AVAILABILITY OF PHOSPHORUS TO PHYTOPLANKTON AND ITS IMPLICATIONS FOR PHOSPHORUS MANAGEMENT STRATEGIES[1]

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INTRODUCTION

One of the questions associated with the development of a cost-effective phosphorus management strategy for a waterbody concerns whether the control program should be based on total phosphorus or on algal available phosphorus entering the waterbody. Until now, eutrophication control programs have been based largely on the control of any form of phosphorus that was amenable to control, irrespective of whether the phosphorus was in a form which could support algal growth.

Thus far, with few exceptions eutrophication control programs in the Great Lakes and other areas have been largely directed toward the control of phosphorus inputs from domestic wastewaters. These programs have included complete elimination of phosphorus input from this source via diversion of wastewaters to another waterbody, limitation of wastewater treatment plant effluent P concentrations to 1 mg P/L and limiting the phosphorus in detergent formulations. Major wastewater diversions have taken place in the Madison, Wisconsin lakes, from Lake Washington in Seattle, Washington and others. Dramatic improvements in eutrophication-related water quality have been found in several waterbodies where wastewater diversion has occurred, the most notable example being Lake Washington.

A second method for P control that has been attempted in several locations is the limitation of the P content in detergent formulations. These limitations have ranged from a few percent by weight allowable phosphorus, such as in Ontario, Canada (2.2% P allowed in formulations), to "complete" detergent P bans where the P content is limited to "trace" amounts. "Trace" is generally translated to a maximum of 0.5% P in the formulation. In the early 1970s the complete bans, such as passed in Indiana and Dade County, Florida, resulted in a decrease in phosphorus content of domestic wastewaters of about 50 to 60%. Today, with the voluntary decrease in the phosphorus content in detergent formulations that has taken place across the U.S., a complete phosphorus ban would be expected to reduce the phosphorus concentration in domestic wastewater treatment plant influents where no P limitations are already in effect, by 30 to 35%.

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Several years ago, Michigan enacted a detergent P ban. It has been found by comparison of P concentrations in Michigan domestic wastewater treatment plant influents before and after initiation of the ban, that the phosphorus concentration in domestic wastewaters generally decreased by 20-35%, although some cities such as Detroit showed no apparent decrease in domestic wastewater P concentration after initiation of the ban. The smaller percent concentration decrease was generally found for cities with a high percentage of the total flow to the municipal system coming from industrial wastewater sources. Attempting to control eutrophication by detergent P bans is generally of questionable value because of the relatively small reduction in phosphorus input that can be achieved by this approach. Thus far there have been no documented cases where there have been measurable improvements in water quality in lakes or impoundments because of detergent P limitation.

In the Great Lakes region, the primary approach to eutrophication control has been to establish limitations on phosphorus loads from domestic wastewater treatment plants based on what could be readily removed by chemical treatment processes (iron, alum or lime addition). Several years ago, when domestic wastewaters contained around 10 mg/L P (late 1960s to early 1970s), it was found that 90% removal of phosphorus could be attained without greatly increasing the cost of domestic wastewater treatment. This reduction translated into a 1-mg/L P effluent concentration. With the decrease in the phosphorus content of domestic wastewaters because of voluntary reductions in the phosphorus content of detergent formulation, domestic wastewaters today typically contain on the order of 5-7 mg/L P. It is generally found today that P removal to 1 mg/L P can be achieved at a maximum total cost on the order of 0.25 cents per person per day for the population served, for treatment plants serving 10,000 people or more. The treatment of domestic wastewaters for phosphorus removal has not yet produced a dramatic improvement in Great Lakes water quality, although it is expected that some measurable improvement will be found in the lower Great Lakes and some parts of the Upper Great Lakes as a result of achievement of the 1 mg/L P limitation in domestic wastewaters. It is generally agreed that this approach has halted Great Lakes eutrophication-related water quality deterioration, but that measures will have to be taken to reduce further the P load to see a significant improvement in eutrophication-related water quality in the lower Great Lakes.

Somewhat fortuitously, the phosphorus control programs that have been initiated have focused on what are generally considered to be available forms of phosphorus, since the forms of phosphorus in effluents from domestic wastewater treatment plants not practicing phosphorus removal are believed to be in chemical forms largely available to support algal growth (i.e., algal-available phosphorus). With attention being given to reducing the phosphorus load from other sources as well as additional removal from domestic wastewaters, increasing emphasis must be placed on assessing the algal availability of phosphorus from controllable sources in order to develop cost-effective management strategies. This assessment is of particular significance to the Great Lakes because of the 1978 U.S.-Canada Water Quality Agreement [1] committing the U.S. and Canada to further reductions in P loads to the Great Lakes. This paper reviews the current state of information on the algal availability of phosphorus from major sources contributing P to the Great Lakes, methods for assessing the algal availability of phosphorus and the importance of developing phosphorus management strategies based on algal-available phosphorus rather than on total phosphorus. Although the focal point of the paper is the Great Lakes, the results are equally applicable to waterbodies throughout the world.

PREVIOUS STUDIES ON AVAILABLE P INPUTS TO THE GREAT LAKES

The amount of algal available phosphorus in an aquatic system is a function of a complex set of physical, chemical and biological processes. Attempts have been made to assess the amounts of sediment and soil-associated phosphorus available for aquatic plant growth, using both chemical fractionation and biological procedures. Although a variety of biological techniques have been used, the preferable method involves the use of a standardized batch algal culture test, such as that recommended by the U.S. EPA [2,3]. In this algal culture test (bioassay), all conditions needed to support algal growth are optimal for a particular alga, except for the phosphorus concentration. The phosphorus needed for algal growth in the test culture must be derived from the total P present in the water sample being investigated. A set of standard algal cultures is prepared in which various levels of available P are added to culture media and inoculated with algae. A calibration curve is developed, based on the standards, to relate the available phosphorus in the cultures to the algal biomass present on the plateau of the resulting growth curve. The amount of algal biomass present in the test water sample at the end of a 1- to 2-week incubation period (i.e., on the growth plateau) is compared to the calibration curve to estimate the amount of phosphorus in the sample that became available to the algae during the incubation period. Other biological tests have been employed by some investigators in order to short-cut the several-week incubation period. As discussed in subsequent sections of this paper, a number of these procedures have significant limitations in their ability to estimate algal available phosphorus in a sample.

The chemical extraction techniques have their basis in the soils literature, where empirical correlations have been developed between the amount of phosphorus extracted from soils with various reagents under certain laboratory conditions and the growth of terrestrial crops on these soils. NaOH is believed to extract from particulates phosphorus associated with iron and aluminum (sometimes called “nonoccluded” P). These forms have been generally found to be available to terrestrial crops. Dilute HCl extracts some calcium phosphates-apatite, which are largely unavailable or very slowly available to support the growth of terrestrial vegetation. Although a number of investigators have applied these procedures directly to aquatic systems, few have investigated the appropriateness of these soil extraction techniques for determining the algal availability of suspended particulate, atmospheric, or sediment-associated P. There may be difficulty in applying procedures designed for the measurement of root uptake of P from soils to the estimation of algal uptake of P from aqueous systems since the conditions of uptake are somewhat different.

Tributary Inputs

One of the early studies of availability of particulate P for algal growth examined the availability of phosphorus associated with sediments from certain Dutch lakes. They indicated that most (approximately 90%) of the P entering these lakes is stored in their sediments. Since primary production in these lakes was high, they suggested that either phosphorus is rapidly regenerated by algae, or there is a regeneration of the sediment-associated phosphorus. As a result of algal assays run in which sediment was the only P source, it was found that 7-30% of the sediment P became available for algal growth during the 3- to 4-week assays. From chemical analyses, they determined that the extractable portion of the sediment phosphorus decreased during the assay by an amount approximately equal to the amount taken up by algal cells.

Golterman [5] found that only a small amount of the phosphate in Frisian marine sediments (total P content 0.9 mg P/g) was available for growth of *Scenedesmus*. He estimated the amount available was equivalent to that portion extracted with NTA (0.01 N) which is said to be on the order of magnitude of the sum of calcium and iron phosphates bound in the sediments. Golterman [5] indicated that recently sorbed phosphate is biologically and chemically different from structural phosphate molecules, in that it tends to become available for algal growth. The P firmly bound to clay or humic compounds is not readily available to support algal growth.

Golterman [5] and Golterman, *et al.* [4] have indicated that "$FePO_4$" and hydroxyapatite are available to stimulate algal growth, whereas $Ca_3 (P0_4)_2$ shows little availability. This is not in agreement with data reported by the IJC Pollution From Land Use Activities Reference Group (PLUARG) with respect to hydroxyapatite [6]. In algal assays, PLUARG found that in cultures receiving soluble orthophosphate as a P source, there was an immediate and rapid increase in primary production. Cultures receiving only erosional materials from Lake Erie shoreline bluffs, in which most of the P was in the form of insoluble apatite, showed a maximum of 20% of the average response to soluble ortho-P spikes. They concluded that there was not enough release of P from the bluff material to support high levels of productivity. This point is discussed further in subsequent sections.

One of the most comprehensive studies concerned with assessing algal available P was conducted in 1972-1973 by Cowen and Lee [7,8] and Cowen [9], who studied the algal availability of particulate P in stormwater runoff from Madison, Wisconsin and tributary waters to Lake Ontario. They evaluated a variety of chemical and physical extraction techniques (acid, base and anion exchange resin) for estimating the fraction of P that becomes available to algae during an 18-day period, using a number of bioassay techniques. Bioassays were run on the separated particulates (without drying) in Algal Assay Procedure (AAP) medium (minus P), on the filtered tributary water after autoclaving or on the particulates in AAP (-P) medium after autoclaving. A variety of other procedures were also used, including chloroform treatment followed by incubation, and short and long dark incubations of tributary water and lakewater with tributary particulates added with anion exchange resin to determine microbial and organic mineralization contributions to available P. Dark incubations of tributary water and lakewater with tributary particulates added were conducted with and without anion exchange resin to determine the effect of soluble P concentration on P release from particulates.

Urban runoff samples were collected by Cowen and Lee [7,8] and Cowen [9] during 12 runoff events between August 1972 and March 1973 from eight locations in Madison, Wisconsin receiving runoff from residential, commercial and urban construction land areas. Acid-extractable inorganic particulate P (extraction with concentrated (0.083N) HCL + H_2SO_4) ranged from 13 to 60% of the total particulate phosphorus (PP_T) in the individual samples; means for the variety of urban land-use fell into the 33-46% PP_T range. Between 9 and 49% PP_T was extracted using a base (NaOH) treatment. Mean values for various land uses ranged from 22 to 27% PP_T. The anion exchange resin extraction was designed to measure that fraction of inorganic P (P_i) involved in solid-solution exchange. From 2 to 28% of PP_T was extracted from the urban runoff samples collected, with mean values for different urban land areas varying from 13 to 17% PP_T. There was no discernible difference in percent extractable P_i in particulates from the urban land areas evaluated. With the particulates from runoff as the only source of P for *Selenastrum* in P-free AAP medium, between 8 and 55% of the PP_T became available for growth (based on comparison of amount of algae present after 18 days in test water with that in the AAP standard assays). While the amount of P from Madison urban runoff extracted with acid was greater than that extracted with NaOH, which was greater than that with anion exchange resin, the overall means did not vary greatly (between 15 and 38% PP_T). The mean percent P available from PP_T as measured by *Selenastrum* growth was 30%, which is in the midst of that range. In 6 of the 10 samples tested by base extraction, the percent PP_T extracted and the percent PP_T used by *Selenastrum* for growth were within 10%; in 7 of the 13 samples tested using anion exchange resin extraction, and in 4 of the 13 samples extracted with acid, the extraction and bioassay results varied by less than 10% of the PP_T. This indicates that the NaOH and anion exchange resin extractions were, for the samples evaluated, a better estimator of the amount of PP_T available for *Selenastrum* growth than add extractions. As discussed by Cowen and Lee [8], specific conclusions regarding the appropriateness of particular chemical extractions for predicting availability of P could not be made on the basis of their data; a host of other factors influence the eventual availability of particulate P in various aquatic systems. The effective availability would, because of these factors, likely be lower than that predicted by *Selenastrum* growth and would likely be better predicted for these samples by anion exchange resin extraction. In general, there was little evidence of mineralization of organic particulate P In the urban runoff. Release of P from particulates was apparently controlled by physical-chemical sorption-desorption and precipitation-dissolution reactions.

