formation. The abrupt morphological demarcation of varnish from rock indicates that varnish material is derived from sources external to the rock. On coarsely crystalline quartz none of the varnish material can be due to alteration of the underlying rock. The presence of a variety of clay minerals precludes direct synthesis from solution. Thus, the clay must be transported to the rock surface. The dependence of varnish development on the porosity and surface roughness of the underlying rock (*1*) may reflect the importance of capillary movement of water in clay transport. Wind transport of clays may be significant in varnishing of outcrop exposures where large distances make water transport unlikely. In this case, moisture might influence retention of windborne clays.

Clay may be an active agent in desert varnish formation. It may serve as a medium for capillary movement of varnishing solutions. Deposition of the ferromanganese oxides within the clay matrix could then cement the clay layer. The clay may aid in the deposition. Illite is known to fix manganese under the *p*H and oxidation-reduction conditions at which varnish forms (*15*). In this way the clay and oxide phases may be mutually dependent: the clay depending on the oxides for resistance to erosion; the oxides depending on the clay for transport and deposition. This would explain why neither pure clay nor pure ferromanganese oxide coatings are associated with desert varnish.

Infrared analyses of varnish from diverse localities in Arizona and New Mexico indicate that our varnish characterization from the Mojave Desert can be generalized to these areas.

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12. Although 0.2 sodium atom per 12 oxygens was present in the extracted varnish, there was negligible sodium in the untreated varnish. We assume that the sodium was introduced in the extraction procedure.
13. The percentage composition of the residue was: Fe_2O_3, 65; H_2O, 24; CaO, 7; K_2O, 2; and MgO, 2.
14. The Mn/Fe ratio varied from 10:1 to 2:1; the typical percentage composition of the residue was: $MnO_2 + Fe_2O_3$, 69; H_2O, 20; BaO, 4; Al_2O_3, 3; CaO, 3; and MgO, 1.
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17. We thank R. P. Sharp for helpful discussions regarding field localities and the preparation of this manuscript, H.-W. Yeh for providing mixed-layer clay standards, and especially the L. S. B. Leakey Foundation and the John A. McCarthy Foundation for financial support. Contribution No. 2786, Division of Geological and Planetary Sciences, California Institute of Technology.

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Great Lakes Eutrophication: The Effect of Point Source Control of Total Phosphorus

Abstract. *A mathematical model of the Great Lakes total phosphorus budgets indicates that a 1 milligram per liter effluent restriction for point sources would result in significant improvement in the trophic status of most of the system. However, because large areas of their drainage basins are devoted to agriculture or are urbanized, western Lake Erie, lower Green Bay, and Saginaw Bay may require non-point source controls to effect significant improvements in their trophic status.*

Accelerated eutrophication, resulting primarily from phosphorus additions due to human activities, is generally regarded as one of the major causes of the deterioration of the Great Lakes water quality (*1*). The governments of Canada and the United States recognized this fact in the Great Lakes Water Quality Agreement between the two countries signed by Prime Minister Trudeau and President Nixon in April 1972. This agreement requires that the phosphorus concentration of effluents from all large municipal waste treatment plants discharging into Lake Erie or Lake Ontario or the international section of the St. Lawrence River be limited to 1 mg/liter (*2, 3*).

Recently, the International Joint Commission, the unitary body set up by the two countries to consider problems related to the boundary waters, suggested carrying this limitation a good deal further. In their *Fourth Annual Report on Great Lakes Water Quality* (*4*), that body recommended to the governments involved that the 1 mg/liter effluent limitation be extended to all point source discharges of phosphorus throughout the entire Great Lakes system.

Implementing a limitation of 1 mg/liter for the point discharges around the Great Lakes is a multibillion dollar proposition. Thus, it is of great interest to determine what changes in water quality can be expected from the imposition of such a limitation. A mathematical model of the total phosphorus budgets for the Great Lakes has been developed that can address this question (*5*).

