Reports

Effect of Restricted Use of Phosphate-Based Detergents on Onondaga Lake

Abstract. *A marked decrease in the concentration of total inorganic phosphate in the epilimnion and hypolimnion of Onondaga Lake, New York State, has been observed during the 1½ years between July 1971 and January 1973. This decrease has been correlated to the implementation of phosphate-limiting legislation. The response of characteristic plankton species has been investigated.*

One of the tools available to environmental regulatory agencies in the control of cultural eutrophication is the establishment of composition limitations for waste-creating consumer products with high levels of nutrients. Detergents are the main consumer products contributing nutrients to acquatic environments. It has been estimated that 10^9 kg of phosphorus enters the nation's waters annually through the use of phosphate-based detergents; this accounts for 30 to 40 percent of the phosphorus entering the aquatic environment (*1*).

Sharp reductions in the concentration of condensed inorganic phosphorus have been observed in Onondaga Lake (north of Syracuse, New York) following the implementation of legislation limiting the percentage of phosphorus allowed in detergents. The legislation, which affects municipal discharges in the urban watershed influent to Onondaga Lake, was enacted both locally and by the state. The Common Council of the City of Syracuse first enacted legislation limiting the phosphate composition in detergents to 8.7 percent, effective on 1 July 1971. New York State, following the example of Syracuse (as well as Erie County, Suffolk County, and Bayville in other parts of the state), enacted similar legislation (*2*), effective on 1 January 1972. After each legislative implementation, reductions in condensed inorganic phosphorus in Onondaga Lake were observed (see Table 1).

A monitoring program for Onondaga Lake has been carried out since 1968 (*3*). Grab samples, collected every 2 weeks at 3-m intervals from the surface to the bottom at a station located in the southern basin, have shown decreases of 85 and 76 percent in the average condensed inorganic phosphate concentrations in the epilimnion and hypolimnion, respectively. The orthophosphate concentrations were found to decline by 47 and 15 percent, respectively, over the same period of time. The concentrations of condensed inorganic phosphate and orthophosphate from January 1970 to January 1973 are shown in Figs. 1 and 2.

Standard analytical procedures were used to determine the concentrations of total orthophosphate, total inorganic phosphate, and the derived value for total condensed inorganic phosphate (*4*). The determination of orthophosphate involved the formation of molybdophosphoric acid, which is subsequently reduced to the intensely colored molybdenum blue complex by stannous chloride. The concentration of molybdenum blue is determined by comparing the absorbance of the sample at 625 nm to that of prepared standards. For the determination of total inorganic phosphate the sample was digested with sulfuric acid in an autoclave for 30 minutes. The analysis of the resulting orthophosphate component was then conducted as outlined above. The analytical procedures were checked against standard samples and found to have a precision of approximately 2 percent and an accuracy within 5 percent. The same analyses were also periodically conducted by using the Technicon 94-70W method outlined for the AAII model. The method involves reduction of molybdophosphoric acid by ascorbic acid and subsequent spectrophotometric analysis. The analytical methods agreed within 5 percent.

Onondaga Lake is approximately 11.7 km^2 in area and has an approximate volume of 14×10^{10} liters and an average annual residence time for lake water of 122 days. Eight natural and man-made major tributaries discharge into the lake. Only the discharge from the Syracuse metropolitan sewage treatment plant showed a significant decrease in the load of condensed inorganic phosphorus. The concentration of total inorganic phosphate in the plant effluent declined from an average of 5.46 mg/liter in 1970 to 2.49 mg/liter in 1972. This decrease of 54.4 percent compares well with the 57.4 percent decline in the average total inorganic phosphate concentration in the lake over the same period. The other sources and sinks within Onondaga Lake were essentially the same before and after the legislation.

In the past 5 years, a characteristic seasonal succession of phytoplankton has been observed within the lake. There is little growth of plankton in the winter, when the lake is covered by ice; a diatom population develops in the spring; and the green algae *Chlorella, Scenedesmus obliquus, Scenedesmus quadricauda*, and *Oocystis parva* dominate the summer period. Blue-green algae of the genus *Aphanizomenon* follow the die-off of the greens, and dominate the late summer and early fall.