Data were collected for Cowen and Lee [8] and Cowen [9] for two urban-residential areas in the Genesee River Basin. Eight samples were collected from both stations between October 1972 and June 1973. The mean percents acid extractable PP_T of PP_T were 30 and 48%, which were comparable to the mean 33 to 46% found for Madison, Wisconsin urban runoff. The apparent available P from 18-day *Selenastrum* bioassays on the 16 samples from the two Genesee River Basin sites ranged from <1 to 34% PP_T, typically on the order of the apparent availability found for Madison, Wisconsin runoff.

Cowen and Lee [8] and Cowen [9) also collected data on seven water samples from three streams in the Genesee River Basin draining crop, brush and pastureland, collected between November 1972 and June 1973. In a separate sampling program they collected 34 tributary water samples from 4 major New York tributaries to Lake Ontario (Black, Oswego, Genesee and Niagara Rivers) between August 1972 and June 1973. The samples from the Genesee River Basin draining nonurban areas showed about 20-35% PP_T extracted with acid, 13-18% PP_T extracted with NaOH, and 6 to 17% PP_T extracted with anion exchange resin. Apparent availability to *Selenastrum* of the particulate-associated P in these samples ranged from about <3 to 10%, but as high as 20% when the samples were autoclaved prior to inoculation and assay. The four Genesee River mouth water samples collected as part of the Lake Ontario, New York tributary sampling program showed that 21-79% PP_T was base-extractable, and 6-31% PP_T was extractable with anion exchange resin. These results were comparable to the other set of Genesee River Basin samples. The other New York tributary samples were not evaluated for chemically extractable forms, but they were evaluated using bioassays. The whole river water samples from the New York tributaries evaluated showed very low P availability, typically <5% of the total PP_T. The difference between P chemically extracted and that taken up by *Selenastrum* may have been due, according to Cowen and Lee, to competition for P by native algae and bacteria present in the sample at the time of collection. When samples were autoclaved prior to inoculation and incubation, availability of particulate P increased to 26-57% PP_T

Cowen and Lee proposed that the short-term resin extraction incubation carried out in the dark may give a better estimate of readily available PP_T than bioassay of the natural PP_T alone, since the resins would take up all the P that would normally be taken up by the algae and bacteria. This amount could readily be determined using this technique. They also suggested, without further substantiation, that by autoclaving river water particulates in AAP (-P) (without filtration) a better estimate of potentially available P can be obtained.

Cowen and Lee [7] concluded that in the absence of site specific data, an upper-bounds estimate could be made of the available P in urban runoff or tributary waters using the following equation:

$$\text{Available P} = \text{TSP} + 0.3\ PP_T \qquad (1)$$

where TSP is the total soluble P, or where there is a large soluble organic P contribution, soluble reactive P (SRP); and PP_T is the total particulate P. Subsequently it has been found by one of the authors (Lee) that due to factors affecting P availability in the receiving waters, namely particle residence time in the photic zone, and the optimum nature of algal assay tests, a more appropriate estimate of the ultimate availability of tributary water phosphorus would be:

$$\text{Available P} = \text{SRP} + 0.2\ PP_T \qquad (2)$$

A number of recent investigators have cited the work of Sagher [10] to ascribe a major significance to NaOH extractable inorganic phosphorus (P_i) in assessing the algal availability of tributary particulate phosphorus. Sagher [10] proposed a method for assessing the “availability” of particulate P, in which NaOH extractable P_i + dissolved P_i are determined in a soil/water system (to which P-starved algae have been added) at the beginning of the assay and after 48-hr incubation. The difference between the NaOH-P_i + dissolved P_i at those two times supposedly gives an estimate of the amount of P “available” to algae. The evaluation of this method was based on two sets of experiments. One set involved correlating NaOH-extractable P_i and dissolved P_i to algal numbers during 30-day bioassays, and the other involved measuring the change in concentrations of the various P_i forms over a 48-hr period in a laboratory sediment-soil-algae system.

Sagher's "growth-related" P uptake experiments involved measuring the amounts of NaOH and HCl extractable P before and during 30-day bioassays, using three soil horizon samples from a Wisconsin Miami silt loam soil and *Selenastrum* cultures. NaOH-extractable P_i generally showed decreasing trends in the bioassays in which the soil was the only P source, indicating to Sagher that the .NaOH-P_i fraction was highly mobile and was the source of replenishment of phosphorus for the algae. In one of the three experiments the NaOH-P_i fraction increased. It was assumed that organic P contribution to available P would be negligible, but that aspect was not investigated by Sagher [10]. Sagher found that, in assays not receiving supplemental available P over the 30-day bioassay period, the total P_i decreased by 2, 37 and 54% in the three soil samples. These decreases corresponded to decreases in the NaOH extraction P of -50 (i.e., increased by 50%), 82 and 65% respectively. These numbers were mathematically manipulated to yield what he termed microbial P to estimate what had been taken up and used by algae.

Correlating P_i concentrations with corresponding cell numbers over the culture period (at 0, 15 and 30 days), as Sagher did as part of this experiment, is not appropriate if the goal is to assess the capability of chemical procedures to estimate the amount of P available for algal growth. Using the initial levels, it should be possible, if the procedure is valid, to predict some endpoint algal biomass. While the correlation between "microbial P" decrease and microbial P based on cell numbers at the end of the incubation period made by Sagher was often not strong, there was an apparent relationship between the initial NaOH-P_i and the number of *Selenasrnim* cells present at the end of the incubation period which was not discussed by Sagher. It should be noted again, however, that the correlations made between algal numbers and NaOH extractable P_i were based on samples of three horizons on one soil. As discussed by Sagher, in order to make any generalized statements about such relationships, a much wider variety of samples needs to be evaluated using this procedure.

Sagher [10] also conducted a series of experiments on the <20-μ fraction of six soil samples from two watersheds in Wisconsin, in which dissolved P, NaOH-P_i and HCI-P_i fractions were measured over 48-hr periods in soil-water-*Selenastrum* bioassays to determine shorter-term availability or uptake by algae. He found that after 48-hr incubation, generally 60-70% of the initial NaOH-P_i plus dissolved P_i were removed from solution. According to Sagher, this translated into an algal assimilation of 70-90% of the initial NaOH-P_i plus dissolved P_i.

Sagher [10] conducted the same type of experiments on simulated runoff, in which an equivalent of 4.6 in. (11.7 cm) rainfall were applied to two plots of agricultural land and runoff was collected. The percentage of NaOH-extractable plus dissolved P_i available from these unfractionated samples was 10-30% higher than that typically found by Sagher using the fractionated soil samples and the fraction of NaOH-P_i that became available. The dissolved P_i concentrations in the runoff were comparatively high. This suggests that this approach, if truly applicable to land runoff, may be highly specific to certain types of land.

While Sagher's recommended procedures appear to have some applicability to the algal availability of the phosphorus in shoreline erosion such as occurs from the bluffs of Lake Erie, and from certain types of soils, it may not be appropriate for assessing the availability of tributary particulate P at the point where the tributary empties into a waterbody, such as one of the Great Lakes, because of the differences in the nature of the materials. This point will be discussed further in a subsequent section. Further, there are several aspects of Sagher's methodology which could distort the results obtained. The soil samples were dried prior to processing which would likely change their sorption/desorption character for representing tributary suspended matter. In the soil preparatory step to fractionate particle size, the soil was leached for about six hours, and (although not specified in the procedure, it was ultimately recommended) the suspension was stored for several days. These steps alter the "initial" concentrations of the various P_i forms and likely do not result in a consistent error across a variety of soil samples. Sagher used a very limited number of soil samples from a restricted geographical area. The general applicability of his procedures must be evaluated. As discussed by Sagher, his method of separating "dissolved P_i" may have not separated out some finely divided particulates/colloidal forms which were included in the "dissolved" fraction.

Sagher [10] also proposed an indirect chemical method for assessing available P, which only required analysis of the soil suspension. This was based on the "fact that essentially all of the soil runoff NaOH-P_i (0.1 N NaOH extraction for one hour)" assumed from the context of Sagher's thesis to include dissolved P_i, "present in the bioassay system was assimilated by P-limited *Selenastrum* after (assumed to be *during*) the 48-hr incubation period." Examination of the data base presented on five soil samples from two watersheds shows that "essentially all available" ranged from 66 to 94% available (with a mean of 79% available) in those assays not spiked with P; those spiked showed much less NaOH-P_i utilization. This procedure would not likely be applicable to soils with high organic content since it does not take into account the mineralization of organic P that would take place over time in a lake. From an overall point of view, the work of Sagher alone, as indicated by Sagher as well, is not adequate justification for use of the NaOH extractable P_i as a measure of biologically available particulate P at the tributary/lake interface. Therefore, those studies discussed below which have relied on the Sagher [10] work for justifying the use of NaOH extraction as a measure of available P must be viewed in light of this potentially significant deficiency.

Sagher, *et al.* [11] conducted four-week bioassays and chemical fractionation studies on seven samples of Wisconsin lake sediments to determine the availability of sediment P to algae. P-starved algae were added to mixtures of wet sediment and algal assay medium with and without added P. Chemically, availability was assessed in terms of a decrease in total P_i concentration (HCl extractable P_1 plus dissolved P_i concentration), which was mathematically converted to increases in microbial P. They indicated that typically on the order of 50-95% (average of about 75%) of the total HCl-extractable P_i was available to algae (i.e., was converted to microbial P). Most of that which became available was from the NaOH extractable P rather than from apatite-P. They found that on the average of about 74% of the NaOH-P_i plus dissolved P_i (50-93% range) was removed during the course of the 3- to 4-week bioassays. Sagher [10] found that on the average approximately 79% of NaOH extractable P_i + dissolved P_i in soils was removed by algae in short-term (48-hr) uptake studies. One of the major differences between these two sets of results [10,11] was in the rate of decrease in extractable P_i levels. Sagher [10] reported that essentially all of the NaOH-P_i (actually approximately 65-75%) was removed by algae within a 48-hr period, while Sagher, *et al.* [11] reported that the rapid decline in dissolved P_i in one of their sediment-PAAP (Provisional Algal Assay Procedure medium) systems in the first few days was likely a function of P_i sorption by the sediment particles. Sagher, *et al.* found that uptake of sediment P_i generally gradually occurred over one to two weeks of exposure.

Sagher, *et al.* [11] did not provide any substantial discussion of the use of this approach for predicting the significance of sediment P_i in affecting algal growth in natural water systems, or the relationship between initial P_i levels and resulting algal biomass. Further, there was generally a poor agreement between microbial P based on *Selenastrum* counts and that based on the chemical procedure, pointing to deficiencies in one or both methods of assessing microbial P uptake. The amount of uptake of P_i also appeared to have depended to some extent on the type of algae assayed. Based on the limited data provided by Sagher, *et al.*, there appears to be some relationship between the log of cell numbers present at the end of the bioassay system. The slope of this straight line relationship appeared to be the same as that between the log of the number of cells after 30 days vs. initial dissolved P_i plus NaOH-P_i from treated soils from the work of Sagher [10]. Greater growth per unit concentration of NaOH-P_i + dissolved P_i was found than per unit total P_i which would be expected, since in general, the sequential HCl extractable (i.e., Ca-P) fraction has been found to be considerably less available than NaOH-extractable P_i.

Sagher, *et al.* [11] pointed out that one of the potential limitations to their approach was its inability to account for available P present as mineralizable P_O (organic P) in sediments. In general, the results of this study of sediment available P by Sagher, *et al.* should not be directly applicable to assessing the availability of phosphorus associated with suspended sediments in a tributary river to algae in receiving waters, mainly because of the general difference in character of the two types of particulates (i.e., sediment and river suspended particulates).

Huettl, *et al.* [12] used five of the Wisconsin soils tested by Sagher, [10] to evaluate the use of aluminum-saturated strong-acid cation exchange resin-extractable P as a measure of the availability of soil particulate P to aquatic algae. While they concluded that for 24-hr exposure periods the resin extractable P averaged 98% of that found to be “available” to algae by bioassay, it is unclear how those authors assessed algal uptake. It appears that they may have used Sagher’s [10] proposed method of taking the difference between the sum of dissolved P_i plus NaOH-P_i before and after incubation with algae, or perhaps they used Sagher’s results for the soils he evaluated.

