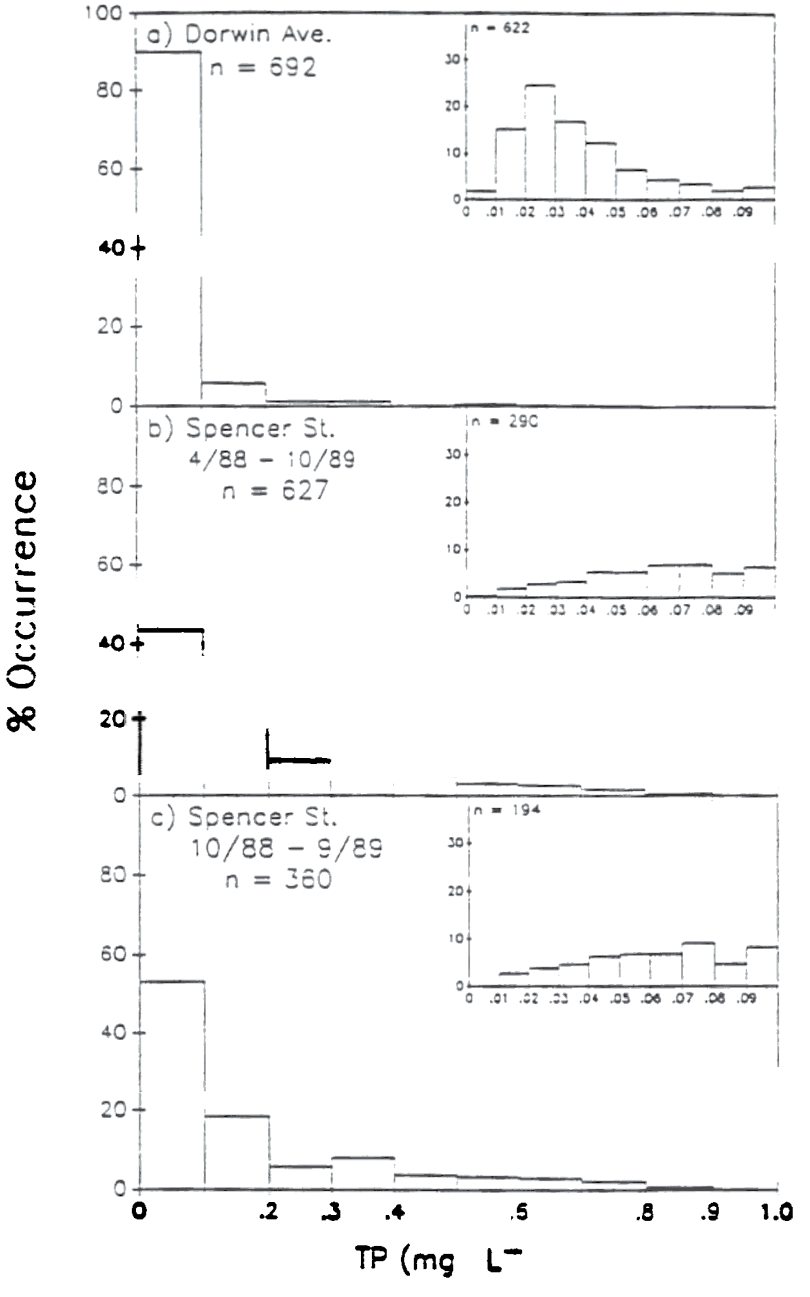

Figure 47. Distributions of TP concentrations in Onondaga Creek: a) Dorwin Avenue, over the interval April 1988 - October 1989, b) Spencer Street, over the interval April 1988 - October 1989, and c) Spencer Street, over the interval October 1988 - September 1989.

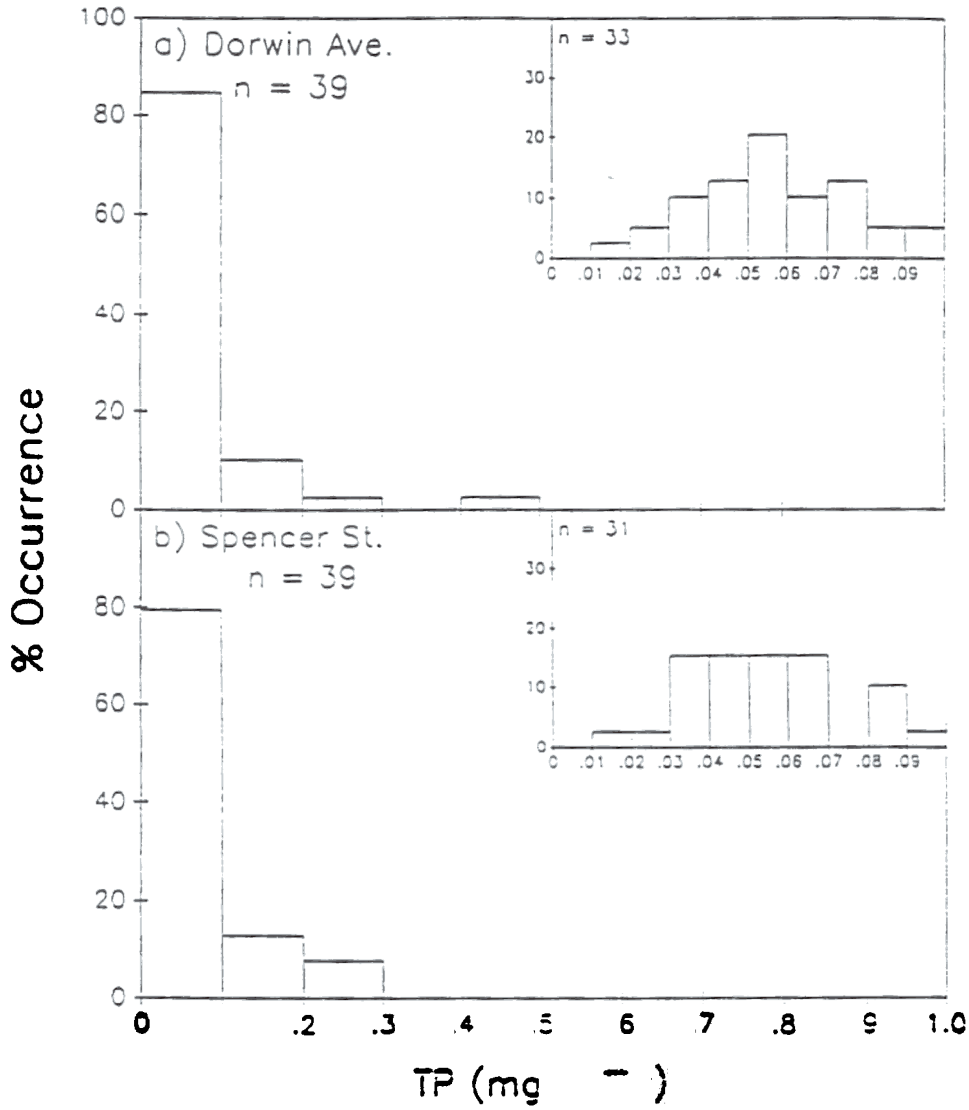

Figure 48. Distributions of TP concentrations in Onondaga Creek over the 1990-1991 interval: a) Dorwin Avenue, and b) Spencer Street.

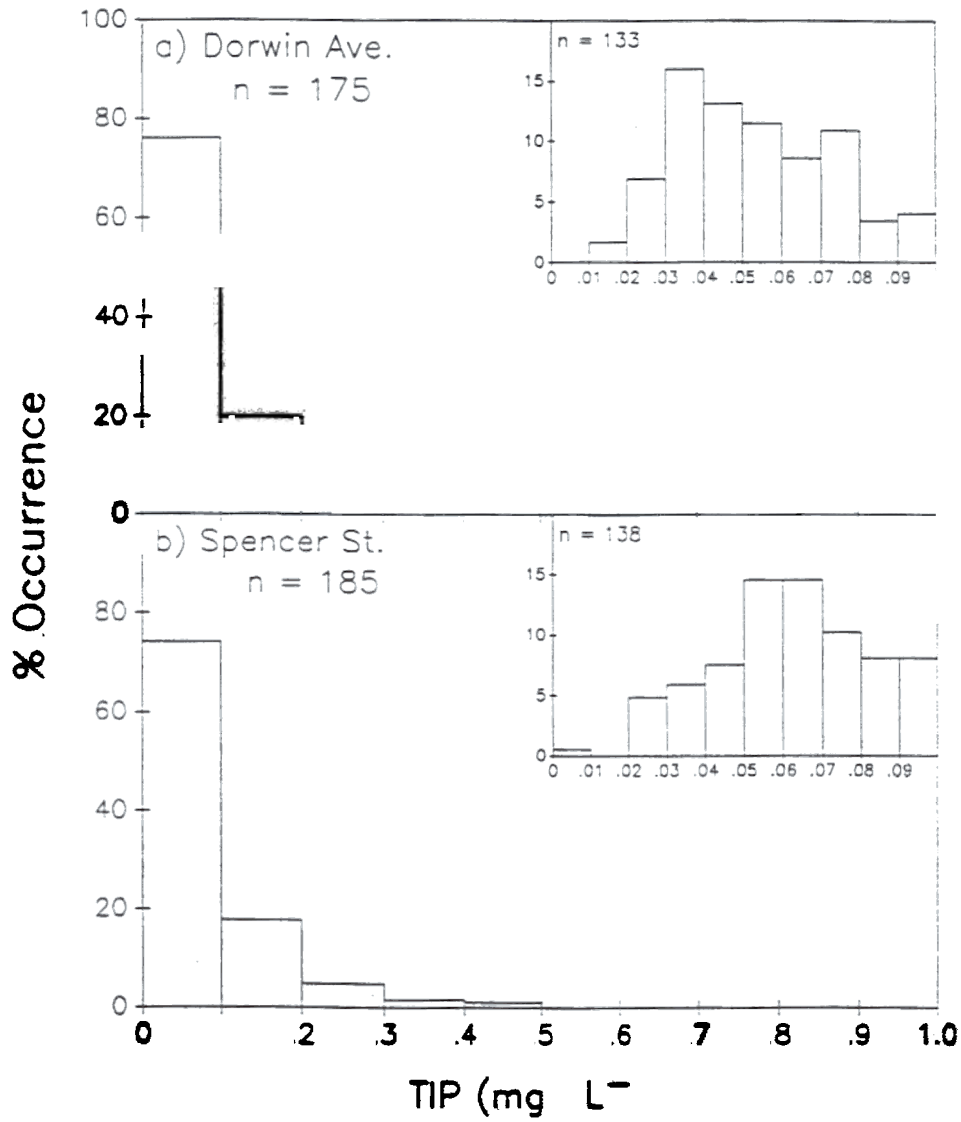

Figure I. Distributions of TIP concentrations in Onondaga Creek, 1983-1989: a) Dorwin Avenue, and b) Spencer Street

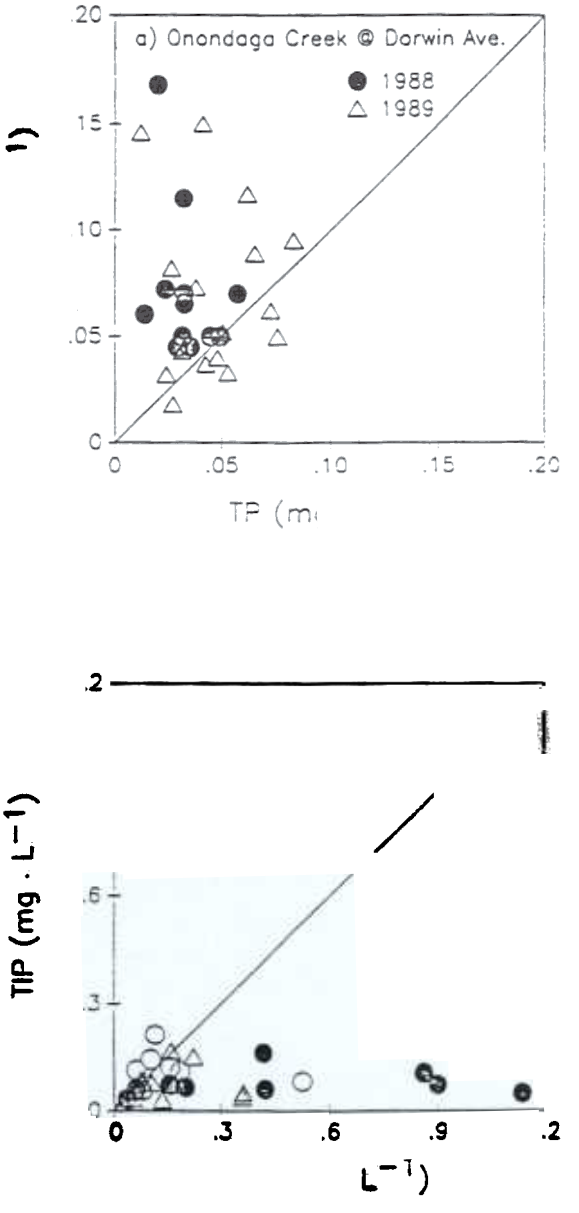

Figure II. Comparison of TIP and TP concentrations for different samples collected on the same day from Onondaga Creek: a) Dorwin Avenue, and b) Spencer Street.

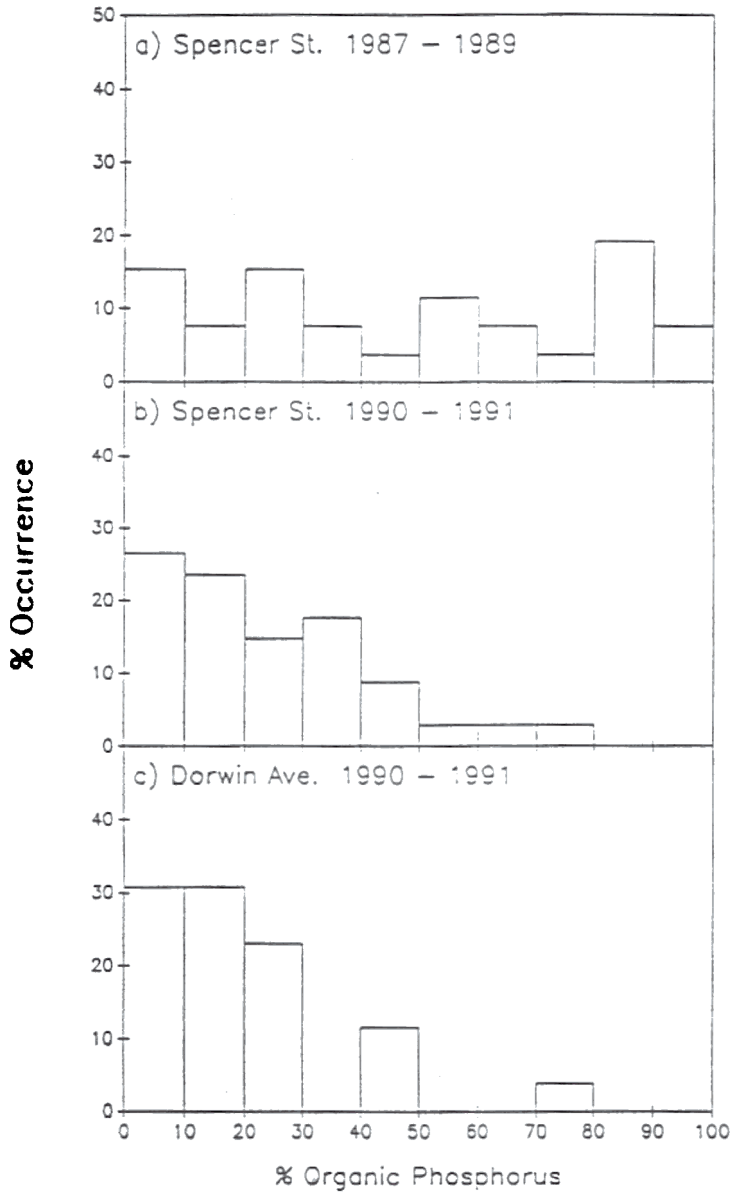

Figure III. Distributions of the contribution of organic P to TP in Onondaga Creek: a) at Spencer Street, 1987-1989 b) at Spencer Street, 1990-1991, and c) at Dorwin Avenue, 1990-1991.

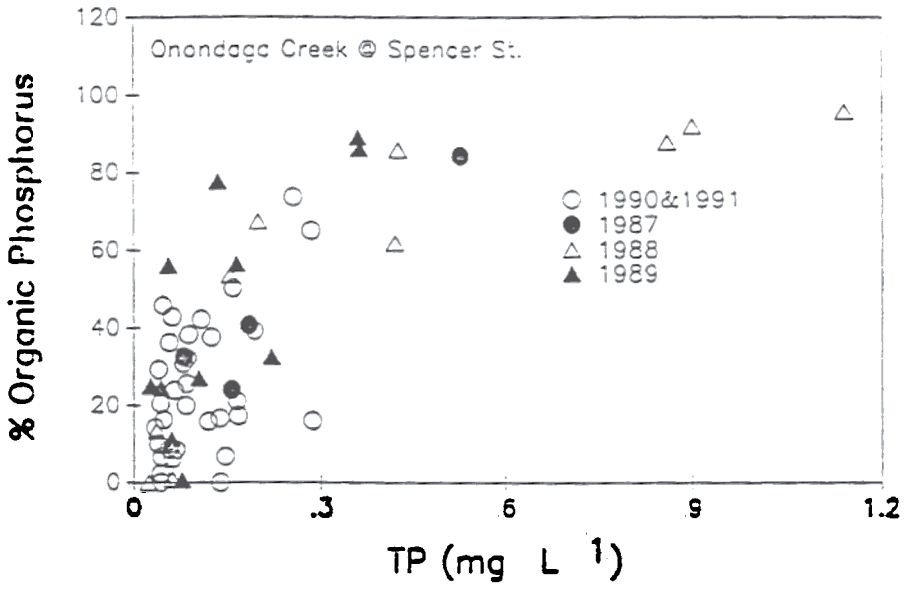

Figure IV. Evaluation of the relationship between organic P and TP concentrations in Onondaga Creek at Spencer Street over the period 1987-1990.

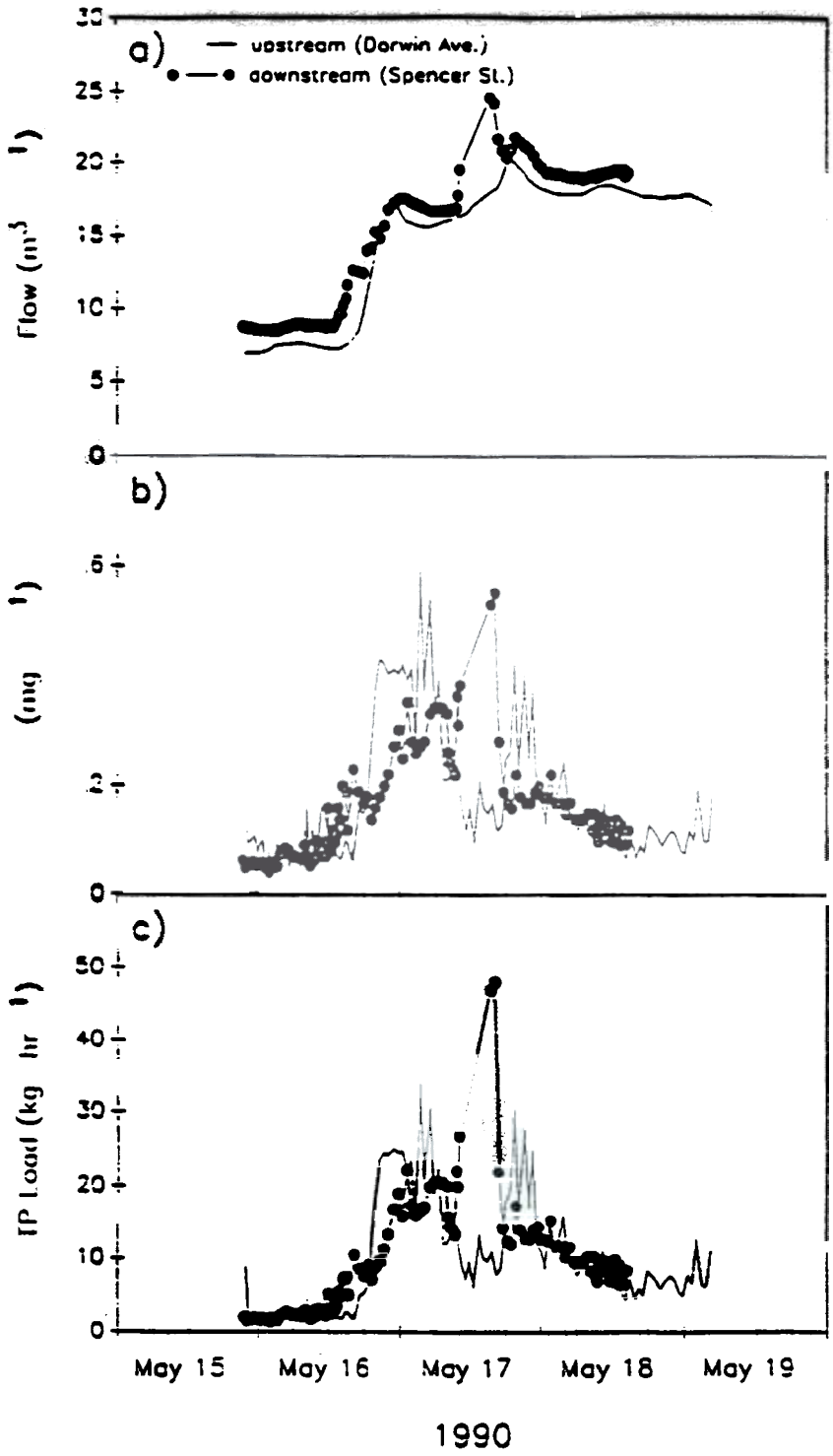

Figure 49. Time series of instantaneous loading conditions for Onondaga Creek for the May 15 - May 19 interval for Dorwin Avenue and Spencer Street: a) flow, b) TP concentration, and c) TP loads.

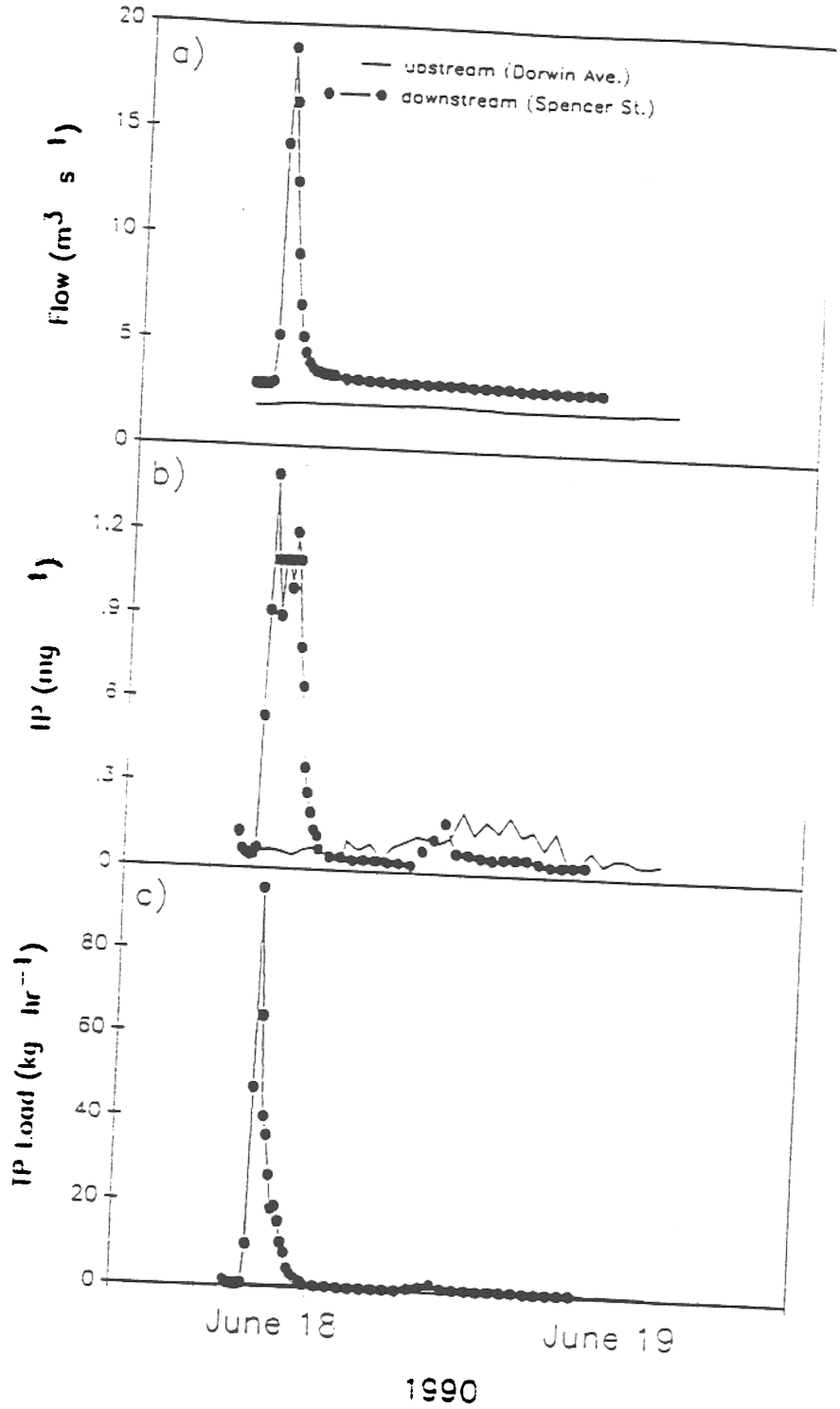

Figure 50. Time series of instantaneous loading conditions for Onondaga Creek for the June 18 - June 19 interval for Dorwin Avenue and Spencer Street: a) flow, b) TP concentration, and c) TP load.

