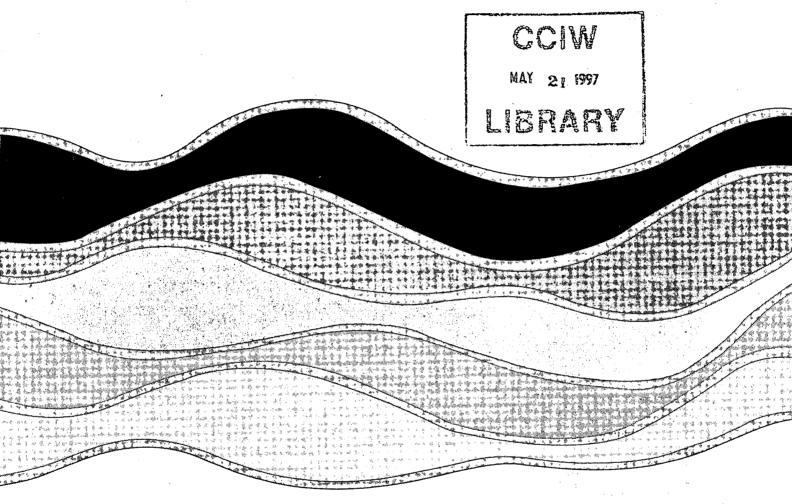
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TD 226 N87 No. 94-58 c.1 LAKE ONTARIO WATER QUALITY TRENDS, 1969 TO 1992:

SOME OBSERVATIONAL NUTRIENT-SCIENCE FOR PROTECTING A MAJOR AND VULNERABLE SOURCE OF DRINKING WATER

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NWRI Contribution No. 94-58

LAKE ONTARIO WATER QUALITY TRENDS, 1969 TO 1992: SOME OBSERVATIONAL NUTRIENT-SCIENCE FOR PROTECTING A MAJOR AND VULNERABLE SOURCE OF DRINKING WATER

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MANAGEMENT PERSPECTIVE

This paper is an empirical study of chemical indicators of biological water-quality, using 25 years of monitoring data for Lake Ontario offshore surface waters. (Trace toxic contaminants are not considered in this paper.) The paper focuses on long-term trends and extends the knowledge gained earlier by the author's Lake Ontario Water Chemistry Atlas (1984).

The main conclusions are: while Lake Ontario's food chain may now be starved of phosphate, caution and understanding are necessary if the external phosphorus loading is to be increased - nitrate in summer in surface waters must not be depleted in the future, to avoid the growth of dangerous blue-green algae that can produce surface scums and algal toxins.

Table: Simplified summary of changes in water quality parameters in Lake Ontario, (offshore, upper 20m), arranged in order of percent change, 1970's to 1990.

Parameter	Time of Year	Percent change 1970's to 1990
Nitrate (+nitrite)	August	Large increase
Nitrate (+nitrite)	Mar/Apr	+29.%
Soluble reactive P	August	always low
Particulate organic		-12.%
Particulate N	August	-21.%
Secchi reciprocal	August	-44.%
Total chlorophyll a	August	-51.%
Total phosphorus	Mar/Apr	-56.%
Soluble reactive P	Mar/Apr	-75.%

SOMMAIRE À L'INTENTION DE LA DIRECTION

La présente communication est une étude empirique des indicateurs chimiques de la qualité biologique de l'eau, étude fondée sur 25 années de données de surveillance des eaux de surface situées au large dans le lac Ontario. (Les contaminants toxiques à l'état de traces ne sont pas examinés ici.) La communication porte sur les tendances à long terme et développe les connaissances acquises antérieurement par l'auteur de l'Atlas de la chimie de l'eau du lac Ontario (1984).

Voici les principales conclusions : même s'il est à peu près certain que la chaîne alimentaire du lac Ontario manque aujourd'hui de <u>phosphate</u>, il faudra faire preuve de prudence et de jugement avant d'augmenter la charge externe de phosphore - il ne faudra pas laisser s'épuiser le <u>nitrate</u> dans les eaux de surface pendant la saison estivale, afin d'éviter la croissance des algues bleues nocives, qui peuvent former de l'écume en surface et des toxines algales.

I dedicate this paper to my dear wife: Carmelita Barreda Dobson, and also to the many staff members of the Canada Centre for Inland Waters who gathered the data, archived it, and computed median values for the selected offshore area of Lake Ontario.

The Laurentian Great Lakes have many uses, including their function as a source of drinking water for the human population of their basins. Therefore we should "handle" the Great Lakes with great care. Table 1 is my subjective ordering of uses according to their relative importance. Apart from human uses, we should also care about plankton and fish in the lake - they should be healthy and without chemical contamination.

TABLE 1: Major human uses of Lake Ontario - an approximate valuation

- 1. Drinking water supply
- 2. Fishing (commercial and sport)
- 3. Transportation
- 4. Recreation (boats and beaches)
- 5. Industrial water supply
- 6. Waste disposal: sewage
- 7. Waste disposal: industrial

The decision was made in the Great Lakes community to reduce the abundance of planktonic algae, and the shore weed *Cladophora*, in Lake Ontario by reducing the loading to the lake of the limiting nutrient: phosphorus. Action taken included reducing the phosphorus content of detergents in Ontario and some of the U.S. Great Lakes states, starting in 1970, and also by precipitating phosphorus at municipal sewage treatment plants, in 1976 and after. The present report is an attempt to learn about the effects produced, within Lake Ontario, by this important and costly remedial action.