Basically Huettl, *et al.* [12] have shown that, for several soils from central Wisconsin, an aluminum-treated cation exchange resin yields about the same extractable P as the decrease in NaOH extractable P and dissolved P’ from an algae-containing suspension. Using the same type of particulate material, but longer-term bioassays in which algal biomass was measured, Cowen [9] and Cowen and Lee [8] found essentially the same general relationship. It is therefore concluded that with these types of samples, the results of all of these procedures are essentially the same. It is, however, important to emphasize that these relationships would not necessarily hold for other soil-suspended river particulate samples. Also, for other systems, tests on soils and on suspended particulates may not yield similar results. Further, Huettl, *et al.* have presented an inappropriate critique of previous studies involving growth bioassays when they state, "Because several days were allowed for cell growth, the relationships between test results (i.e., those of Chiou and Boyd [13] , Cowen and Lee [8], and Porcella, *et al.* [14]) and P availability may be invalid for estimating short-term availability. Short-term availability of P is important in surface waters because the time that eroded soil particles are present in the photic zone prior to settling may be relatively short." Studies on the aqueous environmental chemistry of phosphorus have shown that the P present in the photic zone of a waterbody can be of minor significance in determining the overall phytoplankton biomass in the waterbody. The photic zone may be a relatively thin band of water compared to the mixed layer above the thermocline or bottom. Wind or other current-induced mixing is normally sufficiently great in waterbodies so that available P present in that portion of the mixed layer below the photic zone must be included in any assessment of the phytoplankton growth that will occur in a waterbody. Further, as shown by Stauffer and Lee [15], in some waterbodies even available P below the thermocline can, as a result of thermocline migration, play an important role in regulating phytoplankton growth within waterbodies. Most importantly, it is well known that there is appreciable release of P from sediments under both toxic and anoxic conditions. This was demonstrated by Lee, *et al.* [16] for Lake Mendota, Wisconsin. Therefore, in general, the short-term bioassays recommended by Huettl, *et al.* [12] and Sagher [10] can produce an erroneous estimate of the available P associated with a particular sample. Even the extended bioassays of the type used by Cowen and Lee [8] may be too short to measure properly the amount of P from particulate matter entering a waterbody that would typically become available for algal growth. The insufficient duration of the bioassays done by Huettl, *et al.* [12] and Sagher [10] points out the importance of designing the bioassay system so that it properly reflects the environmental chemistry of P in aquatic systems.

Li, *et al.* [17] evaluated the uptake of various forms of sediment P by the aquatic macrophyte *Myriophyllum spicatum* by determining changes in the concentration of total inorganic P, nonoccluded (NaOH extractable) P_3, exchangeable P_i using radioisotopes of P and plant tissue P after exposure to eight Wisconsin lake sediment samples. Wet sediment was mixed with P-free liquid growth medium and allowed to settle for one week. *M. Spicatum* were added, and when roots appeared (one week later) an additional 9 liters of P-free medium were added. After three more weeks the macrophytes were harvested, 9 liters of medium were removed and replaced with fresh medium. Two more growth cycles were conducted on the same sediment in the same manner. The growth response was proportional to the mass of sediment P added. Results from addition of 43.4 mg sediment P/test culture were used for comparison across sediments since addition of additional P resulted in no biomass increase but did result in luxury uptake of P. The uptake of dissolved phosphorus was not discussed. It should be noted, however, that in light of the contact time between the sediments and water prior to and during the assays, there would likely have been, at least in the first run, considerable dissolved P_3 in the surrounding waters, which perhaps could have been taken up by the plants. Li, *et al.* reported that the results of the three runs on the sediment sample were variable but comparable. Some mineralization of the sediment organic P occurred, generally less than 10% of the total P_O.

The percentage plant uptake of total sediment P_i, 13-17%, was considerably below the 60-95% microbial uptake of sediment P_i found by Sagher, *et al.* [11] in sediments from the same lakes that Li, *et al.* examined. For calcareous sediments tested, 33-50% of the nonoccluded P_i was taken up by the plants, considerably less than the 60-85% found by Sagher, *et al.* [11]. From 43 to 85% of the total exchangeable P_i was available to the macrophytes. For noncalcareous sediments, 18-24% of the nonoccluded P_3 was available, whereas 33-44% of the exchangeable P_3 was available. Nonoccluded appeared more available in calcareous than noncalcareous sediments. Since such differences were not observed for exchangeable P availability, it was concluded that radioisotopically exchangeable P_i is more representative of the available fraction.

Williams, *et al.* [18] investigated the algal availability of various forms of phosphorus associated with 5 Lake Ontario bluff erosional material samples, 3 tributary suspended solids samples from Lake Ontario tributaries, 2 samples from Lake Erie tributaries, and 12 samples collected from the top few centimeters of lake sediments from the Lake Ontario basin. Although the availability of the tributary suspended solids is being given particular emphasis in this chapter, Williams, *et al.* presented only a generalized discussion in their synopsis paper of the results of all samples. Bioassays were conducted in which about 100 mg dry solid equivalent of wet sediment was mixed with 500 ml culture media and algae and incubated for 12 days. It was concluded that apatite P is generally not available to algae, and that algal uptake of P was linearly related to the nonapatite inorganic P (NAIP) present. Uptake averaged about 75% of the NAIP added; in no case was all the NAIP utilized. Algal P uptake was even more closely related to the NaOH extractable P_3, which they found by correlation to be about 70% of the NAIP. The amount of algal uptake of P was not related to the total P content (8-50% of the total P was taken up); however, it was found that the higher percentage uptakes were in samples having higher total P content.

Williams, *et al*. pointed out that P utilized under laboratory conditions should be considered as only potentially available, as those optimum conditions would not likely prevail in the environment. Actual exposure time of the algae to the particulates would be a major factor governing the actual amount of utilizable particulate P in the environment. Suspended solids in streams generally contain large amounts of silt-size particles of clay and silt aggregates, which tend to settle more readily than smaller sized particles, thus perhaps further reducing realized availability of particulate P.

Caution should be exercised in using Williams, *et al.*'s availability percentages because their data may have been biased by sample handling. They froze their sediment samples prior to assaying, which may have substantially altered their characteristics and behavior in the test system.

Logan [19], Logan, *et al.* [29], Verhoff, *et al.* [21] and Verhoff and Heffner [22] undertook a study of the biological availability of particulate phosphorus entering Lake Erie as measured by chemical fractionation, and the rate of availability (uptake) of P in river waters. Logan, *et al.* [20] reported on both aspects of the study, while the other three works cited above presented the results of parts of this study.

Logan [19] and Logan, *et al*. [20] analyzed 66 samples from 36 tributaries in the U.S. portion of the Lake Erie watershed in an attempt to determine the short-term and longer-range P availability potential. The solids fraction that was considered available in the short-term was the NaOH extractable form; the difference between the citrate-dithionite-bicarbonate (CDB) extractable and the NaOH extractable P was considered to represent the portion which potentially can be released over long periods of time during anoxia. The HCl-P_3 was considered unavailable. No work was done, however, to substantiate the validity of these assumptions. They found that when averaged on a geographical regional basis, the NaOH extractable P represented about 30-40% of the total inorganic P in the particulate samples, except for the New York area in which this fraction was 14% of the total inorganic P. Data presented indicated that the NaOH-P was 6-15% of the total particulate P concentration (PP_T). The fraction potentially available over a long term (which includes short-term availability), the (NaOH + CDB) - P_3 fraction, represented on the average 17-27% of the total sediment P content for all four geographical areas. These percentage estimates may be somewhat in error due to the fact that the measured and calculated total P values differed.

Logan [19] and Logan, *et al.* [20] pointed to the importance of assessing the individual character of the systems being considered in using chemically derived P bioavailability estimates. According to those authors, the key factors are the rate at which P becomes available, the duration of the exposure period, and the potential for reexposure of algae to particulate P.

Verhoff, *et al.* [21], Verhoff and Heffner [22] and Logan, *et al.* [20] attempted to assess the rate of conversion of total P to available forms in three Lake Erie tributaries. In interpreting the fraction of unavailable P that may become available in terms of natural water systems, the conversion rate must be considered in light of the characteristics of the receiving water, such as the retention time of the particulates in the waterbody or in the photic zone. Verhoff and Heffner collected a water sample from each of the four Lake Erie tributaries during major storm events. They prepared triplicate 12- to 14-liter subsamples of each river water, added AAP nutrients (without P), and incubated for 100 days or more, periodically harvesting the supernatant for determination of algal P uptake (assumed to be the same as insoluble P). The centrifugate was returned to the assay tank. For the Sandusky River, 0.087% of the total P in the sample was removed by algae per day over the 80-day incubation period. This rate was 0.268% and 0.191% per day for the Honey Creek and Broken Sword samples, respectively. According to Logan, *et al.* [20], there was insufficient growth in the Cattaraugus Creek (NY) sample test to make a harvest. Verhoff and Heffner indicated that the Cattaraugus Creek contained a substantially greater apatite (nonavailable) fraction of total P than the others, and consequently should stimulate much less growth. Verhoff and Heffner indicated that this assessment corresponded to the results of Cowen and Lee [8] for western New York samples. However, examination of the Cowen and Lee study showed that when their tributary samples were autoclaved prior to assay, considerably greater P availability in the samples was found. As discussed previously, Cowen and Lee attributed the lower growth in the New York samples to competition for P by native algae and bacteria, rather than the presence of "unavailable" (apatite) P as suggested by Verhoff and Heffner.

Verhoff and Heffner found that their conversion rates "corresponded favorably" with a number of literature values. However, the literature values cited were for conversion of P in the dark, indicating a rate of mineralization of organic P to dissolved inorganic P, rather than the removal of particulate inorganic forms of P by microbes for assimilation. Verhoff and Heffner's conversion rates are considerably less than rates reported for conversion of various extractable forms of P to algal P reported by Sagher, *et al.* [11] and Sagher [10]. The rates may have been limited by the apparent lack of mixing of the settled sediments and overlying water. Further, since indigenous populations were used, this represents net microbial uptake rate, rather than algal uptake rate; what may be available to zooplankton may not be the same as that available to algae. As pointed out by Logan, *et al.* [20] with reference to this work, there may have been preferential removal of the fine particles as a result of the harvest method; also, at the end of incubation, substantial amounts of algae were present in the sediment which would not have been accounted for in the microbial removal of P. Further, Verhoff and Heffner reported problems with algae growing on the sides of the flasks, and crusts forming on the surface of the sediments. This may have affected the results of their work. If their conversion rates are appropriate, on the order of 30-50% of the total P in these river waters would become available in a year's time. By then substantial amounts of the P would be removed from the lake or photic layer by settling and could result in minimal effect on the lake's productivity.

Logan, *et al.* [20] showed that during the incubation period of about 100 days, generally about 40% of the NaOH extractable P in the sediment was removed, leaving several hundred pg/g NaOH extractable P in the sediment. The Cattaraugus sample showed only 6% remova] of NaOH-extractable P and was the only one to show a decrease in the HCl-extractable fraction (after NaOH extraction). The other three samples all showed increases in this fraction ranging from 4 to 50%. This was generally not observed by other investigators. Based on the work of other investigators, the 40% removal of NaOH-P_i is low. Because of reported problems with loss of sample during the procedure, the results of the fractionation portion of this experiment may be unreliable.

Logan, *et al.* [20] commented on the significance of these findings relative to Lake Erie. Sediments from the more urbanized tributary areas and high clay areas should have the highest bioavailable P load, based on the fact that their character is reportedly representative of the native soil P levels. Since these areas of the Lake Erie Basin drain to the shallower western basin, their impact on algal production may be more significant. This is all under the assumption that the chemical analysis of a soil or river sediment accurately predicts ultimate P availability. However, controlling the sediment load to the Lake will cause proportionately less available P ta be removed, since the available P is supposedly more prevalent in the fine-grained materials; the suspended solids control programs tend to be better at removing the larger-size fractions. Logan, *et al.* suggested that since the availability of sediment P to algae is kinetically controlled, dynamic P lake models may be more appropriate for predicting future change in the individual basins than static P-loading models. Based on what is known about the applicability of the P loading models of Vollenweider [23] and Rast and Lee [24], this statement lacks technical foundation. The applicability of various P-loading models, as influenced by the availability of the P load, will be discussed in a subsequent section.

Armstrong, *et al.* [25] investigated the amounts and fractionation of P forms in particulates from several locations (generally near the mouth) of five Great Lakes tributaries draining mostly rural, agricultural and forested areas, including the Genesee (above Rochester, New York), Grand, Maumee, Menomonee (draining mainly urban areas) and Nemadji Rivers. Composite water samples were collected during particular flow periods at various times over a year. Armstrong, *et al.* processed the data by averaging the data for all sampling sites in each tributary. The averaged flow and suspended solids levels were fairly representative of historical data according to those authors. Samples of Lakes Michigan and Erie recessional shoreline material were also examined. The maximum amount of "available" P in the river particulate matter was assumed in this study to be equal to the NaOH-extractable portion, although Armstrong, *et al.* did not evaluate the appropriateness of this assumption. The fraction of the total particulate P (PP_T) which was taken up by an anion exchange resin over an 18-hr period was considered to be the fraction most readily available for use by algae. The percent NaOH extractable P of PP_T for the five tributaries ranged from 14 to 37%, a range which compares well with that of Cowen and Lee [8] and Cowen [9], of 22-27% NaOH-P for urban runoff, and 11-28% for Genesee River samples. The resin extractable fraction was 7-17% of the PP_T, representing 43-50% of the NaOH-P fraction as averaged for each tributary. The resin P fraction also compared well with that found by Cowen and Lee [8] and Cowen [9]. The organic P fraction of the particulates was not measured by Armstrong, *et al.*, since they indicated this fraction is mineralized very slowly, yielding only a small fraction of available P. They did not, however, present any data to support this position. Armstrong, *et al.* suggested that the mechanism of the uptake of NaOH-P was desorption due to low solution phosphorus concentration, which is maintained by P-deficient algae. Cowen and Lee [8] also found that the amount of extractable P increased when dissolved P levels in the water were lower.