In 1972, the first full growth season after the implementation of phosphate-limiting legislation, *Aphanizomenon* was absent in the succession. Instead, the green algae blooms continued through the summer and fall with cell counts comparable to those measured in previous years. The observed decline and subsequent elimination of blue-green algae when the concentration of condensed inorganic phosphate decreased 85 percent and the concentration of orthophosphate decreased 47 percent in the photic zone is consistent with results reported by Shapiro (*5*). Shapiro found that addition of CO_2 or lowering of the *p*H stimulates a shift in a mixed

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population from blue-green to green algae. He also indicated that the addition of nutrients resulted in dominance by blue-green algae. In Onondaga Lake, both the *p*H and the total inorganic carbon concentration were essentially unchanged after the phosphate-limiting legislation went into effect. In the photic zone the *p*H and total inorganic carbon were found to be 7.69 and 18.7 mg/liter, respectively. It therefore appears that the alteration of the phytoplankton seasonal succession is the result of reducing the phosphorus concentrations in the photic zone. Although there were climatological variations between 1970 and 1972, they do not seem to be of sufficient magnitude and intensity to account for the observed plankton variations.

It should be noted that the concentrations of inorganic and organic nitrogen, the total organic carbon, and the biochemical oxygen demand were essentially the same during the time period being evaluated.

An increase in the phytoplankton diversity index was also observed following the implementation of the detergent phosphate legislation. An increase in Margalef's (*6*) average diversity index from 0.695 to 0.801 most likely reflects a higher degree of stability within the phytoplankton community. This increase in the diversity of the phytoplankton community may indicate a general improvement in the trophic status of the lake. Most significant to the residents in the vicinity of the lake is the fact that the objectionable floating scums attendant with the presence of the blue-green algae might be eliminated from future plankton seasonal successions. This would also have the effect of increasing dissolved oxygen, which is removed from the epilimnion during aerobic decomposition of the nonviable algal mass. The green algae, which are more acceptable ecologically because of their more direct linkage to the food chain, together with more uniform concentrations of dissolved oxygen may lead to the development of a more productive environment for higher aquatic organisms.

Caution must be taken in applying these results to other lakes, which may differ greatly from Onondaga Lake in water chemistry, chemical stratification, and stability of minerals (*7*). Onondaga Lake is dimictic in that it undergoes two periods of circulation per year; the major circulation occurs in the fall. Chemical contributions to the lake in the form of $CaCl_2$ and NaCl from a soda ash manufacturer establish a density structure which impedes the rate of vertical mixing. Industrial and municipal point sources and natural nonpoint sources in the form of salt springs have established a steady-state concentration of chlorides of approximately 1750 mg/liter. Among lakes of its size in the East, Onondaga Lake has one of

Table 1. Change in the concentration of condensed inorganic phosphorus (P) in the epilimnion and hypolimnion of Onondaga Lake following the implementation of local and state legislation restricting phosphorus in detergents. The changes are from the baseline values, 0.73 and 0.81 mg/liter.

Period of observation	Dates	Epilimnion P (mg/liter)	Epilimnion Change (%)	Hypolimnion P (mg/liter)	Hypolimnion Change (%)
Before legislation	1 January 1970 to 30 June 1971	0.73		0.81	
After urban legislation was implemented	1 July 1971 to 31 December 1971	0.22	− 69.8	0.58	− 28.4
After state legislation was implemented	1 January 1972 to 31 December 1972	0.11	− 84.9	0.19	− 76.5