The model is generally based on Vollenweider's phosphorus loading concept (*6*), the major premise of which is that a lake's trophic state is primarily determined by its phosphorus levels. Recent evidence has lent strong support to this assumption (*7*). While the phosphorus loading concept is typically represented by graphical correlations, the present model takes a more mechanistic approach. As a detailed description of the present approach is published elsewhere (*5*), only a brief overview is given here.

The basic forcing functions of the model are variables, such as population and land use, which represent human activities in each drainage basin. A waste source submodel uses empirical relationships to translate these variables into phosphorus loadings. At present, three categories of waste sources of total phosphorus are considered: domestic sources, land runoff, and atmospheric inputs (*8*).

Domestic sources are the sewered waste water from residences, businesses, and institutions and are primarily due to human waste and detergents. The phosphorus load from domestic sources is computed as a function of human population multiplied by per capita loading factors for both human waste and detergents. The amount of removal achieved by presently existing waste treatment facilities and losses of phosphorus during streamflow to the lake are also calculated (*9*). Land runoff sources are calculated as a function of land area devoted to a specific land use times areal runoff factors for each use. At present, the land use categories being considered are urban, forest, pasture, and cropland for Canada and the same scheme, with cropland divided into row and close grown crops, for the United States (*10*). The contribution from atmospheric sources (that is, rainfall, snowfall, and dustfall) is taken as the product of lake surface area and measured areal atmospheric loading rates.

These loadings are combined and serve as input to a budget model that idealizes the lakes and major embayments as completely mixed systems. The model accounts for exchange between lakes (*11*) and in-lake losses. The latter is represented as a first-order loss, which is parameterized by an apparent settling velocity for total phosphorus (*12*). The model is expressed mathematically as a set of ordinary differential equations; these can be solved for in-lake total phosphorus concentration, which in turn can be interpreted as a measure of eutrophication (*13*).

The model agrees reasonably well with both presently measured loadings (r = .89) and concentrations (r = .94) for the Great Lakes (*5*). For this reason, the model can be used with some confidence to investigate the effect of limiting point source effluents to 1 mg/liter.

The 1 mg/liter effluent can be translated into a model variable by assuming that 570 liters per capita per day is typical of the volume of waste generated by each inhabitant of the basin (*14*). Multiplying 570 liters per capita per day by 1 mg/liter yields an equivalent per capita loading rate of 0.21 kg of total phosphorus per capita per year as the treatment objective. All other parameters in the model are set at 1970 values, and the results are as shown in Fig. 1. The height of each bar represents the present concentration for each lake with contributions indicated for several man-induced and natural loads and with the improvement due to the 1 mg/liter effluent represented by the dashed line. Additionally, the result of total removal of phosphorus from domestic sources (that is, a 0 mg/liter effluent) is shown. To assist in interpretation of the results, total phosphorus concentration is related to trophic state by assuming that mesotrophy is bounded by concentrations of 10 and 20 μg of phosphorus per liter (*13*).