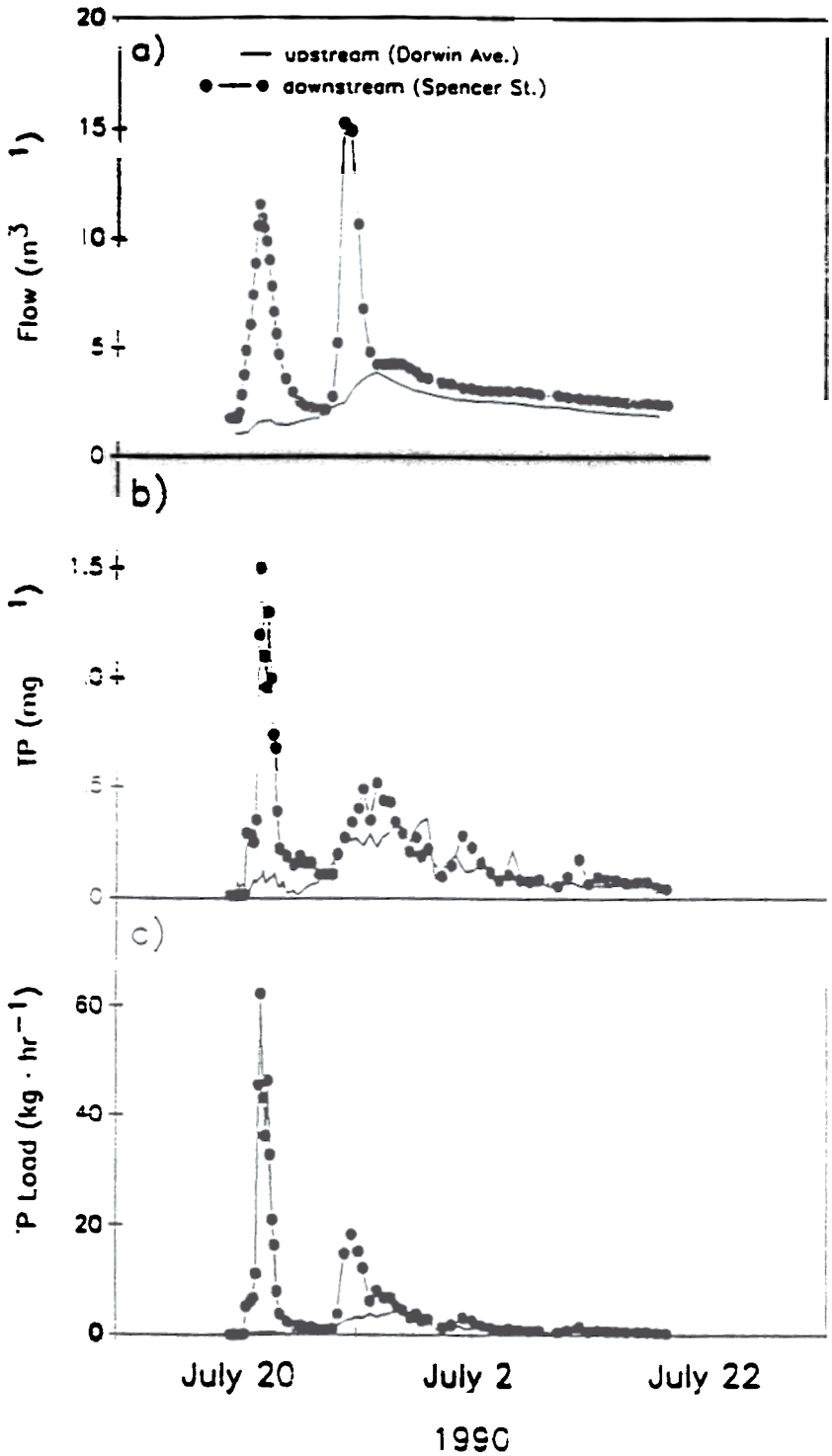

Figure 51. Time series of instantaneous loading conditions for Onondaga Creek for the July 20 - July 22 interval for Dorwin Avenue and Spencer Street: a) flow, b) TP concentration, and c) TP loads.

for references please see Chapter State of Onondaga Lake

A COMPARATIVE ANALYSIS OF PHOSPHORUS DATA FOR ONONDAGA LAKE, AND IMPLICATIONS

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March 1994

Background

Phosphorus (P) has long been recognized as the most critical nutrient controlling phytoplankton growth, and related aesthetic water quality features, in most lakes (Carlson 1977, Dillon 1975, Hutchinson 1973, Vollenweider 1968). Elevated inputs of P to lake ecosystems, associated with man's activities (e.g., disposal of treated sewage, agricultural wastes, etc. enhances phytoplankton growth, and causes deleterious consequences, such as reduced clarity and increased hypolimnetic oxygen depletion. The accelerated "aging" of lakes associated with elevated loadings of P is described as cultural eutrophication. Onondaga Lake's profound cultural eutrophication problems have been well documented (Effler 1994 ; they are largely the result of the effluent load of P received from METRO

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Appendix II
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in orms of P are routinely measured
is y studies. Total phosphorus (TP)
Vo ophic state e.g., Carlson 1977,
me al dissolved phosphorus (TDP) is
be samples. Most TDP is assumed to
co ort phytoplankton growth. A third
soluble reactive phosphorus (SRP);
OP that is usually assumed to be
in plankton. Particulate phosphorus
(PP), a measure of phytoplankton biomass in many productive systems, is calculated as the difference of paired TP and TDP analyses (PP = TP-TDP).

"There are two basic approaches for quantifying the

relationship between phytoplankton growth and nutrient availability; both have been widely applied in mathematical models. The first approach, based on Monod (1942) kinetics, relates growth rate to the external (dissolved) nutrient concentration:

$$G(N) = \frac{[P]}{K_p + [P]} \tag{1}$$

in which G(N) = the fraction of the maximum specific growth rate (range 0 to 1) achieved at phosphorus concentration [P] ($mg \cdot L^{-1}$) and K_p is the half-saturation constant ($mg \cdot L^{-1}$), a measure of the organism's efficiency in acquiring phosphorus. Phosphorus available to algae is typically characterized as soluble reactive phosphorus (SRP), however, other dissolved forms (e.g., nonreactive or organic phosphorus) can support growth (Berman 1970, Taft et al. 1977). The second approach, based on Droop (1968) kinetics, relates growth rate to the internal (or stored) nutrient concentration:

$$G(N) = 1 - (Q_o/Q) \tag{2}$$

in which Q = the cell quota (mass nutrient · unit biomass^{-1}) and Q_o is the minimum cell quota, i.e. the internal phosphorus concentration where growth ceases.

The Monod model offers the advantage of directly relating growth to water column phosphorus levels. The disadvantage of the Monod approach is that it ignores the well-documented phenomenon of luxury uptake, where nutrients including phosphorus are acquired and stored at levels well beyond the immediate demand for growth. By drawing on internal nutrient stores, algae

can grow at near maximum rates during periods of water column nutrient depletion. The Droop model overcomes this problem by relating growth to internal nutrient levels, thus accommodating the luxury uptake - storage phenomenon. The Droop approach requires a mass balance on the internal nutrient pool, considering contributions through nutrient uptake from the external environment and losses through the demand for growth

The additional kinetic complexity required by the Droop model limits its management application. DiToro 1980) recognized this in modeling nutrients and phytoplankton in Lake Erie (see also DiToro and Connolly, 1980). He suggested that since the pool size response to the external environment is rapid compared with the response to demands for growth (nutrient uptake rate > growth rate , algae would achieve a cellular equilibrium when the rate of change in external nutrient levels is slow relative to the rate of growth. Under these conditions, i.e. a relatively stable external nutrient environment, the linkage between growth rate and nutrient resources may be fairly represented by the simpler Monod model". (Effler 1994, P.3-36 and 3-37)

Accurate P concentrations are critical for the upper productive layers if the development of reliable mechanistic models for phytoplankton growth are to be supported (e.g., Bowie et al. 1985 In particular, accurate SRP or TDP data are necessary to support the Monod approach. Additionally, PP concentrations are required if the Droop framework is adopted

The Department of Drainage and Sanitation of Onondaga County

(D&S) have been measuring P species in Onondaga Lake since late 1960's. The Upstate Freshwater Institute (UFI) has been monitoring P species in the lake since 1987. The comparative analysis presented here demonstrates historic and on-going shortcomings in the D&S monitoring program for P. An analysis conducted by Walker (1991 and UFI's on-going analysis of available data bases for the lake (Effler 1994) indicate that problems of the D&S monitoring program are not limited to P species. Walker (1991) used statistical and graphical methods and limnological reasoning to identify and "flag" anomalous values in a comparative analysis of data bases available for Onondaga Lake. Walkers's (1991 perspective was the adequacy of the various data sets to support the depiction of long-term trends. UFI's review has been more demanding for certain parameters, because of the intention of certain parties to utilize D&S's data base to support development and testing of mechanistic models. Some of the problems identified in the D&S data base to date are summarized in Table 1 below. It's important to continue to identify and characterize the problems of the various data bases for the lake to avoid errors in evaluation of the lake's status with respect to standards goals, to identify trends, to avoid the development of faulty management models for the lake.

Errors in Selection of P Species

UFI has monitored the fundamental three P species included in most limnological programs, TP, TDP, and SRP. In contrast, until 1990 D&S monitored total inorganic P (TIP), dissolved

TABLE 1: Problems with the Onondaga County Department of Drainage and Sanitation Data Base for the Onondaga Lake System

Parameter	Problem Description	Reference
dissolved oxygen (DO)	false low in epilimnion, false high in hypolimnion 1976-1981, data rejected	Walker 1991
	presence of DO near lake bottom when reduced species present, 1972-1988	Walker 1991
temperature	false high in hypolimnion, 1979-1981 data rejected	Walker 1991
pH	unexplained long-term instabilities; faulty data identified for various yrs	Walker 1991, Doerr and Effler 1994
hydrogen sulfide	false low in 1972-1974 (rejected), suspicious differences noted in other years	Walker 1991
phosphorus (P)	monitored total inorganic P instead of total P until 1989	Effler and Whitehead 1994, Effler et al. 1994, this report
soluble reactive P	false high values in upper productive waters of lake for much of summer	this report
chloride	unreliable lake concentrations, 1979 and 1982	Doerr et al. 1994
total inorganic P for tributaries and related loads	unreliable during periods of lower concentrations, before 1989	Effler 1992, Effler and Whitehead 1994

inorganic P (DIP), and SRP (described as ortho-P by D&S, in most instances), in both tributaries and the lake. D&S's selection of P species is fundamentally flawed for monitoring water quality features related to P and to support mechanistic phytoplankton models

The TIP method, described as "Total Acid Hydrolyzable Phosphorus" in Standard Methods (Method 4500-P B2; APHA 1989), uses a hot sulfuric acid digestion procedure. It includes reactive phosphorus as well as acid hydrolyzable forms of

phosphorus (condensed phosphates and higher molecular weight inorganic species Some natural waters contain organic phosphate compounds that are hydrolyzed to ortho-phosphate under these digestion conditions. The TIP method is not intended to include organic forms of P. This omission totally compromises the trophic state indicator value of the measure, by the systematic exclusion of phytoplankton biomass, often a major component of TP in the upper productive waters of eutrophic lakes. Further, TIP measurements instead of TP for the tributaries eliminates the use of TP loading/trophic state relationships (e.g., Vollenweider 1968, 1975) for the lake. Measurement of DIP instead of TDP eliminates measurement of dissolved organic forms of P, forms that are available for phytoplankton uptake during periods of SRP depletion through enzymatic activity (Connors 1993).

The analysis of paired TP and TIP data collected by D&S from the upper waters (0,3, and 6 m depths) of the lake in 1990 (Figure 1 illustrates the limitations of the TIP parameter. Total inorganic P was in general substantially lower than TP and it represented a variable fraction of TP (Figure 1 Further, the relationship between TIP and TP (Figure 1 may have limited utility in generating estimates of TP concentrations for earlier (e.g., before 1986) years, as there appears to be little reason to assume it would remain uniform over the decreases in P loading (Effler and Whitehead 1994 and in-lake concentrations Effler et al. 1994 that have occurred. In contrast, TIP is a good estimator of TP in the hypolimnion of Onondaga Lake, because most

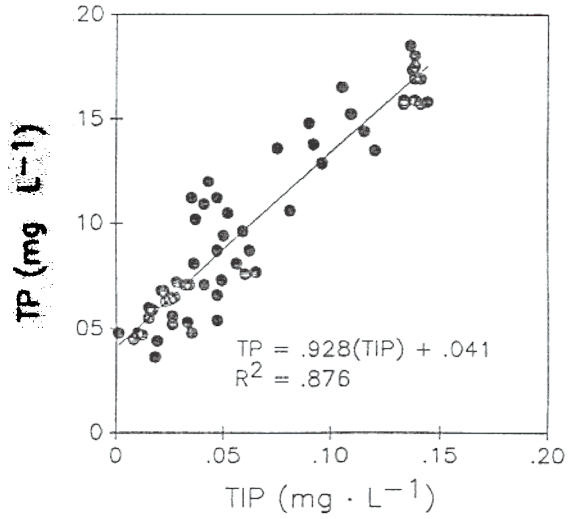

Figure 1. Evaluation of the relationship between TIP (total inorganic phosphorus) and TP in the upper waters (0, 3, and 6 m) of Onondaga Lake in 1990. (from Effler *et al*. 1994).

of the P on this layer is in the form of SRP.

Detection Limit Problems with SRP

Stearns and Wheler (1993) has reported on the results of a "sample splitting" QA/QC program conducted in 1991 with three participating entities, D&S, UFI, and the New York State Department of Environmental Conservation (NYSDEC), for SRP. These "splits" were evaluated at two depths, 1 and 16 m, corresponding to the upper productive waters and the hypolimnion during summer, respectively. When analyzed together (lumping 1 and 16 m results) a strong relationship, implying equivalency, emerged (Figure 2, Stearns and Wheler 1993). However, a quite different picture emerges when the evaluation is separated for epilimnion (Figure 3a and hypolimnion (Figure 3b). Measurements of D&S are systematically higher for the upper productive layer (Figure 3a), where issues of nutrient limitation and related inputs for phytoplankton models are so critical. It should be noted that "false high" observations are much more common at these low concentrations, rather than "false low" measurements, because of the susceptibility to contamination at these lower concentrations. Further, it should be noted that the very low SRP concentrations documented for substantial portions of the summer of 1992 are consistent with coincident high levels of alkaline phosphate activity that is known to occur only under conditions of highly depleted SRP Connors 1993 Near equivalency is observed at the higher concentrations that prevail in the hypolimnion (Figure 3b). This is expected because the potential for bias in analysis from contamination is greatly

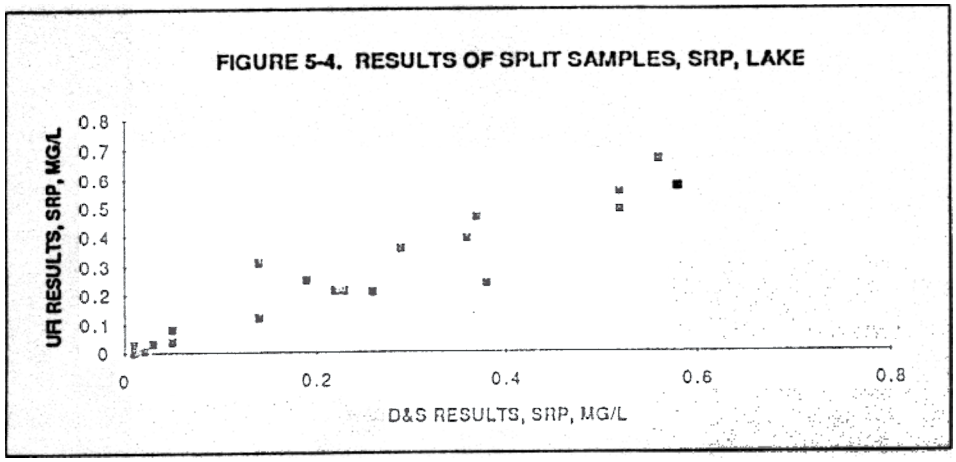

Figure 2. Evaluation of relationship between UFI and D&S measurements of SRP in split samples from depths of 1 and 16 m (lumped together) in 1991. (from Stearns and Wheler 1993).

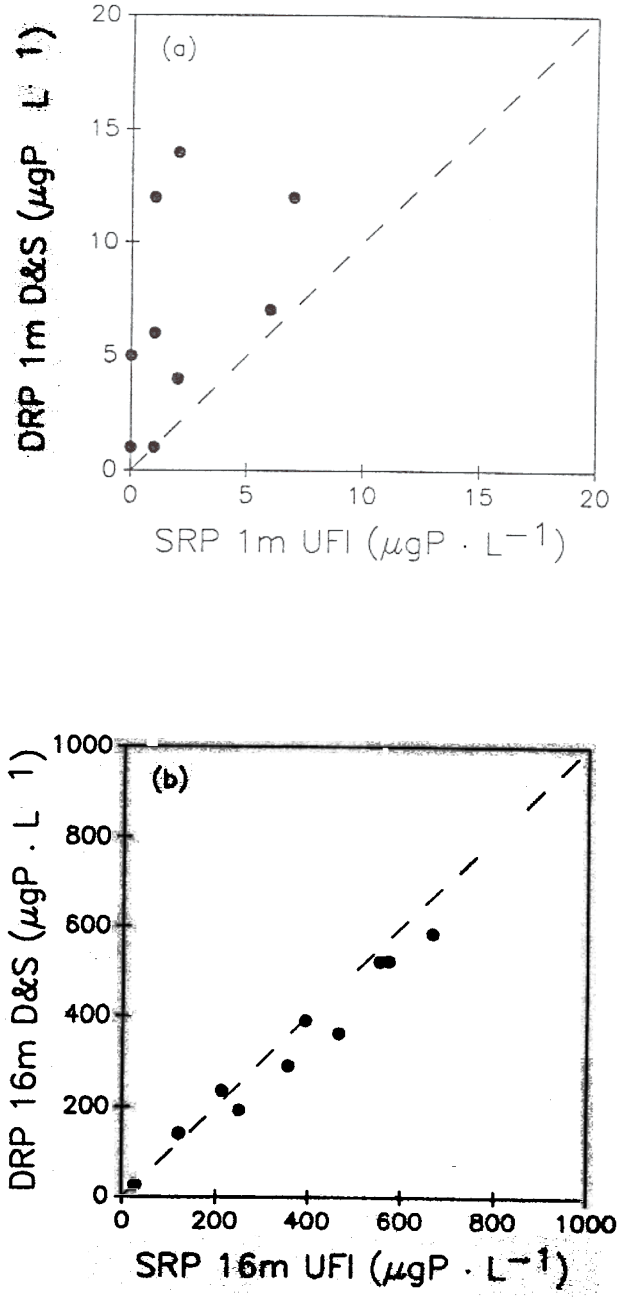

Figure 3. Evaluation of relationship between UFI and D&S measurements of SRP on split samples in 1991: a) 1 m depth, and b) 16 m depth.

reduced at the higher concentrations common to the hypolimnion The performance of the relationship for the "lumped" data (Figure 2) is greatly biased by the observations for the hypolimnion (Figure 3b). This is misleading for the conditions in the upper productive waters, so critical to phytoplankton-based aspects of water quality.

Comparison of temporal trends in near-bottom (18 m) waters over the 1987-1990 interval indicates a general consistency in the D&S and UFI data at the higher concentrations common to that depth interval (Figure 4). This is consistent with detection limit problems for D&S that are manifested only at lower concentrations. The temporal distribution for the hypolimnion in 1985 (Figure 4a) depicted in the D&S data base appears to be anomolus, and inconsistent with established limnological paradigms (e.g., progressive increases in hypolimnetic SRP during summer stratification). The elevated SRP concentrations in spring in 1986 (Figure 4b) are consistent with the documented failure of spring turnover to occur in that year (Effler and Perkins 1987).

According to Stearns and Wheler 1993 the limit of detection until early May of 1990 for the SRP test was 0.01 mg L^{-1} This corresponds to the use of a path length of 1 cm in this spectrophotometric test. This limit of detection is inappropriate to support phytoplankton models, as lower concentrations commonly observed in the upper productive layers of even eutrophic lakes that are limiting to growth can not be resolved. For example, values of Kp (see equation 1 are

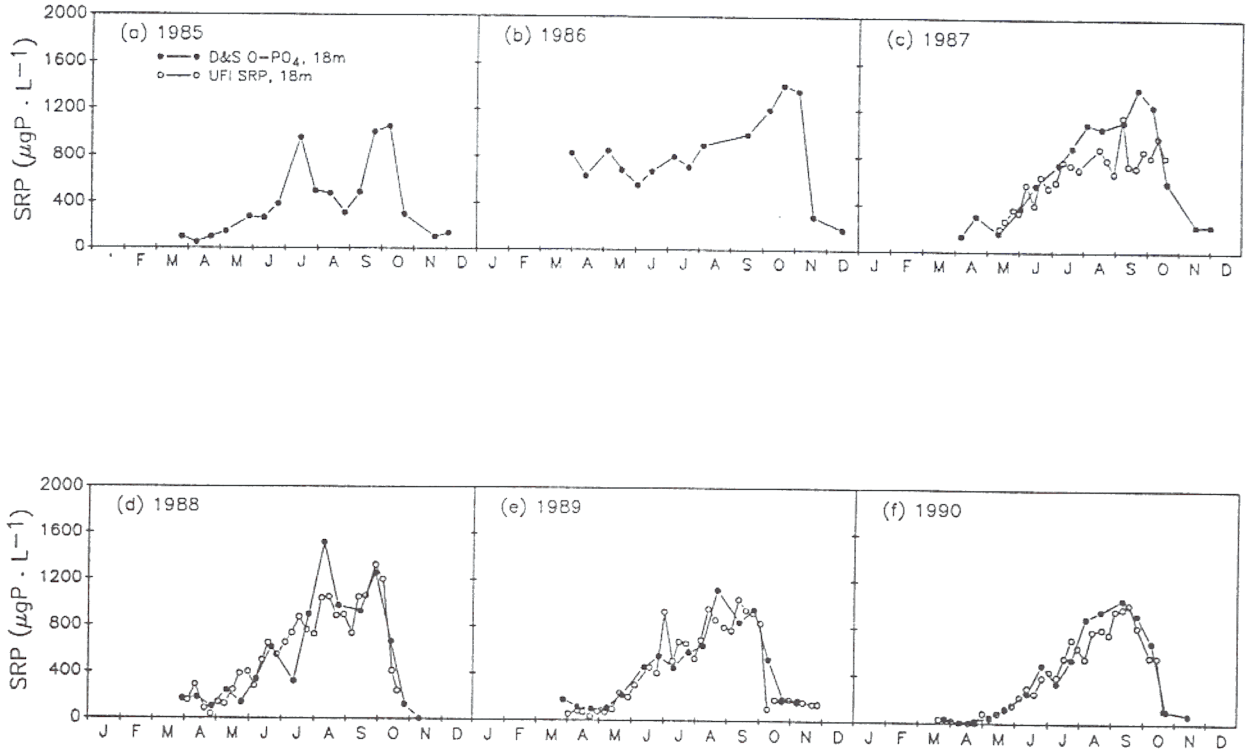

Figure 4. Temporal distributions of SRP at 18 m depth: a) 1985, b) 1986, c) 1987, d) 1988, e) 1989, and f) 1990. Comparisons of D&S and UFI data for 1987-1990.

mostly substantially lower than 10 $\mu g \cdot L^{-1}$ (see Bowie et al. 1985). Apparently an effort was made to improve their capability to resolve lower concentrations by using longer path lengths in

test, as detection limits of 5 $\mu g \cdot L^{-1}$ for a portion of May and 1 $\mu g \cdot L^{-1}$ thereafter were reported for the rest of 1990 (Stearns and Wheler 1993). UFI has utilized a 10 cm path length throughout its program

Review of D&S monitoring data for the upper waters over the period 1985-1991, particularly when compared with UFI data available for most of the interval, makes it clear these claims

detection limits are not operationally met. This is illustrated in Figures 5 and 6, which depict the seasonal distribution of SRP in the near surface waters of Onondaga Lake over the 1985-1991 interval, over the full range of observations

over the lower concentration range observed during the summer, respectively. Note that the UFI concentrations during summer are dramatically lower most of the time, reflecting the outcome of uptake by algae Figures 5 and 6). The irregular increases reported by UFI are consistent with the dynamics of phytoplankton biomass documented for the lake (Auer et al. 1990, Chapter 6), corresponding to clearing events (periods of minimum phytoplankton biomass) when uptake is suppressed and external loading and recycle continue. Exceptions are the abrupt increases in the summer of 1988 which we attribute to contamination problems (Figure 5d and 6b). Note that the match between the UFI and D&S date becomes better at the higher concentrations of spring and fall (Figures 5 and 6). Review of

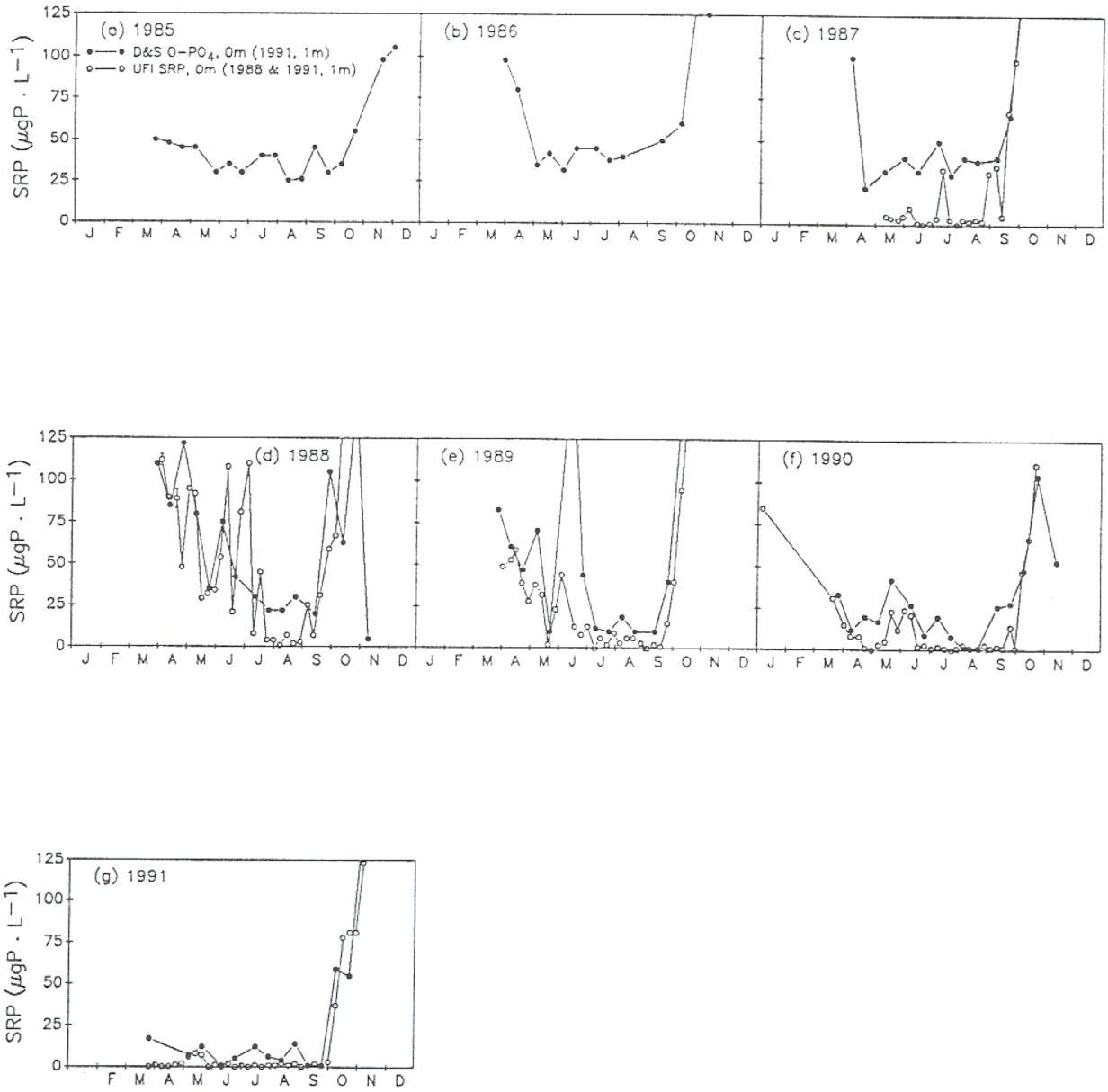

Figure 5. Temporal distributions of SRP in the upper waters (0 or 1 m): a) 1985, b) 1986, c) 1987, d) 1988, e) 1989, f) 1990, and g) 1991. Comparisons of D&S and UFI data for 1987-1991.