Examination of P fractions associated with various particle size fractions led Armstrong, *et al.* to conclude that the particle size fractions all had similar percentages of the various P fractions measured. Recessional shoreline samples showed only 1-4% of the particulate P was extractable with NaOH. Greater than 68% of these materials were HCl extractable. "Available" P loads (based on dissolved P and NaOH-P being available) were calculated for the five tributaries investigated by Armstrong, *et al.* [25]. Between 23 and 58% of the total P loads (mean of 44%) were calculated to be available. Using the approach developed by Cowen and Lee [7,8] and Cowen [9], Lee and Jones [26] determined the percent available P load to Lake Ontario from the four major U.S. tributaries. As shown in Table I, between 30 and 46% of the total P loads from these rivers is potentially available. This compares well with the estimates of Armstrong, *et al.* [25] for a variety of tributaries to each of the Great Lakes.

Table I. Distribution of Total and Soluble Orthophosphate Tributary Load from Major U.S. Tributaries to Lake Ontario[a]

Tributary River	Mean Total P Load (metric tons/day)	Mean Soluble Ortho P Load (metric tons/day)	Soluble Ortho P/ Total P (%)
Niagara	20.8	2.4	12
Genesee	1.8	0.34	20
Oswego	2.9	0.92	32
Black	0.5	0.08	16

Tributary River	Potentially Available P/ Total P (%)	Percent of U.S. Tributary Total P Load	Percent of U.S. Tributary Soluble
Niagara	30	80	64
Genesee	36	7	9
Oswego	46	11	25
Black	32	2	2

[a] Adapted from Casey, *et al.* [28] after Lee and Jones [26].

Monteith and Sonzogni [27] reported on the "available" P in over 160 U.S. Great Lakes shoreline soils representing 49 soil profiles. Available P was reported as the P fraction extracted in 2 hr with 0.05 N HCl. As discussed by Monteith and Sonzogni, although this technique may not be the most appropriate for assessing biological availability, those data were the only ones provided which may even roughly approximate the amount of available P in the particulate shoreline soils. The literature cited by those authors which discuss the use of mild acid extraction for estimating available forms indicates that it very likely provides an overestimate of both short-term and long-term contaminant availability. For the soils evaluated in that study, an average of 43% of the total soil P was extracted as orthophosphate by dilute HCl. From the data presented, they indicated that there appeared to have been more 0.05 N HCl extractable P associated with the clayey fraction than with the sandy or loamy soil fractions.

Thomas [29] summarized data derived during Task D studies of PLUARG. Water samples were collected from ten Great Lakes tributaries (Bronte Creek, Humber, Credit, Welland, Niagara, Grand, Cedar, Thames, Saugeen and Nottawasaga Rivers) and analyzed, generally monthly, for bulk mineralogical properties and forms of P. The concentrations of NAIP (nonapatite inorganic P), organic P and apatite P in each river were highly variable over the annual cycle, but the annual mean values (when expressed as a percentage of the total sediment P) were fairly constant. What was termed “available P” (NAIP) was on the order of 20-40% of the tributary particulate total P, which is on the same order as that found to be potentially available by Cowen and Lee [7,8] and Cowen [9]. According to Thomas, available sediment (particulate) P as measured by these chemical techniques represents 0.9, 3.6 and 1.2% of the total P loadings to Lakes Huron, Erie, and Ontario, respectively. These estimates cannot be compared directly to those of Lee and Jones [26] or Armstrong, *et al.* (25], since Thomas’ estimates of available P do not include the soluble P in the tributaries. Thomas also concluded from the data that there was little variation in the texture and mineralogy of particulates in the streams, indicating consistency in sediment sources, mixing and transport, and that the particulates reflect the basin soils. Further, he indicated that based on these data, available P cannot be predicted by land use or form but must be measured for individual lakes or watersheds.

It is important to note that this study did not include any assessment of available P using bioassay techniques. As is discussed in other parts of this review, the authors have reservations about the ability of NaOH extraction of particulate matter to assess the biologically available P associated with Great Lakes tributary particulates in some cases, especially those with elevated organic P content. It has recently been learned, however, that Thomas and co-workers have subsequently conducted bioassay studies on these tributary waters and that these data will be published in the near future. Such data will potentially allow a much better assessment of how well the NaOH extraction procedure applied to particulate matter plus the soluble orthophosphate approximates the amount of algal-available P in a variety of tributary waters.

Atmospheric Inputs

A number of investigators have attempted to assess the atmospheric contributions of phosphorus to waterbodies. While most of these investigators determined various chemical fractions of P in their rainfall and dustfall samples, only Cowen [9] and Cowen and Lee [8] did studies to determine the availability of the P from this source to algae. Cowen [9] and Cowen and Lee [8] conducted bioassays with *Selenastrum* on particulates from three samples of Madison, Wisconsin snow collected in April 1973. In genera!, the total soluble P concentrations were the same as the dissolved reactive P level. Less than 25% of the particulate P in these snow samples was available to *Selenastrum* in 18 days. One sample did not show any detectable growth. Cowen and Lee collected 13 precipitation samples from various locations within New York State. These samples contained small amounts of dissolved reactive P, compared to the total soluble P. Bioassays with *Selenastrum* on the total sample showed that in only three samples was the algal available P more than 10% of the total P concentration. In 12 of the samples, the percent algal available P was less than the percent dissolved reactive P.

Brezonik [30] reviewed the literature on atmospheric contributions of a variety of chemicals and found that ortho-P was typically on the order of 0-0.005 mg P/L, and total P on the order of 0.02-0.15 mg P/L. He also reported on the concentrations of P in rainwater collected August 31-September 1, 1969, at nine stations near Gainesville, Florida. Total P ranged from 0.02 to 0.65 mg P/L and ortho-P from 0.004 to 0.043 mg P/L; soluble ortho-P ranged from 7 to 66% of the total P. Phosphorus was also measured every 5-10 minutes during two storm events in the summer of 1969 at Gainesville, Florida. Both total and ortho-P decreased over time after start of the rainfall. The ortho-P fraction was 50-100% of the total P in the samples evaluated.

Brezonik [30] also presented literature values for P in snowfall. For the two studies cited for snowfall, ortho-P levels were 33 and 30 µg P/L, the former being 58% of the reported total P. A summary by Brezonik of literature estimates of the percent of the total P load contributed by rainfall shows that it ranges from a few percent to as much as 74%.

Murphy [31] evaluated the phosphorus in 89 samples of rainwater collected from atop a 10-rn high building in a densely populated urban Chicago area. Air particulates were also collected using a high volume air sampling pump. The average concentrations of total P in rainfall were 0.034 mg P/L, and soluble orthophosphate (52 samples) was 0.012 mg P/L. Concentrations were found to be higher in lower volume rainfall events and lower in higher volume events. Concentration in eight snowfall samples ranged from 0.016 to 0.054 mg P/L, and 0.006 to 0.196 mg P/L for “orthophosphate” (assumed to be determined on unfiltered sample), with most concentrations in the 0.02.0.05 mg P/L range.

Peters [32] collected eight rainwater samples, six samples of rainwater plus dustfall, and one snow sample from a pasture-forest area above the eastern shore of Lake Memphremagog, near Montreal, Canada. Samples were analyzed for total P (TP), soluble P (SP) and soluble reactive P (SRP). Although these samples were frozen prior to analysis, the author indicated that this type of preserving did not affect the integrity of Lake Memphremagog samples evaluated. He did not, however, evaluate the reliability of this preservation technique for their atmospheric samples. Using radiotracer techniques, Peters concluded that on the order of 38% of the atmospheric P was exchangeable, which he equated with being available for algal growth.

A total of 188 precipitation samples was collected from six locations around Lake Michigan and analyzed for total P by Murphy and Doskey [33]; 131 of these were also analyzed for dissolved reactive phosphate. Weighted (unclearly defined) average total P concentrations for the six stations ranged from 0.016 to 0.036 mg P/L; weighted average dissolved reactive P ranged from 0.006 to 0.014 mg P/L. The higher concentrations were typically found at the stations at the south end of the lake. On a stationwide average, soluble ortho-P ranged from 30 to 56% of the total P concentration. A series of 23 rainfall samples was chemically fractionated further to determine the amount of hydrolyzable, organic and total reactive P in the samples. The weighted average dissolved reactive P was 0.01 mg P/L; hydrolyzable (less dissolved reactive P), 0.0044 mg P/L; organic P, 0.009 mg P/L; and total reactive, 4.68 mgP/L.

Twenty-two snow samples from four of the above cited locations were also analyzed by Murphy and Doskey [33]. Total P ranged from 0.07 to 0.058 mg P/L (mean 0.026 mg P/L) and dissolved reactive P from 0.002 to 0.024 mg P/L (mean 0.007 mg P/L). On a per sample basis, soluble reactive P was 39% of the total P. In a number of samples, the total reactive P concentration was considerably greater than the dissolved reactive P. Murphy and Doskey [33] concluded that 50% of the total P present in precipitation is a reasonable estimate of the amount of P that will ultimately become available, although they did not conduct any bioassays to substantiate this conclusion.

Délumyea and Petel [34,35] studied atmospheric inputs of phosphorus along the shore of and on Lake Huron between April and October 1975. It is important to note in reviewing their results that what they have termed "available" P is operationally defined as the soluble ortho-P plus that leached at pH 2 in H_2 SO_4. It does not, however, have any demonstrated relationship to that fraction which is available to stimulate algal growth in the lake water. Concentrations of acid-leached P in six, monthly, integrated samples of rainfall and dry fallout from each of 11 shoreline stations showed concentrations to be highly variable from month to month, ranging from a few µg/L to 0.7 mg/L. Although they reported some problems due to sample loss through evaporation, especially in the summer, average concentrations appeared to be highest in June and September and lowest in August.

Total soluble phosphorus concentrations in 21 event rain samples collected from eight shoreline stations between June and October 1975 were also highly variable, ranging from a few tenths of a µg P/L to 36 µg/L. Concentrations appeared to be highest in mid-July, decreasing through October.

Availability of Soluble Orthophosphate

A review of the literature on the availability of soluble orthophosphate, generally defined as molybdate reactive phosphate that will pass through a 0.45-µ pore size membrane filter, leads to the conclusion that this form of phosphorus is usually readily available to support algal growth. However, under certain conditions, the soluble molybdate reactive P may not be readily available. A number of investigators, notably Rigler [36,37] and Lean [38,39], have reported that substantial parts of the soluble molybdate reactive phosphorus is not available to support algal growth. On the other hand, Walton and Lee [40] have found, using algal assay procedures and a variety of waters, that there was a good correlation between the expected algal growth (based on the soluble orthophosphate content of water samples) and the actual growth achieved under standardized culture conditions. Examination of the conditions governing the results of these studies shows that the two groups of investigators were working in markedly different concentration ranges. Rigler and Lean worked with water samples having soluble ortho-P concentrations in the µg P/L range, whereas Walton and Lee [40] worked with waters having concentrations of 10 µg P/L. It is well known that the molybdate method is not necessarily specific for soluble orthophosphate, but includes other forms of P and other materials, such as arsenate, usually present in trace amounts in aquatic systems. At higher P levels, the soluble ortho-P dominates the other P forms and many interfering substances. It is therefore not surprising to find at low concentrations of phosphorus, at or near those that are generally believed to limit algal growth, that there would be a greater discrepancy between molybdate reactive P and that found available through bioassay.

From a phosphorus management strategy point of view, the fact that the molybdate test does not accurately measure algal available phosphorus at a few µg P/L concentration levels or less is of no major consequence since P control programs must be directed toward those sources which have concentrations well above that level.