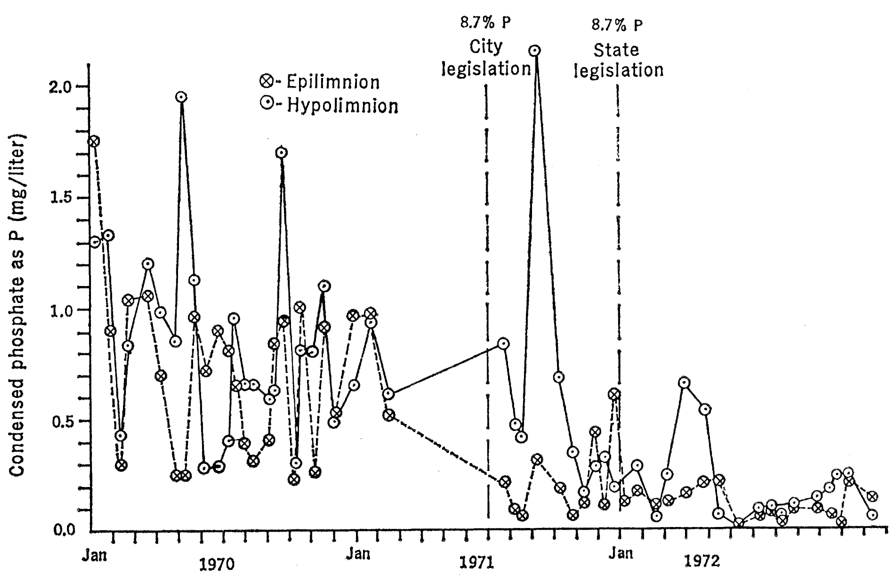

Fig. 1. Condensed inorganic phosphate concentration in Onondaga Lake.

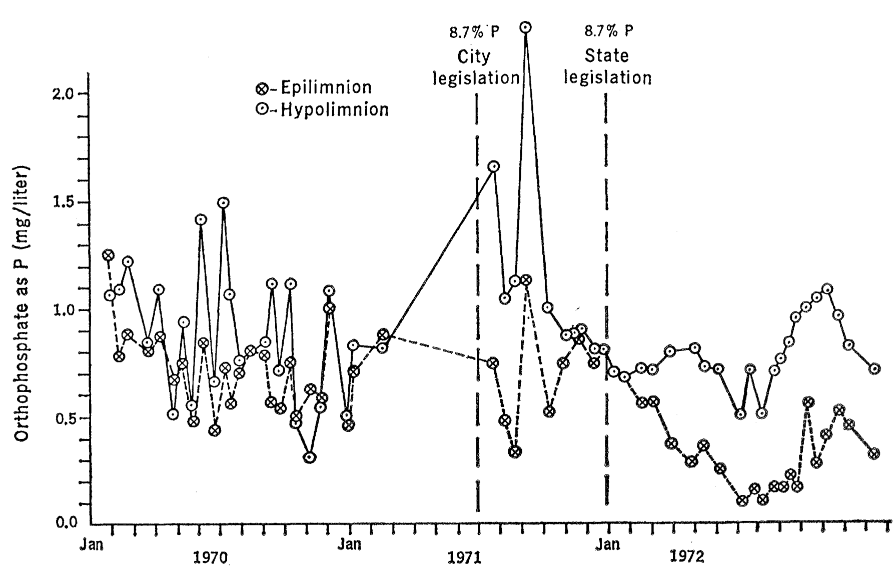

Fig. 2. Orthophosphate concentration in Onondaga Lake.

the highest concentrations of dissolved solids.

The high calcium concentrations are a major factor in the continuous formation of phosphate-bearing minerals such as hydroxylapatite [$Ca_5(PO_4)_3OH$] and fluorapatite [$Ca_{10}(PO_4)_6F_2$] throughout the lake. In addition, the lake is oversaturated with calcite ($CaCO_3$) throughout the year except during the middle and late winter when the *p*H falls below 7.

Since Onondaga Lake serves as a receptacle for an area that is almost entirely urban, there is little contribution of phosphorus from natural and agricultural sources. Preliminary estimates of the influent total inorganic phosphorus indicate that approximately 71 percent can be accounted for by municipal point-source discharges, 19 percent by municipal nonpoint sources (combined sewer overflows), 1 to 2 percent by industrial sources, and 8 to 9 percent by agricultural and natural sources (*8*). Natural sources have been reported to account for 26 to 41 percent of the phosphorus discharged to the receiving water bodies in the continental United States. It has been predicted that elimination of phosphates from detergents might result in the reduction of the average total phosphorus concentrations in receiving waters from 0.26 to 0.18 mg/liter for a reduction of 37.7 percent (*9*). The legislation limiting phosphates in detergents has had a much more pronounced effect on Onondaga Lake, reducing the average concentration of total inorganic phosphorus from 1.74 to 0.74 mg/liter—a net change of 57.4 percent.