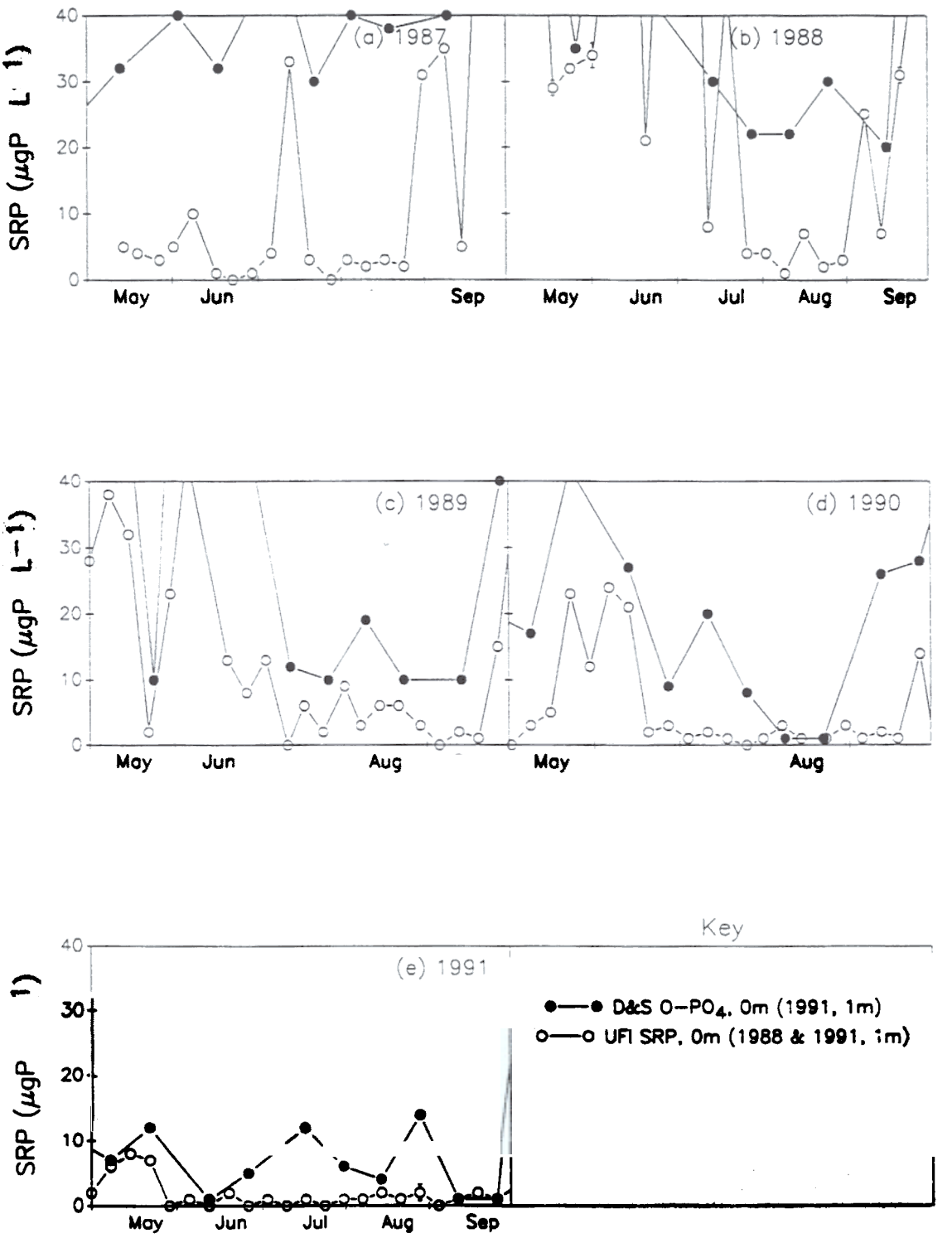

Figure 6. Comparison of temporal distributions of SRP in the upper waters, D&S and UFI, expanded scale: a) 1987, b) 1988, c) 1989, d) 1990, and e) 1991.

the distributions reported by D&S over the 1985-1988 period indicates the effective detection limit for SRP was closer to 25 $\mu g \cdot L^{-1}$ (e.g., approximate value of minima reported each year), instead of 10 $\mu g \cdot L^{-1}$ According to Monod kinetics (equation (1)) and the D&S SRP data the lake was essentially nutrient-saturated continuously (see review of Bowie et al. 1985, for listings of Kp values). A strongly contrasting picture emerges from the UFI data base, values of SRP frequently were ≤ 1 $\mu g \cdot L^{-1}$ These values are highly limiting according to Monod kinetics. Independent analyses (Connors 1993) support the position that some limitation prevails. However, the analysis of Auer et al. (1994) supports the Droop framework over the Monod for Onondaga Lake. They concluded only a modest level of limitation prevails because of effective use of other dissolved fractions of P (e.g. represented as TDP-SRP), fractions not included in the D&S program.

Some improvement in resolution of lower concentrations in the upper waters by the D&S program is indicated starting in 1989; minimum concentrations of about 10 $\mu g \cdot L^{-1}$ are reported on several occasions. Yet further decreases in the detection limit of SRP for the D&S program are apparent in 1990, as specified by Stearns and Wheler (1991), and 1991. Concentrations approaching about 1 $\mu g \cdot L^{-1}$ were reported on several occasions. In sharp contrast, UFI documented such concentrations over rather protracted periods of time (based on rather frequent measurements) in these two years. Clearly the D&S program continued to fail to accurately resolve SRP concentrations over

the 1989-1991. The SRP data base of D&S can not be used to support the development of mechanistic phytoplankton models

Implications of Limitations in D&S Phosphorus Data Base for Proposed Phytoplankton Submodel (to Calcite Model), RI/FS

Allied's consultants argued originally for an overly complex modeling approach for calcite, that included among over submodels, a mechanistic phytoplankton submodel. They identified the D&S data base as more than adequate to support the development and testing of such a model. The model, as recently described, was to be applied over the 1985-1990 interval. The issue of the interval is crucial, as it brackets the period from pre-to post-closure over which a major reduction in $CaCO_3$ precipitation occurred. Accurate P data for the appropriate species are essential to support such an effort. For example, P data cannot be subject to calibration. The model framework presently being used by Allied consultants already has many degrees of freedom; i.e., many coefficients are subject to the tuning process.

The state of the D&S P data base is such that it cannot support a phytoplankton modeling effort, for any portion of the intended 1985-1990. First, because of the flaws in the selection of P species monitored by D&S, the P cycle cannot be appropriately modeled, and related model simulations tested. For example, there is not a P measurement that includes the contribution from phytoplankton biomass. The omission of a measurement that included dissolved organic P is also seriously flawed, as phytoplankton apparently use this pool during periods

of SRP depletion in Onondaga Lake Auer et al. 1994, Connors 1993). Second, the problems of the D&S program with regards to inadequate detection/ resolution of concentrations of dissolved species, particularly SRP (as manifested in the analysis above) make these data unacceptable for support of a phytoplankton model throughout the period of interest (1985-1990).

The UFI P species data base is adequate to support related needs of a phytoplankton model. However, unfortunately it does not extend back to the pre-closure period. While a strictly post-closure phytoplankton model may have some utility in supporting predictions of seasonal precipitation/deposition of $CaCO_3$, this may be of less value to Allied's consultants. longer term (1985-1990) modeling effort offered the opportunity of bringing METRO into the analysis. Other factors, besides the inadequate P data base, argue against the phytoplankton model efforts initiated by Allied's consultants. They are addressed in our review of their draft calcite report

References

APHA. 1989. Standard Methods for the Analysis of Water and Wastewater. 17th Edition. American Public Health Association, Washington, D.C.

Auer, M.T., Effler, S.W., Storey, M.L., and Sze, P. 1994. Phytoplankton, in Chapter 6. Biology. In: S.W. Effler (editor), State of Onondaga Lake, submitted to the Onondaga Lake Management Conference, Syracuse, NY.

Berman, T. 1970. Alkaline phosphate and phosphorus availability in Lake Kinnert. Limnol. Oceanogr. **15:** 663-674.

Bowie, G.L., et al. 1985. Rates, Constants, and Kinetic Formulations in Surface Water Quality Modeling. 2nd Edition. EPA/600/3-85/040. U.S. Environmental Protection Agency, Athens, Georgia.

Carlson, R.F. 1977. A trophic states index for lakes. Limnol. Oceanogr. **22:** 361-368.

Connors, S.W. 1973. Determination of Phytoplankton Phosphorus Limitation and the Associated Effects of Stormwater Discharges on Onondaga Lake, New York. Masters Thesis. Michigan Technological University, Houghton, MI.

Dillon, P.J. 1975. The phosphorus budget of Cameron Lake, Ontario: The importance of flushing rate to the degree of eutrophy of lakes. Limnol. Oceanogr. **20:** 28-39.

DiToro, D.M. 1980. Applicability of cellular equilibrium and Monod theory to phytoplankton growth kinetics. Ecol. Model. **8:** 201-218.

————, and Connolly, J.P. 1980. Mathematical Models of Water Quality in Large Lakes, Part 2: Lake Erie. EPA/600/3080-065. Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Duluth, MN.

Droop, M.R. 1968. Vitamin B_{12} and marine ecology. IV. The kinetics of growth, uptake, and inhibition in Monochrysis lutheri. J. Mar. Biol. Assoc. U.K. **49:** 629-636.

Doerr, S.M., and Effler, S.W. 1994. A Comparative Analysis of pH Data for Onondaga Lake. Submitted to the New York State Department of Environmental Conservation, Albany, NY.

————, ————, Whitehead, K.A., Auer, M.T., Perkins, M.G., Heidtke, T.M. 1994. Chloride model for polluted Onondaga Lake. Water Res. **28:** 849-861.

Effler, S.W. 1992. Unsolicited report, submitted to R. Ott, concerning the Onondaga County data base for total inorganic phosphorus for Onondaga Creek. February 26, 1992.

———————— (editor). 1994. State of Onondaga Lake. Submitted to the Onondaga Lake Management Conference. Syracuse, NY.

————————, Driscoll, C.T., Doerr, S.M., Addess, J. and Brooks, C.M. 1994. Phosphorus, in Chapter 5. Chemistry. In: S.W. Effler (editor), State of Onondaga Lake, submitted to the Onondaga Lake Management Conference, Syracuse, NY.

————————, and Perkins, M.G. 1987. Failure of spring turnover in Onondaga Lake, NY., U.S.A. Water, Air, Soil Pollut. 34: 285-291.

————————, and Whitehead, K.A. 1994. Tributaries and Discharges, Chapter 3. In: S.W. Effler (editor), The State of Onondaga Lake. Report submitted to the Onondaga Lake Management Conference, Syracuse, NY.

Hutchinson, G.E. 1973. Eutrophication: The Scientific background of a contemporary practical problem. Amer. Sci. 61: 269-279.

Monod, J. 1942. Recherches sur la croissance des cultures bacteriennes. Hermann, Paris, France.

Stearns & Wheler. 1993. Onondaga Lake Cooperative Monitoring Program 1991 Annual Report. Submitted to the Department of Drainage and Sanitation, Onondaga County, Syracuse, NY.

Taft, J.L., Loftus, M.E., and Taylor, W.R. 1977. Phosphate uptake from phosphomonoesters by phytoplankton in Chesapeake Bay. Limnol. Oceanogr. 22: 1012-1021.

Vollenweider, R.A. 1968. Scientific Fundamentals of the Eutrophication of Lakes and Flowing Waters and Particular Reference to Nitrogen and Phosphorus as Factors in Eutrophication. Technical Report DAS/C81/68, Organization for Economic Cooperation and Development, Paris, France.

————————. 1975. Input-output models with special reference to the phosphorus loading concept in limnology. Schweiz. Z. Hydrol. 33: 53-83.

————————. (Ed.) 1982. Eutrophication of Waters: Monitoring, Assessment and Control. Organization of Economic Cooperation and Development, Paris, France.

Walker, W.W. 1991. Compilation and Review of Onondaga Lake Water Quality Data. Report submitted to Onondaga County Department of Drainage and Sanitation. Syracuse, NY.

UPSTATE FRESHWATER INSTITUTE

January 16, 1996

Mr. T. Larson
Bureau of Central Remedial Action
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NYS DEC
50 Wolf Road
Albany, N.Y. 12233-7010

Dear Mr. Larson:

Enclosed you will find a reasonably detailed analysis of phosphorus (P) input information utilized by HydroQual in their eutrophication submodel of the calcite ($CaCO_3$) model for Onondaga Lake. UFI is not supportive of the eutrophication model as a management tool because efforts to establish its credibility have not been successful. It is important to reflect on the role of the eutrophication submodel in the RI/FS. Simply stated, it's not particularly critical to the RI/FS (this has been my position from the outset). Basically if seasonal and long-term credibility could be demonstrated, it would allow the accommodation of the influence of primary productivity on the seasonality and potential long-term changes in chemical equilibrium conditions that quantify the thermodynamic tendency for the precipitation of calcite.

Despite reductions in P loading to Onondaga Lake over the 1970-1990 period, the available evidence indicates the phytoplankton of the lake remain nearly nutrient-saturated. Thus it appears unlikely that a substantial change (e.g., remediation) in phytoplankton production has occurred. In the absence of a strong phytoplankton signature (systematic change) over this, or some portion of this interval, there is little to gain by a phytoplankton submodel for the RI/FS.

Even if a eutrophication submodel was desired or needed, the temporal limits of credible testing are greatly constrained by the availability of reliable P data. The necessary (simultaneous) suite of reliable tributary and lake P data to support model testing are available only since 1987. Application of the phytoplankton submodel to earlier intervals would be highly speculative. The potential role of the facility's cooling water operation is particularly problematic. Unfortunately, Onondaga County's monitoring program is almost a complete loss for support of eutrophication model testing, because of

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inaccurate laboratory analyses and the failure to measure total phosphorus. This time constraint on model testing (≥ 1987) further limits the utility of a eutrophication submodel in the RI/FS process. Certainly Allied Signal wants the submodel to extend to before the facility closed to be able to include a primary production factor/explanation for the observed major reduction in $CaCO_3$ precipitation.

In conclusion, I can not recommend the acceptance of the complex seasonal calcite model (that includes the eutrophication submodel) by NYSDEC because the credibility necessary to justify management application(s) can not be demonstrated, due to the lack reliable data. Recommendations concerning selection among the remaining model framework alternatives for the calcite issue will emerge as other portions of our review are completed.

Sincerely

S.W. Effler

S.W. Effler, Ph.D.
Director of Research

PHOSPHORUS

Phosphorus Loading

Accurate specification of phosphorus loading is a fundamental component in the development of a credible eutrophication model. A model that is calibrated to inaccurate phosphorus loads is not a credible management tool; i.e calibration achieved only as a result of compensating errors in other source/sink processes The evidence is compelling that much of the phosphorus load input adopted by HydroQual is inaccurate

1.1 METRO

METRO is the dominant source of P to Onondaga Lake (Effler et al. 1996). The disparity in estimates of METRO's contribution by Onondaga County's various consultants is interesting. Stearns Wheler's estimates Onondaga County 1991-1993 for the 1990-1992 interval ranged from 56 to 75%, and HydroQual indicates 65 to 75% (for an unspecified period; letter to R Mustico from W. Shepard, Nov 14, 1995 However, Onondaga County (1996) has recently indicated the METRO contribution is about 50%. It is essential to accurately determine the P load from METRO to support the testing of a credible eutrophication model for Onondaga Lake (cf Doerr et al. 1996), and to fairly evaluate management options under consideration for METRO.

HydroQual appears to be unfamiliar with the available data for the METRO facility. HydroQual based their loading estimates on TIP annual loads (i.e., single number per year reported by

Onondaga County (1971-1985) for the 1970-1984 period. Estimates for the 1985-1989 period were based on TIP measurements made by the County as part of the County's monitoring program (e.g., ~ 24 observations per year) Apparently 1990 estimates were based on TP measurements from the County program (TP analysis introduced in mid-1989). The adoption of these protocols has greatly compromised the accuracy of the TP loads developed by HydroQual Further, it's inexplicable that the County did not provide proper oversight on this issue, as part of HydroQual's analysis of the deep-water discharge proposal.

The short-comings in the HydroQual loads have two basic components, temporal resolution and the limitations of TIP as a surrogate of TP (Effler et al. 1996, Effler and Whitehead 1994) Daily monitoring of TP concentration in the METRO effluent commenced in 1980. Samples were 24 h time composites through mid-October of 1988, thereafter they were flow-weighted composites. These data, as well as all other County data, are in the public domain. Assuming the TP analyses were accurate, this monitoring program (a permit requirement) is capable of supporting loading estimates that should nearly reflect the "true" load from the facility. The accuracy of the METRO effluent TP concentration data base of Onondaga County is supported by paired measurements (n = 453 made by UFI in 1989 and 1990 (Effler and Whitehead 1994; note no similar independent check on the County's TIP measurements has been made). What is the explanation for HydroQual not making use of the daily TP concentrations in developing TP loads for METRO? Further, the

less frequent (~ 24 per year) TIP data available before 1980 should have been available from Onondaga County instead basing loads on annual estimates).

The use of annual loads is inconsistent with the stated seasonal goals of the HydroQual eutrophication model, particularly for such a high flushing rate system. HydroQual does not specify what assumptions they made concerning the seasonality of the loads. Temporal uniformity throughout the year cannot be supported (e.g., Effler and Whitehead 1994; Doerr et ;al 1996). Doerr et al. (1996) found TP predictions for upper waters of the lake to be "moderately sensitive to the timing of loads, as indicated by the comparison of model output for the detailed daily loads versus simulations for the simplification of temporally uniform hydrologic and TP loads at the annual average values". TP loads must be more temporally detailed than annual to support credible seasonal predictions in this high flushing rate (Effler and Whitehead 1994 lake

Effler and Whitehead (1994 developed an empirical relationship between TIP and TP concentrations for METRO based on paired data available from the County from early 1990 through July 1991. The limitations of this expression (and those for the tributaries) were emphasized Aware of these limitations, HydroQual (1995; P.1-35) utilized this relationship to generate TP loads for the 1970-1989 interval based on TIP concentrations In the letter from S.W. Effler to J. Fitzpatrick of July 25, 1995, UFI indicated TP loads based on TIP were highly uncertain and inappropriate to support model testing. Of course, using

temporally limited TIP data when frequent TP data are available should not be considered acceptable, unless equivalent loading estimates emerge from the two data sets

The short-comings in the TIP-TP relationship for METRO are further demonstrated here by comparison of TIP and TP concentrations in METRO's effluent for samples collected on the same day in each year over the 1980-1990 interval (Figure 1) The relationship is weak in most of the years, TIP concentrations exceed TP values in several cases, and there are indications of potential systematic changes in the relationship over the interval. Particularly noteworthy is the much greater disparity between the TIP and TP measurements in 1980, before chemical precipitation treatment for P removal was initiated. This suggests the potential for major underestimation of the METRO TP load based on TIP before 1981, and indicates a change in the composition of P in the effluent from before to after the addition of treatment for P removal. This analysis (Figure 1) is not supportive of the use of the empirical expression of Effler and Whitehead (1994) to generate credible estimates of TP loads from TIP (concentrations or loads) for the 1980-1989 interval, nor the 1970-1979 period. These findings are particularly interesting in light of the claimed insights of Allied's consultants, "Because the composition of P in municipal treatment plants is fairly well known and documented, for there to be significant error in the P loading estimate, the composition of P in the tributaries would have to change significantly" (Allied Signal letter of Nov. 14, 1995

Apparently there have been some variations in the composition of P in the effluent over the 1980-1989 period (e.g., Figure 1 Extension of the TP-TIP relationship to earlier years < 1980 introduces yet greater uncertainty and the potential for greater systematic errors; e.g., additional changes in treatment (primary through 1978, secondary until mid-1981).

UFI has investigated the relative errors in annual TP loads from METRO that would result from basing the estimates on TIP measurements 24 per year. We have partitioned the contributions of frequency of sampling (daily vs twice/mo) and the use of TIP as a surrogate (and adopting the Effler and Whitehead (1994 expression). The error introduced by the limited frequency (but use of TP concentration data) is modest in most cases, the median for the 1980-1989 period is 7.6% (Figure 2a and b). However, the error resulting from limited frequency of sampling was more than 15% for 1980, and more then 20% for 1983 The combined error introduced by adopting the TIP-TP relationship (i.e., in addition to infrequent (2/mo) sampling) is substantial (e.g., compare Figure 2b and d) The maximum error associated with the combined effects of frequency and TIP as a surrogate is nearly 40% (Figure 2d), the median for the 1980-1989 period is 15% (Figure 3b). The error was greater than 10% in 8 of 10 years, and greater than 15% in 5 of 10 years.

The HydroQual METRO annual loads for the 1980-1989 period are compared to the UFI loads in Figure 3. The UFI loads are the basis of evaluation; a fair representation as the available data (daily TP concentrations) were fully utilized (Effler et al.

1996, Effler and Whitehead 1994). HydroQual loads are in error by more than 20% in 6 years of the 10 year interval; the maximum error was 38%, the median was 22%. The introduction of systematic errors of this magnitude into the eutrophication model is unacceptable, particularly when accurate loads are available Calibration with these erroneous loads indicates there are compensating errors in other parts of the model (e.g., model matches data for the wrong reasons)

A summary of the data available to support TP loading estimates for the METRO effluent for the 1970-1990 period, and related choices HydroQual made to support testing of their eutrophication model, is presented in Table 1. Loading estimates inherently become more accurate moving from the second column to the fifth column of Table 1. Throughout the entire period HydroQual has made choices that diminish the reliability of loading estimates from the dominant source of P to Onondaga Lake These choices have compromised HydroQual's model testing/ calibration effort (consider the errors indicated in Figure 3) Is there an explanation for these choices? The available TP concentration data for METRO limit credible eutrophication modeling efforts to > 1980. Subsequent treatment of the lake P data base further shrinks the appropriate eutrophication modeling period.

2 Tributaries

Accurate estimates of tributary loading are essential to support testing of a eutrophication model for Onondaga Lake

TABLE 1: Phosphorus Data to Support TP Loads from METRO, and HydroQual's Choices (x)

Year	Annual TIP Load Estimate[1]		TIP Measurements (2/mo) Effluent[2]		TP Measurements Effluent 2/mo[2]		Daily[3]
1970	yes	x	yes				
1971	yes	x	yes				
1972	yes	x	yes				
1973	yes	x	yes				
1974	yes	x	yes				
1975	yes	x	yes				
1976	yes	x	yes				
1977	yes	x	yes				
1978	yes	x	yes				
1979	yes	x	yes				
1980	yes	x	yes				yes
1981	yes	x	yes				yes
1982	yes	x	yes				yes
1983	yes	x	yes				yes
1984	yes	x	yes				yes
1985	yes		yes	x			yes
1986	yes		yes	x			yes
1987	yes		yes	x			yes
1988	yes		yes	x			yes
1989	yes		yes	x			yes
1990					yes	x	yes

1 from annual Onondaga County reports
2 public domain data available from Onondaga County, 1985-1990 data in Walker (1991) data base
3 public domain data submitted to NYSDEC monthly

Accurate tributary loads are particularly critical to support representative projections (following rigorous model testing that establishes model credibility) of related water quality characteristics for management scenarios that include diversion of METRO HydroQual's estimates of tributary loading of TP well as other P fractions) are inaccurate. This compromises overall model testing and will tend to cause misleading results for model projections of water quality for METRO diversion scenarios

Responses of Allied Signal (letter to R. Mustico of November 14, 1995) and HydroQual (letter to S.W. Effler of December 1995) on this matter are inexplicable and inappropriate. These responses have attempted to address only the limitation of TIP as a surrogate of TP to support estimates of tributary TP loading. Indeed this is a problem. The responses on this issue flawed, and will be addressed subsequently. More importantly, the TIP-TP issue is minor compared to the unacceptable quality of County tributary data through 1989 As indicated in the letter to J. Fitzpatrick of July 15, 1995 (item 6, paragraph 3), "in an unsolicited report to R. Ott of Drainage and Sanitation in 1992 I indicated the loads from Onondaga Creek were false high, apparently associated with inappropriate laboratory protocol" Through 1989 Onondaga County's laboratory used a 1 cm path length for absorbance measurements for tributary P analyses; an inappropriate choice for the concentrations that prevailed Effler and Whitehead 1994 Standard Methods (APHA 1989) recommends a path length of at least 5 cm in the concentration

range of 0.01 to 0.25 $mg \cdot L^{-1}$ The report to R. Ott should be available to HydroQual from its client, Onondaga County. The report also describes alternate (other than Onondaga County) tributary P data bases (also see Effler et al. 1991, Effler and Whitehead 1994, Heidtke and Auer 1992). The P concentrations in Onondaga Creek (the largest tributary input) reported by the County were systematically false high in 1988 and 1989, almost certainly as a result of the inappropriate analytical protocol used in the analysis (described above). In the absence of clear evidence to the contrary, it must be assumed that this problem prevailed from the start of the County's program for all the tributaries and all measured P species, because the same inappropriate laboratory protocol was used throughout that interval These false high concentrations, and the attendant false high loads, compromise testing of the eutrophication model and application of the model for the METRO diversion scenario. These errors in tributary loading will tend to result in the understatement of the benefit of METRO diversion (see HydroQual report to Onondaga County, 1995)

Arguments presented by Allied Signal (letter to R. Mustico of November 14, 1995 and HydroQual (letter to S.W. Effler of December 27, 1995) attempt to minimize the importance of the inherent uncertainties in the empirical expressions developed by Effler and Whitehead (1994) in developing loads. Part of the argument includes the following quote from Effler and Whitehead (1994 these regression equations "represent a basis to recreate the historic TP loading picture for the lake over the period of

TP monitoring". This cannot be interpreted as an endorsement by Effler and Whitehead (1994) to use such relationships to support model testing. Clearly their intent was to make the most (from a historic loading perspective) of a bad (poor data) situation. These researchers continue to not support the use of the TIP-TP relationships to recreate loads for model testing purposes. It is a moot issue in light of the over-riding data quality problems of the County's tributary data discussed above. It is noteworthy that Effler, Brooks and Whitehead (1996) recently indicated in the peer-reviewed literature that reliable estimates of total loading (TP) from tributaries are available only for ≥ 1987. The 1987-1989 loads presented in that work are based on different data (on TP measurements, see Effler and Whitehead 1994) than incorporated in the County (i.e., HydroQual) estimates of TIP loads

Further, in light of the demonstrated variability in the TIP-TP relationship for METRO over the 1980-1989 interval, what are the compelling arguments for accepting such an approach for the tributaries Under these circumstances, HydroQual would need to demonstrate the veracity of such expressions over a range of years The inaccuracy of the tributary TIP measurements (see report to R. Ott) overrides this issue

Allied Signal's consultants (letter to R. Mustico of November 14, 1995) and HydroQual (letter to S.W. Effler of December 27, 1995) present a scenario related to the TIP-TP tributary issue concerning the potential uncertainty associated with the organic P (OP) fraction. The scenario, "if the fraction

of OP in the tributaries was underestimated for historical conditions", was poorly conceived. If the report to R. Ott, cited in the letter to J. Fitzpatrick of July 25, had been reviewed appropriately, Allied Signal's consultants would recognize that the more appropriate scenario would be this fraction of P, as well as all the other fractions, have often been overestimated because of short-comings in the County's laboratory program.