There is another condition under which the molybdate-reactive phosphate at greater than 10 µg P/L levels will not correspond well to algal available P in the standard assay procedure. As discussed by Cowen and Lee [8] this may occur for those samples which contain large amounts of biodegradable organic carbon. Under these conditions, large bacterial populations may develop in the algal cultures which will absorb the phosphorus as part of respiration, making it unavailable for algal growth. Aquatic bacteria, because of their generally higher growth rates compared to algae, can out-compete algae for P, provided that there is a sufficient concentration of organic carbon to support bacterial growth. While this has not been investigated, it is likely that bacterial absorption of P would only temporarily make the P unavailable for algal growth. Upon bacterial death and lysis, substantial parts of the P in bacterial cells would be released and made available for algal growth. The algal assays on high oxygen demand high BOD waters would tend to show lower P availability than would be realized in the water over extended periods of time. Therefore, caution should be exercised in interpreting results of algal assays for available P.

Summary of Studies on Algal Availability of P from Diffuse Sources

Cowen and Lee [7,8] and Cowen [9] have conducted essentially the only large-scale study to examine the relationships between biological availability of P as measured by bioassay-determined cell growth and a variety of chemical extraction methods. Other studies, such as those of Sagher [10] and Sagher, *et al.* [11], have demonstrated a relationship between an amount of P removed from various soil P fractions and converted to algal P uptake, and the percentage of the total particulate P represented by the soil P fractions. The amount of particulate P available to algae, according to the studies of Cowen and Lee, is approximately equal to an amount between that extracted by an anion exchange resin and by NaOH, the latter giving a long-term maximum. This amount is often approximately equal to 10-30% of the particulate P concentration. Sagher's [10] study indicated that the NaOH P removed by the algae represented on the order of 30-40% of the initial total inorganic P concentration of the soils. If the sediment organic matter were taken into account in his computations, a range of percent total particulate P available on the order of that found by Cowen and Lee would likely be approached.

The results of NaOH extractions on Great Lakes area soils and sediments performed by investigators whose work is discussed herein, have typically shown that 10-30% of PP_T is extractable. This is in close agreement with the finding of Cowen [9] and Cowen and Lee [7,8], which showed available P from urban and rural drainage was approximately equal to soluble reactive P + 0.2 times the particulate P. A number of these investigators have generally agreed that this range would represent a maximum, long-term availability based on ideal laboratory conditions; the realized availability of particulate P would likely be somewhat less than the NaOH extractable amount. However, if it is assumed, based on the work of Cowen and Lee, and Sagher and others, that the NaOH extractable P is a crude estimate of the algal available part of the particulate P in a Great Lakes tributary water sample, then it may be concluded that the relationship developed by Cowen and Lee is a suitable approach for generally estimating the amount of algal available P entering a waterbody. There has been sufficient work done to substantiate this relationship in the Great Lakes basin so that it can be used for development of P management strategies for the control of phosphorus from "typical" land and urban runoff. There are situations where this procedure should not be used without verification. Some of these systems are discussed below and in subsequent sections of this paper.

Although several investigators have reviewed either experimentally or through the literature the question of the availability of organic P fractions, none have focused on this issue. They have assessed that in the time frame considered (generally several weeks' exposure), mineralization of organic P to readily available forms is negligible. For the most part, however, these investigators have not dealt with high organic P systems. This issue should receive attention, especially since (as discussed in another section of this chapter) as erosion control practices are put into effect, the proportions of sediment P fractions entering tributaries and lakes may change. An example of this is the "no till" agricultural practice designed to limit soil erosion. It has been observed that while this practice may reduce the amount of NaOH-P or other sediment inorganic P fractions entering a water, it may significantly increase the organic P load. The significance of this change relative to eutrophication-related water quality is not known at this time. It does indicate, however, since the organic P fractions are not extracted by NaOH or anion exchange resins, that before such extraction procedures are adopted as standard techniques for determining "biologically available" particulate P, the availability of the organic P fraction in higher organic P systems should be evaluated. It also points to the importance of assessing through bioassays the suitability of chemical extraction techniques for estimating availability of particulate phosphorus for a wider variety of systems.

It should be noted that, in reviewing the literature on this topic it has been found that many investigators have not provided sufficient detail and clarity of presentation in their reports to enable a reviewer to ascertain what was actually done in many cases. All papers and reports devoted to this and related topics should contain a detailed, clearly presented experimental procedures description to enable other investigators to duplicate their work should they choose to do so. While this is applicable to all scientific and engineering studies, it is especially important for studies of available forms of contaminants since the answers obtained in these studies are highly dependent upon how the experiments were conducted.

IMPACT OF P QUALITY

The eutrophication program of the Organization for Economic Cooperation and Development (OECD) has demonstrated for the U.S. [24,41], as well as internationally (unpublished), that strong correlations exist between the P loads to waterbodies (lakes, impoundments and estuaries) normalized by mean depth and hydraulic residence time, and the phytoplankton biomass, as measured by planktonic algal chlorophyll and Secchi depth. It is evident that P is the primary controlling factor in the overall trophic state of many lakes and impoundments. Further, it is possible to quantitatively predict a waterbody's eutrophication-related water quality based on the normalized phosphorus load using the OECD eutrophication modeling approach. Lee and Jones [26] and Lee, *et aI.* [42] have demonstrated that the OECD modeling approach is applicable to the Great Lakes.

While it is possible to relate P load to eutrophication-related water quality in lakes and impoundments, no such relationships exist at this lime for rivers and streams. There are no meaningful P load or concentration limits that can be used to estimate the impact of a particular P source on eutrophication-related water quality in a stream or river. It is evident, however, that streams and rivers can have much higher concentrations of available P without producing significant deterioration of water quality than can lakes, impoundments, estuaries and marine waters.

The discharge of P to a stream or river may have a markedly different effect on a downstream lake or impoundment compared to the effect that would result if P were discharged directly to the lake or impoundment. These differences result from the fact that the algal availability of the phosphorus can change between the point where it enters the stream or river, and where it enters the lake or impoundment. Although it is possible that some unavailable P forms may be converted to available forms in transit downstream to a waterbody, the predominant reaction likely causes available forms to be converted to unavailable forms. This would be of particular significance for wastewater treatment plants located some distance inland from the waterbody of concern, since for some river systems appreciable parts of the available forms of phosphorus would be converted to unavailable forms during river transport to the lake or impoundment. This is the result of sorption reactions, and in calcareous areas, precipitation of phosphorus, and the incorporation of P into aquatic plant biomass occurring within the stream, which results in part of the P becoming refractory and therefore unavailable to support downstream aquatic plant growth. In a similar vein, the OECD studies [24,43] have shown that arms or bays of a larger lake can be effective nutrient traps, in which available P entering the area is converted to a substantial extent to unavailable forms through phytoplankton growth and subsequent death. Such situations can result in the main body of a water-body having much better water quality than would be predicted based on the total P load to the entire waterbody (including the arm or bay).

From a P management strategy point of view, it is certainly inappropriate to require the same degree of P removal from wastewaters discharged directly to a waterbody as from wastewaters discharged to a tributary of the waterbody, especially if the discharge is a considerable distance upstream from the waterbody. There is need for studies to define the aqueous environmental chemistry of P in river and stream systems. They should be focused on determining the amount of P available at the point of entry into the river or stream systems which remains available at the lake/tributary interface. It certainly behooves those municipalities located considerable distances inland from the waterbody of concern to support studies of this type. Such studies could prove to be highly cost-effective in reducing the treatment costs associated with P removal. It is important to emphasize that the factors governing conversion of available P to unavailable P are reach-of-stream specific. Therefore, studies of this type conducted on one stream are likely to have limited applicability to another stream or to a different reach of the same stream.

While the above discussion has focused on wastewater treatment plant effluent, it is equally applicable to other P sources such as agricultural runoff. It is apparent for the Great Lakes basin, as well as other areas, that the amount of algal-available P that reaches the Great Lakes, per acre of crop under identical farming and other conditions, is less for those farms located considerable distances inland compared to those on the lake's shore. Greatest attention in developing P control measures for diffuse sources should be given to control of the available forms of P from those sources adjacent to the lakes.

AVAILABLE PHOSPHORUS IN DOMESTIC WASTEWATER TREATMENT PLANT EFFLUENTS

Current Great Lakes Practice

Domestic wastewaters represent a significant source of phosphorus for the Great Lakes. It is generally assumed that the P present in domestic wastewaters is available to support algal growth. However, this has not been demonstrated and it is reasonable to expect that at least some part of the total P (especially colloidal P and the nonreadily settleable organic P fraction) in domestic wastewater treatment plant effluents is not available to support algal growth. This unavailable portion would likely constitute even a greater percentage of the total P in an effluent that has been treated for phosphorus removal because, as discussed by Lee [44] , some of the phosphorus would be tied up with iron or aluminum as particulate P. Studies on the direct addition of iron and aluminum salts to lakes to reduce water column P concentration have shown that the P incorporated in hydrous oxide floc is not readily returned to the water column over extended periods of time and is essentially made unavailable for algal growth. There is a need to conduct studies on the amount of P that is available for algal growth in secondarily treated wastewater, as well as wastewater treated for P removal. The characteristics of such studies are discussed in a subsequent section.

It should be noted that concomitant with P removal by alum or iron precipitation techniques, a number of toxic chemicals, such as heavy metals, organic materials, etc., are also removed. Further, there is generally a reduction in the classical pollutant load (BOD, suspended solids, etc.) to the receiving water. With increased emphasis being placed on improving the quality of municipal effluents over that typically attained with secondary treatment, it is possible that the focal point of increased removal of contaminants from wastewater effluents should shift from phosphorus to other chemicals. It is important to conduct studies which properly define the costs and the benefits associated with removal of toxic chemicals by iron and alum precipitation techniques to develop management strategies for those contaminants from municipal wastewater sources. In developing these strategies, the availability of the contaminants to aquatic life must be assessed properly. It is well known [45,46] that iron and aluminum hydrous oxides are efficient scavengers of many toxic materials, and can convert some of them to forms unavailable to aquatic life. Lee [45], in his review of the role of hydrous oxides in the control of contaminants in aquatic systems, pointed out that there are often marked differences in the abilities of freshly precipitated (*in situ* precipitated) and aged hydrous metal oxides to remove contaminants from aquatic systems. Malhotra, *et al.* [47] found that the removal of P from a wastewater effluent by Fe and Al precipitation was much more effective when the hydrous oxide floc was formed *in situ* in the presence of P, compared to the addition of preformed floc.

Proposed Great Lakes Practice

Domestic wastewater treatment plants throughout the Great Lakes' Basin, and in other areas as well, are practicing phosphorus removal by the addition of alum, lime or iron. As discussed above, with these techniques a 1 mg P/L effluent concentration is readily attainable at low cost. The 1978 Great Lakes Water Quality Agreement [1] calls for additional phosphorus removal from domestic wastewaters to at least 0.5 mg P/L for municipalities situated in the drainage basin of the lower Great Lakes to achieve the proposed phosphorus loads in the Agreement. There are several aspects of this objective that must be considered, one of the most important of which is the expected improvement in water quality which would result from achieving the 0.5-mg P/L level. This topic has been reviewed in detail by Lee and Jones [26] and Lee, *et al.* [42]. They have found, based on total P load and using the OECD eutrophication modeling approach, that the reduction in effluent concentration to 0.5 mg P/L will result in a nonperceptible change in water quality in the open waters of the Great Lakes (Table II), compared to the 1 mg P/L effluent limitations of the 1972 Great Lakes Water Quality Agreement.

As discussed by Lee and Jones [26], the potential changes in nearshore water quality must be evaluated on a case-by-case basis. In general, however, it is doubtful that there would be many locations in the nearshore waters where a significant additional improvement in water quality would result from wastewater treatment plants in a region further reducing effluent P concentrations from 1 to 0.5 mg P/L. Therefore, considering the significant increase in cost associated with reducing domestic wastewater treatment plant effluent P concentrations from 1 to 0.5 mg P/L, and a possible lack of improvement occurring in Great lakes water quality as a result of this further reduction, it does not appear that adoption of a general requirement that all domestic wastewater treatment plants in the lower Great Lakes Basin must achieve 0.5 mg P/L effluent concentration is technically valid or cost-effective. However, for those waterbodies in which it appears that a significant impact on water quality would result from decreasing effluent total P concentrations from 1 to 0.5 mg P/L, studies should be conducted to determine the amount of available P that will be removed by this action, since much of the total P in a 1-mg P/L effluent which has been treated for P removal may be tied up with hydrous iron or aluminum oxides and therefore unavailable for algal growth in the receiving waters.