The present work on Lake Ontario is empirical - it is measuring and not modelling. Our observations of water quality began in 1966 and became more reliable after 1968. By now the long term trends of some of the parameters indicating water quality are apparent. The data are being examined with critical respect. The data from our Lake Ontario monitoring and surveillance cruises are stored in the CCIW computer file known as the

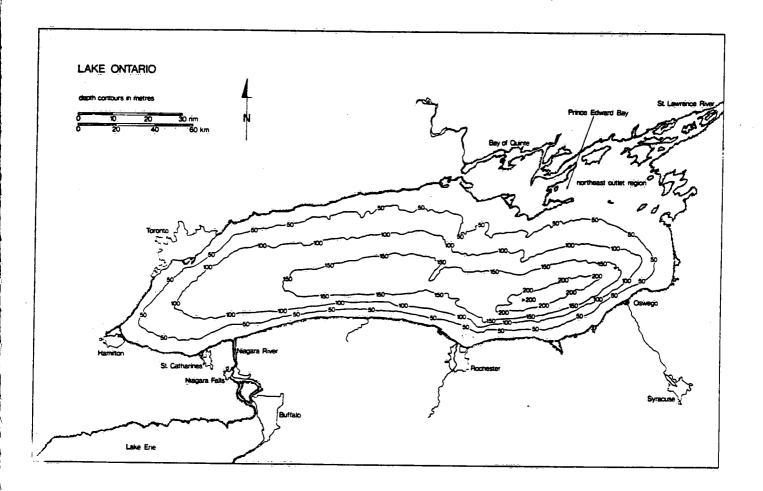
STAR Great Lakes data file. We computed statistically-robust median values by cruise for many nutrient-related parameters to discern trends which we thought would show the lake's response to society's external phosphorus loading reductions that began in the 1970's. For the present study, nutrient data were selected from the offshore waters, on each cruise, by the practical criterion that a station's sounding be greater than 100 metres (Figure 1). Further, the data were selected only from the upper 20 metres. In this work, "winter" means March and April, and "summer" means August. During March/April, dissolved nutrients were at their seasonal peak; and during August, plankton indicators were high but less variable than during July (see Figure 2, seasonal cycle of particulate nitrogen).

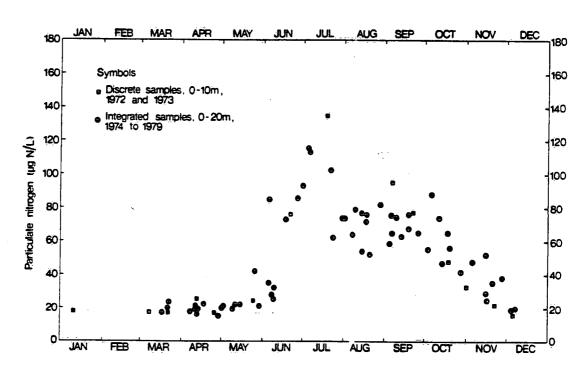
Results:

Note: The method of curve fitting in this work is a simple way of mild smoothing, mentioned briefly in Holloway (1958). Adjacent pairs of median values in each time-series are averaged, and adjacent pairs of these first smoothed values are averaged once more. In the trend graphs, the median values and mildly smoothed curves are shown together - it is easy to see whether there are regular gradual changes, or more random values and an unreliable oscillating curve.

Referring to Figure 3: during the 1970's decade in Lake Ontario, the median value of total phosphorus (TP) in March and April was about 22 μ g P/L (until 1977). By 1980, the values had dropped rapidly to about 15 μ g P/L, and by 1985, the late winter median had dropped less rapidly to 11. In 1991 and 1992, the values were about 9, slightly below the established goal of 10 μ g P/L. The reason for this trend was, very likely, the reduction of external phosphorus loadings to Lake Erie and Lake Ontario. The phosphorus content of detergents was reduced after 1972 in some Great Lakes regions, and, from 1976, less phosphorus was discharged from municipal sewage treatment facilities. By 1990 a major adjustment of Lake Ontario water quality had been

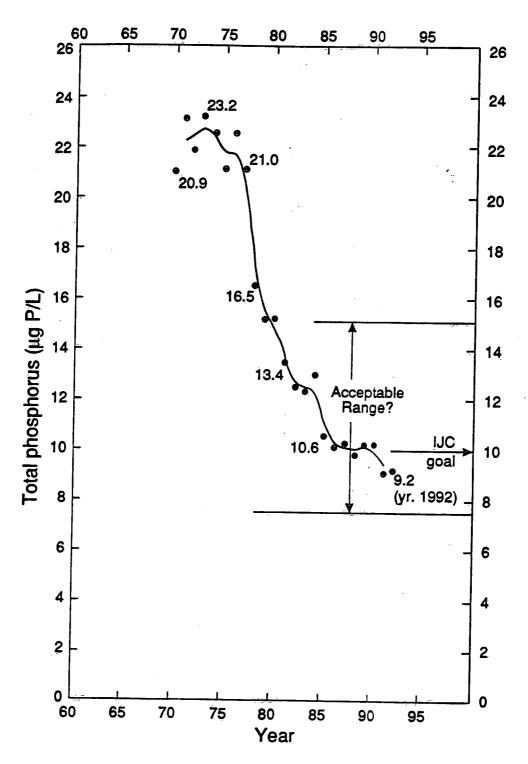
FIGURE 1





Lake Ontario, particulate nitrogen in offshore near-surface waters, cruise-mean values in the years 1972 to 1979.