More problematic is the modeling philosophy that emerges concerning this scenario. Performance characteristics of the eutrophication model, that incorporates many degrees of freedom (e.g., many coefficients for which there are not system-specific determinations), is used as a basis to evaluate the potential for short-comings in loading data. This approach is inappropriate; it turns the model testing process on its head. We would be most interested in literature citations where this practice has been adopted, under similar circumstances (e.g., non-conservative substance(s), many degrees of freedom in the model, major uncertainties in so many years of loading data).

HydroQual indicated in its letter of December 27, 1995 (p.11 that UFI has similarly evaluated model input data based on model performance, citing the chloride model of Doerr et al. (1994). The circumstances were distinctly different in that work; contrasting features of the Doerr et al. (1994) modeling effort include:

1. conservative substance modeled, i.e., no reaction terms,

2. loads much more well defined,
3. similarity of Cl^- concentration data from different laboratories established for a number of years (e.g. see Figure 4 of Walker 1991) of the modeled period
4 clear in-lake signatures in seasonal structure manifested in most years, and
5. a striking long-term structure manifested associated with the closure of the Allied Signal facility

The circumstances of the HydroQual eutrophication model are strikingly different, and unsupportive of the use of the model to evaluate loads

1. P, and its various species, are far from conservative The P cycle is complex, and its representation in the HydroQual model is complex (e.g., many "knobs to turn" in calibration),
2. loads are poorly defined, related to poor choices in species to monitor and laboratory protocol by Onondaga County, and
3. poorly defined in-lake temporal signatures (short-and long-term) of important P species, particularly in the upper waters of the lake, because of poor choices in species to monitor and laboratory protocol by Onondaga County.

Interestingly, HydroQual failed to indicate that Doerr et al.'s (1994) identification of the County's lake data as probably flawed was based on more than model performance "Further, limited data from a alternate source (Walker 1991) differ greatly

(from the County D&S data) in several instances in these years" (p.856, Doerr et al. 1994). Other aspects of HydroQual's responses to UFI comments concerning the County's chloride data will be provided in a separate communication.

Consistent with the structure of HydroQual's (1994, 1995 model, they have split the P load into five fractions: 1 dissolved inorganic P or PO_4^{3-}, 2) labile dissolved organic P (LDOP), 3 refractory dissolved organic P (RDOP), 4 labile particulate organic P (LPOP), and 5) refractory particulate organic P (RPOP). Very rarely would any monitoring program have direct estimates of all of these fractions. Such partitioning for the tributaries is of course fatally compromised by the use of Onondaga County data that is unreliable through at least 1989 (see above) However, even under the hypothetical case of accurate tributary data, this partitioning of the fractions necessarily introduces uncertainty in loading conditions. The County program through 1989 could have only supported credible specification of two fractions, dissolved inorganic (PO_4^{-3} P and LDOP. The apportioning of the other three forms appears quite arbitrary (equally, sum of these three components equal to the residual of TP and TIP). Such an approach should not be accepted until its implications are fully demonstrated and found acceptable

1.3. Internal Loading Associated with Allied's Use of the Lake as a Source of Cooling Water

The use of the hypolimnion as a source of cooling water by Allied Signal resulted in the net transfer of water from the

lower enriched hypolimnion to the productive epilimnion because of reductions in density associated with increases in temperature (Effler and Owens 1986, 1987). This artificial cycling of water if of particular concern with regards to P and eutrophication modeling for the period before Allied Signal closed (1986) as it represents a potentially important internal load associated with the operation of the facility. Our position that this operation caused a potentially important internal load is based on: 1 the high flow rates that prevailed in certain years, e.g., 2.3 to 3.6 $m^3 \cdot s^{-1}$ (e.g., average METRO flow is ~ 3.2 $m^3 \cdot s^{-1}$ for much of the summers of 1980 and 1981 (Effler and Owens 1987), 2) the very high P concentrations that develop(ed) in the lake's hypolimnion (Auer et al 1993, Doerr et al. 1996, Driscoll et al. 1993, Effler 1996 and 3 the highly available form of P in the hypolimnion (Effler 1996). Effler and Owens (1987) estimated this internal load was about 20% of the external load over the April-October interval of 1980 and 1981; it was estimated to be the single largest source over the June August interval of 1981. Unfortunately, the Effler and Owens (1987) estimates must be considered uncertain as a result of their uncertainty in the depth of the deep water intakes, because of the strong vertical gradients in P concentrations that prevail within the hypolimnion for much of the summer (Doerr et al. 1996, Effler 1996)

Several forms of data would be necessary to develop adequate estimates of this internal load:

1) detailed operating information for the cooling water intakes for all years, including:

a) identity of intake (was it a shallow or deep-water intake? and period of operation,

b) withdrawal rate, accurately temporally resolved.

2) depth of intake(s) This information has been requested Allied Signal by NYSDEC at a RI/FS meeting. The information has not been provided. It is crucial that information be accurate (e.g., engineering drawings perhaps checked against recent underwater survey).

3 accurate P data from the lake over the period of cooling water withdrawal.

These internal loads (if emanating from depth ≥ those assumed by Effler and Owens 1987) need to be seasonally resolved. Extending such estimates to earlier than 1980 may be problematic, as P loads routed to Ninemile Creek via the West Flume may have been significantly diminished by in-stream reaction with the $CaCO_3$ deposits (e.g., Effler et al. 1991) formed from Allied Signal's wastebed discharges. HydroQual needs to accurately estimate this potentially important internal load before it includes any of the years during which Allied Signal operated the deep (hypolimnion) cooling water intakes in the eutrophication model. HydroQual needs to quantitatively address the issue of the extent to which the absence of a detailed treatment of the cooling water operation has impacted other features of their water quality model analysis

1.4. Changes in TP Loading Adopted for the METRO Deep-Water Discharge Proposal

The HydroQual TP loading story changes abruptly in their

analysis of the METRO deep-water proposal (HydroQual 1995) late in the report (paragraph 1, under 3.2 Initial Projections) HyrdroQual indicates the TP loading estimates for the 1985 -1990 period were, "revised" based on comparisons with values presented in a Effler and Canale (1993) reference. Why were these changes not incorporated in the appropriate earlier section of the report that described the development of loads? I am unaware of a "water quality model documentation report" prepared by Effler and Canale. I am unaware of any report/manuscript prepared with that authorship in that year. UFI did prepare a report in 1993 (Canale et al. 1993 that included TP loading estimates for 1987-1990. No loads for 1985 and 1986 were included. HydroQual indicates changes were made, but differences apparently persisted in the loads from the UFI values "our revised estimates are within 10 percent of those reported by Is this a result of more averaging procedures (e.g., average erroneous loads with representative loads to get less erroneous loads)? These loads for the METRO deep-water analysis are apparently different from those incorporated in the RI/FS analysis (HydroQual and PTI 1994). HydroQual's documentation of development of these modified loads is woefully inadequate, and the supporting citations and statements are inaccurate. HydroQual acknowledged deterioration in certain features of model performance as a result of these modifications in TP loading. It's highly likely these performance characteristics would further deteriorate if the most representative loads were adopted for the 1987-1990 period.

2.0 Lake Phosphorus Data

2.1 SRP

The response of Allied Signal's consultants on November 1995 are quite different than those of HydroQual on December 1995 concerning the SRP/orthophosphorus detection limit problem of D&S for upper water samples. In the November 14 response, Allied's consultants could not explain the disparity between the D&S concentrations and HydroQual's calibration values for 1987 and 1990 (" in 1987 D&S mid-summer surface concentrations in Figure 6[+] are about 30 to 40 µg/L, whereas in the calibration plot they are about 10 to 20 µg/L. The cause for this disparity is not clear" In the December 27, response, HydroQual indicates both D&S and UFI data are included in the calibration plot values, implying this is the reason for the previously unexplained disparity. Why is the "story" changing? How were the D&S and UFI data averaged? HydroQual indicates averaging protocols would be clearly described throughout the response (p.1 of HydroQual response) - however, it remains far from clear how the SRP calibration plot data were arrived at (Figure 15, HydroQual response).

Effler and Doerr (1994 concluded that the SRP concentration data base of D&S was inaccurate; specifically, most of epilimnion values are false high as a result of detection limit problems Substantial evidence was presented in support of this

[+] the legend Figure 6 of the Effler and Doerr memo (1994) was corrected by memo in March of 1995 (i.e., before release of Allied Signal; see attached), apparently this correction was not passed along to Allied Signal.

position. Allied's consultants (November, 1995) and HydroQual (December 1995) present no evidence in defense of the D&S epilimnetic SRP data HydroQual acknowledges "that much of the D&S epilimnion SRP data may suffer from detection limit problems" - this is an understatement, as there is no evidence presented to the contrary.

In sharp contrast to the D&S P data base, much of the UFI P data base has been subjected to rigorous peer-review as part of the publication of related research manuscripts (e.g., Auer et al. 1993, Connors et al. 1996, Driscoll et al. 1993). In particular, the detailed time distributions of SRP (as well as dissolved organic P) in the upper waters of Onondaga Lake for the summers of 1989-1992 were subjected to rigorous review as part of an intensive analysis of P pools and alkaline phosphatase activity (Connors et al. 1996)

Averaging of D&S's erroneous SRP data with UFI's representative data is an entirely unacceptable manner in which to develop calibration data for this parameter. HydroQual's resulting calibration data set for SRP in the epilimnion (e.g 10 to 20 $\mu g \cdot L^{-1}$ in 1987, 5 to 10 $\mu g \cdot L^{-1}$ in 1989 (Allied Signal's consultants, November, 1995) is far from representative of conditions that prevailed. What is the justification for averaging such disparate data sets, particularly in light of the known non-linear response of phytoplankton within this range of concentrations? Allied's consultants indicate that the "biased-high" (HydroQual, December, 1995)/ "high D&S detection" limits (Allied Signal, November, 1995) calibration data were

largely ignored - and that the more realistic model projections ~ 2 $\mu g \cdot L^{-1}$ minimum, claimed to be similar to UFI measurements) emerged from calibration. This is instead apparently a result of judgment, that would have been better applied in the development of the calibration data. The implication that the 2 $\mu g \cdot L^{-1}$ minimum prediction in calibration emerged because of the limited ranges of related model coefficients is an assertion, that would be quite an undertaking to demonstrate in a statistically rigorous manner (e.g., Storey et al. 1993).

It is noted that Allied Signal's consultants chose not to respond to P issues related to Onondaga County's unfortunate selection of species to monitor. In particular, there is not a P measurement that includes the contribution of phytoplankton biomass. The lack of a measure of dissolved organic P is also a problem, as phytoplankton apparently use this pool during periods of SRP depletion in Onondaga Lake (Connors et al 1996). These omissions in the data base are fatal limitations for the rigorous testing of a eutrophication model. Credible and appropriate epilimnetic P data, necessary to develop a credible eutrophication model, are available only since 1987. This condition is even more temporally limiting than the availability of reliable METRO loading data

3.0 Implications for Eutrophic Model Testing

Consider now, in light of the foregoing limitations identified in this analysis, the implications for testing the eutrophication model for the 1970-1990 period. It's fair to say that major changes in external P loading occurred over this

period (e.g., Effler et al. 1996, Effler and Whitehead 1994) However, the reduction in external loading from the dominant source (METRO) is poorly defined before 1980, the interval over which the largest portion of the load reduction occurred (Effler and Whitehead 1994). Tributary loads based on Onondaga County data through 1989 are unreliable and almost certainly false high This eliminates quantification of any significant systematic changes that may have occurred in this smaller component of external loading. The change in internal loading, associated with Allied Signal's use of the lake as a source of cooling water (that potentially had as seasonal structure critical to summer phytoplankton growth), that may have resulted from operational variations before closure and almost certainly occurred with the closure of the facility, remain largely unquantified. The loading picture is unfortunately very poorly defined, particularly with respect to the major changes that occurred.

The lack of reliable calibration data sets for in-lake concentrations of various P species (particularly for the upper productive layers) before 1987 fatally compromises eutrophication model testing that focuses on the 1970-1990 period. Performance of a eutrophication model in simulating P species, particularly TP (i.e., includes contributions from phytoplankton biomass) and SRP (e.g., representation of P available to support phytoplankton growth), is a critical basis for evaluating model credibility. We indicated previously the importance of also having reliable measurements of DOP. The County did no measure TP in the lake until part way through 1989. UFI's TP data base starts in 1987

Though measurements of SRP (ortho-P) are available from Onondaga County's program since 1970, the situation for SRP is really no better than for TP, because the County's SRP measurements from the upper layers are unreliable. Effler and Doerr (1994 established the County's SRP data were unreliable (false high) associated with detection limit problems (apparently HydroQual largely concedes this point). Consider the SRP situation within the context of HydroQual's (letter of December 27, 1995) Figure 15. The calibration data sets of 1987, 1989 and 1990 are false high due to the inclusion of D&S data with UFI data. Corrections can be made for these years by eliminating the D&S data. However, all the earlier data (from D&S) are unreliable. No reliable adjustments of D&S data are possible (e.g., note, there are not indications that the degree of the detection limit problem has been uniform). Thus there is no basis to test the interannual and seasonal structures predicted by the HydroQual model (Figure 15, letter of December 27, 1995; e.g., increased degree and period of SRP depletion from the 1970's to 1980's) and therefore the model's credibility.

The selection of the 1970-1990 period for model testing is conceptually flawed for application to METRO management alternatives presently under consideration. Instead, the focus should be testing a eutrophication model for the range of conditions that presently prevail (e.g., Doerr et al. 1996).

References

Auer, M.T., Johnson, N.A., Penn, M.R., and Effler, S.W. 1993. Measurement and verification of rates of phosphorus release for a hypereutrophic urban lake. Hyrobiologia 253: 301-309.

Canale, R.P., Doerr, S.M., and Effler, S.W. 1993. Total Phosphorus Model Report - Onondaga Lake, 1987-1990. Report submitted to Central New York Regional Planning and Development Board, Syracuse, NY.

Connors, S.D., Auer, M.T., and Effler, S.W. 1996. Phosphorus pools, alkaline phosphatase activity, and phosphorus limitation in hypereutrophic Onondaga Lake, NY. Lake Reservoir Manage. (in press)

Doerr, S.M., Canale, R.P., and Effler, S.W 1996. Development and testing of a total phosphorus model for Onondaga Lake, N.Y. Lake Reservoir Manage. (in press).

Doerr, S.M., Effler, S.W., Whitehead, K.A., Auer, M.T., Perkins, M.G., and Heidtke, T.M. 1994. Chloride model for polluted Onondaga Lake. Wat. Res. 28: 849-861

Driscoll, C.T., Effler, S.W., Auer, M.T., Doerr, S.M., and Penn, M.R. 1993. Supply of phosphorus to the water column of productive hardwater lake: controlling mechanisms and management considerations. Hydrobiologia 253: 61-72

Effler, S.W (ed. 1996. Limnological and Engineering Analysis of a Polluted Urban Lake. Prelude of Environmental Management of Onondaga Lake, New York Springer-Verlag, NY (in press)

Effler, S.W Brooks, C.M., Addess, J.M., Doerr, S.M., Storey, M.L., and Wagner, B.A 1991 Polluted loadings from Solvay waste beds to lower Ninemile Creek, New York.

Effler, S.W., Brooks, C.M., and Whitehead, K.A 1996. Domestic waste inputs of nitrogen and phosphorus to Onondaga Lake, and water quality implications Lake Reservoir Manage. in press).

Effler, S.W., and Doerr, S.M. 1994. A comparative analysis of phosphorus data for Onondaga Lake, and implications Report submitted to NYSDEC, Albany, NY

Effler, S.W., and Owens, E.M. 1986. The density of inflows to Onondaga Lake, U.S.A., 1980 and 1981 Wat. Air Soil Pollut 28: 105-115

Effler, S.W., and Owens, E.M. 1987. Modifications in phosphorus loading to Onondaga Lake, U.S.A., Associated with alkali manufacturing. Wat. Air Soil Pollut 32: 177-182.

Effler, S.W., and Whitehead, K.A. 1994. Tributaries and Discharges (Chapter 3). In S.W. Effler (ed. State of Onondaga Lake Management Conference Syracuse, NY.

Heidtke, T.M., and Auer, M.T. 1992. Partitioning phosphorus loads: Implications for Lake restoration J. Wat. Resour. Plans Manage. 118: 562-579

HydroQual. 1995. Hydrodynamic Evaluation of METRO Outfall Relocation in Onondaga Lake, and Application of the Onondaga Lake Eutrophication Models in the Evaluation of METRO Treatment Alternatives and Wasteload Allocation. Report to Onondaga County, Syracuse, NY

HydroQual and PTI. 1994. Onondaga Lake RI/FS: Calcite Modeling Report. Prepared for Allied Signal Inc. Solvay, New York

Onondaga County. 1996 Proposed Municipal Compliance Plan. Syracuse, NY

Onondaga County. 1971-1993. Onondaga Lake Monitoring Program Annual Report of Department of Drainage and Sanitation, Onondaga County, Syracuse, NY

Storey, M.L., Auer, M.T., Barth, A.K., and Graham, J.M. 1993. Site-specific determination of kinetic coefficients for modeling algal growth. Ecol. Model. 66: 181-196

Walker, W.W. 1991. Compilation and Review of Onondaga Lake Water Quality Data, Report submitted to Onondaga County, Syracuse, NY.

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Communication No. 4 to HydroQual Concerning Onondaga Lake: Review of HydroQual's Phosphorus Loading Estimates and Associated Protocols, and Comments on HydroQual Responses Concerning UFI's Analysis of the Phosphorus Data Base of Onondaga County

This letter is the fourth concerning HydroQual's modeling analyses of Onondaga Lake. This communication focuses on phosphorus (P), specifically P loading and P data used for model testing. This correspondence does not address the model framework for P and related processes (perhaps in later communications). The treatment of P loading represents an expansion of UFI's review; most of the material has not been presented to you previously. The discussion of lake P data represents our comments on your related responses presented in the HydroQual letter of December 27, 1995, and the AlliedSignal letter of W. Shephard of November 14, 1995.

For the record, we reiterate (see letter of October 2, 1995) UFI's reasons for participating in this dialogue: "1) our past work on Onondaga Lake, 2) the implications if the model is used as the basis of management action, 3) the ongoing controversy about scientific analysis and studies on the Lake, 4) the conflicting interests of Onondaga County and AlliedSignal in these matters, and 5) our commitment to the rehabilitation of Onondaga Lake based on unimpeachable scientific analysis".

A eutrophication model can not be rigorously tested for Onondaga Lake for the 1970-1990 period because of the lack of appropriate and reliable P concentration data for the lake and its inputs for much of that interval. Testing of such a model should instead focus on a much shorter period (since 1987) for which an appropriate and credible data set exists. An exceptional opportunity has been missed to track and simulate the effects of major reductions in external, and perhaps internal, P loading that occurred through the mid-1980's. This is unfortunate for lake managers in general, but particularly those concerned with remediation of Onondaga Lake. The responsibility for this lost

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opportunity lies with Onondaga County, associated with the short-comings in their monitoring program, as delineated herein.

Despite additional descriptions provided in your letter of December 27, 1995, the documentation of various procedures related to P can still be described as incomplete and cryptic. For example, how were seasonal loads developed from annual loads? Attached you will find a reasonably detailed review of HydroQual's protocols for developing P loads, comments on HydroQual's response to UFI's concerns regarding the quality of Onondaga County lake P data, and our evaluation of the implications for eutrophication modeling. Some of the more salient features are listed below.

1 Inaccurate annual TIP loads were used by HydroQual to drive a seasonal eutrophication model, despite the availability of more temporally detailed data, including daily TP concentrations from METRO since 1980.

2 Despite being aware of the potential inherent limitations, described by Effler and Whitehead (1994), HydroQual applied empirical TIP-TP relationships to estimate TP loads for model testing from TIP data. Additional analyses presented here indicate this practice introduces substantial error in loading estimates from the dominant source, METRO.

3. HydroQual has not recognized (and apparently has not been informed by Onondaga County) that Onondaga County P data for tributaries through 1989 are unreliable because of short-comings in the County's laboratory program.

4 HydroQual (letter of December 27, 1995) has used the performance characteristics of a eutrophication model, in the absence of successful rigorous model testing, as a basis to evaluate the potential for short-comings in loading data.

5. The potentially important role of Allied Signal's cooling water operation in cycling P within the lake has not been considered in HydroQual's analysis. This issue also needs to be considered for other constituents being modeled.

6 Inaccurate model calibration data for the concentration of soluble reactive P in the upper waters were developed by the inexplicable averaging of UFI data with erroneous County data.

7 HydroQual has not recognized the extent to which the short-comings in Onondaga County's monitoring program has limited the period over which rigorous testing of eutrophication model for Onondaga Lake is possible.

Revisions in loading estimates are not recommended for the period before 1987, because the lack of reliable lake and tributary P data precludes eutrophication model testing for that period.

I am sure that we all agree that it is to everyone's advantage to make absolutely sure that all scientific work on Onondaga Lake stands up to rigorous scrutiny. We have undertaken this correspondence in that spirit.

Please feel free to contact me with any questions you may have concerning the contents of this communication (315-466-1309).

Sincerely,

S.W. Effler, Ph.D.
Director of Research

cc: Mr. Walter Shepard, Allied Signal, Inc.
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Mr. Timothy Larsen, NYSDEC
Mr. Ronald Sloan, NYSDEC
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PHOSPHORUS

1.0 Phosphorus Loading

Accurate specification of phosphorus loading is a fundamental component in the development of a credible eutrophication model. A model that is calibrated to inaccurate phosphorus loads is not a credible management tool; i.e., calibration achieved only as a result of compensating errors in other source/sink processes. The evidence is compelling that much of the phosphorus load input adopted by HydroQual is inaccurate.

1.1 METRO

METRO is the dominant source of P to Onondaga Lake Effler et al. 1996). The disparity in estimates of METRO's contribution by Onondaga County's various consultants is interesting. Stearns and Wheler's estimates (Onondaga County 1991-1993 for the 1990-1992 interval ranged from 56 to 75%, and HydroQual indicates 65 to 75% (for an unspecified period; letter to R. Mustico from W Shepard, Nov. 14, 1995) However, Onondaga County (1996) has recently indicated the METRO contribution is about 50% It is essential to accurately determine the P load from METRO to support the testing of a credible eutrophication model for Onondaga Lake (cf. Doerr et al 1996), and to fairly evaluate management options under consideration for METRO.

HydroQual appears to be unfamiliar with the available data for the METRO facility HydroQual based their loading estimates on TIP annual loads (i.e., single number per year reported by

Onondaga County (1971-1985) for the 1970-1984 period. Estimates for the 1985-1989 period were based on TIP measurements made by the County as part of the County's monitoring program (e.g., ~ 24 observations per year. Apparently 1990 estimates were based on TP measurements from the County program (TP analysis introduced in mid-1989) The adoption of these protocols has greatly compromised the accuracy of the TP loads developed by HydroQual Further, it's inexplicable that the County did not provide proper oversight on this issue, as part of HydroQual's analysis of the deep-water discharge proposal.

The short-comings in the HydroQual loads have two basic components, temporal resolution and the limitations of TIP as a surrogate of TP (Effler et al. 1996, Effler and Whitehead 1994) Daily monitoring of TP concentration in the METRO effluent commenced in 1980. Samples were 24 h time composites through mid-October of 1988, thereafter they were flow-weighted composites. These data, as well as all other County data, are in the public domain. Assuming the TP analyses were accurate, this monitoring program (a permit requirement) is capable of supporting loading estimates that should nearly reflect the "true" load from the facility. The accuracy of the METRO effluent TP concentration data base of Onondaga County is supported by paired measurements (n = 453 made by UFI in 1989 and 1990 Effler and Whitehead 1994; note no similar independent check on the County's TIP measurements has been made What is the explanation for HydroQual not making use of the daily TP concentrations in developing TP loads for METRO? Further, the

less frequent 24 per year TIP data available before 1980 should have been available from Onondaga County (instead of basing loads on annual estimates)

The use of annual loads is inconsistent with the stated seasonal goals of the HydroQual eutrophication model, particularly for such a high flushing rate system. HydroQual does not specify what assumptions they made concerning the seasonality of the loads. Temporal uniformity throughout the year cannot be supported (e.g., Effler and Whitehead 1994, Doerr et ;al. 1996 Doerr et al. (1996) found TP predictions for the upper waters of the lake to be "moderately sensitive to the timing of loads, as indicated by the comparison of model output for the detailed daily loads versus simulations for the simplification of temporally uniform hydrologic and TP loads at the annual average values" TP loads must be more temporally detailed than annual to support credible seasonal predictions in this high flushing rate (Effler and Whitehead 1994 lake.