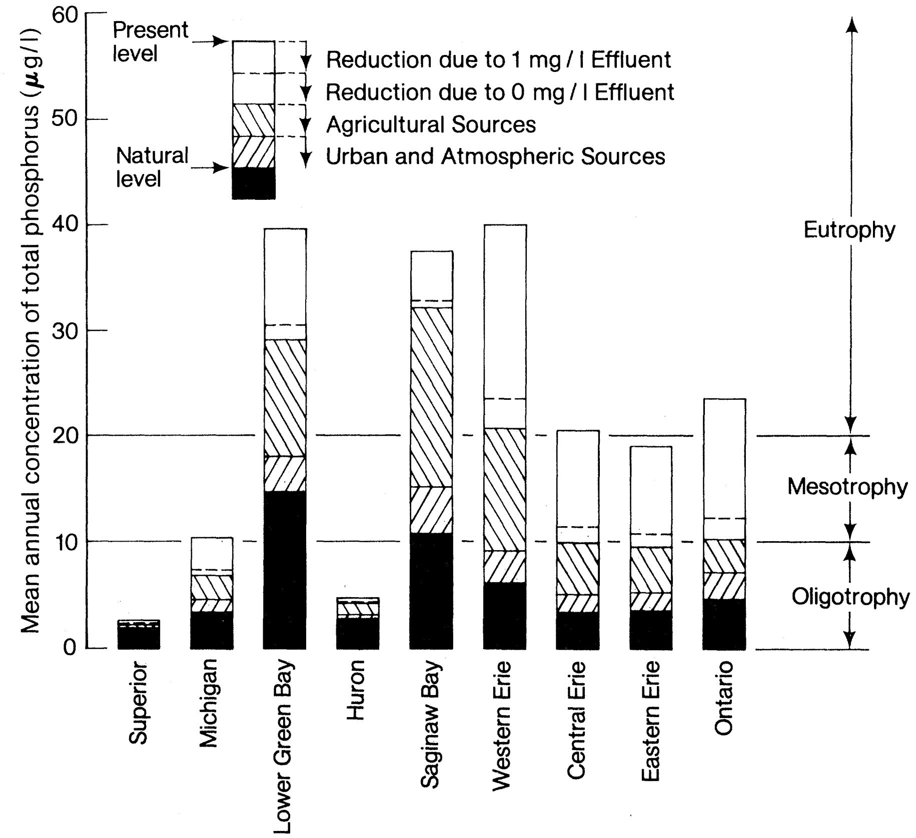

Fig. 1. Total phosphorus concentrations (micrograms per liter) resulting from various treatment schemes for the Great Lakes.

The immediately obvious observation is that the 1 mg/liter effluent restriction will significantly improve water quality over much of the Great Lakes. The concentration of total phosphorus in the central and eastern basins of Lake Erie and in Lake Ontario will fall from levels of 20 μg/liter or above to values approaching 10 μg/liter. Lake Michigan will return to more oligotrophic conditions well below 10 μg/liter. The effects in Lake Superior and Lake Huron will be relatively minor, but these lakes are still classified as oligotrophic, and the limitation will help maintain this condition.

However, in the western basin of Lake Erie and in Saginaw Bay and lower Green Bay (from Long Tail Point to Sturgeon Bay) the results are somewhat different. According to the model, these areas have naturally higher phosphorus concentrations than other areas in the Great Lakes system. These levels have been raised substantially by large inputs through runoff from land that has undergone intensive agricultural and urban development. The high natural concentrations are primarily the result of all three water bodies having large drainage basins relative to their size.

For these three areas the model predicts that the 1 mg/liter limitation will not bring the total phosphorus concentration below 20 μg/liter. Thus, to restore the trophic conditions in lower Green Bay, Saginaw Bay, and western Lake Erie to levels that more nearly approach their natural state and that would be considered generally satisfactory, further management actions could be required. An examination of Fig. 1 shows that these drainage basins have large inputs from land runoff and suggests that, in addition to the point source limitation, steps to reduce diffuse sources could be necessary to bring about return to acceptable trophic conditions (*15*).