FIGURE 2



Median values of total phosphorus in Lake Ontario, offshore, upper 20 m., March/April, 1970 to 1992. Figure 3.

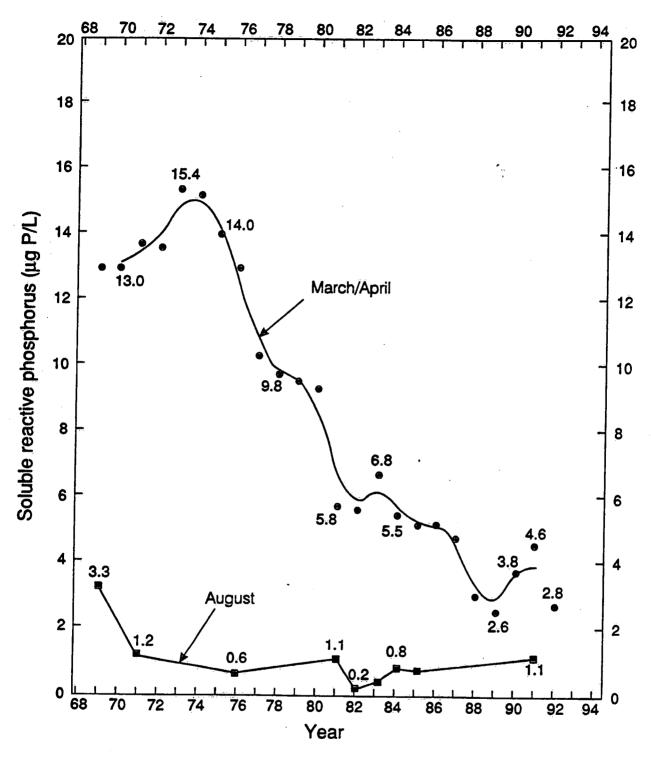
accomplished. This remedial measure was done to fulfil the Great Lakes Water Quality Agreements of 1972 and 1978, between the United States and Canada. In the Agreements, the lake management goals for phosphorus were expressed in terms of: (1) annual external phosphorus loadings to the two lakes, Erie and Ontario; and (2) the within-lake concentration of total phosphorus in "spring". In this present paper, the trends of a number of other nutrient concentrations and plankton abundance indicators, also surveyed in Lake Ontario from about 1970, will be presented and discussed, to increase our knowledge of changes that have been taking place in this lake.

There is controversy in aquatic science about what is being measured in soluble reactive phosphorus, "SRP". I will assume in this paper that SRP indicates approximately the readily bioavailable fraction(s) not yet depleted by the phytoplankton. SRP concentrations in Lake Ontario are maximal in winter, and minimal in the surface layer during summer (Dobson, 1984, Figure 57).

Figure 4 of the present paper indicates the trends of SRP medians over about 20 years in upper, offshore Lake Ontario waters. This phosphorus fraction was about $1.0 \mu g$ P/L each August, near the detection limit of the test, indicating that phosphorus was probably one of the limiting factors for plankton biomass in August of these years.

The March-and-April SRP values peaked in 1973 at 15.4 μ g P/L, and then declined to 6 μ g P/L by 1982. After that, the slope of the trend was less but the median values declined further, to the range 2.6 to 4.6 in the last five years, 1988 to 1992.

My associate Klaus L.E. Kaiser has suggested that if the trend of winter SRP during the 1980's decade continues into the 1990's, then winter SRP would approach zero in just a few years, and then the food web populations would collapse and die off. Kaiser's interpretation raises important questions: Is there enough phosphorus in Lake Ontario? And is it now necessary to add somewhat more each year from the municipal sewage treatment plants? (The cost would be less than at present.)



Median values of soluble reactive phosphorus in Lake Ontario, offshore, upper 20 m., winter and summer, 1969 to 1992. Figure 4.

Nitrate is the most abundant inorganic ionic nitrogen species in Lake Ontario waters in winter (March/April). Ammonia has been low, about 10 μ g N/L, in winter and summer over the years, and nitrite was usually only a trace. The test for nitrate also detects nitrite, but in these data, nitrate was much more abundant than nitrite.

Referring to Figure 5: the median value of nitrate in March and April was 247 μ g N/L in the year 1969, rose to 403 μ g N/L in 1987, declined a bit to 360 in 1990, and then was 384 in 1992.

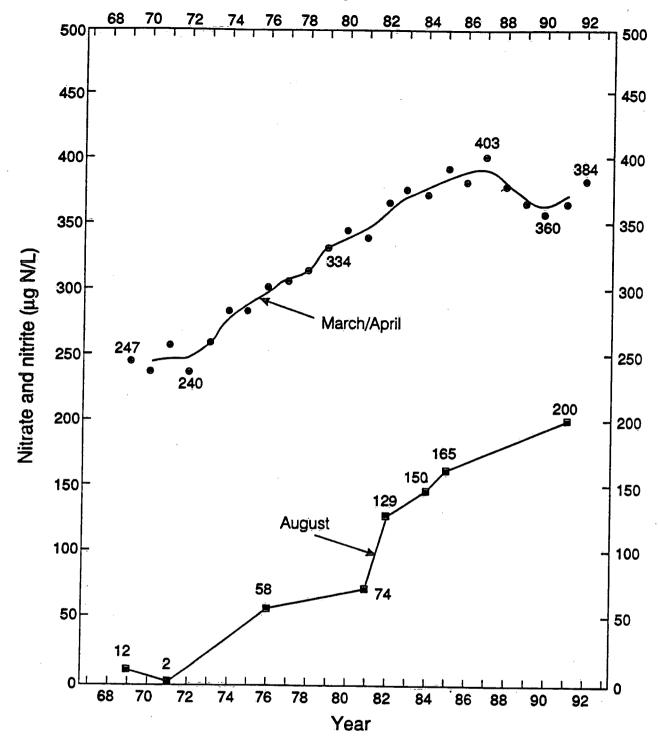
Nitrate has been increasing in all the Great Lakes (Dobson, 1981), even in Lake Superior (Bennett, 1986), partly due to acid rain.