Effler and Whitehead (1994) developed an empirical relationship between TIP and TP concentrations for METRO based on paired data available from the County from early 1990 through July 1991. The limitations of this expression (and those for the tributaries) were emphasized Aware of these limitations HydroQual (1995; P.1-35) utilized this relationship to generate TP loads for the 1970-1989 interval based on TIP concentrations. In the letter from S.W. Effler to J. Fitzpatrick of July 25, 1995, UFI indicated TP loads based on TIP were highly uncertain and inappropriate to support model testing. Of course, using

temporally limited TIP data when frequent TP data are available should not be considered acceptable unless equivalent loading estimates emerge from the two data sets.

The short-comings in the TIP-TP relationship for METRO are further demonstrated here by comparison of TIP and TP concentrations in METRO's effluent for samples collected on the same day in each year over the 1980-1990 interval (Figure 1 The relationship is weak in most of the years, TIP concentrations exceed TP values in several cases, and there are indications of potential systematic changes in the relationship over the interval Particularly noteworthy is the much greater disparity between the TIP and TP measurements in 1980, before chemical precipitation treatment for P removal was initiated. This suggests the potential for major underestimation of the METRO TP load based on TIP before 1981, and indicates a change in the composition of P in the effluent from before to after the addition of treatment for P removal. This analysis (Figure 1 is not supportive of the use of the empirical expression of Effler and Whitehead (1994) to generate credible estimates of TP loads from TIP (concentrations or loads) for the 1980-1989 interval, nor the 1970-1979 period These findings are particularly interesting in light of the claimed insights of Allied's consultants, "Because the composition of P in municipal treatment plants is fairly well known and documented, for there to be significant error in the P loading estimate, the composition of P in the tributaries would have to change significantly" (Allied Signal letter of Nov. 14, 1995).

Apparently there have been some variations in the composition of in the effluent over the 1980-1989 period (e.g Figure 1 Extension of the TP-TIP relationship to earlier years < 1980) introduces yet greater uncertainty and the potential for greater systematic errors; e.g , additional changes in treatment (primary through 1978, secondary until mid-1981)

UFI has investigated the relative errors in annual TP loads from METRO that would result from basing the estimates on TIP measurements 24 per year) We have partitioned the contributions of frequency of sampling (daily vs twice/mo) and the use of TIP as a surrogate (and adopting the Effler and Whitehead (1994) expression). The error introduced by the limited frequency (but use of TP concentration data) is modest in most cases, the median for the 1980-1989 period is 7.6% (Figure 2a and b) However, the error resulting from limited frequency o sampling was more than 15% for 1980, and more then 20% for 1983 The combined error introduced by adopting the TIP-TP relationship (i.e., in addition to infrequent (2/mo sampling) is substantial (e.g., compare Figure 2b and d). The maximum error associated with the combined effects of frequency and TIP as a surrogate is nearly 40% (Figure 2d), the median for the 1980-1989 period is 15% (Figure 3b) The error was greater than 10% in 8 of 10 years and greater than 15% in 5 of 10 years

The HydroQual METRO annual loads for the 1980-1989 period are compared to the UFI loads in Figure 3 The UFI loads are the basis of evaluation; a fair representation as the available dat (daily TP concentrations) were fully utilized (Effler et al

1996 Effler and Whitehead 1994) HydroQual loads are in error by more than 20% in 6 years of the 10 year interval the maximum error was 38% the median was 22% The introduction of systematic errors of this magnitude into the eutrophication model is unacceptable, particularly when accurate loads are available Calibration with these erroneous loads indicates there are compensating errors in other parts of the model (e.g., model matches data for the wrong reasons)

A summary of the data available to support TP loading estimates for the METRO effluent for the 1970-1990 period, and related choices HydroQual made to support testing of their eutrophication model, is presented in Table 1. Loading estimates inherently become more accurate moving from the second column to the fifth column of Table 1. Throughout the entire period HydroQual has made choices that diminish the reliability of loading estimates from the dominant source of P to Onondaga Lake These choices have compromised HydroQual's model testing/calibration effort (consider the errors indicated in Figure 3) Is there an explanation for these choices? The available TP concentration data for METRO limit credible eutrophication modeling efforts to >=1980. Subsequent treatment of the lake P data base further shrinks the appropriate eutrophication modeling period.

1.2 Tributaries

Accurate estimates of tributary loading are essential to support testing of a eutrophication model for Onondaga Lake

TABLE 1: Phosphorus Data to Support TP Loads from METRO, and HydroQual's Choices (x)

Year	Annual TIP Load Estimate[1]		TIP Measurements (2/mo) Effluent[2]		TP Measurements Effluent 2/mo[2]		Daily[3]
1970	yes	x	yes				
1971	yes	x	yes				
1972	yes	x	yes				
1973	yes	x	yes				
1974	yes	x	yes				
1975	yes	x	yes				
1976	yes	x	yes				
1977	yes	x	yes				
1978	yes	x	yes				
1979	yes	x	yes				
1980	yes	x	yes				yes
1981	yes	x	yes				yes
1982	yes	x	yes				yes
1983	yes	x	yes				yes
1984	yes	x	yes				yes
1985	yes		yes	x			yes
1986	yes		yes	x			yes
1987	yes		yes	x			yes
1988	yes		yes	x			yes
1989	yes		yes	x			yes
1990					yes	x	yes

1 from annual Onondaga County reports
2 public domain data available from Onondaga County, 1985-1990 data in Walker (1991) data base
3 public domain data submitted to NYSDEC monthly

Accurate tributary loads are particularly critical to support representative projections (following rigorous model testing that stablishes model credibility) of related water quality characteristics for management scenarios that include diversion of METRO HydroQual's estimates of tributary loading of TP (as well as other P fractions) are inaccurate. This compromises overall model testing and will tend to cause misleading results for model projections of water quality for METRO diversion scenarios

Responses of Allied Signal (letter to R Mustico of November 14, 1995 and HydroQual (letter to S.W. Effler of December 27, 1995) on this matter are inexplicable and inappropriate These responses have attempted to address only the limitation of TIP as a surrogate of TP to support estimates of tributary TP loading Indeed this is a problem The responses on this issue are flawed, and will be addressed subsequently More importantly, the TIP-TP issue is minor compared to the unacceptable quality of County tributary data through 1989 As indicated in the letter to J. Fitzpatrick of July 15, 1995 (item 6, paragraph 3) "in an unsolicited report to R. Ott of Drainage and Sanitation in 1992 I indicated the loads from Onondaga Creek were false high apparently associated with inappropriate laboratory protocol" Through 1989 Onondaga County's laboratory used a 1 cm path length for absorbance measurements for tributary P analyses an inappropriate choice for the concentrations that prevailed (Effler and Whitehead 1994) Standard Methods (APHA 1989) recommends a path length of at least 5 cm in the concentration

range of 0.01 to 0.25 $mg \cdot L^{-1}$ The report to R Ott should be available to HydroQual from its client Onondaga County The report also describes alternate other than Onondaga County tributary P data bases also see Effler et al. 1991 Effler and Whitehead 1994, Heidtke and Auer 1992) The P concentrations in Onondaga Creek (the largest tributary input) reported by the County were systematically false high in 1988 and 1989, almost certainly as a result of the inappropriate analytical protocol used in the analysis (described above In the absence of clear evidence to the contrary, it must be assumed that this problem prevailed from the start of the County's program for all the tributaries and all measured P species because the same inappropriate laboratory protocol was used throughout that interval These false high concentrations, and the attendant false high loads, compromise testing of the eutrophication model and application of the model for the METRO diversion scenario These errors in tributary loading will tend to result the understatement of the benefit of METRO diversion (see HydroQual report to Onondaga County 1995)

Arguments presented by Allied Signal letter to R Mustico of November 14, 1995 and HydroQual letter to S W Effler of December 27, 1995 attempt to minimize the importance of the inherent uncertainties in the empirical expressions developed by Effler and Whitehead (1994 in developing loads Part of the argument includes the following quote from Effler and Whitehead 1994 these regression equations "represent a basis to recreate the historic TP loading picture for the lake over the period of

monitoring". This cannot be interpreted as an endorsement by Effler and Whitehead (1994 to use such relationships to support model testing. Clearly their intent was to make the most (from a historic loading perspective) of a bad (poor data) situation. These researchers continue to not support the use of the TIP-TP relationships to recreate loads for model testing purposes. It is a moot issue in light of the over-riding data quality problems the County's tributary data discussed above. It is noteworthy that Effler, Brooks and Whitehead (1996) recently indicated in the peer-reviewed literature that reliable estimates of total loading TP from tributaries are available only for ≥ 1987 The 1987-1989 loads presented in that work are based on different data (on TP measurements see Effler and Whitehead 1994 than incorporated in the County (i.e., HydroQual estimates of TIP loads.

Further, in light of the demonstrated variability in the TIP-TP relationship for METRO over the 1980-1989 interval, what the compelling arguments for accepting such an approach for tributaries. Under these circumstances, HydroQual would need to demonstrate the veracity of such expressions over a range of years. The inaccuracy of the tributary TIP measurements (see report to R. Ott) overrides this issue.

Allied Signal's consultants (letter to R Mustico of November 14, 1995) and HydroQual (letter to S.W Effler of December 27, 1995) present a scenario related to the TIP-TP tributary issue concerning the potential uncertainty associated with the organic P (OP) fraction. The scenario, "if the fraction

of OP in the tributaries was underestimated for historical conditions", was poorly conceived If the report to R Ott, cited in the letter to J. Fitzpatrick of July 25, had been reviewed appropriately, Allied Signal's consultants would recognize that the more appropriate scenario would be this fraction of P. as well as all the other fractions, have often been overestimated because of short-comings in the County's laboratory program

More problematic is the modeling philosophy that emerges concerning this scenario Performance characteristics of the eutrophication model, that incorporates many degrees of freedom e.g many coefficients for which there are not system-specific determinations), is used as a basis to evaluate the potential for short-comings in loading data This approach is inappropriate it turns the model testing process on its head. We would be most interested in literature citations where this practice has been adopted, under similar circumstances e.g., non-conservative substance(s), many degrees of freedom in the model, major uncertainties in so many years of loading data).

HydroQual indicated in its letter of December 27, 1995 p.11 that UFI has similarly evaluated model input data based on model performance, citing the chloride model of Doerr et al 1994) The circumstances were distinctly different in that work; contrasting features of the Doerr et al 1994) modeling effort include:

1. conservative substance modeled, i.e., no reaction terms

2. loads much more well defined

3 similarity of Cl^- concentration data from different laboratories established for a number of years (e.g see Figure 4 of Walker 1991 of the modeled period,

4 clear in-lake signatures in seasonal structure manifested in most years, and

5. a striking long-term structure manifested associated with the closure of the Allied Signal facility.

The circumstances of the HydroQual eutrophication model are trikingly different, and unsupportive of the use of the model to evaluate loads

1 P, and its various species, are far from conservative 'he P cycle is complex, and its representation in the HydroQual model is complex (e.g., many "knobs to turn" in calibration),

2 loads are poorly defined, related to poor choices in species to monitor and laboratory protocol by Onondaga County, and

3. poorly defined in-lake temporal signatures short-and long-term) of important P species, particularly in the upper waters of the lake, because of poor choices in species to monitor and laboratory protocol by Onondaga County

Interestingly, HydroQual failed to indicate that Doerr et al 's 1994) identification of the County's lake data as probably flawed was based on more than model performance "Further limited data from a alternate source (Walker 1991 differ greatly

(from the County D&S data) in several instances in these years" (p.856, Doerr et al. 1994). Other aspects of HydroQual's responses to UFI comments concerning the County's chloride data will be provided in a separate communication.

Consistent with the structure of HydroQual's (1994, 1995) model, they have split the P load into five fractions: 1) dissolved inorganic P or PO_4^{3-}, 2) labile dissolved organic P (LDOP), 3) refractory dissolved organic P (RDOP), 4) labile particulate organic P (LPOP), and 5) refractory particulate organic P (RPOP). Very rarely would any monitoring program have direct estimates of all of these fractions. Such partitioning for the tributaries is of course fatally compromised by the use of Onondaga County data that is unreliable through at least 1989 (see above). However, even under the hypothetical case of accurate tributary data, this partitioning of the fractions necessarily introduces uncertainty in loading conditions. The County program through 1989 could have only supported credible specification of two fractions, dissolved inorganic (PO_4^{-3}) P and LDOP. The apportioning of the other three forms appears quite arbitrary (equally, sum of these three components equal to the residual of TP and TIP). Such an approach should not be accepted until its implications are fully demonstrated and found acceptable.

1.3. Internal Loading Associated with Allied's Use of the Lake as a Source of Cooling Water

The use of the hypolimnion as a source of cooling water by Allied Signal resulted in the net transfer of water from the

lower enriched hypolimnion to the productive epilimnion because of reductions in density associated with increases in temperature (Effler and Owens 1986, 1987 This artificial cycling of if of particular concern with regards to P and eutrophication modeling for the period before Allied Signal closed 1986) as it represents a potentially important internal load associated with the operation of the facility. Our position that this operation caused a potentially important internal load is based on 1 the high flow rates that prevailed in certain years, e.g., 2.3 to 3.6 $m^3 \cdot s^{-1}$ (e.g., average METRO flow is ~ 3.2 m^3 s^{-1} for much of the summers of 1980 and 1981 (Effler and Owens 1987 2 the very high P concentrations that develop(ed) in the lake's hypolimnion (Auer et al. 1993, Doerr et al. 1996, Driscoll et al 1993, Effler 1996 and 3) the highly available form of P in the hypolimnion Effler 1996) Effler and Owens (1987 estimated this internal load was about 20% of the external load over the April-October interval of 1980 and 1981; it was estimated to be the single largest source over the June August interval of 1981 Unfortunately, the Effler and Owens (1987) estimates be considered uncertain as a result of their uncertainty in the depth of the deep water intakes, because of the strong vertical gradients in P concentrations that prevail within the hypolimnio for much of the summer (Doerr et al. 1996, Effler 1996

Several forms of data would be necessary to develop adequate estimates of this internal load

1 detailed operating information for the cooling water intakes for all years, including:

a) identity of intake (was it a shallow or deep-water intake? and period of operation,

b) withdrawal rate accurately temporally resolved

2) depth of intake(s). This information has been requested from Allied Signal by NYSDEC at a RI/FS meeting. The information has not been provided. It is crucial that information be accurate (e.g., engineering drawings perhaps checked against recent underwater survey

3 accurate P data from the lake over the period of cooling water withdrawal.

These internal loads if emanating from depth ≥ those assumed by Effler and Owens 1987) need to be seasonally resolved Extending such estimates to earlier than 1980 may be problematic, as P loads routed to Ninemile Creek via the West Flume may have been significantly diminished by in-stream reaction with the $CaCO_3$ deposits e.g., Effler et al. 1991 formed from Allied Signal's wastebed discharges. HydroQual needs to accurately estimate this potentially important internal load before it includes any of the years during which Allied Signal operated the deep (hypolimnion) cooling water intakes in the eutrophication model HydroQual needs to quantitatively address the issue of the extent to which the absence of a detailed treatment of the cooling water operation has impacted other features of their water quality model analysis

1.4. Changes in TP Loading Adopted for the METRO Deep-Water Discharge Proposal

The HydroQual TP loading story changes abruptly in their

analysis of the METRO deep-water proposal (HydroQual 1995 in the report (paragraph 1, under 3.2 Initial Projections) HyrdroQual indicates the TP loading estimates for the 1985 -1990 period were, "revised" based on comparisons with values presented in a Effler and Canale (1993) reference. Why were these changes not incorporated in the appropriate earlier section of the report that described the development of loads? I am unaware of a "water quality model documentation report" prepared by Effler Canale I am unaware of any report/manuscript prepared with authorship in that year UFI did prepare a report in 1993 (Canale et al 1993) that included TP loading estimates for 1987-1990. No loads for 1985 and 1986 were included. HydroQual indicates changes were made, but differences apparently persisted in the loads from the UFI values "our revised estimates are within 10 percent of those reported by Is this a result of more averaging procedures (e.g., average erroneous loads representative loads to get less erroneous loads)? These loads for the METRO deep-water analysis are apparently different from those incorporated in the RI/FS analysis (HydroQual and 1994 HydroQual's documentation of development of these modified loads is woefully inadequate, and the supporting citations and statements are inaccurate HydroQual acknowledged deterioration in certain features of model performance as a result of these modifications in TP loading It's highly likely these performance characteristics would further deteriorate if the most representative loads were adopted for the 1987-1990 period.

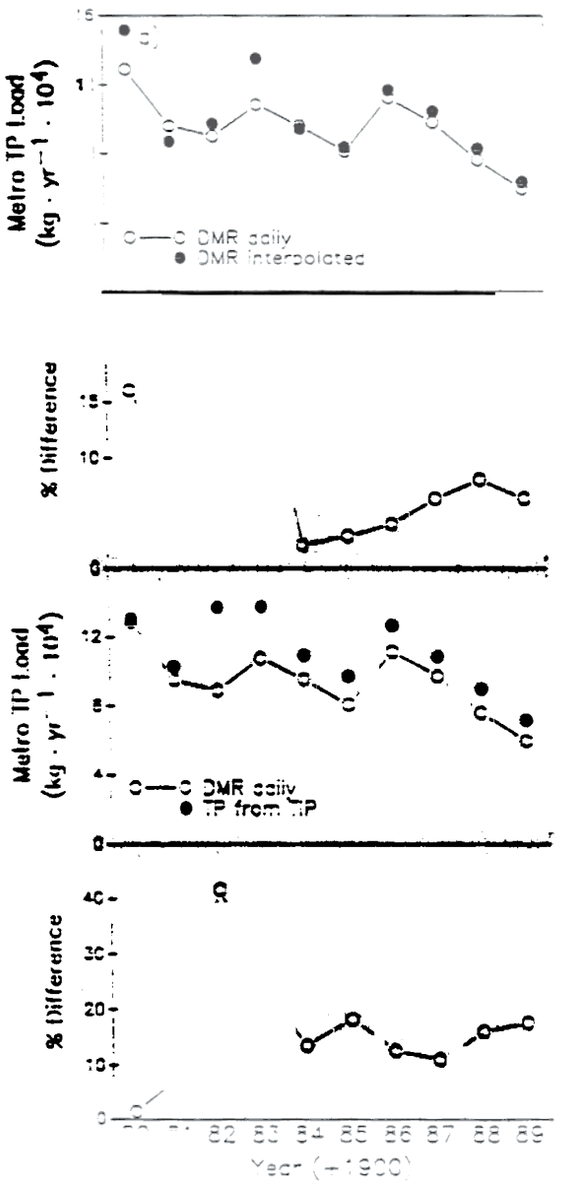

Figure 2. Errors in METRO loading estimates associated with monitoring frequency and use of TIP as a surrogate measure of TP for the 1980-1989 interval: a) comparison of annual estimates of METRO TP load from daily versus biweekly TP measurements, b) error from biweekly program, as percent difference, c) comparison of annual estimates of METRO TP load from daily TP measurements versus biweekly TIP measurements, and d) error from biweekly TIP program, as percent difference.

2.0 Lake Phosphorus Data

2.1 SRP

The response of Allied Signal's consultants on November 14 1995 are quite different than those of HydroQual on December 27 1995, concerning the SRP/orthophosphorus detection limit problem of D&S for upper water samples In the November 14, 1995 response, Allied's consultants could not explain the disparity between the D&S concentrations and HydroQual's calibration plot values for 1987 and 1990 (" in 1987 D&S mid-summer surface concentrations in Figure 6+ are about 30 to 40 µg/L, whereas in the calibration plot they are about 10 to 20 µg/L The cause for this disparity is not clear" In the December 27, 1995 response, HydroQual indicates both D&S and UFI data are included in the calibration plot values implying this is the reason for the previously unexplained disparity. Why is the "story" changing? How were the D&S and UFI data averaged? HydroQual indicates averaging protocols would be clearly described throughout the response (p.1 of HydroQual response -- however, remains far from clear how the SRP calibration plot data were arrived at (Figure 15, HydroQual response)

Effler and Doerr 1994) concluded that the SRP concentration data base of D&S was inaccurate; specifically, most of the epilimnion values are false high as a result of detection limi problems Substantial evidence was presented in support of this

+ the legend Figure 6 of the Effler and Doerr memo (1994) was corrected by memo in March of 1995 (i.e., before release of Allied Signal; see attached), apparently this correction was not passed along to Allied Signal.

position. Allied's consultants (November, 1995) and HydroQual December 1995) present no evidence in defense of the D&S epilimnetic SRP data. HydroQual acknowledges "that much of the D&S epilimnion SRP data may suffer from detection limit problems" this is an understatement, as there is no evidence presented to the contrary

In sharp contrast to the D&S P data base, much of the UFI P data base has been subjected to rigorous peer-review as part of the publication of related research manuscripts (e.g., Auer et al 1993 Connors et al 1996, Driscoll et al. 1993). In particular, the detailed time distributions of SRP (as well as dissolved organic P) in the upper waters of Onondaga Lake for the summers of 1989-1992 were subjected to rigorous review as part of an intensive analysis of P pools and alkaline phosphatase activity (Connors et al 1996

Averaging of D&S's erroneous SRP data with UFI's representative data is an entirely unacceptable manner in which to develop calibration data for this parameter. HydroQual's resulting calibration data set for SRP in the epilimnion e.g 10 to 20 $\mu g \cdot L^{-1}$ in 1987, 5 to 10 $\mu g \cdot L^{-1}$ in 1989 (Allied Signal's consultants, November, 1995 is far from representative of conditions that prevailed What is the justification for averaging such disparate data sets, particularly in light of the known non-linear response of phytoplankton within this range of concentrations? Allied's consultants indicate that the "biased-high" (HydroQual, December, 1995)/ "high D&S detection" limits (Allied Signal, November, 1995) calibration data were

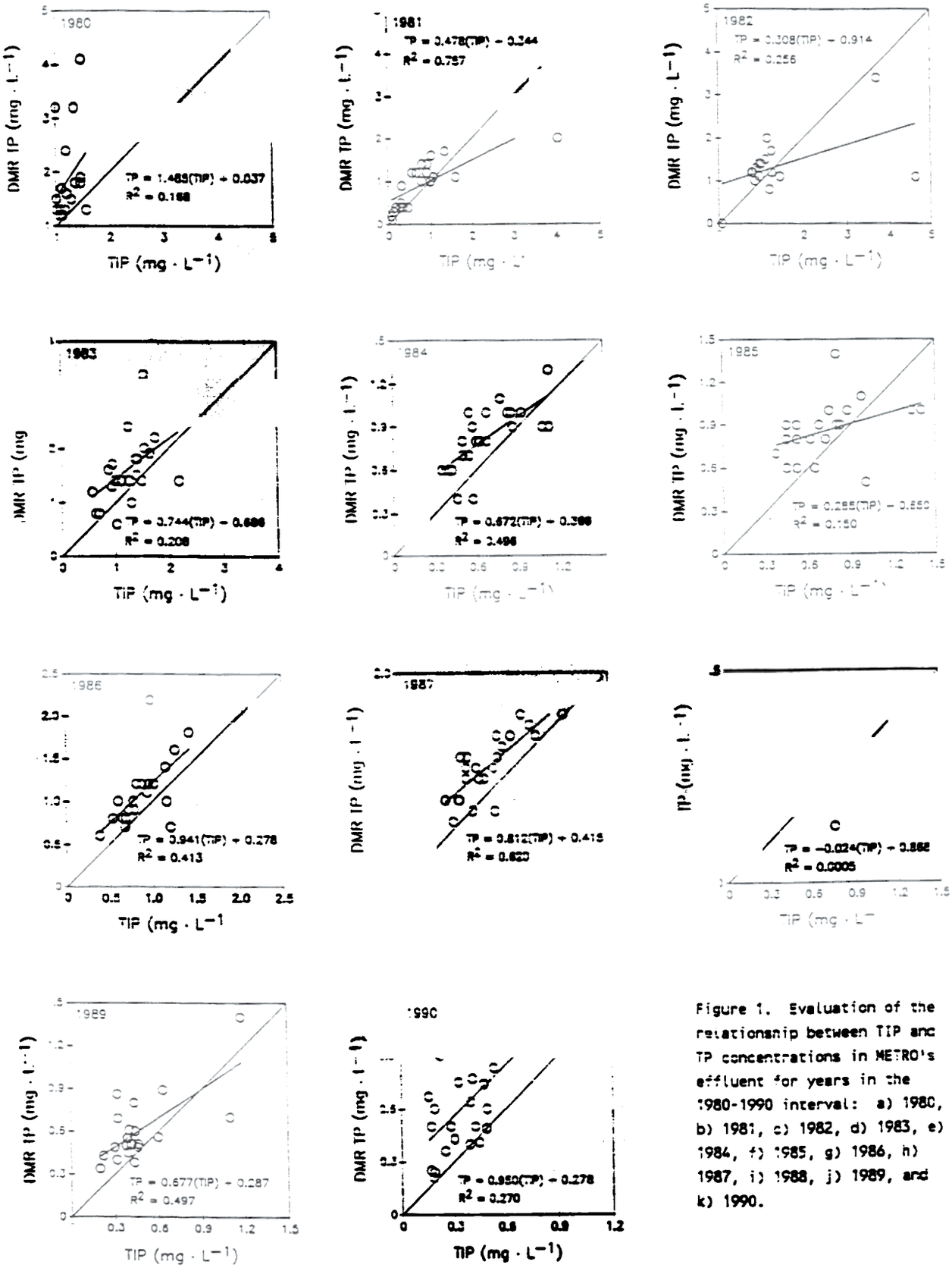

Figure 1. Evaluation of the relationship between TIP and TP concentrations in METRO's effluent for years in the 1980-1990 interval: a) 1980, b) 1981, c) 1982, d) 1983, e) 1984, f) 1985, g) 1986, h) 1987, i) 1988, j) 1989, and k) 1990.