Table II. Summary of Predicted Changes in Water Quality in the Great Lakcs Under the Base Loads, Reduction Scenarios and 1978 Water Quality Agreement Target Loads[a]

Lake	Base Load	Detergent Phosphate Reduction Scenario	1.0 mg/L Effluent Limitation Scenario	0.5 mg/L Effluent Limitation Scenario	Target Load
Chlorophyll-a (µg/L)					
Superior	1.0	0.9	0.9	0.9	0.9
Michigan	2.0	2.0	1.8	1.8	1.8
Huron	1.2	1.2	1.2	1.2	1.1
Erie	5.0	4.7	4.1	3.8	3.3
Ontario	2.3	2.3	2.1	1.9	1.7
Secchi Depth (m)					
Superior	9.1	9.2	9.3	9.3	9.3
Michigan	6.0	6.2	6.4	6.4	6.5
Huron	7.9	7.9	8.0	8.0	8.3
Erie	3.8	3.9	4.1	4.3	4.7
Ontario	5.7	5.7	6.0	6.2	6.7
Hypolimnetic Oxygen Depletion ($g\ O_2/m^2/day$)					
Erie (Central Basin)	0.43-0.75	0.40-0.67	0.38-0.61	0.36-0.58	0.32-0.52

[a] See Lee and Jones [26] or Lee, *et al.* [42] for the basis of these estimations.

Although for the Great Lakes, little additional improvement in water quality will likely be achieved by reducing domestic wastewater treatment plant effluent P concentration to below 1 mg P/L, there may be situations in which removal of P below that readily attainable by iron, alum or lime treatment (i.e., below 1 mg P/L) will result in a significant improvement in water quality in the receiving waters. There are parts of the U.S., such as near Lake Dillon near Vail, Colorado, where municipal wastewater treatment plants are required to achieve 0.2 mg P/L in their effluents. The cost-effectiveness of and water quality benefits to be realized by achieving this concentration in domestic wastewater treatment plant effluents being discharged to Lake Dillon is under investigation [48]. The appropriateness of having domestic wastewater treatment plant effluent limitations of less than 1 mg P/L in other areas must be evaluated on a case-by-case basis, with both short-term and long-term bioassays being used to assess the availability of phosphorus in the treatment plant effluent.

The Detroit, Michigan situation, in which the municipality's wastewater discharges are considerably above the 1 mg P/L effluent standard (apparently because of a hydraulic overloading of the plant) represents a special case in which work should be done to determine how much of the so-called excess total phosphorus load is available to support algal growth in Lake Erie. The Detroit treatment plant, like a number of others in major metropolitan areas, receives large amounts of industrial wastes which contain appreciable quantities of iron. Therefore it is possible that most of the phosphorus currently discharged from the plant is not in a form that is available to support algal growth. Therefore, further reduction in the effluent P concentration may have little or no impact on eutrophication-related water quality in Lake Erie. It is conceivable for treatment plants that are hydraulically overloaded and have excess P in their effluents, that the addition of alum to the effluent could be a short-term, cost-effective way of reducing the available P content of the effluent. The P would be tied up in the aluminum hydrous oxide floc, and would be incorporated into the sediments as the floc settles in the receiving waters. This approach represents a modified version of direct lake treatment with alum or iron for phosphorus control. Recent work by the authors has shown significant potential for the use of water treatment plant alum sludge as a means of removing P from wastewaters and aquatic systems. If further work substantiates these initial findings, this approach could significantly reduce the cost of P removal under certain situations.

Approach for Assessing Available P in Domestic Wastewaters

The approach for assessing available P in wastewaters must be different from that used to assess P availability in soils, river suspended sediments and urban drainage. The studies on the amounts of available P in domestic wastewater treatment plant effluents must involve long-term bioassays. Chemical extraction tests such as NaOH extraction will likely not be reliable in estimating availability of P in the effluents because such tests do not properly assess the availability of organic P. There is also some question about the algal availability of some forms of iron and aluminum phosphate present in domestic wastewater treatment plant effluents and in aquatic systems which are solubilized by NaOH. It should also be noted that U-tube culture systems which employ a membrane to separate the P source from the culture may also prove to be highly unreliable in estimating available P in domestic wastewater effluents because of bacterial and other growths on the membrane during long-term tests, which could interfere with the transfer of phosphorus from the leaching-mineralization part of the tube to the algal culture.

Some investigators have assumed that disappearance of soluble orthophosphate from an algal culture can be directly equated with algal uptake of phosphorus and, therefore, its availability to support algal growth. There are situations where this assumption is erroneous. The only proper way to assess availability is to measure growth (the increase in biomass). What may appear to be uptake of soluble ortho-P may actually be precipitation of phosphorus with calcium, iron or aluminum species. Further, P could be sorbed onto detrital organic remains of algae and/or bacteria, and yet be counted as “available” P. There is a substantial marine literature which shows that P tends to strongly sorb onto organic aggregates arising from the polymerization of apparently dissolved, most probably colloidal organic and inorganic molecules present in aqueous systems. Further, as discussed in the section of this chapter devoted to condensed phosphates and their ability to support algal growth, there are biochemical transformations of phosphorus compounds which produce soluble forms not measured by the molybdate test without acid hydrolysis, and which are not immediately available to support algal growth. The long-term availability of these compounds needs to be determined.

All investigators should be extremely cautious about trying to short-cut bioassays involving measurement of algal growth as a measure of phosphorus availability. This is especially true for domestic wastewater effluents. It is emphasized that growth experiments should not be based on growth rates, but rather on actual biomass yield under established plateau conditions.

It is evident from the above discussion that a considerable research effort should be undertaken on the amounts of P in domestic wastewater treatment plant effluents that are or can become available to support algal growth in aquatic systems. Although it probably is appropriate to assume that chemical precipitation techniques removing P to 1 mg/L levels in domestic wastewater treatment plant effluents are cost-effective in removing available P, the efficacy of P removal to less than 1 mg/L in the effluents should be based on the amounts of algal-available P being removed, which has not yet been defined. As with other sources of phosphorus, consideration must be given not only to P availability in the effluents, but the availability of P over extended periods of time under the conditions that will prevail in the receiving waters. Particular attention must be given to the iron-phosphate systems because reducing conditions such as occur in anoxic hypolimnia tend to promote the release of iron-bound P from sediments. It should be noted, however, that even under extended periods of anoxia, appreciable quantities of P in sediment are not released to overlying waters under conditions that would promote release. Therefore, even particulate iron hydrous oxide phosphate that enters an anoxic hypolimnion would likely only partially become available to support algal growth. Small amounts of money spent on research in defining algal available P in domestic wastewater treatment plants and in receiving waters could save large amounts of money in the control of P from domestic wastewater.

Studies on the availability of P in domestic wastewater treatment plant effluents must be conducted to include a substantial number of samples collected over an annual cycle from several different types of treatment processes, such as iron or alum addition to the primary settling tank, iron or alum addition to the activated sludge system and the tertiary use of iron, alum or lime in the secondary settling tank or final sedimentation tank. It is possible that significant seasonal differences in algal availability of P will be found among treatment plants using the same removal processes, as well as among different processes. A few grab samples from a limited number of treatment plants could readily result in development of information not representative of the typical situation.

Condensed Phosphate

Today detergent phosphate represents about 20-35% of the total P concentration in domestic wastewaters in areas where no detergent P limitations are in effect. Detergent P is typically in the form of pyro- and tripolyphosphates (condensed phosphates). It is generally believed that these forms of phosphorus are readily available to support algal growth, based on the supposition that there is rapid and complete hydrolysis of the condensed phosphate to soluble orthophosphate during secondary wastewater treatment. While hydrolysis appears to be rapid during conventional secondary treatment, examination of the literature raises questions about the extent of this hydrolysis to soluble orthophosphate. In a study of hydrolysis of condensed phosphates in algal culture systems [49], it was found that the bacteria present in the algal culture and/or extracellular phosphatases excreted by the algae caused a rapid hydrolysis of pyro- and tripolyphosphate. However, this hydrolysis did not result in the formation of soluble orthophosphate, or in the same number of algal cells as found in standard cultures containing equivalent amounts of soluble orthophosphate. Typically, for the same phosphorus concentration, condensed phosphate produced about half as many cells as soluble orthophosphate. Based on the studies by Cowen and Lee [49], it appears that as part of the enzymatic hydrolysis of the condensed phosphate, part of the P is converted to a form which is not measured in the standard molybdate test for soluble orthophosphate, and which is also not available to support algal growth in the several-week incubation period used in these tests. It is not known at this time whether extended periods of incubation would cause conversion of this unidentified form of P to soluble orthophosphate available to support algal growth. Obviously, this is an area that needs attention to evaluate the significance of phosphorus used as a builder in detergents, in stimulating algal growth in the aquatic environment. It is possible that up to 50% of the P present in detergents in the form of condensed phosphates may be converted to forms not available to algae as part of enzymatic hydrolysis.

OTHER FACTORS THAT NEED CONSIDERATION

The review of the literature in an earlier section showed that the amount of algal available phosphorus in a sample of Great Lakes tributary water can be estimated by using the sum of the soluble orthophosphate concentration and about 0.2 times the particulate phosphorus content. It was further shown that for many systems, the anion exchange resin-extractable P and hydroxide-extractable P provide reasonable estimates of the amount of phosphorus that will become available to support alga] growth in about a two- to three-week culture period. There are several important limitations and factors that must be considered in the use of this information on the development of a phosphorus management strategy for a waterbody. Some of these factors are discussed in this section of this paper.

Organic Phosphorus Sources

The studies that have been conducted thus far on algal available phosphorus have considered predominantly inorganic systems or were conducted for sufficiently short periods of time so as to preclude the mineralization of organic P to orthophosphate. There are some situations in which particulate or soluble organic phosphorus represents significant parts of the total P content of an aquatic system. In these types of systems, the hydroxide extraction or anion exchange procedures for estimating available P are not reliable and should not be used. Further, the standard algal assay procedures only assess the amount of organic P that becomes available during the course of the bioassay test, typically 2-3 weeks. It is likely that the rates of mineralization of most organic phosphorus compounds will be such that a much longer incubation period would be needed to assess their long-range availability.

As noted previously, this situation could be of particular significance in agronomic practices in that in shifting from normal to minimum to no-till farming practices, the availability of P in the particulates derived from the land may be drastically altered. Under normal tillage practices, it is expected that 10-30% of the P associated with the erosional particulate matter would become available to support algal growth. Under no-till conditions, where erosion is minimal, the character of the particulate matter will be substantially different from that of normal tillage; it will be predominantly organic, rather than inorganic in nature. The availability of P from the organic particulate matter from no-till systems is unknown at this time. It is possible that, although switching to a no-till method of farming would reduce erosion, it might increase the overall net flux of available phosphorus from a unit area of land. This is an area that needs immediate attention in order to develop meaningful, cost-effective programs for the control of phosphorus from agricultural sources.

Another farming practice which has been shown to result in a particularly significant increase in the amount of P derived from agricultural lands is the spreading of manure on frozen soil. In some years when the spring thaw occurs while the soil is still frozen, the P associated with the manure is carried to a nearby watercourse, rather than being incorporated into the soil. Further discussion of the significance of manure spread on frozen land as a cause of water quality deterioration has been presented by Sonzogni and Lee [50].

Other nonpoint sources of P which have been found to have large amounts of organic phosphorus present are wetlands and marshes. Lee, *et al.* [51] found that marsh drainage from several Wisconsin marshes contained relatively large amounts of apparently soluble organic phosphorus compounds. Those investigators did not, however, determine the rate at which these compounds would be converted to orthophosphate through mineralization processes. Wetlands would also be expected to contribute large amounts of particulate organic phosphorus to downstream waterbodies. In the upper Midwest during the late winter-early spring high flow periods, the organic phosphorus present in detrital plant remains is transported from marshes to nearby watercourses [51]. Lee, *et al.* [51] and Jones and Lee [52] reported that over the annual cycle the amount of phosphorus entering many wetlands is expected to be approximately equal to the amount transported from the wetlands during high flow. As Jones and Lee [52] pointed out, although total P_{in} may equal total P_{out} for many wetlands, the presence of wetlands could have a significant impact on the algal availability of phosphorus from various sources. This is of importance with respect to not only conventional wetlands systems, but also those used for treatment of domestic wastewaters. With increasing attention being given to this method of wastewater disposal, it is important that the efficacy of such systems be judged in terms of their ability to remove algal available P over the annual cycle.

From a Great Lakes phosphorus management strategy point of view, the effect of wetlands in changing the forms of P that enter the Great Lakes is likely to be small because of the relatively small amount of wetland area in the Great lakes watershed. The above-mentioned phenomenon could, however, be important in localized areas of the Great Lakes or for other lakes. There is need to determine both short-term and longer-term availability of phosphorus present in wetland drainage. With this type of information, it would be possible to assess the significance of wetlands in affecting the phosphorus management strategy for a waterbody.