Referring again to Figure 5: the median values of nitrate in offshore near-surface waters of Lake Ontario during August were 12 μ g N/L in 1969, 2 μ g /L in 1971, then rose to 200 μ g/L by 1991. Nitrate in August could be called "the nitrate residual" or "the excess nitrate". In the most recent years, this excess nitrate could not be accumulated by the plankton whose growth in August was more strongly limited by shortage of phosphorus. For managing the plankton of Lake Ontario, the increasing residual nitrate is probably "healthy" provided that phosphorus control continues. Without P-control, Lake Ontario phytoplankton would "bloom" because NO₃ and HCO₃ are now abundant.

Excess nitrate probably suppresses nitrogen fixation and also suppresses surface scums of blue-green algae. These would occur if nitrate were to be depleted. Further, sometimes blue-green algae produce toxic substances, so perhaps excess nitrate protects the drinking water from having such chemicals before or after treatment.

From the nitrate trend curve for August we learn that, around 1970, nitrate would have been a limiting factor, (co-limiting with phosphorus), or perhaps would have allowed nitrogen fixation. But after about 1980, nitrate was in excess, allowing phosphorus to be the one limiting factor controlling plankton growth. Therefore we might expect that, after





Median values of (nitrate and nitrite) in Lake Ontario, offshore, upper 20 m., winter and summer, 1969 to 1992. Figure 5.

1980, phosphorus external loading control would cause a response in Lake Ontario of less plankton, as desired.

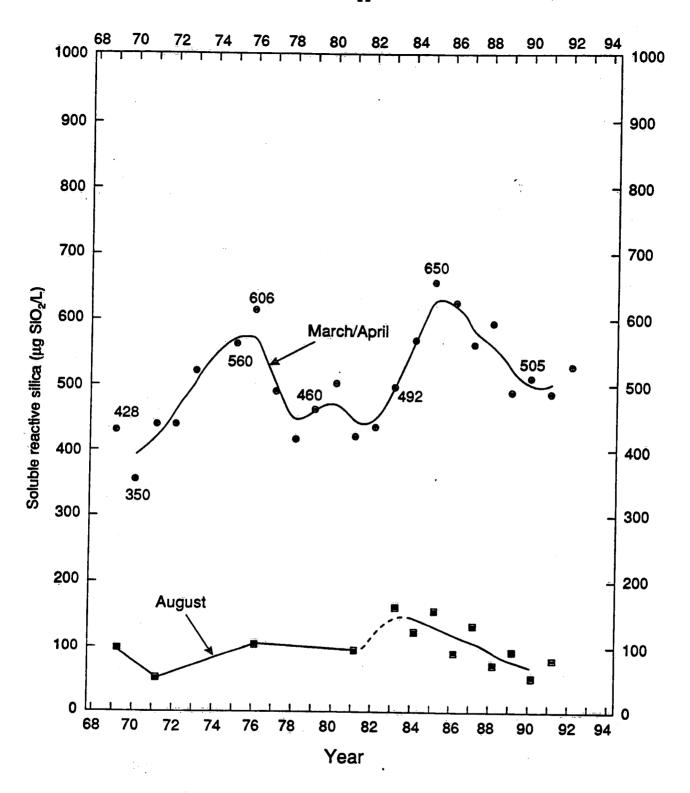
Smith (1983) presented evidence from 17 lakes showing that blue-green algae were abundant, relative to other algae, when the waters had low ratios of total nitrogen to total phosphorus. Further he proposed that "nitrogen fertilization" might keep blue-greens low in abundance. The nitrate trend in Lake Ontario may have the same beneficial effect.

In Figure 6, for soluble reactive silica: again the data are from offshore near-surface waters of Lake Ontario. In March and April, the median values appear to cycle, with peaks in 1976 and 1985, and a broad trough in between. A long-term trend cannot be inferred.

In August, 1969 to 1991, the median value ranged from 50 to 150 μ g SiO₂/L, much lower than in March and April. The depletion in summer is probably caused by diatoms, which are common phytoplankton with shells or "frustules" composed of silica.

There are methods for quantifying particulate biogenic silica, (Krausse et al., 1983), but such measurements were not made on our Lake Ontario surveys. Diatoms dominate the winter and spring phytoplankton communities in surface waters of Lake Ontario (Munawar and Nauwerck, 1971), but in summer the diatoms decline because of enhanced sedimentation and a shortage of silica. The spring crop of diatoms is found to have settled into the deep and bottom waters by summer (Dobson, 1984). For future water quality surveys of Lake Ontario, I suggest measurements be made of soluble reactive silica and, also, particulate biogenic silica, to know more about the diatoms.