Though measurements of SRP (ortho-P) are available from Onondaga County's program since 1970, the situation for SRP is really no better than for TP, because the County's SRP measurements from the upper layers are unreliable. Effler and Doerr (1994) established the County's SRP data were unreliable (false high) associated with detection limit problems (apparently HydroQual largely concedes this point) Consider the SRP situation within the context of HydroQual's (letter of December 27, 1995) Figure 15. The calibration data sets of 1987, 1989 and 1990 are false high due to the inclusion of D&S data with UFI data. Corrections can be made for these years by eliminating the D&S data However, all the earlier data from D&S) are unreliable. No reliable adjustments of D&S data are possible (e.g., note, there are not indications that the degree of the detection limit problem has been uniform) Thus there is no basis to test the interannual and seasonal structures predicted by the HydroQual model Figure 15, letter of December 27, 1995; e.g increased degree and period of SRP depletion from the 1970's to 1980's), and therefore the model's credibility

The selection of the 1970-1990 period for model testing is conceptually flawed for application to METRO management alternatives presently under consideration. Instead the focus should be testing a eutrophication model for the range of conditions that presently prevail (e.g. Doerr et al. 1996)

period e.g Effler et al 1996 Effler and Whitehead 1994 However the reduction in external loading from the dominant source METRO) is poorly defined before 1980, the interval over which the largest portion of the load reduction occurred (Effler and Whitehead 1994 Tributary loads based on Onondaga County data through 1989 are unreliable and almost certainly false high This eliminates quantification of any significant systematic changes that may have occurred in this smaller component of external loading. The change in internal loading, associated with Allied Signal's use of the lake as a source of cooling water that potentially had as seasonal structure critical to summer phytoplankton growth), that may have resulted from operational variations before closure and almost certainly occurred with the closure of the facility, remain largely unquantified The loading picture is unfortunately very poorly defined, particularly with respect to the major changes that occurred

The lack of reliable calibration data sets for in-lake concentrations of various P species particularly for the upper productive layers before 1987 fatally compromises eutrophication model testing that focuses on the 1970-1990 period Performance of a eutrophication model in simulating P species, particularly TP e includes contributions from phytoplankton biomass) and SRP e.g representation of P available to support phytoplankton growth is a critical basis for evaluating model credibility. We indicated previously the importance of also having reliable measurements of DOP. The County did no measure TP in the lake until part way through 1989 UFI's TP data base starts in 1987

largely ignored and that the more realistic model projections (~ 2 $\mu g \cdot L^{-1}$ minimum, claimed to be similar to UFI measurements) emerged from calibration. This is instead apparently a result of judgment, that would have been better applied in the development of the calibration data. The implication that the 2 $\mu g \cdot L^{-1}$ minimum prediction in calibration emerged because of the limited ranges of related model coefficients is an assertion, that would be quite an undertaking to demonstrate in a statistically rigorous manner (e.g., Storey et al. 1993).

It is noted that Allied Signal's consultants chose not to respond to P issues related to Onondaga County's unfortunate selection of species to monitor. In particular, there is not a P measurement that includes the contribution of phytoplankton biomass. The lack of a measure of dissolved organic P is also a problem, as phytoplankton apparently use this pool during periods of SRP depletion in Onondaga Lake (Connors et al. 1996 These omissions in the data base are fatal limitations for the rigorous testing of a eutrophication model. Credible and appropriate epilimnetic P data, necessary to develop a credible eutrophication model, are available only since 1987 This condition is even more temporally limiting than the availability of reliable METRO loading data

3.0 Implications for Eutrophic Model Testing

Consider now, in light of the foregoing limitations identified in this analysis, the implications for testing the eutrophication model for the 1970-1990 period. It's fair to say that major changes in external P loading occurred over this

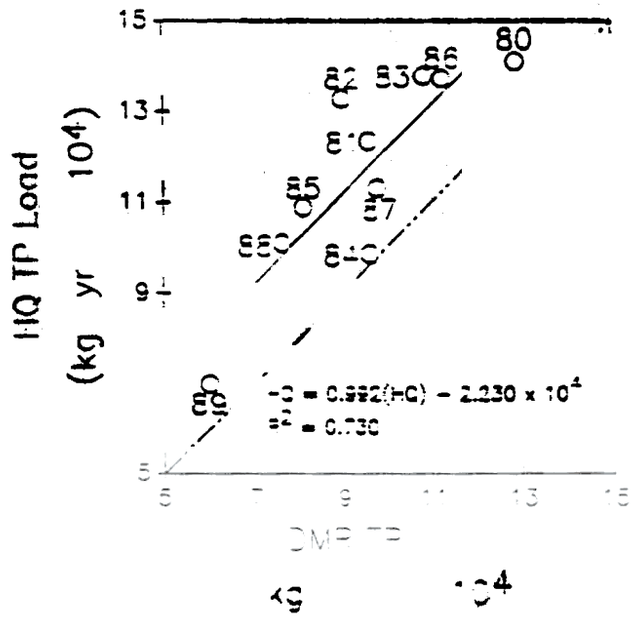

Figure 3. Comparison of annual TP loads from METRO for the 1980-1989 interval, Hydroqual (HQ) versus from daily monitoring report (DMR) TP data.

References

Auer, M.T Johnson, N.A Penn, M.R., and Effler, S.W 1993. Measurement and verification of rates of phosphorus release for a hypereutrophic urban lake. Hyrobiologia 253: 301-309.

Canale, R.P., Doerr, S.M., and Effler, S.W 1993. Total Phosphorus Model Report - Onondaga Lake, 1987-1990. Report submitted to Central New York Regional Planning and Development Board, Syracuse, NY

Connors, S.D Auer, M.T., and Effler, S.W. 1996. Phosphorus pools, alkaline phosphatase activity, and phosphorus limitation in hypereutrophic Onondaga Lake, NY. Lake Reservoir Manage in press).

Doerr S.M., Canale, R.P and Effler S.W 1996. Development and testing of a total phosphorus model for Onondaga Lake, N.Y Lake Reservoir Manage. in press

Doerr, S.M., Effler S.W., Whitehead K.A., Auer, M.T. Perkins, M.G., and Heidtke, T.M 1994 Chloride model for polluted Onondaga Lake Wat. Res. 28: 849-861

Driscoll, C.T., Effler, S.W., Auer, M.T., Doerr, S.M., and Penn, M.R 1993 Supply of phosphorus to the water column of productive hardwater lake: controlling mechanisms and management considerations Hydrobiologia 253: 61-72

Effler S.W (ed 1996 Limnological and Engineering Analysis of a Polluted Urban Lake. Prelude of Environmental Management of Onondaga Lake New York Springer-Verlag NY (in press

Effler, S.W Brooks, C.M., Addess, J.M., Doerr, S.M., Storey M.L., and Wagner, B.A. 1991. Polluted loadings from Solvay waste beds to lower Ninemile Creek, New York

Effler S.W Brooks, C.M and Whitehead, K.A. 1996. Domestic waste inputs of nitrogen and phosphorus to Onondaga Lake, and water quality implications Lake Reservoir Manage in press)

Effler, S.W., and Doerr, S.M 1994. A comparative analysis of phosphorus data for Onondaga Lake, and implications Report submitted to NYSDEC, Albany, NY.

Effler S.W and Owens, E.M 1986 The density of inflows to Onondaga Lake, U.S.A., 1980 and 1981. Wat. Air Soil Pollut 28: 105-115

Effler, S.W., and Owens, E.M 1987 Modifications in phosphorus loading to Onondaga Lake, U.S.A., Associated with alkali manufacturing Wat. Air Soil Pollut 32: 177-182.

Effler, S.W and Whitehead, K.A 1994. Tributaries and Discharges (Chapter 3) In S.W Effler ed. State of Onondaga Lake Management Conference Syracuse, NY.

Heidtke, T.M., and Auer, M.T. 1992 Partitioning phosphorus loads: Implications for Lake restoration. J. Wat. Resour. Plans Manage. 118: 562-579

HydroQual 1995 Hydrodynamic Evaluation of METRO Outfal Relocation in Onondaga Lake and Application of the Onondaga Lake Eutrophication Models in the Evaluation of METRO Treatment Alternatives and Wasteload Allocation Report to Onondaga County, Syracuse, NY

HydroQual and PTI. 1994 Onondaga Lake RI/FS: Calcite Modeling Report Prepared for Allied Signal Inc Solvay New

Onondaga County 1996. Proposed Municipal Compliance Plan. Syracuse, NY

Onondaga County 1971-1993. Onondaga Lake Monitoring Program Annual Report of Department of Drainage and Sanitation Onondaga County, Syracuse, NY

Storey, M.L., Auer, M.T., Barth, A.K., and Graham, J.M. Site-specific determination of kinetic coefficients for modeling algal growth Ecol. Model. 66: 181-196.

Walker, W.W 1991. Compilation and Review of Onondaga Lake Water Quality Data, Report submitted to Onondaga County, Syracuse, NY

Domestic Waste Inputs of Nitrogen and Phosphorus to Onondaga Lake, and Water Quality Implications[1]

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ABSTRACT

Effler, S. W., C. M. Brooks and K. A. Whitehead. 1996. Domestic waste inputs of nitrogen and phosphorus to Onondaga Lake, and water quality implications. Lake and Reserv. Manage. 12(1):127-140.

The recent history of loading of total phosphorus (TP) and nitrogen (N) species to Onondaga Lake, NY, from an adjoining domestic waste treatment facility (METRO), and related impacts on the lake, are documented. The discharge from METRO represents an extraordinary contribution to the inflow of the lake; e.g., in most years it is the largest source of water during the month of August. Approximately a 20-fold reduction in effluent TP concentration has been achieved by METRO over the 1970-1993 period, in response to a detergent ban and increased levels of treatment. The TP loading from the facility decreased about 5-fold over the 1977-1992 interval. A significant level of nitrification has been achieved during the warmer months since the late 1980s, but this has been attended by increased effluent concentrations of nitrite (NO_2^-). METRO presently contributes approximately 60, 90, and 80% of the total external loads of TP, ammonia, and total N, respectively. The extremely high prevailing external total loads of TP and total N, approximately 8 and 200 $g/m^2/y$, respectively, severely impact the lake. Recurring degradations associated with the cultural eutrophication of the lake include excessive concentrations of phytoplankton, poor clarity, rapid loss of oxygen from the hypolimnion, and lake-wide oxygen depletion during the fall mixing period. Related water quality standards for transparency and oxygen are violated. A state guidance value for summer epilimnetic TP concentration of 20 $\mu g/L$ is exceeded by a factor of ≥ 3 annually. Standards to protect aquatic life against the toxic effects of free ammonia and NO_2^- are violated by a large margin routinely in the upper waters in summer. METRO is the appropriate focus for related remediation efforts.

Key Words: domestic waste, phosphorus, nitrogen, external loads, cultural eutrophication, clarity, free ammonia, nitrite, standards, violations.

Anthropogenic inputs of phosphorus (P) and nitrogen (N) can have important water quality implications for receiving waters. Phosphorus loading is the principal regulator of primary productivity in most lakes (e.g., Vollenweider 1975, 1982, Wetzel 1983). Extreme cases of cultural eutrophication are manifested as conspicuous water quality problems, such as phytoplankton blooms, poor clarity, and rapid depletion of hypolimnetic dissolved oxygen (DO) associated with the decay of depositing phytoplankton. Reduction of external P loading has been a frequently applied lake restoration technique to eliminate or ameliorate these unwanted characteristics (Cooke et al. 1993). A rather wide range of lake response (e.g., degree of success) to P-based management has been observed (e.g., Edmondson and Lehman 1981, Larsen et al. 1981, Welch et al. 1986). Nitrogen, in the form of ammonium ion (NH_4^+) and nitrate (NO_3^-), is also an important plant nutrient, though rarely limiting in fresh waters (Harris 1986, Wetzel 1983). Ammonia and its organic precursors can represent a significant oxygen sink (Bowie et al. 1985, Harris 1986), and unionized ammonia (or free ammonia, NH_3) and nitrite (NO_2^-) are toxic to fish (Russo and Thurston 1977, USEPA 1985) at low concentrations.

Effluent from domestic wastewater treatment plants is an important anthropogenic source of P and N (Brezonik 1972, Thomann and Mueller 1987, Vollenweider 1975); concentrations vary greatly depending on the level of treatment (Thomann and Mueller 1987). Here we characterize and quantify the loading of P and N from a domestic wastewater treatment plant to Onondaga Lake, NY, and document recent changes in loading in response to management actions. Further, selected features of the impacts of this discharge on the water quality of the lake are described.

[1]Contribution No. 142 of the Upstate Freshwater Institute.

Particular emphasis is given to the status of the lake with respect to numerical regulatory standards.

Recent History of METRO

In 1960, Onondaga County completed construction of a domestic wastewater treatment facility, the Metropolitan Syracuse Wastewater Treatment Plant (METRO), that served most of the residents in the Onondaga Lake watershed. The facility, located on the southeastern shore of the lake (Fig. 1), provided primary treatment. A combined sewer system (i.e., carries domestic waste and runoff) serves this region. METRO was designed to treat an average flow of 2.19 m^3/s (50 million gallons/d (MGD)), and could accommodate a peak flow of 7.45 m^3/s (170 MGD). According to the original plans for the facility, the METRO effluent was to be pumped around the lake, combined with effluent from a small treatment facility located about 2 km east of the lake, and discharged to the Seneca River (Fig. 1). The diversion part of the plan was never executed; instead the METRO effluent was discharged to the southern end of Onondaga Lake (Fig. 1). By the early 1970s the METRO facility was overloaded, with associated manifestations of poor performance (USEPA 1974).

Major upgrades to METRO were made from the late 1970s to the early 1980s. The facility provided secondary treatment by 1979, with the contact stabilization modification of activated sludge. This form of biological treatment was not expected to achieve significant ammonia removal (e.g., nitrification) in this climate (e.g., USEPA 1974). Advanced, or tertiary treatment, in the form of P removal by chemical precipitation, was on line by mid-1981. This process was unusual in that P was precipitated by addition of calcium enriched ionic waste (0.28 m^3/s (6.5 MGD), by design) from a nearby chemical manufacturer (Effler and Hennigan 1996). The effluent standard for total P (TP), established for facilities of this size in the Great Lakes watershed, is 1.0 mg/L. The upgraded facility was designed to treat an average flow of 3.5 m^3/s (80 MGD). Flows up to 5.26 m^3/s (120 MGD) receive full treatment and are discharged to the lake via a shoreline outfall. Peak flows of 9.77 m^3/s (223 MGD) can be accommodated. Flows in excess of 5.26 m^3/s (120 MGD; e.g., during runoff events) receive incomplete treatment (primary treatment and chlorination; "by-pass" flow) and are discharged at a depth of about 6 m. The alternatives of discharging METRO effluent to the Seneca River or directly to Lake Ontario were dismissed during these upgrades because the assimilative capacity of the river was judged to be inadequate and the cost for the Lake Ontario discharge option was considered too great (USEPA 1974).

Tertiary treatment was interrupted for significant periods during 1981, 1982, and 1983, usually in response to operational problems caused by the reception of the industrial ionic waste (excessive precipitation of $CaCO_3$, which occluded pipes and coated tanks). The closure of the industry in 1986 required the development of an alternative chemical treatment methodology. Phosphorus is now precipitated with ferrous sulfate, a much more widely used approach. The facility irregularly fails to meet its New York State permit requirements for total suspended solids, BOD, setteable solids, pH, TP, and residual chlorine.

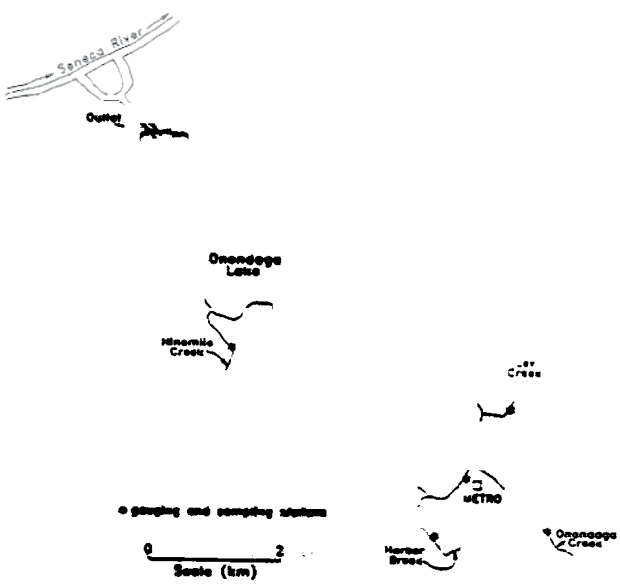

Figure 1.–Onondaga Lake with the positions of METRO, significant tributaries, and approximate locations of flow gauges and monitoring sites.

Methods

Onondaga Lake is a medium sized (surface area of 12 km^2 and mean depth of 10.9 m), high flushing rate (average of 3.9 flushes/y), dimictic, urban lake that adjoins Syracuse, NY. Since closure of the chemical manufacturer (1986), summer stratification has been established by May and the onset of complete fall turnover has occurred by mid-to-late October (Effler and Owens 1996). More background information on the lake, including the history of the development of the area, the lake's setting, morphometry, hydrology, and selected features of its degraded state, is available from Effler and Hennigan (1996).

The analysis presented here uses data collected as

Table 1: Salient features of supporting monitoring programs.

Monitoring Component	Responsible Party	Parameters[1]	Description
hydrology			
tributary	USGS	flow	continuous gauges since early 1970s
METRO	Onondaga County[2]	flow	continuous measurements
METRO effluent concentrations	Onondaga County	TIP	2/mo, 1970-1979
		T-NH_3, TKN	2/mo, 1970-1979
		T-NOx	2/mo, since 1970
	Onondaga County[2]	TP	daily, since 1980
	Onondaga County[2]	T-NH_3	5d/wk, since 1989
	Onondaga County[2]	TKN	2d/wk, since 1989
	authors	NO_2^-	2/mo 1991 and 1992; 2-3 d/wk part of 1993
tributary concentrations	P - by authors N - Onondaga County and authors	TP, T-NH_3, NO_3^-, NO_2^- TKN	2/mo routinely, augmented in certain years by more frequent measurements by authors[3]
lake measurements	authors	T-NH_3, NO_2^-, TP - DO, temp., pH Secchi disc, Chl[4]	general: weekly, routine deep water site (19 m), ≤ 2 m depth profiles Hydrolab Surveyor 3 (since 1991) 12 cm diameter, black/white quadrant

[1] chemical analyses according to APHA (1980, 1985).
[2] Onondaga County (METRO) permit requirements, reported monthly to NYSDE.
[3] details of augmented portions of program presented by Effler and Whitehead (1996).
[4] chlorophyll.

part of several monitoring programs, including: 1) measurements made at METRO as part of its permit requirements, 2) tributary flow measurements made by the United States Geological Survey, starting in the early 1970s, 3) measurements made by the authors, and 4) results reported by Onondaga County (1971-1994) as part of an annual monitoring program. Salient features of these programs that support this analysis are specified here (Table 1).

As the impact of the METRO facility has come under closer scrutiny in recent years, sampling frequency and the number of parameters measured in the facility's effluent have both increased (Table 1). Daily TP monitoring commenced in 1980. Earlier monitoring of P in the plant's effluent was limited to bi-monthly (2/mo) analyses of total inorganic P (TIP; described as "total acid hydrolyzable phosphorus" by the American Public Health Association (APHA 1989)). Values of TIP are systematically lower than TP measurements because organic (particularly particulate) forms of P are not detected (weaker digestion procedure for TIP (APHA 1989)). Onondaga County (1971-1990) also measured TIP, instead of TP, in Onondaga Lake and its tributaries until 1989. The more frequent monitoring of the various N species in the METRO effluent was dictated by modifications in the permit requirements in 1989 (Table 1). Samples from the lake tributaries, and METRO until 1980, were grab type. Samples from METRO over the 1980-1988 interval were time composites, thereafter they have been flow-weighted composites.

We commenced our monitoring program for TP in the tributaries and the lake in 1987. All N and P analytes were measured according to standard methods (e.g., APHA 1985, 1989). Chlorophyll *a* and phaeophytin concentrations in the lake were measured according to Lorenzen (1967) through 1986. Thereafter total chlorophyll was measured according to Parsons et al. (1984). The lake was monitored at a deep water location in the south basin (Fig. 1) found to be generally representative of lake-wide conditions (Effler 1996).

Annual loads were based on summation of daily loading estimates for METRO and the tributaries (Fig. 1); other sources of N and P are insignificant by comparison. Daily estimates for METRO were the product of daily flows and daily concentrations. Concentrations for days without measurements (e.g., < 1980) were estimated by time interpolation. Estimates for the pre-1980 period utilized an empirical expression based on paired TP and TIP measurements, developed by Effler and Whitehead (1996). Tributary daily loading estimates were developed using FLUX (version 4.4,

1990), loading analysis software developed by Walker (1987). The details of the development of the tributary loads were described by Effler and Whitehead (1996).

The USEPA (1985) developed criteria intended to protect against the toxic effects of NH_3, that were subsequently adopted as standards by the State of New York. Both the standards (acute and chronic) and the fraction of total ammonia (T-NH_3) that exists as NH_3 are functions of temperature and pH. Thus they are subject to substantial seasonal variations in systems such as Onondaga Lake (e.g., Effler et al. 1990). The protocols to estimate NH_3 concentrations and the standards, as a function of pH and temperature, were reviewed by Effler et al. (1990). These procedures were used to evaluate the status of Onondaga Lake with respect to these standards.

The depletion of hypolimnetic DO in Onondaga Lake is represented by the "areal hypolimnetic oxygen deficit" (AHOD; $g/m^2/d$). AHOD has been widely used as an indicator of trophic state (Hutchinson 1957, Mortimer 1941, Wetzel 1983). Mortimer (1941) proposed limits of 0.25 $g/m^2/d$ for the upper limit of oligotrophy and 0.55 $g/m^2/d$ for the lower limit of eutrophy. Estimates of AHOD (e.g., Wetzel and Likens 1991) could not be made for those years in which spring turnover did not occur (an impact of the chemical manufacturing facility, see Effler and Owens 1996, Effler and Perkins 1987), as the lower layers were not replenished with oxygen following the winter depletion (e.g., Effler and Perkins 1987).

METRO Inputs

Hydrology

Selected features of the hydrologic budget of Onondaga Lake for the 1971-1989 period were reviewed by Effler and Hennigan (1996). The effluent flow into the lake from METRO over this period was about 19% of the total inflow. We know of no other lake in the United States that receives this much of its inflow as treated wastewater. The next largest contribution of treated domestic waste to an inland lake in New York State is the Ithaca WWTP (0.44 m^3/s or 10 MGD), which represents < 2% of the total inflow received by Cayuga Lake.

The situation for Onondaga Lake is even more severe than implied by the annual average inflow, when the seasonality of runoff for the watershed is considered (Fig. 2). The relatively constant volume of effluent discharged from METRO in combination with the strong seasonality in hydrologic loading from tributaries

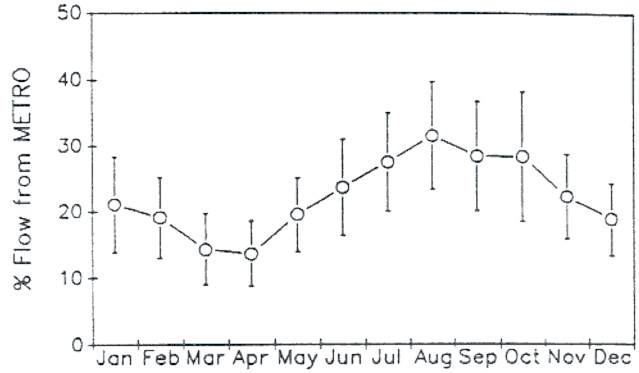

Figure 2.–Seasonality in the contribution of the METRO discharge to total inflow to Onondaga Lake, average monthly % for period 1971-1989, with ± 1 standard deviation bars.

(Effler and Hennigan 1996) results in major seasonality in the contribution of METRO to total inflow, though substantial interannual variability is observed (Fig. 2). METRO's contribution is smallest in spring (e.g., about 13% on average for April) and largest in mid- to late summer (e.g., about 31% on average for August; Fig. 2), when primary productivity (e.g., Wetzel 1983) and recreational demands are greatest. The METRO discharge represented 28%, on average, of the total inflow to the lake over the critical water quality interval of June-September, for the 1971-1989 period. This wastewater input was the single largest source of water to the lake for the month of August in 14 y over the 1971-1989 interval.

Phosphorus

Annual average TP concentrations in the METRO effluent for the 1970-1993 period are presented here (Fig. 3a), but corresponding estimates of loads are not presented for the 1970-1976 interval (Fig. 3b), because short-comings in this portion of the data base make estimates for those years unreliable. Reliable estimates of total loading from tributaries are limited to the 1987-1993 interval (Fig. 3b). Relative contributions of METRO to total loading are presented for 1987 and 1989 as insets (Fig. 3b). METRO loads correspond to the fully treated effluent, with the exception of 1993. The relative contributions of partially treated "by-pass" (e.g., runoff events) discharges to the facility's TP load were minor (e.g., < 8%; Effler and Whitehead 1996), except in 1993, when about 22% of the released flow did not receive full treatment. This was due to unusually high spring runoff and construction activity at METRO. Substantial disparity exists within this monitoring record with respect to temporal coverage and analytical methods (e.g., TIP versus TP; Table 1). METRO effluent TP concentrations and loading information became

more reliable starting in 1980 when daily monitoring of TP commenced (Table 1).

Substantial reductions in effluent TP concentrations (Fig. 3a) and loads (Fig. 3b) have occurred in response to related management efforts, which include a ban on high-P detergents in Onondaga County (Murphy 1973), the addition of secondary treatment, the addition of tertiary treatment, and, most recently, improvements in tertiary treatment. Though poorly quantified, the single largest reduction was apparently associated with the detergent ban (Fig. 3a). Substantial short-term variations in TP concentrations in the plant's effluent have been observed throughout the period of daily monitoring (since 1980). Concentrations in excess of the standard (> 1 mg/L) have been documented annually, though only infrequently since 1989 (Effler and Whitehead 1996); 213 violations occurred in 1983, but only 25 in 1989. The annual average TP concentration in the METRO effluent over the 1989 - 1992 interval was about 0.6 mg/L, substantially less than the state standard of 1.0 mg/L. This represents a nearly twenty-fold reduction in the annual average TP concentration in the facility's effluent since 1970 (Fig. 3a).