Mineralization of Phosphorus

In assessing the longer-term availability of phosphorus, consideration must be given to the regeneration or mineralization of the phosphorus present in algal cells. There is considerable controversy in the literature about the extent to which algae are degraded. From their studies on axenic algal cultures, they determined that bacteria and microfauna increase the rate and extent of aerobic algal decomposition. Mixtures of autotrophic and heterotrophic organisms had a refractory portion of 12-86% that was not degraded within a year under aerobic conditions. Older cultures exhibited a narrower range of 30-70%, while the mean of 75 different cultures was 40% refractory material.

Force, *et al.* [54] studied nutrient regeneration of algae in laboratory tests. According to them, the two major factors controlling this regeneration are: (1) the extent of organic decomposition; and (2) the initial nutrient content of the algal cells. With respect to the latter, Force, *et al.* pointed out that in algae which have taken up ‘luxury” phosphorus, the extra P is loosely bound in the cells and is therefore more readily released than P more tightly bound within the cell. They suggested that the critical initial P content of algae, above which excess P regeneration occurs, is about 03% by weight. They concluded that after 0.5-1 year of decomposition under aerobic conditions, an average of 50% (range of 0-94%) of the initial P remained refractory (undecomposed), whereas under anaerobic conditions 40% of the P remained refractory. According to Force, *et al.*, this difference between aerobic and anaerobic regeneration is not significant. Two additional comments were made concerning these results. First, regeneration values determined in that study related to the maximum rate of decomposition, and second, other means of essentially permanently removing regenerated or other phosphate from the water (e.g., precipitation, sorption) were not considered. It is likely, therefore, that Force, *et al.*’s estimate of the amount of P regeneration from algae is an overestimate of what would actually be expected to be available in the environment. The results of their studies were consistent with the conclusions of the American Water Works Association Committee [55] review, that 30-70% of algae and associated organics are readily degraded. The remainder is resistant to degradation, being consumed at a rate of a few percent per year.

Golterman [5] concluded that the phosphate not returned from algae into the biochemical cycle was about 1-5% per cycle through algae. He pointed out, however, that this could represent a significant amount over a 200-day growing season. With growth cycles of 5-10 days, this could represent a loss (i.e., phosphate made unavailable) of 20-100% of the phosphate taken up. The product formed in this P-cycle is detrital phosphorus which is resistant to bacterial attack.

DePinto and Verhoff [56] investigated nutrient regeneration from algal cultures by growing axenic cultures of *Chorella* and *Selenastrum* for about seven days, then placing them in the dark, inoculating some with bacteria. They indicated that the rate and extent of algal regeneration was dependent on initial concentrations of available P as well as the amount of bacteria present. For initial concentrations of 186 μg P/L in the assay medium, soluble ortho-P regeneration in the dark ranged from about 80 to 95% over 1-2 months. For initial concentrations of 80 μg P/L, regeneration of soluble ortho-P in the dark was about 30-50%. Assuming that there is a real dependence of regeneration on the initial concentration, the upper ranges of percent regeneration found by DePinto and Verhoff would not be expected in the field because very few P-limited waterbodies would be expected to contain 0.2 mg/L available P during the summer when temperatures are at the levels evaluated by DePinto and Verhoff. Because of their experimental design, it would therefore be expected that their estimates of regeneration would be high. Their regeneration estimates also represent a one growth cycle regeneration; it may be expected that each time the regenerated phosphorus is reused, 50-70% of it will become refractory. The amount of regeneration found by DePinto and Verhoff is similar to that found by Jewel and McCarty [53] and Force, *et al.* [54] for regeneration over a year's time. Their rate data, however, would not be expected to be applicable to natural water systems because of the nature of their experimental design. One of the common problems encountered by investigators in this area is designing a test system which can properly simulate natural water conditions.

While the range of values for the unmineralizable P fraction of dead algae found in the literature is wide, it appears that on the order of half of the P content of dead algal cells remains unavailable. The amount of mineralization of algal P to available P depends to a large extent on the specific physical, chemical and biological characteristics of the area of concern. These results have important implications in the development of a P management strategy. For example, the development of refractory organic compounds is an important mechanism in some river systems by which P is converted from available to unavailable forms. The same situation exists within arms or bays of waterbodies.

Other Forms of Phosphorus

There are a number of commercially used organic P compounds which may potentially stimulate algal growth in receiving waters. These compounds include P-C, P-O-C, and P-O-P ring and chain bonded materials, such as those used in treatment of cooling waters for industrial cooling towers. Some of these compounds would likely enter aquatic systems as blow-down to storm or municipal sewers. Generally, the polymeric inorganic compounds are hydrolyzed in aquatic systems. While some of the organic P compounds are resistant to hydrolysis, they would be expected to eventually hydrolyze at least in part to soluble orthophosphate. It is possible that these compounds would show a phenomenon similar to that found by Clesceri and Lee [49] for condensed phosphate of only partially hydrolyzing to soluble orthophosphate. While the authors are not aware of the amount of these compounds used, they speculate that this use is small, compared to the total P load to the Great Lakes and therefore represents an insignificant factor in developing a P management strategy for the Great Lakes. While likely unimportant in the Great Lakes system, P used in cooling towers, as well as in industrial processes, could be significant in influencing water quality in other waterbodies. This would have to be investigated on a case-by-case basis for each particular waterbody. When it appears that the total P load from these sources is potentially important, then studies should be done to ascertain what part of that total P load enters the waterbody in a form available to support algal growth.

IN-LAKE AVAILABILITY AND LOAD-RESPONSE MODELING

Thus far, this discussion has focused on the availability of P in samples of water or particulate matter from various sources, such as agricultural runoff, domestic wastewaters, etc. Also, consideration has been given to the availability of P in samples of river water obtained at the lake-tributary interface. What is needed, however, is an assessment of the amount of P contributed to the lake or waterbody of concern which is available to support algal growth within the body of water. Numerous investigators, such as Cowen and Lee [8], have pointed out that what may be available to an algal culture in a sample of water from a particular source over a two-week incubation period will not likely be the same as what becomes available in the lake. There is a wide variety of physical, chemical, and biological processes which influence the algal availability of P in aquatic systems. Unfortunately, in the early 1970s the U.S. EPA and other agencies greatly curtailed funding for research on the aqueous environmental chemistry of phosphorus. We know very little more about the actual behavior of P in aquatic systems than was known in the 1960s when funds were available. It is certainly likely that the attempts to simulate environmental systems in laboratory beakers or jugs, for such purposes as measuring the rate and extent of mineralization of organic forms of P, the slow release of P from apatite species, and similar kinds of reactions, are likely to have limited applicability to real world situations. For example, it is generally stated in the literature that apatite phosphorus is not available to support algal growth. This statement is typically based on relatively short-term (i.e., a week or two) laboratory experiments. However, longer-term experiments such as those of Gerhold and Thompson [57] have shown that P in at least some forms of apatite is available to support algal growth. This is confirmed by the work of Golterman [5] and Golterman, *et al.* [4].

This raises an interesting question concerning the erosion of Lake Erie and Lake Ontario bluffs. It is generally stated that this erosion does not contribute to the fertilization of these lakes [6]. However, examination of the results of algal culture experiments [6] on the erosional material derived from the bluff erosional material where the predominant form of P is apatite shows that these erosional materials are not available to support algal growth. When one considers the total amount of erosion that takes place (estimated to contribute 40% of the total P load to Lake Erie), and the fact that the previously conducted growth experiments [6] only incorporated a few weeks of incubation, there could be appreciable algal growth in these lakes resulting from bluff erosional material where the predominant form of P is apatite. To determine the actual significance of apatite erosion from Lake Erie bluffs or other sources, a much better understanding of the behavior of apatite P in the lake system of concern must be achieved. The same is true of P from other sources, such as erosional material from land runoff, particulate P in wastewater effluents or atmospheric dustfall.

Because it is unlikely that funding will become available to provide the types of information needed, it is reasonable to ask whether a P management strategy can be developed based on available P inputs. There are those who advocate that because of the many unknowns about the behavior of P in aquatic systems, the only appropriate approach is to base a P management strategy on the total phosphorus input, without any attempt to assess what part of the total will be unavailable. This is essentially the policy which has been followed until now. However, in the future such an approach could be tremendously wasteful of the financial resources available for pollution control with little actual improvement in eutrophication-related water quality in the lakes. Therefore, there is substantial agreement that P management strategies should be based on the best information available on the amounts and sources of available forms of P that enter the lakes.

Development of P Management Strategies

The first step in the development of a P management strategy is to determine the amounts of P derived from each principal source. Next, assuming that all P from each source is 100% available, an estimation must be made of the potential improvement in water quality that will result from controlling each source to the extent possible. The estimate should be based on the OECD eutrophication modeling approach described below. If it appears that the controllable P from a given source will have a significant impact on water quality, then consideration should be given to the amount of total P from that source likely to become available to support algal growth. It may be possible to use some of the generalized relationships discussed earlier in this paper (such as 20% of the particulate P from diffuse sources being available for algal growth). It may be necessary, however, to conduct laboratory and field studies to evaluate for the particular aquatic system in question, the amount of algal available P contributed from each potentially significant source. It has been recommended that there is a need to standardize bioassay procedures being used to assess the availability of P. Such an approach, however, will not necessarily improve the quality of the data generated. While general guidelines on how to conduct such a test should be formulated, a “cook book” approach which provides step-by-step instructions should be avoided. All bioassays conducted to assess P availability must be tailored to some extent to fit the particular system under investigation. All users of such bioassays must be thoroughly familiar with their appropriate use and limitations.

Standardization of methods and approaches has carried through to the design of treatment plants for P and other contaminant removal. The approach typically used today in the design of wastewater treatment works and the development of control programs for diffuse sources is based on what is readily achievable in conventional treatment (i.e., 90% removal of some contaminants from domestic wastewaters), rather than the characteristics of the receiving waters. However, in the l980s, in the U.S., waste load allocation under the provisions of best available treatment (BAT) will require that contaminant control programs be based on the characteristics of. the receiving waters. This approach requires a case-by-case evaluation of the costs and water quality benefits that will be derived from a particular control program. Much greater emphasis will have to be placed on field and laboratory studies designed to measure the impact of a contaminant from a particular source on receiving water quality. Because of the fact that many contaminants such as P exist in unavailable form in sources and aquatic systems, the heart of the field evaluation program will have to be devoted to defining the part of the contaminant load that is available to affect water quality in the waterbody in question. As discussed earlier for P removal in wastewater treatment plants to 0.5 mg P/L in the effluent, the expenditure of funds for defining, quantifying and assessing the significance of available forms of contaminants could be highly cost-effective in helping to design contaminant control programs that minimize cost, yet provide maximum environmental protection.

The key to the above-mentioned process is the availability of a reliable load-response model that can predict for any given contaminant control program, the improvement in water quality that will arise from program implementation. The OECD eutrophication study provides a technically valid approach for assessing load-response relationships for P-based eutrophication control programs. The characteristics of this modeling approach and its ability to handle available forms of P are discussed below.