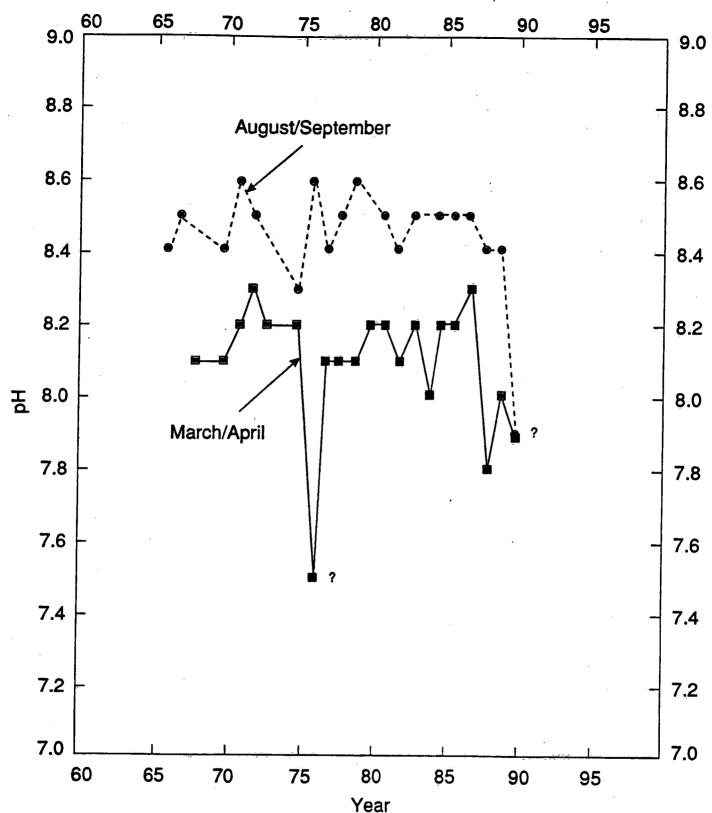
The pH median values shown in Figure 7 for March/April and August/September over many years, should be considered only approximate. It is difficult to have accurate measurement better than to the nearest 0.1 pH units. The pH data will not be closely studied here — they are shown only to demonstrate that the pH values in Lake Ontario



Median values of soluble reactive silica in Lake Ontario, offshore, upper 20m., winter and summer, 1969 to 1992.

Figure 6.





Median values of pH in Lake Ontario, upper 20 m., offshore, 1966 to 1990. The medians are for raw pH data without corrections for temperature.

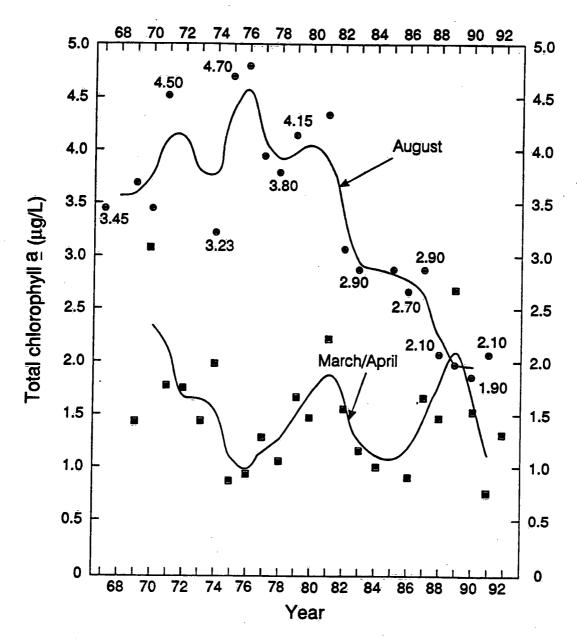
Figure 7.

offshore near-surface waters are usually above 8.0 pH units, proving that Lake Ontario has not been acidified by acid rain. Of course, Lakes Ontario and Erie waters are pH buffered by the dissolution of the surrounding calcite/dolomite rocks. Acidification harms aquatic life at pH values of about 5 or less.

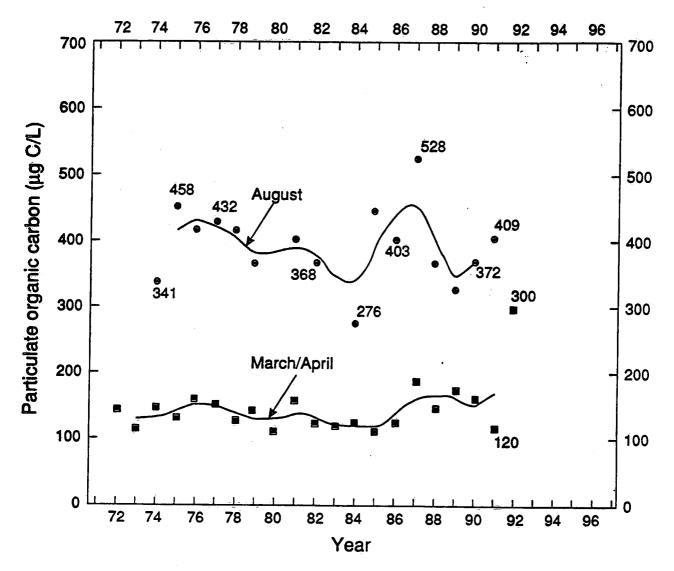
Referring to Figure 8, the median values of total chlorophyll <u>a</u> in March/April appear to be cyclical, with troughs near 1976 and 1985, and peaks near 1981 and 1989. In August during years before 1982, chlorophyll <u>a</u> median values were about $4 \pm 1 \mu g/L$. August values were less, near 2.9 $\mu g/L$ in five years 1982 to 1987. Finally, August medians were lowest, about 2.0 $\mu g/L$, in four recent years, 1988 to 1991.