The time course of estimated annual TP loads from METRO over the 1977-1993 interval (Fig. 3b) generally tracks that of the average concentrations (Fig. 3a). Note the increased load for 1993 (e.g., about 70% greater than for the previous 3 y), associated with the unusually high spring runoff (about 50% of the 70% increase) and construction activity (about 20% of the 70% increase) in the absence of an increase in the estimated tributary load (Effler et al. 1994). Tributary loading estimates for the 1991-1993 interval are less than those obtained for the 1987-1990 period. The cause(s) of this apparent decrease is presently unknown; it is not in response to a specific management action. METRO's contribution to the total annual TP load in 1987 was nearly 75%, and in 1989 it was about 60% (Fig. 3b). The 1987 case is considered generally representative of the facility's contribution when it operated at the 1 mg/L effluent standard, while the 1989 case reflects the improved performance of tertiary treatment (e.g., 0.6 mg/L) achieved in recent years since switching to ferrous sulfate treatment (e.g., Fig. 3a).

The prevailing external TP loading rate (i.e., sum of METRO and tributary inputs) is extremely high from the perspective of widely used semi-empirical, or screening, trophic state models (e.g., Vollenweider 1975). The average annual areal TP loading rate for the 1989-1992 interval, 7.8 $g/m^2/y$, for an average hydraulic overflow rate (annual average total inflow rate for the same period, divided by the surface area of the lake) of 39 m/y, corresponds to highly eutrophic conditions (cf. Vollenweider 1975).

A substantial portion of the total TP load to Onondaga Lake is subject to management reduction (Fig. 4). This includes the entire METRO contribution, which could be eliminated by diversion around the lake (also see Effler and Doerr 1996). Additionally, a portion of the tributary load could be eliminated. For example about 5-10% of the total TP load to the lake emanates from combined sewer overflows (Effler and Whitehead 1996), which discharge to lake tributaries after runoff events (Effler and Hennigan 1996). Perhaps another 3-6% of the total TP load could be eliminated by effective management practices in the rural portions of the lake's watershed (cf. Effler and Whitehead 1996). About 25-32% of the total load (or 60-80% of the tributary load) is probably not subject to further

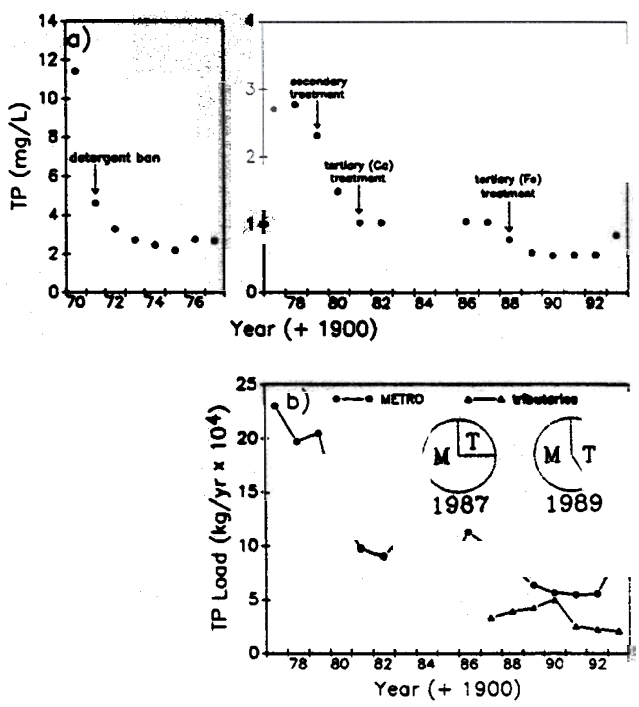

Figure 3.–Annual conditions: (a) METRO effluent average TP concentrations (y-axis segmented in time to resolve recent changes), and (b) METRO and tributary TP loads, with contributions for two selected years; M-METRO, and T-tributaries.

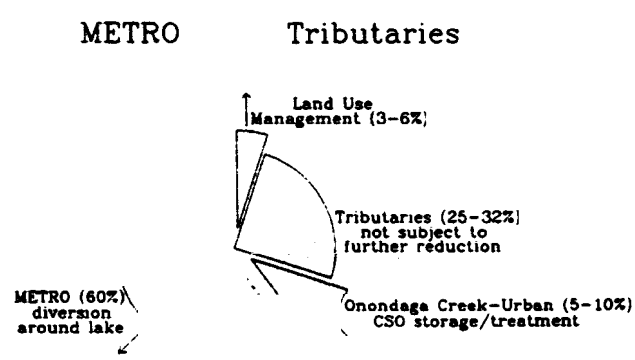

Figure 4.–Partitioning external TP loading to Onondaga Lake; identification of manageable fractions (arrows).

reduction. Clearly METRO should be the primary focus for P-based remediation efforts for the lake. Internal loading from the enriched hypolimnion to the productive upper waters during summer stratification, mediated by vertical mixing, presently is only about 10% of the annual external load (e.g., Auer et al. 1993). This internal load would decrease by more than a factor of two if the METRO input was eliminated (e.g., following the establishment of new steady-state conditions for the lake's sediments (Penn 1994)).

Nitrogen Species

Essentially all of the N discharged from METRO before the addition of biological treatment was as organic-N or T-NH_3. More than 50% was as organic-N (Effler and Whitehead 1996). Essentially no nitrification was achieved in the facility following the addition of biological treatment (e.g., see Fig. 5a) until the late 1980s (e.g., Fig. 5b and c), though there was a shift to greater concentrations of T-NH_3 and reduced concentrations of organic-N (Effler and Whitehead 1996). The seasonal distributions of N species in METRO's effluent presented for 1988 (Fig. 5b) and 1989 (Fig. 5c), that depict nitrified effluent for portions of the warmer (e.g., Fig. 5d) months, are generally representative of conditions since 1988.

The most conspicuous seasonal pattern in nitrogen species for 1988 and 1989 is associated with the operation of the nitrification process in the warmer months; in particular, T-NH_3 concentrations were lower and T-NO_x (NO_3^- plus NO_2^-) concentrations were higher (Fig. 5b and c), while total N concentrations remained relatively constant. The seasonality in nitrification in 1988 and 1989 (Fig. 5b and c) largely reflects the influence of temperature (Fig. 5d) on the kinetics of this microbial process (Bowie et al. 1985), and is consistent with observations for other contact stabilization facilities in north temperate climates (USEPA 1975). The details of the timing and extent of the nitrification process have differed year-to-year. For example, nitrification was achieved over a shorter period, and to a less complete extent, in 1988 (Fig. 5b) compared to 1989 (Fig. 5c). These interannual differences are probably attributable to modest differences in plant operation (e.g., sludge age).

Monitoring of the NO_2^- species in the METRO effluent has not been a permit requirement. However, limited monitoring conducted by the authors (Fig. 6) indicates NO_2^- represents a significant fraction of T-NO_x during the active nitrification period of summer. The dynamics of NO_2^- generally tracked those of T-NO_x during the summer of 1993. At times NO_2^- represented as much as 30% of T-NO_x during this interval (Fig. 6). Increases in NO_2^- concentrations have been observed in the plant's effluent in other recent years during summer (unpublished data, S.W. Effler). Thus, in an effort to reduce the load of T-NH_3 to Onondaga Lake, the loading of another potentially toxic species, NO_2^- has increased. These results, and the subsequently documented violations of the state standard for this

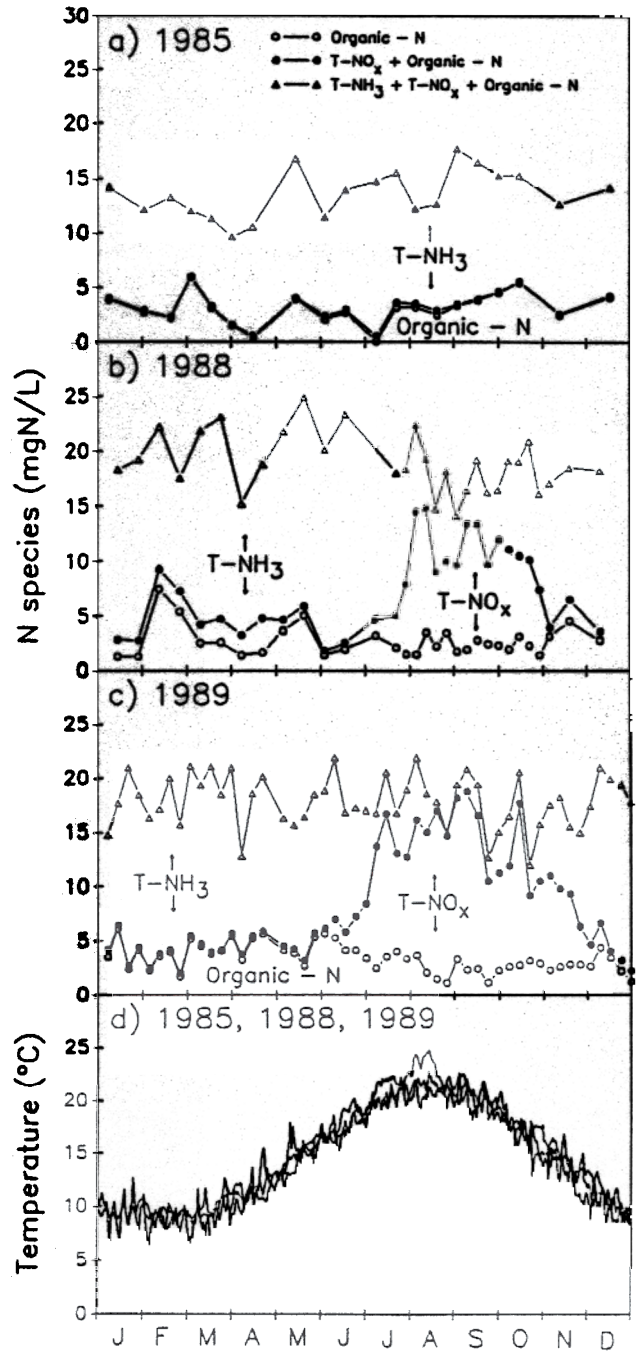

Figure 5.–Temporal distributions in the METRO effluent; (a) concentrations of N species in 1985, (b) concentrations of N species in 1988, (c) concentrations of N species in 1989, and (d) temperature for 1985, 1988, and 1989.

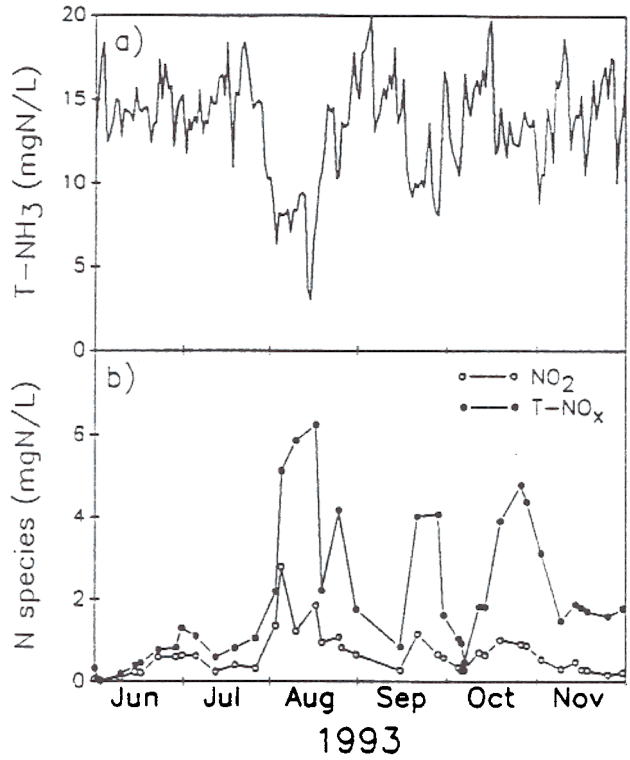

Figure 6.–Time series of selected N species in METRO's effluent in the June-November interval of 1993: (a) T-NH_3, and (b) T-NO_x and NO_2^-.

species in the lake, indicate that NO_2^- should be monitored routinely in the plant's effluent, and that the "trade-off" between the benefit of seasonal nitrification and the increase in NO_2^- loading to the lake

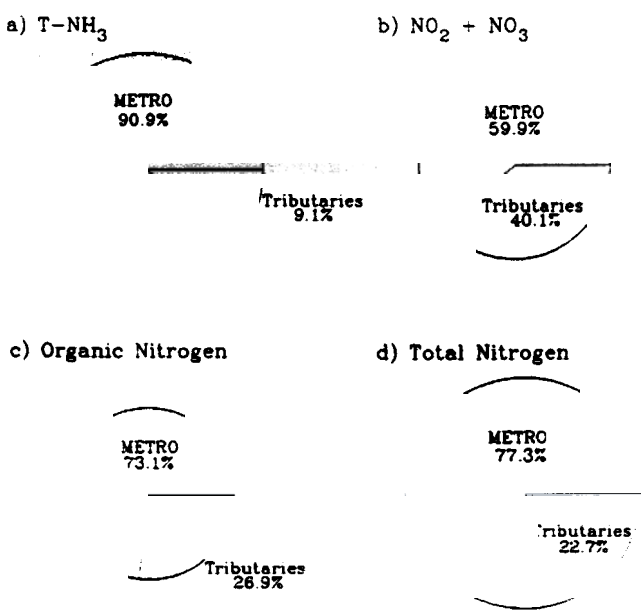

Figure 7.–Contributions of METRO and tributaries to loading of N species and total N to Onondaga Lake in 1989: (a) T-NH_3, (b) T-NO_x, (c) organic-N, and (d) total N. Relative areas of "pies" for three N species proportional to contribution of each to total N loading.

should be evaluated.

METRO is the dominant source of N to Onondaga Lake. The contributions of the METRO discharge to the loading of selected N species and total N (Fig. 7) for 1989, are representative of conditions that continue. The annual areal loading rate for total N to the lake (about 200 $gN/m^2/y$) exceeds by a factor of 1.5 the highest value included in the N loading compilation of Brezonik (1972). METRO represents about 90% of the T-NH_3 load (Fig. 7a), 60% of the T-NO_x load (Fig. 7b), 70% of the organic-N load (Fig. 7c), and about 80% of the total N load (Fig. 7d).

Manifestations of Cultural Eutrophication

The paleolimnological analysis of Rowell (1996) shows that Onondaga Lake was oligo-mesotrophic to mesotrophic before colonial development of the watershed. Here we describe the highly eutrophic conditions that continue to prevail in the lake despite the reductions in P loading achieved at METRO (Fig. 3).

Lake TP Concentrations

The TP concentration in the upper productive layers of a lake is a widely used indicator of trophic state (e.g., Auer et al. 1986, Chapra and Dobson 1981, Vollenweider 1975, 1982). There is no numerical standard for TP in the State of New York, but there is a narrative standard, ".... none in amounts that will result in growths of algae, weeds, and slimes that will impair the best usages", and a recently established guidance value (open to some regulatory discretion) of 20 µg/L, as the mean summer epilimnetic TP concentration (New York State Department of Environmental Conservation (NYSDEC) 1993). The guidance value is based on empirical relationships with aesthetic effects for primary and secondary recreation (e.g., Kishbaugh 1993). This value is generally consistent with the upper bounds of mesotrophy proposed for TP concentrations by various researchers (see Auer et al. 1986, Chapra and Dobson 1981, Vollenweider, 1975, 1982).

Concentrations of TP were high in 1987, the highest in 1988, were lower in the 1989-1992 interval, and increased in 1993 (Table 2). The lowest margin of exceedance of the NYSDEC guideline value was nearly a factor of 3. Further, the TP concentration in all the years was substantially above levels described as indicative of eutrophy (e.g., Auer et al. 1986, Chapra and Dobson 1981, Vollenweider 1975, 1982).

Table 2.–Indicators of eutrophy for Onondaga lake, for the mid-May to mid-September interval.

Year	TP* (µg/L) $\bar{x}$	Chl+ (µg/L) $\bar{x}$	Chl+ (µg/L) median	SD** (m) $\bar{x}$	SD** (m) median	AHOD (g/m³/d)
1978		70*	55	.93	1.0	
1981				.92	1.0	1.7
1985		63	59	.84	.85	
1986		37	20	.77	.75	
1987	105	72	46	1.42	1.3	1.7
1988	140	33	29	1.93	1.5	
1989	74	36	24	2.22	1.7	1.9
1990	76	28	21	2.32	1.7	1.1
1991	56	36	21	2.90	2.0	1.4
1992	63	20	20	2.66	1.95	1.5
1993	90	26	22	3.05	1.8	

* TP – epilimnetic summer average TP concentration; volume-weighted average for 0-8 m, mid-May to mid- September.
+ Chl - epilimnetic average chlorophyll; summation of chlorophyll *a* plus phaeophytin for 1978, 1985, 1986; as total chlorophyll in other years.
** SD - Secchi disc transparency.

The central role that loading from METRO plays in regulating TP concentrations in Onondaga Lake is evidenced by the strong linear relationship that has prevailed between the summertime mean epilimnetic TP concentration and the TP load from METRO over the April-September interval (Fig. 8). The lake responds rapidly to significant changes in loading because of its high flushing rate (Effler and Hennigan 1996). Approximately 97% of the year-to-year differences in epilimnetic TP concentrations over the 1987-1993 interval (with the exception 1988) can be explained by changes in METRO TP loading. The year 1988 is an outlier, with several possible explanations. For instance, the tributary monitoring program (Table 1) may not have captured the added loading associated with a sewer line break along one of the tributaries in that year (Effler and Whitehead 1996). More probably, incorrect high measurements of TP concentration in the lake were included in the observations for that year. Clearly lake TP concentrations are highly responsive to loads received from METRO (Fig. 8). It is unfortunate that the appropriate monitoring TP data for the lake are not available to document the response to earlier reductions in METRO loading (Fig. 3).

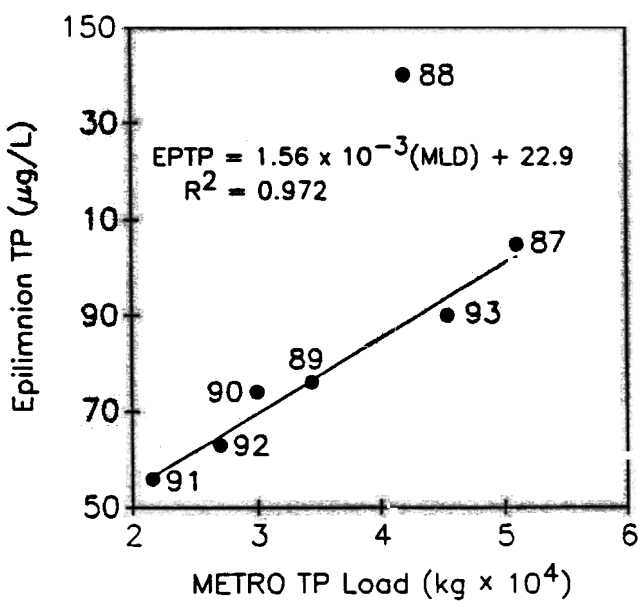

Figure 8.–Relationship between epilimnetic summer average TP concentration in Onondaga Lake and METRO loading over the April-September interval. Years designated by last two digits.

Phytoplankton and Clarity

Before closure of the soda ash facility (1986), chlorophyll concentrations tended to remain high (e.g., > 30 µg/L; Auer et al. 1996) throughout the productive period of late spring to early fall. Stronger fluctuations have been observed since 1987, characterized by distinctly lower and more abrupt

minima (e.g., < 3 μg/L) compared to earlier years (Auer et al. 1996). The temporal changes in clarity in the lake are largely driven by the dynamics of phytoplankton biomass (Effler and Perkins 1996). Thus, abrupt increases in Secchi disc transparency (described as "clearing events") have attended the abrupt decreases in phytoplankton biomass and seasonal measures of clarity (Table 2) have improved. Summer average and median chlorophyll concentrations and Secchi disc tranparencies throughout the 1978-1993 interval (Table 2) are indicative of eutrophy (cf. Carlson 1977). The median is provided as a more robust indicator for the highly dynamic conditions that have prevailed annually since the closure of the soda ash/chlor-alkali facility (Auer et al. 1996).

Phosphorus is the limiting nutrient in Onondaga Lake (Auer et al. 1996). However, the available evidence (e.g., Connors et al. 1996) indicates that, despite substantial reductions in TP loading (Fig. 3) and lake concentrations (e.g., Fig. 8, Table 2) over the period of record, only a small degree of P limitation of phytoplankton growth has been achieved (i.e., other factors such light and temperature are regulating (e.g., Field and Effler 1983)). This is consistent with the literature; e.g., Auer et al. (1986) found that TP concentrations > 40 μg/L were essentially saturating in Green Bay, Lake Michigan. Reductions in phytoplankton biomass and increases in clarity in Onondaga Lake since closure of the soda ash/chlor-alkali facility (Table 2) are not a result of increased nutrient limitation, but can instead be attributed to increased zooplankton grazing ("top-down" control; Siegfried et al. 1996). The timing of changes in chlorophyll and Secchi disc transparency, when compared to temporal patterns of TP loading and lake TP concentrations (Table 2), further support this position. First, the distinct improvements in clarity and reductions in phytoplankton biomass (Table 2) emerged before reductions of external TP loading (Fig. 3) and coupled decreases in lake TP concentrations (Fig. 8) occurred. Second, both chlorophyll concentrations and clarity were insensitive to the increases in epilimnetic TP concentration that occurred in 1993 (and perhaps 1988, Table 2). One possible side-effect of increased zooplankton pressure has been the proliferation of nuisance filamentous cyanobacteria (particularly *Aphanizomenon flos-aquae*) which are resistant to grazing. Yet greater reductions in external TP loading would be required to systematically improve related features of water quality (see Effler and Doerr 1996) through P limitation.

Oxygen

The rapid depletion of DO from the lake's hypolimnion and the calculation of the associated AHOD is illustrated here for 1991 (Fig. 9a), based on volume-weighted concentrations (from profiles) below a depth of 10 m. The AHOD value for 1981 (Table 2) has been presented previously (Effler et al. 1986). The average AHOD for the six years for which deter-minations have been made was 1.54 g/m²/d, the range was 1.1 to 1.9 g/m²/d. These values are indicative of a highly eutrophic system (e.g., > 0.55 g/m²/d; Mortimer 1941), and they approach the highest values in data bases used to develop predictive empirical expressions for AHOD (Cornett and Rigler 1979, Walker 1979, Welch and Perkins 1979). We assign no significant temporal trends to the results (Table 2). The substantial year-to-year variability is most likely a result of year-to-year differences in the magnitude and timing of vertical mixing in the lake (Effler et al. 1986, Owens and Effler 1989).

In Onondaga Lake, anoxia is established first in the lowermost layers of the hypolimnion because of oxygen-demanding processes at the sediment-water interface (Gelda et al. 1995). The depth interval of anoxia expands upward in a generally progressive manner, and may for brief periods extend from the lake bottom to within 5-6 m of the surface (e.g., Fig. 9b). The by-products of anaerobic metabolism, particularly methane (CH_4; Addess and Effler 1996) and hydrogen sulfide (H_2S; Effler et al. 1988), start to accumulate after the onset of anoxia. The highest concentrations of these anaerobic by-products develop in the lowermost layers (Fig. 9b), consistent with the localization of methanogenesis and sulfate reduction in the sediments (Effler et al. 1988, Fallon et al. 1980, Rudd and Hamilton 1978).

Lake-wide depletions of DO down to concentrations that violate surface water standards for New York State (< 5 mg/L, as a daily average; < 4 mg/L, at anytime within a day) are common (Fig. 9c) in the upper waters of Onondaga Lake during the approach to fall turnover. This fall DO "sag" phenomenon is illustrated as the average DO concentration in the upper 5 m of the lake over the September-November interval of 1990 (Fig. 9d). During that period, the DO concentration violated the standard for more than 2 weeks. Substantial year-to-year variations in the timing and severity of this phenomenon (e.g., Fig. 9c) are attributed largely to meteorological variability (Effler 1996, Gelda and Auer 1996). The exodus of most fish from the lake (e.g., to the Seneca River) during this low DO period has been documented by Tango and Ringler (1996). The severe oxygen depletion in autumn that results from oxidation of anaerobic metabolites that accumulate in the hypolimnion during summer (e.g., Fig. 9b) is a particularly severe and conspicuous manifestation of the cultural eutrophication of the lake (Effler et al. 1988, Addess and Effler 1996).

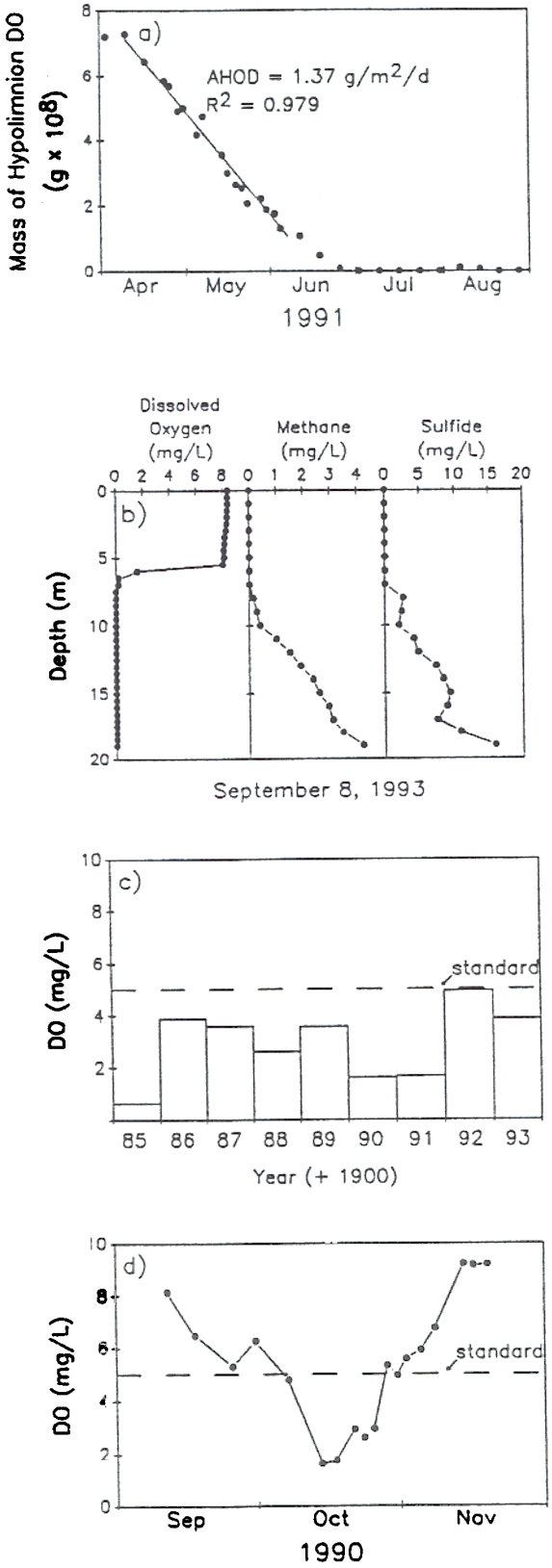

Figure 9.–Oxygen resources of Onondaga Lake: (a) hypolimnetic DO depletion and calculation of AHOD for 1991, (b) selected paired vertical profiles of DO, CH_4, and H_2S (Sept. 8, 1993), (c) annual fall DO minimum for upper 5 m, 1985-1993, and (d) fall DO (0-5 m average) sag and recovery in 1990.