It is evident that the limitation of detergent phosphate composition to 8.7 percent phosphorus by weight has had a discernible effect on the chemical and biological composition of the lake. Perhaps, therefore, a harder look should be given to the use of this type of legislation by State and Federal regulatory agencies in the control of cultural eutrophication. Due to present domestic fiscal policy limitations, legislation of this nature may be one of the effective methods of controlling eutrophication in the immediate future.

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Mars: Mariner 9 Spectroscopic Evidence for H_2O Ice Clouds

Abstract. *Spectral features observed with the Mariner 9 interferometer spectrometer are identified as those of H_2O ice. The measured spectra are compared with theoretical calculations for the transfer of radiation through clouds of ice particles with variations in size distribution and integrated cloud mass. Comparisons with an observed spectrum from the Tharsis Ridge region indicate H_2O ice clouds composed of particles with a mean radius of 2.0 micrometers and an integrated cloud mass of 5×10^{-5} gram per square centimeter.*

Ground-based observations indicate that several distinct types of clouds occur in the martian atmosphere including yellow clouds, assumed to be composed of blowing surface dust, and white clouds, assumed to be condensed volatile substances (*1*). White clouds fall into two classes: (i) diffuse clouds with no particular aerographic location and (ii) discrete clouds at relatively fixed aerographic locations (*2*). Discrete clouds have been observed in the Nix Olympica–Tharsis Ridge area by Slipher (*3*), in the near-encounter pictures of Mariner 7 (*4*), and in the Mariner 9 orbital pictures (*5*). Although it has been suspected that the white clouds are composed of H_2O ice (*6*), to date no direct spectral evidence has been found. We present here spectroscopic data indicating the existence of H_2O ice clouds on Mars in the region of the shield volcanoes of the Tharsis Ridge. Estimates are given for the cloud particle size and the integrated cloud mass.

Spectra of Mars have been obtained between 200 and 2000 cm^{-1} with a resolution of 2.4 cm^{-1} by the infrared interferometer spectrometer (IRIS) carried by the Mariner 9 spacecraft. The observed spectral interval includes the molecular absorption features of both CO_2 and H_2O. Observations of these spectral features and their use in determining surface pressure, thermal structure, and the amount of H_2O vapor have appeared in the literature (*7*). Broad absorption features, indicative of particulate (dust) absorption, have also been observed during the Mariner 9 mission. Spectra obtained in the later part of the mission show additional broad absorption features which differ in position and width from those of the dust clouds. These broad absorption features were found to correspond closely to those expected for H_2O ice clouds.

Figure 1A presents a comparison of spectra observed in the Tharsis Ridge region and the lower Arcadia region with theoretical calculations for an H_2O ice cloud. The spectrum measured over lower Arcadia shows an approximately constant brightness temperature except for the CO_2 absorption band centered at 667 cm^{-1} and the rotational H_2O vapor absorption lines below 400 cm^{-1}. In contrast, the Tharsis Ridge spectrum exhibits a strikingly broad absorption feature extending from 550 to 950 cm^{-1} with a second broad absorption region evident between 225 and 350 cm^{-1}. Superimposed on the latter is a sharp spectral feature near 227 cm^{-1}. The theoretical H_2O ice cloud spectrum (Fig. 1B), described below, exhibits a similar behavior.

The IRIS fields of view for the two observed spectra are indicated in Fig. 2 by circles superimposed on a Mariner 9 television picture of the same region. Prominent in the picture are the summits of Nix Olympica and of the three shield volcanoes along the Tharsis Ridge as well as the extensive cloud systems to the west of the volcanoes. Because of the substantial processing of the television data, information concerning the optical properties of the clouds cannot be inferred visually from Fig. 2. The cloud-free spectrum is associated with the field of view in the left portion of Fig. 2, whereas the ice cloud spectrum from the field of view in the center of the figure includes the clouds off North Spot and Middle Spot. Since