If total chlorophyll a is a valid indicator of algal biomass [the matter was critically assessed by Tolstoy, 1979], the evidence in Figure 8 would suggest that August algal abundance has declined. Another interpretation would be that an intensifying phosphorus deficiency trend in August has lowered the chlorophyll content of the phytoplankton cells (Healey, 1973) without decreasing algal biomass. A third interpretation of the August data is that the smallest algae pass through the filters used to collect the organisms and that these small algae have become relatively more abundant. A fourth idea is: If bluegreen algae are mostly inedible (Hutchinson, 1973), then the measured decline of chlorophyll in Lake Ontario during August could perhaps indicate a decline of bluegreens, leaving mostly edible algae and zooplankton in the more recent summers. This would explain why particulate nitrogen and particulate organic carbon have declined only slightly, if they include some zooplankton.

The median values of particulate organic carbon, POC, in March and April were in the range of 100 to 200 μ g C/L except for the last year, 1992, when there was a surprising 300 μ g C/L (Figure 9). The sudden jump cannot be interpreted until more years are observed. POC in August was quite variable in the range 276 (1984) to 528 (1987). These two extreme medians were quite close in time, so the second half of the record is erratic and the trend is uncertain. "Particulate organic carbon" includes phytoplankton,



Median values of total chlorophyll <u>a</u> in Lake Ontario, offshore, upper 20 m., summer and winter, 1967 to 1992. Figure 8.



Median values of particulate organic carbon in Lake Ontario, offshore, upper 20 m., winter and summer, 1972 to 1992. Figure 9.

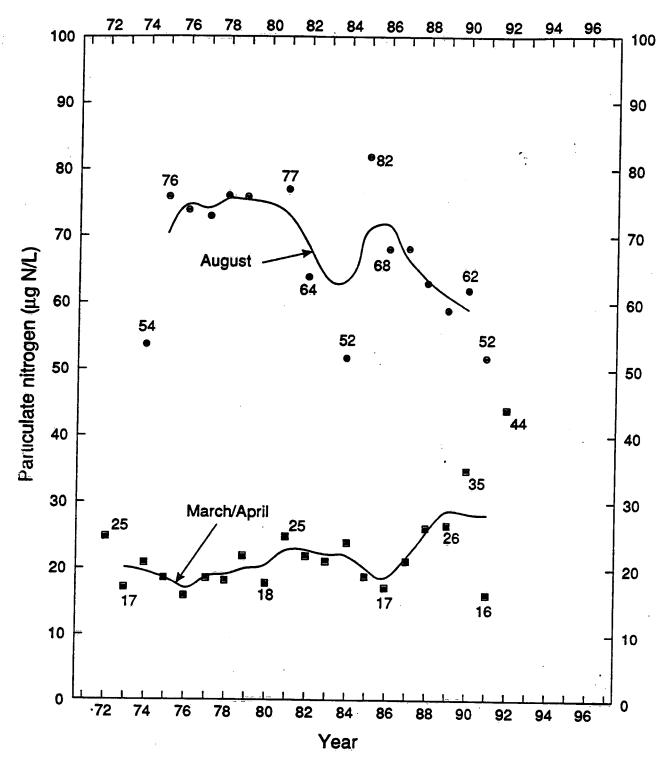
detritus, and small zooplankton, but not precipitated calcite. Perhaps in Lake Ontario POC is mostly "total plankton biomass-carbon".

Particulate nitrogen, PN, shown in Figure 10, is partly in protein of the plankton. "PN" is simpler to measure than POC, because calcite must be excluded in the case of POC. The median values of PN in March and April were near 20 μ g N/L for most of the record, but the medians of the last three years were more erratic. The median values of PN during August (Figure 10) suggest a decline, but that deduction is uncertain because of great variability, especially in the case of 1984 (52 μ g/L) and adjacent 1985 (82 μ g/L).

The traditional and approximate Secchi-disc method was used in our surveys of Lake Ontario water quality. Figure 11 displays the median values of (March/April) and August, 1966 to 1992. In the Figure the scale for the readings in metres is non-linear, and the scale for the transformed reciprocal values is linear, following Postma (1961). The reciprocal values are approximately proportional to the concentration of small particles. In late winter the readings for most of the years were about 6 to 8 m, except 1991, at 4.5 m, and 1992, at 5 m. In August the readings were in a range of 1.5 to 5 m. The August median values were very scattered, and mild smoothing produced a cyclic trend curve which is very uncertain.

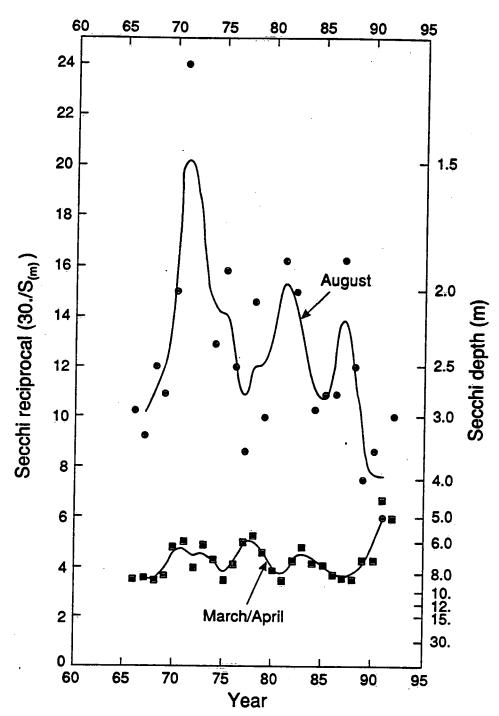
DISSOLVED OXYGEN: A DISCUSSION

When deep temperate lakes are heavily fertilized, they do not develop serious anoxia in their deep waters (e.g., Lake Ontario). If shallow temperate lakes have a cold bottom layer in summer, they develop progressively lower oxygen values in the cold layer even with little fertilization and the cold layer becomes very low in oxygen (e.g., Central Lake Erie) or even seasonally anoxic. The interested reader may want to see: Hutchinson (1938); Charlton (1980); Chapra and Dobson (1981); Vollenweider and Janus (1982). The lake-wide dissolved oxygen regime of Lake Ontario was described by Dobson (1967)