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3. All concentrations presented in this report are for total phosphorus expressed as phosphorus.
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8. The categorization is based on present understanding of phosphorus inputs to the Great Lakes. For example, industrial sources are not included since they generally contribute minor amounts of phosphorus, and measurements on the Great Lakes support this assumption. As an example, Appendix B of (*4*) reports that for 1975 direct industrial sources amounted to less than 5 percent of the direct point sources of total phosphorus to the Great Lakes.
9. Loss of phosphorus in streamflow is presently not well understood and is currently the subject of research in the Great Lakes Basin. It has been suggested [D. B. Baker and J. W. Kramer, *Proc. 16th Conf. Great Lakes Res.* (1973), p. 858] that a sizable fraction of upstream point sources could be lost during streamflow by incorporation into the sediments of the stream or its impoundments. Based on a preliminary analysis of runoff data, we assume that 75 percent of point source phosphorus originating in counties that are not contiguous with a Great Lake or their connecting channels is lost in streamflow. No losses are assumed for on-lake counties. The effect of this assumption on our predictions for western Lake Erie and lower Green Bay is minor, since most of the population lives in close proximity to these water bodies. The effect on Saginaw Bay is more substantial, because the cities of Flint and Saginaw lie in off-lake counties. It should be noted, however, that even if all point sources were assumed to reach Saginaw Bay, land runoff would be still greater for that basin.
10. Areal loading factors for the respective land uses are based on P. D. Uttormark, J. D. Chapin, and K. M. Green [*U.S. Environ. Prot. Agency Rep. EPA-660/3-74-020* (1974)].
11. In the original application (*5*), each of the lakes is treated as a completely mixed system with the exception of Lake Erie, which is divided into its three subbasins. The present model has been extended to treat Saginaw Bay and Green Bay explicitly. Since these bays have open boundaries, both advective and diffusive transport are modeled, with the latter being calibrated by using chloride and heat balances.
12. A general apparent settling velocity of 16 m/year is derived by S. C. Chapra [*Water Resour. Res.* **11**, 1033 (1975)]. This value works well for most of the Great Lakes with the exception of western and central Lake Erie and Green Bay, where the parameter is calibrated to existing data.
13. While total phosphorus concentration is a cause rather than an effect or symptom of eutrophication, it has been used as a measure of lake trophic state by a number of investigators. The present analysis uses values of 10 and 20 μg/liter as bounds for mesotrophy, as suggeste[illegible] P. J. Dillon [*Limnol. Oceanogr.* **20**, 28 (1975)]. While Dillon's scheme is general, H. F. H. Dobson (personal communication) has used Great Lakes data to set the same bounds. It should be noted, however, that all such efforts are approximations to aid interpretation and that the boundaries are more realistically ranges rather than thresholds.
14. *Report to the International Joint Commission on the Pollution of Lake Erie, Lake Ontario, and the International Section of the St. Lawrence River* (International Joint Commission, Washington, D.C., and Ottawa, Ontario, 1969).
15. It should be noted that there are two shortcomings to the present approach. The first is that it does not consider the time that will be required for the predicted improvements to manifest themselves. A lake's response could be retarded by feedback from the sediments in cases where phosphorus levels have grown high owing to prolonged enrichment [see D. W. Schindler, in *Environmental Biogeochemistry*, J. Nriagu, Ed. (Ann Arbor Science, Ann Arbor, Mich., 1976), p. 647]. The effect is discussed in (*5*) with particular emphasis on Lake Erie. The second shortcoming, which is a problem of the phosphorus loading concept in general, is the assumption that phosphorus from all sources is equally available for algal growth. While it is unclear in terms of present understanding how this assumption affects our predictions, the question of phosphorus availability is presently the subject of much research and should be kept in mind when evaluating our results.
16. We thank the following for comments and discussions related to this study: R. Bowden, G. F. Lee, A. P. Pinsak, D. Rockwell, D. Scavia, S. Tarapchak, and N. Thomas. This report is GLERL Contribution No. 99.

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Increasing Photosynthesis by Inhibiting Photorespiration with Glyoxylate

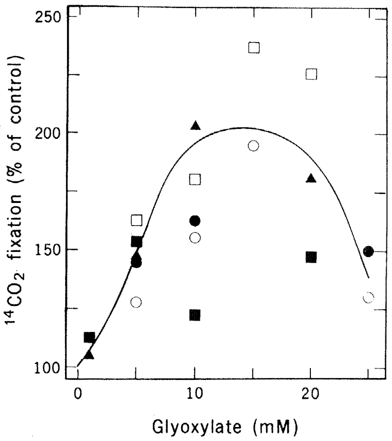
Abstract. *Glyoxylate treatment doubles net photosynthetic carbon dioxide fixation by tobacco leaf disks because inhibition of glycolate synthesis by glyoxylate results in decreased photorespiration. These observations show that photorespiration can be metabolically regulated and suggest that genetic or chemical alteration of pool sizes of certain metabolites can produce plants with increased photosynthesis.*

In most crops at least half the CO_2 assimilated during photosynthesis is lost by photorespiration (*1*, *2*). This rapid loss of CO_2 diminishes net photosynthesis and yields (*3*). The synthesis and subsequent oxidation of glycolate (CH_2OHCOO^-) largely account for the production of photorespiratory CO_2 (*3*). Photorespiration is slow in the few photosynthetically efficient crops (*4*) such as maize, sorghum, sugarcane, and millet, presumably because the rate of glycolate synthesis is slow (*5*). Net photosynthesis is usually greater and crop yields are accordingly higher in these species (*6*).