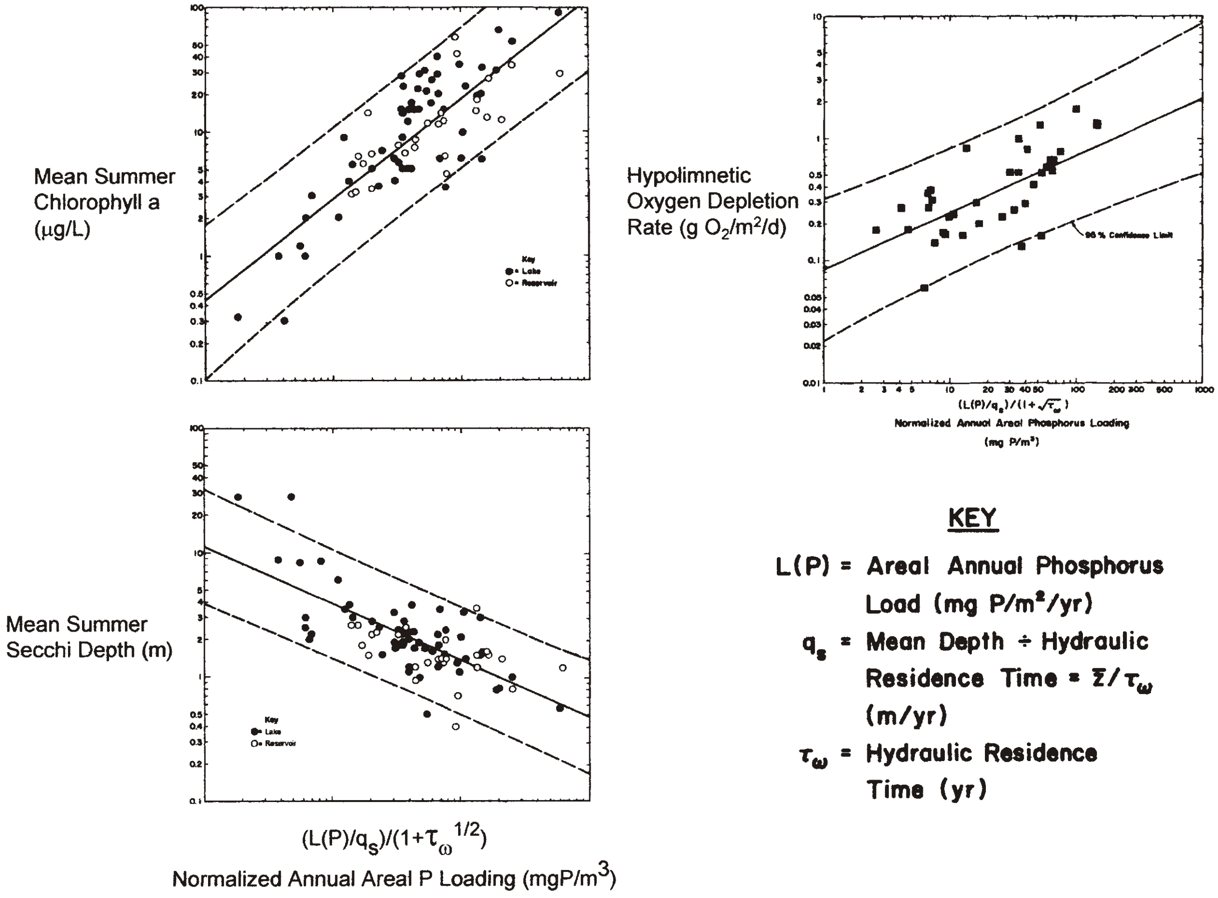
OECD Eutrophication Modeling Approach

The Organization for Economic Cooperation and Development (OECD) eutrophication program conducted an evaluation of P load-eutrophication response relationships for 200 waterbodies in 22 counties based on the work of Vollenweider [58,59,23]. The bulk of the results of the overall OECD eutrophication study has not yet been published, because the project was just being completed at the time of preparation of this paper. However, the results of the US. part of the study have been published [24]. Rast and Lee [24], using Vollenweider’s [58,59,23] framework and the data from the 40 U.S. OECD waterbodies, developed statistical relationships between P load to a waterbody, as normalized by mean depth and hydraulic residence time, and planktonic algal chlorophyll, Secchi depth (water clarity), and hypolimnetic oxygen depletion rate. The authors have had the opportunity to review the results of the total OECD eutrophication study and have found that the load-response relationships for the waterbodies outside the U.S. are essentially the same as those found by Rast and Lee [24] . Further, the authors of this paper have, subsequent to the completion of the U.S. OECD studies, studied approximately 60 waterbodies principally located in the U.S. and including all of the Great Lakes, and found that they fit the same P load-eutrophication response relationships. Thus, there are over 300 waterbodies across the world that fit the P load-eutrophication response relationships developed by Vollenweider [58,59] and Rast and Lee [24].

It is now possible to predict for waterbodies in which the maximum planktonic algal growth is limited by phosphorus, the mean and the maximum [60] planktonic algal chlorophyll, Secchi depth due to phytoplankton light scattering, hypolimnetic oxygen depletion rate and overall fish yield [6], based on mean depth, hydraulic residence time and P load. Figure 1 presents a summary of the relationships developed by Rast and Lee [24] based on the U.S. OECD waterbodies. It should be noted that although the Vollenweider-OECD relationships arc based on total P load, they implicitly consider the available P load. This is because many of the waterbodies included within the OECD study have about the same ratio of point to non-point source P loads. Waterbodies with high percentages of domestic wastewater point source P loads tend to become limited by nitrogen or some other factor, and therefore would not be expected to fit the Vollenweider-OECD load-response relationships. In essence, it appears that there is a relatively constant error relating total P load to available P load for many of the U.S. OECD waterbodies. The remarkable insensitivity of lakes' eutrophication responses to small changes in P loads, such as would be associated with considering total P load vs. available P load for a particular waterbody, effectively overshadows the significance of this error in formulating load-response relationships for a waterbody. Although water quality is generally insensitive to minor changes in P load (such as reducing domestic wastewater treatment plant effluents to 0.5 mg P/L in the Great Lakes basin), such changes may be very expensive to achieve.

In an effort to assess whether the availability of the P load to a waterbody is accounted for in the OECD modeling approach, or causes a bias in the position of a waterbody in the P load-response relationships, the U.S. OECD waterbody data sets and relationships were reexamined. Those waterbodies (or portions thereof) to which the point source total P load (mostly readily available to algae) was less than 50% of the total load (56% of the 45 points) were identified on the U.S. OECD normalized P load-chlorophyll diagram (Figure 1) to determine if they were positioned differently, as a group, from the whole set of OECD waterbodies. It was found that there was no discernible demarcation between the two sets of' data points. Those waterbodies with less than 50% of their P loads from point sources were essentially equally distributed among those waterbodies having greater than 50% of their P loads in readily available forms. This is an indication that the Vollenweider OECD modeling approach handles implicitly in its normalization components, the availability of P load to waterbodies.

Rast and Lee [24] and Lee, *et al.* [4] indicated that altering the P load to a waterbody should result in the load-response point for the given waterbody moving parallel to the U.S. OECD lines of best fit shown in Figure 1. Actually this is in error to the extent that the ratio of available P to unavailable P in the P load being removed from the waterbody deviates from the average ratio for the waterbodies from which the regression lines were derived. If the P control program is directed primarily toward diffuse sources, in which most of the P is in an unavailable form, then it would be expected that there would be less improvement in water quality per unit P removed than would be predicted based on the U.S. OECD lines of best fit. The converse would be true for those control programs directed toward the available forms of phosphorus.



KEY

L(P) = Areal Annual Phosphorus Load (mg P/m^2/yr)

q_s = Mean Depth ÷ Hydraulic Residence Time = $\bar{z}/\tau_\omega$ (m/yr)

τ_ω = Hydraulic Residence Time (yr)

Figure 1. U.S. OECD data applied to phosphorus load, mean chlorophyll *a*, mean Secchi depth, and hypolimnetic oxygen depletion rate relationships [4].

In addition to providing an important engineering tool upon which to develop eutrophication control programs for lakes, impoundments and estuaries, these studies have provided valuable insights into the behavior of various forms of P in waterbodies. First and foremost, it is clear from these and other studies, such as Lee, *et al.* [16], that the sediments of waterbodies are very important sinks for P. This is supported by the P residence time studies of Vollenweider [62] and Sonzogni, *et a1.* [63]. Many waterbodies have been found to have P residence times of a year or less. This means that the P which enters the waterbody each year is either deposited into the sediments or is carried out of the waterbody in its outflow. Although there is release of P from sediments during certain times of the year, which can have near-term effects on water quality, the driving force for eutrophication of many waterbodies is the external P load. Therefore, the long-term, slow release of P from sediments is apparently insignificant in determining overall trophic state for many waterbodies. It is concluded by the authors that available P incubation studies which incorporated incubation periods of a few weeks to a month or so are probably adequate to describe the potentially significant amounts of available P entering waterbodies. It is important to note that the rates of P becoming available in the field vs. laboratory are likely to be markedly different. Also, the P concentrations in the water will likely affect the extent to which P becomes available from particulate forms. Ultra-low P levels in a laboratory study system would tend to cause P to become available which would normally never become available in an actual waterbody. This situation again points to the importance of gaining a much better understanding of P cycling within lakes in order to understand the extent to which particulate P becomes available to support algal growth within the waterbody.

The OECD eutrophication studies have demonstrated that the approach of Miller, *et al.* [64] of using results of algal assays for available forms of P in a particular sample is invalid to estimate the benefits that would be derived by controlling the available P load to a waterbody. One cannot use, contrary to what was implied by Miller, *et al.*, a direct ratio of available load to response for estimating benefits (i.e., a 10% reduction in available load will not necessarily result in a 10% reduction in algal biomass). Consideration must be given not only to the P load, but also the mean depth and hydraulic residence time of the waterbody, and to the fact that the load-response correlation from the OECD studies is a log-log relationship.

Techniques such as measurement of phosphatases, acetylene reduction, etc., developed by Fitzgerald [65,66], provide useful information for assessing the amount of available P in a particular sample. These techniques have application to determining whether the algae present in a sample have been grown under a P-limited or surplus condition. They have little or no applicability, however, to determining the amount of available P in a particular sample.

Other Considerations

Studies on the aqueous environmental chemistry of P must focus attention on nearshore waters, since it is in this region that the greatest uptake and release from particulate matter will occur. Work in this region of a waterbody is especially difficult because of the lack of understanding of the hydrodynamics of these regions, which affects the mixing of nearshore and offshore waters, and the mixing of tributary and nearshore waters, as well as the sedimentation dynamics of particles. The hydrodynamic information coupled with appropriately designed laboratory bioassay tests will provide the kinds of information needed to determine how much of the P load to a waterbody will become available to support algal growth.

In conducting in-lake studies of P availability, particular attention must be given to the role of hydrous iron oxides in controlling P availability. The studies of Jones and Lee [46] showed that hydrous iron oxide plays a dominant role in controlling the amount of algal-available P released from waterway sediments. Failure of U.S. pollution control agencies in the Great Lakes to understand the role of hydrous iron oxides in controlling the release of contaminants from sediments and the use of bulk sediment criteria has resulted in expenditures of over $200,000,000 by the American public for alternative, more expensive methods of dredged sediment disposal involving on-land, rather than open water disposal. As discussed by Jones and Lee [46], the so-called confined disposal could be more detrimental to Great Lakes water quality than the previously used, less expensive open water disposal techniques. Similarly, Plumb and Lee [67] and Lee [45] have demonstrated through the use of algal assays that the approximately 50,000 tons of taconite tailings discharged daily to Lake Superior by the Reserve Mining Company did not represent a source of available P to the lake as a result of the formation of hydrous iron oxide on the surface of the tailings particles, which sorbed any P release from the tailings and made the P unavailable to support algal growth under the toxic conditions that prevail in Lake Superior.

The dynamic modeling approach for estimating load-response relationships attempts to describe the hydrodynamics and aquatic chemistry of phosphorus with particular emphasis on tracking the soluble orthophosphate-available P within aquatic systems. One of the reasons why the dynamic modeling approach has limited predictive capabilities is the fact that the sedimentation and sediment/water exchange processes are not properly modeled. Such modeling is not likely to be accomplished until appropriate studies have been conducted on the behavior of P in aquatic systems. The dynamic models, in considering the availability of the various forms of phosphorus, do not properly reflect the natural water system. There is no justification for claiming that the dynamic modeling approach is a more valid approach for estimating nutrient load-eutrophication response relationships than the statistical approach developed by Vollenweider. Evidence points to the opposite conclusion.

CONCLUSIONS AND RECOMMENDATIONS

Phosphorus management strategies for the Great Lakes and other waterbodies should be based on the control of the algal available P load to the waterbody, rather than the total P load. The available forms of phosphorus from a particular source should be determined by algal bioassays in which the increase in algal biomass is measured. Other bioassay or chemical extraction techniques should only be used after they have been verified for the particular source in question by comparison to the results of concurrently run algal bioassays. It appears that NaOH extractable and anion exchangeable phosphorus correlate fairly well with bioassay-available P for urban drainage and for phosphorus derived from normal tillage agricultural runoff. Neither of these two techniques as normally used would properly assess the availability of organically bound phosphorus. There is a need for P availability studies on domestic wastewater treatment plant effluents, atmospheric dust-fall and precipitation, high organic P sources, such as no-till or minimum-till farming, and wetland drainage.

Research needs to be conducted on the aqueous environmental chemistry of phosphorus in rivers and in lakes with particular reference to defining the amounts of phosphorus that remain or become available within the system, or are converted to unavailable forms. This research should be specifically focused on obtaining information needed for development of phosphorus management strategies. At this time, it is recommended that the available P load from urban stormwater drainage and normal-tillage agricultural runoff that enters the lake directly, or has a limited distance of tributary travel between source and lake, be estimated based on the relationship:

available P = soluble ortho P + 0.2 (particulate P)

Before a P management plan which includes a reduction in the P from domestic wastewater treatment plant effluents below 1 mg P/L is implemented, definitive research must be done to evaluate the amount of available P removed by the treatment proposed. Also, before implementation of minimum or no-till farming for the purpose of controlling P input to a waterbody, studies should be conducted to define the relative amounts of available P derived from normal tillage vs. other farming practices.

Also, studies should be conducted on the amount of condensed P present in domestic wastewater treatment plant influents and in combined sewer overflow, which becomes available to support algal growth in the treatment plant and in the Great Lakes.

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