Median values of particulate nitrogen in Lake Ontario, offshore, upper 20 m., winter and summer, 1972 to 1992.

Figure 10.



Median values of Secchi depths and Secchi reciprocals in Lake Ontario, offshore, winter and summer, 1966 to 1992. The reciprocal values indicate [particles].

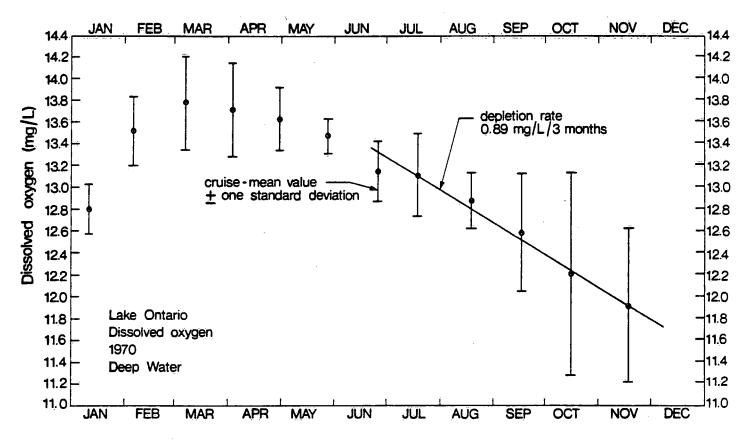
Figure 11.

and Dobson (1984, an atlas). Near-surface waters in the 1970's had supersaturation as high as about 130% in June and July. In the 1970's the main seasonal thermocline during September and October had percent saturation values near 100%. In the Deep Water mass, temperatures colder than 4.00°C and not within 10 m of the lake bottom, the cruise mean values were always greater than 11.0 mg O₂/L. Offshore bottom water, colder than 4.00°C and within 10 m of the bottom, was not consistently sampled; its cruise mean values were above 10 mg O₂/L. For the Deep Water, the yearly cycle in 1970 is illustrated here in Figure 12. Clearly, if the Lake Ontario main basin has always had dissolved oxygen greater than, say, 9.0 mg/L, the zooplankton and fish have had enough dissolved oxygen. They require greater than about 6.0 mg/L for their respiration (Erichsen-Jones, 1952; Davis, 1975). A possible problem, however, is the early summer supersaturation in the upper waters due to seasonal warming and algal photosynthesis. Supersaturation of oxygen and nitrogen can cause gas bubble disease in aquatic organisms (Marsh and Gorham, 1904; Mathias and Barica, 1985) and this may sometimes be a significant problem in Lake Ontario upper waters.

As for long-term dissolved oxygen trends in Lake Ontario: Dobson (1984) found no regular trend in the Deep Water summertime depletion rate. (An update of this has not yet been done.)

Conclusion:

Phosphorus and chlorophyll have declined as expected, but August particulate nitrogen and August particulate organic carbon have declined only slightly. Perhaps we are seeing only a strengthening of phosphorus limitation and reduced chlorophyll per cell (Healey, 1973), and not a decline of algal biomass. Or, perhaps there has been a decline of phytoplankton without much decline of micro-zooplankton.



Lake Ontario, dissolved oxygen (mg/L) in the Deep Water (samples with temperature <4°C and not within 10 m of the bottom), the year 1970, data from 12 cruises of the vessel Martin Karlsen.

FIGURE 12

In the next few years, the sedimentation of zebra mussel larvae, with shells (M.N. Charlton, pers. comm.), may perhaps take the phosphorus concentrations even lower. But if we raise the external phosphorus loading, whose target was 7000 metric tons per year, and which, if increased, might bring more plankton and fish growth, then the resulting nitrate depletion will probably bring blue-green algal scums and algal toxins. Thus for any design of a new P-loading target, we must be careful and knowledgeable.

Acknowledgements:

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APPENDIX

NUTRIENT LIMITATION ASSESSMENT A NEW METHOD APPLIED TO LAKE ONTARIO
OFFSHORE NEAR-SURFACE WATERS IN AUGUST 1969 TO 1991

APPENDIX

A practical method is now described for assessing nutrient limitation of [particulate matter] in 1.0 L water samples. The method could be used for carbon, nitrogen, phosphorus, and silica for diatoms.