Glycolate is synthesized early in photosynthesis (*7*) and is oxidized to glyoxylate ($CHOCOO^-$) and further metabolized by reactions in the glycolate pathway of carbohydrate metabolism (*8*). Photorespiratory CO_2 is released during one or more steps of the pathway (*9*). Blocking glycolate oxidation with α-hydroxysulfonates (*10*), or glycolate synthesis with epoxides such as glycidate (*11*), inhibits photorespiration in disks cut from leaves of the inefficient species tobacco and increases net photosynthesis at least 50 percent.

We have sought ways of regulating the glycolate pathway that slow glycolate synthesis in order to lay a biochemical foundation for genetically altering photorespiration (*12*). Recently, we found that glycolate synthesis is inhibited in tobacco leaf disks when they are floated on solutions of L-glutamate, L-aspartate, phosphoenolpyruvate, or glyoxylate (*13*, *14*). We describe here the inhibition of photorespiration and the doubling of net photosynthesis when leaf tissue is treated with glyoxylate, an intermediate of the glycolate pathway.

Disks floated on 5 to 25 m*M* potassium glyoxylate (*p*H 4.6) showed a 1.2- to 2.3-fold increase in their net rate of photosynthetic $^{14}CO_2$ fixation compared with



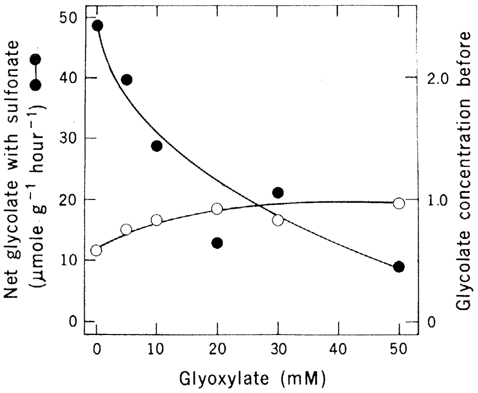


Fig. 1 (left). Effect of glyoxylate concentration on increase in net photosynthetic CO_2 fixation in tobacco disks. Control rates with water were arbitrarily taken to equal 100 percent. In each sample, six 1.6-cm-diameter disks from tobacco leaves (var. 'Havana Seed') whose leaf stomata opened well in the light (*21*) were strung together by a cotton thread and placed in a 75-ml Warburg flask containing 1.0 ml of the solution indicated. After 1 hour at 30°C with an irradiance of 325 μeinstein m^{-2} sec^{-1} (400 to 700 nm) a continuous stream of $^{14}CO_2$ (600 ppm) of known specific radioactivity was passed through the flask at 250 ml min^{-1} (*13*). After 5 minutes the disks were removed to boiling 20 percent ethanol and homogenized, and the amount of ^{14}C fixed was determined. The control rates [micromoles of $^{14}CO_2$ fixed per gram (fresh weight) per hour] were: (●) 60.3, (○) 52.4, (▲) 47.0, (■) 34.4, and (□) 38.0. Fig. 2 (right). Inhibition of glycolate synthesis in tobacco leaf disks floated on glyoxylate solution. In each sample, six 1.6-cm leaf disks were floated in 50-ml beakers on 1.5 ml of either water or the glyoxylate solutions for 1 hour with an irradiance of 390 μeinstein m^{-2} sec^{-1} at 30°C. The disks were then washed twice with 1.5 ml of water and plunged into boiling 20 percent ethanol either directly (○) or after the water had been replaced with 2.5 ml of 10 m*M* α-hydroxy-2-pyridinemethanesulfonic acid for 3 minutes (●). After the killed tissue was homogenized, the glycolate fraction was collected by ion exchange chromatography on Dowex-1 acetate (*5*) and assayed colorimetrically (*11*).