Lake Status With Respect to NH_3 and NO_2^- Standards

NH_3

Ammonia (NH_3) concentrations in the upper waters of Onondaga Lake during the 1988-1993 period routinely violated the chronic non-salmonid toxicity standard and occasionally exceeded the acute non-salmonid standard (Fig. 10). Note that allowable levels of NH_3 are not a constant, but are a function of ambient temperature and pH (cf. Effler et al. 1990) which together determine the unionized fraction of T-NH_3 and the toxicity limits of NH_3. The 1988 conditions were documented earlier by Effler et al. (1990). The spring to early fall interval addressed in this treatment is the most critical because the higher temperatures (Effler and Owens 1996) and pH (Driscoll et al. 1994, Effler et al. 1990) values increase the fraction of T-NH_3 that exists as NH_3. Further, the most severe conditions are observed in the upper waters, rather than the hypolimnion, for the same reasons.

Violations of the acute standard were documented in 1988 and 1989, but not in subsequent years. The acute standard was undoubtedly exceeded, and more nearly approached, on more days than indicated in this analysis (Fig. 10a-f) as a result of photosynthetically - induced diurnal increases in pH. Violations of the chronic NH_3 standard, by a wide margin, is a recurring problem for the upper waters of the lake (Fig. 10 a-f). Violations persist for at least 2 months, and in some years for more than 5 months (Fig. 10a-f).

The year-to-year differences in the severity of NH_3 violations (Fig. 10) are related primarily to interannual differences in the T-NH_3 concentration in spring, and, to a lesser extent, pH. The spring T-NH_3 concentration is regulated largely by the dilution provided by tributary flow. Inflow from the tributaries is highly variable year-to-year (Effler and Hennigan 1996; Fig. 2), while the T-NH_3 load from METRO to the lake during the antecedent winter period is relatively uniform (e.g., Fig. 5b and c). Thus, the highest T-NH_3 concentrations in spring are expected in those years with the lowest tributary inflow during the proceeding winter. We have evaluated the relationship between spring (April) lake T-NH_3 concentrations and antecedent (November-March) tributary inflow within the context of a "dilution" (Manczak and Florczyk 1974) model (Fig. 11). Variations in the inverse of total antecedent tributary inflow explained 65% of the variability in T-NH_3 concentrations observed in the lake in April for the 6 y of the 1988-1993 interval (Fig. 11). The approximate linearity of the relationship is consistent with the

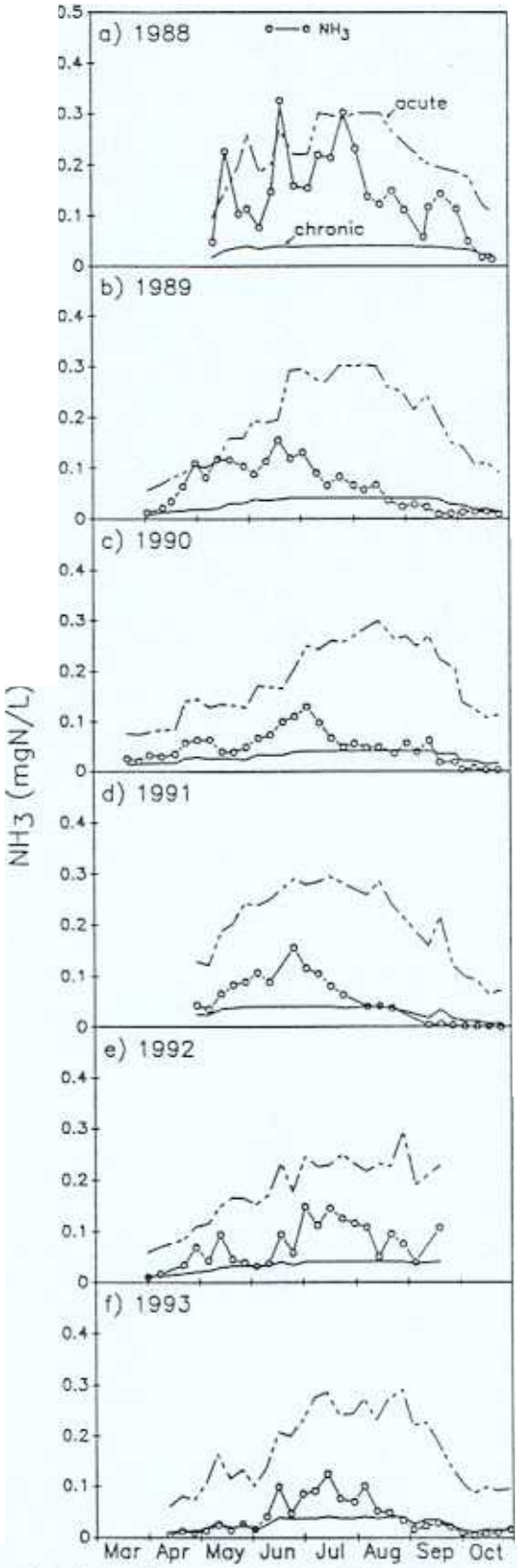

Figure 10.–Comparison of time series of NH_3 concentrations and chronic and acute standards for non-salmonids in the near surface (1 m) waters of Onondaga Lake: (a) 1988, (b) 1989, (c) 1990, (d) 1991, (e) 1992, and (f) 1993.

"dilution" model identified for some fluvial systems (Manczak and Florczyk 1974), where a relatively uniform loading source is diluted to a varying extent according to natural variations in runoff. This analysis indicates that year-to-year differ-ences in T-NH_3 (and therefore NH_3) concentrations in the lake are primarily a result of natural variations in runoff instead of differences in treatment performance at METRO. Year-to-year differences in phytoplankton growth (a sink for T-NH_3) may also contribute importantly to variations in T-NH_3 concentrations in the upper waters of the lake (Canale et al. 1996).

The prevalence and margin of violation of the chronic non-salmonid toxicity criterion for NH_3 and the more infrequent occurrence of violations of the acute standard in the upper waters of Onondaga Lake are consequences of the discharge of domestic waste water. The extent to which the prevailing high NH_3 concentrations impact the diversity, health, and abundance of aquatic life (particularly fish) in the lake is presently unknown. Delineation of the influence(s) of this pollutant is complicated by the myriad of other water quality problems of the lake (Effler 1996).

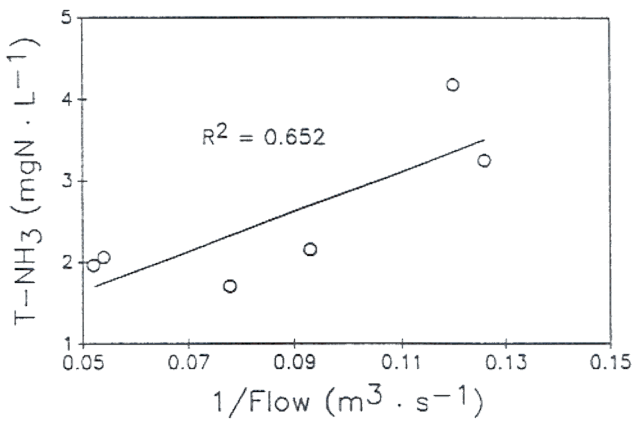

Figure 11.–Relationship between the inverse of the summed tributary inflow for the November-March interval and the subsequent April T-NH_3 concentration in Onondaga Lake, e.g., according to a dilution model.

NO_2^-

Nitrite is an intermediate product in the two stage biochemical process of nitrification. Nitrite is depleted rapidly from the hypolimnion of Onondaga Lake following the onset of anoxia associated with the operation of the denitrification process (e.g., Brooks and Effler 1990). In sharp contrast, generally progressive increases in NO_2^- concentrations are observed in the upper waters of the lake until August (Fig. 12a-f). Violations of the non-salmonid toxicity standard have been documented in each year over the 1989-1993

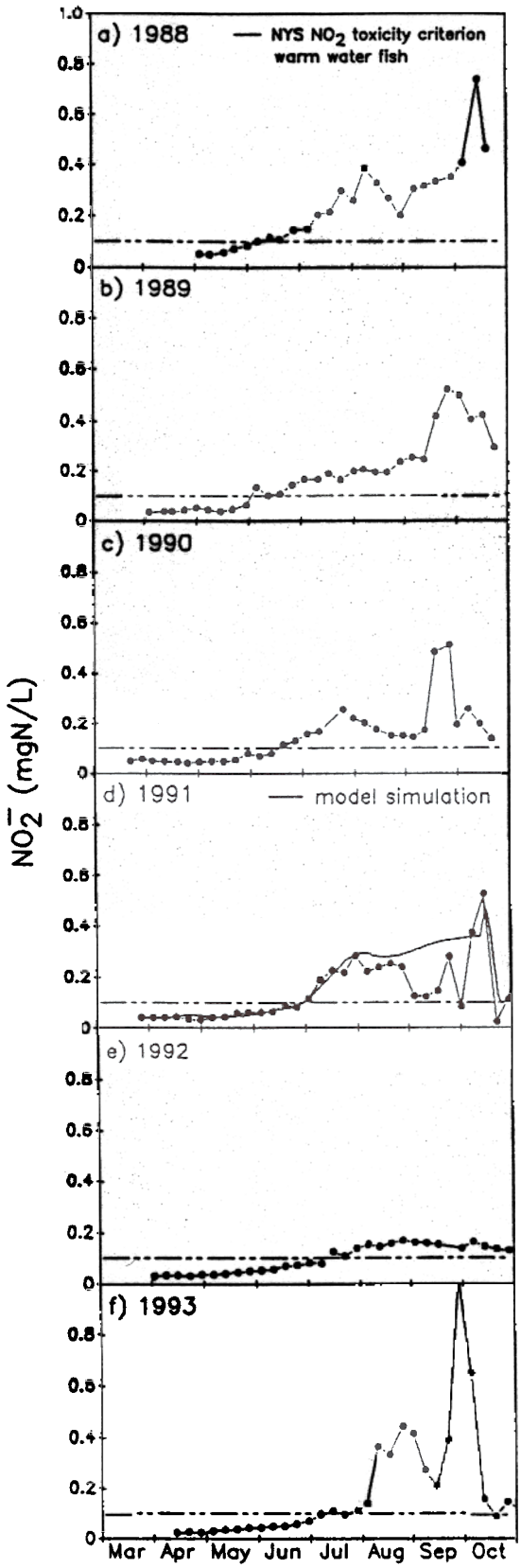

Figure 12.–Time series of NO_2^- concentrations in the near surface waters of Onondaga Lake: (a) 1988, (b) 1989, (c) 1990, (d) 1991, (e) 1992, and (f) 1993. Standard for non-salmonid fish, and mass balance model simulation for 1991, included.

interval (Fig. 12). Rather strong differences have been common after early August, with rather abrupt changes in NO_2^- concentration evident in most years (Fig. 12). Extremely high concentrations of NO_2^-, that represent severe violations of the standard, were observed over the August-October interval in 5 of the 6 years (Fig. 12). Clearly, severe violation of the NO_2^- toxicity standard has been a recurring problem in the upper waters of the lake. Hutchinson (1957) observed that the occurrence of "appreciable" NO_2^- concentrations in surface waters is indicative of sewage contamination. 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, Effler 1996).

A major part of the NO_2^- problem in the lake is the high external loads of NO_2^- received in the warmer months from METRO (e.g., Fig. 6). Application of a conservative substance mass balance model (e.g., loads and flushing accommodated, but no reactions) for NO_2^- has been successful in simulating the observed temporal structure through mid- to late summer in 1991 (Fig. 12d), supporting the important role METRO (95% of the NO_2^- load over the simulation interval of 1991) plays in this problem. It is noteworthy that the available evidence indicates the rate of nitrification in Onondaga Lake in summer is low (Canale et al. 1996), compared to values adopted in the modeling literature (e.g., Bowie et al. 1985). The conservative NO_2^- model fails in the late summer to fall interval (Fig. 12d). The operation of a major sink process in early September and a major source in early October of 1991 is indicated (Fig. 12d), which are not accommodated by the model. The non-conservative behavior of NO_2^- in fall (Fig. 12d) probably reflects temporal imbalances in the rates of the first and second stages of the overall nitrification process, as well as the abrupt increase in internal loading of T-NH_3 to the upper waters of the lake that accompanies the fall mixing period (Brooks and Effler 1990).

Management Perspectives

Clearly the extremely high loads of P and N species received by Onondaga Lake from METRO severely impact the lake, as manifested by the routine violations of several related water quality standards in the lake (Table 3). Degradations from cultural eutrophication, including excessively high concentrations of phytoplankton biomass, poor transparency, rapid depletion of oxygen from the hypolimnion, and lake-wide oxygen depletion during the fall mixing period, are conspicuous and recurring. Standards to protect

Table 3.–Violations/exceedances of numerical standards/guidance value for New York State in Onondaga Lake related to METRO P and N discharges.

Constituent/Attribute	Resource/Use	Standard/Guideline
free ammonia (NH_3)	fishing	toxicity; standard function of pH and temperature; differ for salmonid and non-salmonid fisheries
nitrite (NO_2^-)	fishing	toxicity; < 100 μg NO_2^-/L for non-salmonid, 20 < μgNO_2^-/L for salmonid
dissolved oxygen (DO)	fishing	≥ 5 mg/L, daily average; ≥ 4 mg/L, minimum within a day
clarity (Secchi disc)	swimming	standard for opening a public bathing beach; ≥ 4 ft (or 1.2 m)
total phosphorus (TP)		guidance value; epilimnetic summer average ≤ 20 μgP/L

against the toxic effects of NH_3 and NO_2^- on aquatic life are violated routinely and by a wide margin. Rarely have the signatures of N and P pollution been so clear (Table 3). METRO plays the primary role in all of these problems, and is the appropriate target for related remediation efforts.

At the heart of these water quality problems is the large volume of the METRO discharge to Onondaga Lake. This input of treated waste water represents nearly 30%, on average, of the total inflow received by the lake during summer, and is usually the largest single source of water in the month of August. Despite the major reductions in METRO effluent TP concentrations, and thereby loads and lake concentrations, achieved from increased treatment and other management actions, the lake remains highly eutrophic due to excessive external loading of P. The severity of the violations of the ammonia toxicity standard(s) reflects the lack of year-round nitrification treatment at METRO. While the seasonal nitrification achieved during the warmer summer months at the facility in recent years may have resulted in modest amelioration of the NH_3 problem in the lake, the attendant high NO_2^- loads from the plant contribute greatly to the violations of the NO_2^- toxicity standard in the lake.

References

Addess, J. A. and S. W. Effler. 1996. Summer methane fluxes and fall oxygen resources of Onondaga Lake. Lake and Reserv. Manage. 12(1):91-101.

APHA. 1980, 1985. Standard methods for the examination of water and wastewater. 15th and 16th editions, American Public Health Association, NY.

Auer, M. T., S. W. Effler, M. L. Storey, S. Connors and P. Sze. 1996. Phytoplankton (Biology, Chapter 6). *In:* S. W. Effler (ed.). Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, New York. Springer-Verlag, NY (in press).

Auer, M. T., M. S. Kieser and R. P. Canale. 1986. Identification of critical nutrient levels through field verification of models for phosphorus and phytoplankton growth. Can. J. Fish. Aquat. Sci. 43: 379-388.

Auer, M. T., N. Johnson, M. P. Penn and S. W. Effler. 1993. Measurement and verification of rates of sediment phosphorus release for a hypereutrophic urban lake. Hydrobiol. 253:301-309.

Bowie, G. L., W. B. Mills, D. B. Porcella, C. L. Campbell, J. R. Pagenkopf, G. L. Rupp, K. M. Johnson, P. W. H. Chan, S. A. Gherini and C. Chamberlain. 1985. Rates, constants, and kinetic formulations in surface water quality modeling, 2nd edition, EPA/600/3-85/040. U.S. Environmental Protection Agency. Athens, GA. 455 p.

Brezonik, P. L. 1972. Nitrogen sources and transformations in natural waters. *In:* H. E. Allen and T. P. Kramer (eds.). Nutrients in natural waters. John Wiley and Sons. P. 1-50.

Brooks, C. M. and S. W. Effler. 1990. The distribution of nitrogen species in polluted Onondaga Lake, NY, USA. Wat., Air, Soil Pollut. 52: 247-262.

Canale, R. P. R. Gelda and S. W. Effler. 1996. Development and testing of a nitrogen model for Onondaga Lake. Lake and Reserv. Manage. 12(1):151-164.

Carlson, R. F. 1977. A trophic status index for lakes. Limnol. Oceanogr. 22: 361-368.

Chapra, S. C. and H. F. H. Dobson. 1981. Quantification of the lake topologies of Naumann (surface growth) and Thienemann (oxygen) with special reference to the Great Lakes. J. Great Lakes Res. 7: 182-193.

Connors, S. D., M. T. Auer and S. W. Effler. 1996. Phosphorus pools, alkaline phosphatase activity, and phosphorus limitation in hypereutrophic Onondaga Lake. Lake and Reserv. Manage. 12(1):47-57.

Cooke, G. D., E. B. Welch, S. A. Peterson and P. R. Newroth. 1993. Restoration and management of lakes and reservoirs (2nd Ed.). Lewis, Boca Raton, FL.

Cornett, R. J. and F. H. Rigler. 1980. The areal hypolimnetic oxygen deficit: An empirical test of the model. Limnol. Oceanogr. 25: 672-679.

Doerr, S. M., S. W. Effler, K. A. Whitehead, M. T. Auer, M. G. Perkins and T. M. Heidtke. 1994. Chloride model for polluted Onondaga Lake. Wat. Res. 28: 849-861.

Driscoll, C. T., S. W. Effler and S. M. Doerr. 1994. Changes in inorganic carbon chemistry and deposition of Onondaga Lake, New York. Environ. Sci. Tech. 28: 1211-1218.

Edmondson, W. T. and J. T. Lehman. 1981. The effect of changes in the nutrient income on the condition of Lake Washington. Limnol. Oceanogr. 26: 1-29.

Effler, S. W. (ed.). 1996. Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, NY. Springer-Verlag, NY (in press).

Effler, S. W., C. M. Brooks, M. T. Auer and S. M. Doerr. 1990. Free ammonia in a polluted hypereutrophic urban lake. Res. J. Wat. Pollut. Contr. Fed. 62: 771-779.

Effler, S. W., C. M. Brooks, M. G. Perkins, S. M. Doerr, K. A. Whitehead, B. A. Wagner and C. T. Driscoll. 1994. Onondaga Lake Monitoring Report, 1993. Submitted to the Onondaga Lake Management Conference, Syracuse, NY.

Effler, S. W. and S. M. Doerr. 1996. Water quality model evaluations for scenarios of loading reductions and diversion of domestic waste effluent around Onondaga Lake. Lake and Reserv. Manage. 12(1):181-193.

Effler, S. W., J. P. Hassett, M. T. Auer and N. Johnson. 1988. Depletion of epilimnetic oxygen and accumulation of hydrogen sulfide in the hypolimnion of Onondaga Lake, NY, USA. Wat., Air, Soil Pollut. 39: 59-74.

Effler, S. W. and R. D. Hennigan. 1996. Onondaga Lake, New York: legacy of pollution. Lake and Reserv. Manage. 12(1):1-13.

Effler, S. W. and E. M. Owens. 1996. Density stratification in Onondaga Lake: 1968-1994. Lake and Reserv. Manage. 12(1):25-33.

Effler, S. W. and M. G. Perkins. 1987. Failure of spring turnover in Onondaga Lake, NY, USA. Wat., Air, Soil Pollut. 34:285-291.

Effler, S. W. and M. G. Perkins. 1996. An optics model for Onondaga Lake. Lake and Reserv. Manage. 12(1):115-125.

Effler, S. W., M. G. Perkins and C. M. Brooks. 1986. The oxygen resources of the hypolimnion of Onondaga Lake, NY, USA. Wat., Air, Soil Pollut. 29: 93-108.

Effler, S. W. and K. A. Whitehead 1996. Tributaries and discharges (Chapter 3). *In:* S.W. Effler (ed.). Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, NY. Springer-Verlag, NY (in press).

Fallon, R. D., S. Harris, R. S. Hanson and T. D. Brock. 1980. The role of methane in internal carbon cycling in Lake Mendota during summer stratification. Limnol. Oceanogr. 25: 357-360.

Field, S. D. and S. W. Effler. 1983. Light-productivity model for Onondaga Lake, NY. J. Environ. Eng. Div. ASCE 109: 830-844.

Gelda, R. K. and M. T. Auer. 1995. Development and testing of a dissolved oxygen model for a hypereutrophic lake. Lake and Reserv. Manage. 12(1):165-179.

Gelda, R. K., M. T. Auer and S. W. Effler. 1995. Determination of sediment oxygen demand by direct measurements and by inference from reduced species accumulation. Mar. Freshwat. Res. 46: 81-88.

Harris, G. P. 1986. Phytoplankton ecology, structure, function, and fluctuation. Chapman and Hall, NY.

Hutchinson, G. E. 1957. A treatise of limnology. Vol. I. Geography, physics and chemistry. John Wiley and Sons, NY.

Kishbaugh, S. A. 1993. Applications and limitations of qualitative lake assessment data. Abstract, paper presented at North American Lake Management Society Conference, Seattle, WA.

Larsen, D. P., D. W. Schultz and K. W. Malereg. 1981. Summer internal phosphorus supplies in Shagawa Lake, MN. Limnol. Oceanogr. 26:740-753.

Lewis, W. M. and J. Morris. 1986. Toxicity of nitrite to fish: A review. Trans. Amer. Fish. Soc. 115: 183-195.

Manczak, H. and J. Florczyk. 1974. Interpretation of results from the studies of pollution of surface flowing waters. Wat. Res. 5: 575-584.

Mortimer, C. J. 1941. The exchange of dissolved substances between mud and water (Parts I and II) J. Ecol. 29:280-329.

Murphy, C. B. 1973. Effect of restricted use of phosphate-based detergents on Onondaga Lake. Science 181: 379-381.

New York State Department of Environmental Conservation (NYSDEC). 1993. New York State fact sheet for phosphorus: Ambient water quality value for protection of recreational uses. Bureau of Technical Services and Research, Albany, NY.

Onondaga County. 1971-1994. Onondaga Lake Monitoring Report. Annual report. Syracuse, NY.

Owens, E. M. and S. W. Effler. 1989. Changes in stratification in Onondaga Lake, New York. Wat. Resour. Bull. 25:587-597.

Parsons, T. R., Y. Marta and C. M. Lalli. 1984. A manual of chemical and biological methods for seawater analysis. Pergamon Press, NY.

Penn, M. R. 1994. The deposition, diagenesis and recycle of sedimentary phosphorus in a hypereutrophic lake. Ph.D thesis. Michigan Technological University, Houghton, MI.

Rowell, H. C. 1996. Paleolimnology of Onondaga Lake: the history of anthropogenic impacts on water quality. Lake and Reserv. Manage. 12(1):35-45.

Rudd, J. W. M. and R. D. Hamilton. 1978. Methane cycling in a eutrophic shield lake and its effects on whole lake metabolisms. Limnol. Oceanogr. 23: 337-348.

Russo, R. C. and R. V. Thurston. 1977. The acute toxicity of nitrite to fishes. *In:* R. A. Tubb (ed.). Recent advances in fish toxicity. USEPA, Ecological Res. Series, EPA-600/3-77-085, Corralis, OR.

Siegfried, C. A., N. A. Auer and S. W. Effler. 1996. Changes in the zooplankton of Onondaga Lake: causes and implications. Lake and Reserv. Manage. 12(1):59-71.

Sze, P. 1996. Phytoplankton, composition and abundance (Biology, Chapter 6). *In:* S. W. Effler (ed.). Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, NY. Springer-Verlag, NY (in press).

Tango, P. J. and N. H. Ringler. 1996. The role of pollution and external refugia in structuring the Onondaga Lake fish community. Lake and Reserv. Manage. 12(1):81-90.

Thomann, R. V. and J. A. Mueller. 1987. Principles of surface water quality modeling and control. Harper & Row, NY.

USEPA. 1974. Environmental impact statement on waste water treatment facilities construction grants for the Onondaga Lake drainage basin. Region II, NY.

USEPA. 1975. Process design manual for nitrogen control. Technology Transfer Document. Washington, DC.

USEPA. 1985. Ambient water quality criteria for ammonia - 1984. Office of Research and Development, Cincinnati, OH.

Vollenweider, R.A. 1975. Input-output models with special references to the phosphorus loading concept in limnology. Schweiz. Z. Hydrol. 33: 53-83.

Vollenweider, R.A. (ed.). 1982. Eutrophication of waters: Monitoring, assessment and control. Organization of Economic Cooperation and Development, Paris, France.

Walker, W. W. 1979. Use of hypolimnetic oxygen depletion rate as a trophic state index for lakes. Wat. Resour. Res. 15:1463-1470.

Walker, W. W. 1987. Empirical methods for predicting eutrophication in impoundments. Report 4: Phase III: Applications manual. Technical Report E-81-9. U.S. Army Engineer Waterways Experimental Station, Vicksburg, MS.

Welch, E. B. and M. A. Perkins. 1979. Oxygen deficit - phosphorus loading relation in lakes. J. Wat. Poll. Contr. Fed. 51:2823-2828.

Welch, E. B., D. E. Spyridakis, J. I. Shuster and R. R. Horner. 1986. Declining lake sediment phosphorus release and oxygen deficit following wastewater diversion. J. Wat. Poll. Contr. Fed. 58: 92-96.

Wetzel, R.G. 1983. Limnology (2nd ed.). Saunders College Publ, NY.

Wetzel, R. G., and G. E. Likens. 1991. Limnological analyses (2nd ed.). Springer-Verlag, NY.