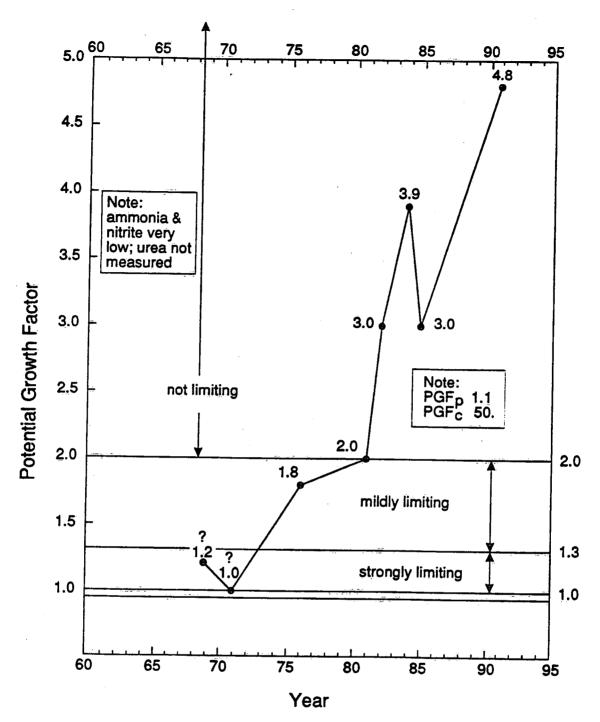
Outline of method: Measure the particulate fraction of the element and measure the soluble reactive fraction(s) in the same sample. Assume that the dissolved organic matter (DOM) is somewhat refractory and somewhat unavailable for rapid plankton growth assume therefore that DOM need not be considered. Thus we assume that the soluble reactive fraction is the only one available for further rapid particulate growth. Then:

(particulate) + (soluble reactive) (particulate)

is a ratio that indicates the potential increase of particulates. We will call the ratio: the 'Potential Growth Factor' (PGF). A ratio of 1.3 would mean that the particulates could increase by one-third, if all the soluble reactive fraction was used. A ratio of 2.0 would indicate a potential doubling of particulates. Thus we can label, and interpret, various ranges of the PGF approximately as follows:

1.0 to 1.3 strongly limiting
1.3 to 2.0 weakly limiting
≥2.0 not limiting

Application to Lake Ontario, Figure A1: For nitrogen, and using averages from many samples each August, we infer strong limitation around 1970, changing to mild limitation until 1980, and 'not limiting' thereafter. Phosphorus in August appeared to be strongly limiting throughout the time-series, with a PGF always near 1.1 Carbon had a PGF of 50, certainly not limiting, due to abundant bicarbonate.



Nitrogen limitation assessment, Lake Ontario, in August 1969 to 1991.

Figure. A1

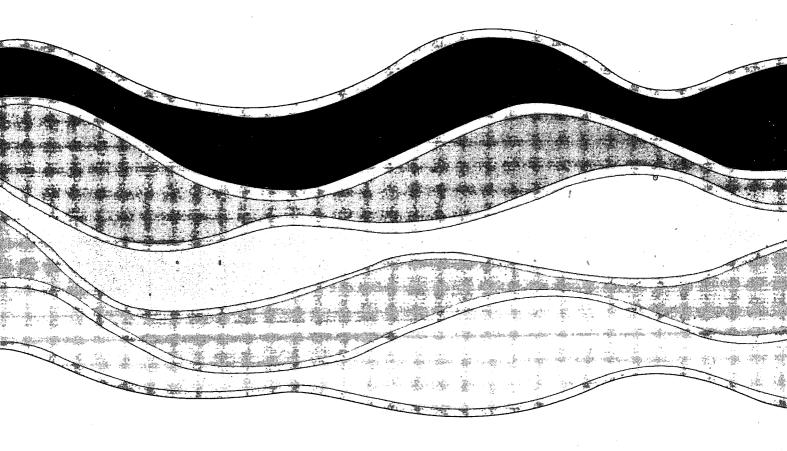
This method may be applicable to many fresh and marine waters, and may be more conclusive and efficient than traditional nutrient enrichment experiments and the use of physiological indicators.

FIGURE CAPTIONS

- Figure 1. Bathymetric map of Lake Ontario.
- Figure 2. Lake Ontario, particulate nitrogen in offshore near-surface waters, cruise-mean values in the years 1972-1979.
- Figure 3. Median values of total phosphorus in Lake Ontario, offshore, upper 20 m, March/April, 1970 to 1992.
- Figure 4. Median values of soluble reactive phosphorus in Lake Ontario, offshore, upper 20 m, winter and summer, 1969 to 1992.
- Figure 5. Median values of (nitrate and nitrite) in Lake Ontario, offshore, upper 20 m., winter and summer, 1969 to 1992.
- Figure 6. Median values of soluble reactive silica in Lake Ontario, offshore, upper 20 m., winter and summer, 1969 to 1992.
- Figure 7. Median values of pH in Lake Ontario, upper 20m, offshore, 1966 to 1990.

 The medians are for raw pH data without corrections for temperature.
- Figure 8. Median values of total chlorophyll <u>a</u> in Lake Ontario, offshore, upper 20 m, summer and winter, 1967 to 1992.
- Figure 9. Median values of particulate organic carbon in Lake Ontario, offshore, upper 20 m, winter and summer, 1972 to 1992.
- Figure 10. Median values of particulate nitrogen in Lake Ontario, offshore, upper 20 m, winter and summer, 1972 to 1992.

- Figure 11. Median values of Secchi depths and Secchi reciprocals in Lake Ontario, offshore, winter and summer, 1966 to 1992. The reciprocal values indicate [particles].
- Figure 12. Lake Ontario, dissolved oxygen (mg/L) in the Deep Water (samples with temperature <4°C and not within 10m of the bottom), the year 1970, data from 12 cruises of the vessel Martin Karlsen.
- Figure A1. Nitrogen limitation assessment, Lake Ontario, in August, 1969 to 1991.



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