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TREATMENT OF INFLOW AS A
LAKE MANAGEMENT TECHNIQUE
FOR PHOSPHORUS CONTROL

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ABSTRACT

The reduction of phosphorus loadings to lakes has been a major focus of many lake restoration/protection strategies for eutrophication control. Treatment of inflowing waters has been suggested as a possible alternative to other phosphorus control programs, particularly the application of extensive land management practices in the drainage basin.

Treatment of inflow was subdivided into two approaches for this report: treatment of impounded inflow and treatment of flowing water by a fixed system. A literature review was made of both types with data on their overall effectiveness for removing phosphorus. In addition, a separate laboratory evaluation was conducted on two techniques using the affinity of aluminum-hydroxide flocculent for dissolved inorganic phosphorus (DIP) by various adsorption/precipitation reactions. Both techniques were shown to remove DIP, but with serious drawbacks.

In general, the most effective treatment of inflow systems are sedimentation basins and wetlands. Sedimentation basins, if properly designed and maintained, should remove 30-50% of the phosphorus from runoff (through particulate settling) with moderately high sediment concentrations. The retention of phosphorus in wetlands is often a function of their hydrology. Spring flushing can often cause low annual DIP retentions even though summer DIP retentions are higher; annual particulate phosphorus retentions can be quite high given that the wetland is not short-circuited by large, defined drainage channels. A combined sedimentation basin/wetland system is recommended in certain situations as an effective system for removing phosphorus from inflowing waters to lakes. Annual phosphorus removal efficiencies should be well over 50%. Other types of fixed bed systems are generally not recommended as a treatment strategy unless the need for phosphorus control can justify their expense and operation costs.

INTRODUCTION

Phosphorus has generally been identified as the major plant nutrient stimulating lake eutrophication (Hutchinson 1957; Vollenweider 1968). Uttormark and Hutchins (1978) summarized lake restoration strategies for phosphorus control in a manner consistent with input/output lake modeling of phosphorus dynamics:

$$\begin{array}{rcccccc} \text{change in lake} & & \text{external} & & \text{net} & & \\ \text{trophic state} & = & \text{phosphorus} & + & \text{internal} & - & \text{outflow} \\ \text{(phosphorus mass)} & & \text{loading} & \underline{\quad} & \text{recycling} & & \text{phosphorus} \end{array}$$

Five techniques to reduce nutrient inflow (external phosphorus loading) were listed: wastewater treatment, wastewater/stormwater diversion, land management practices, product modification (e.g. detergents), and treatment of inflow. The first four management techniques have been applied in many situations in past years and are straightforward. Wastewater treatment and diversion and the elimination of high phosphate detergents have proved effective in some cases for the reduction in point source phosphorus loadings.

In many lake watersheds, point source pollution has not been a problem or has been corrected such that nonpoint sources of phosphorus are the overriding problem. Recently, the U.S. Environmental Protection Agency (EPA) has funded many projects to identify nonpoint sources of pollution from agricultural and urban areas. Plans were developed to improve land management practices and, hence, reduce nonpoint pollution. However, the diffuse nature of this type of phosphorus input to lakes and the socioeconomic difficulties of instituting land management practices on a large scale have negated some of the more impressive loading reductions resulting from point source control. Also, land management practices have not been adequately developed or designed to handle runoff from large storm events when nutrient loadings to lakes are particularly excessive. As a result, loadings accumulated from years of effective control of "normal" events can literally be washed downstream during infrequent floods.

In cases where land management practices to control nonpoint pollution are ineffective or too costly, treatment of inflow might be beneficial. Treatment of inflow might also have applications when reservoirs or impoundments are created on fertile streams that have high baseflow phosphorus concentrations which can sustain in-lake nutrients when lake water flushing rates are high. Treatment might also be applied to upstream lake outlet discharges to reduce downstream lake inputs of phosphorus. Dunst et. al. (1974) originally indicated treatment of inflow was an experimental phosphorus loading reduction technique meriting further development.

Engineering designs for treatment of inflowing streams to lakes have been hampered by problems with handling relatively large and variable flows that have high loads of suspended solids and particulate nutrients, but more moderate concentrations of dissolved nutrients than point source effluents. Although discharges from upstream lakes normally do not have high suspended solids and associated particulate nutrients, washed out algae may contain the largest percentage of phosphorus (organic) during certain times of the year.

However, assurances must be made that the treatment of these large volumes of input waters to the receiving lake does not create problems such as altered pH or residual chemicals (Fe, Al, or other flocculents) in the treated water. Also, in certain cases, the link between upstream channel and lake must be left intact so as not to provide a barrier to aquatic organisms.

This report has three objectives that are discussed in separate sections. The first section is a literature review of techniques for removing phosphorus from flowing waters. Treatment strategies can be subdivided into two general approaches: treatment of impounded inflow or treatment of flowing water by a fixed system. The treatment of impounded inflow can be further subdivided into two categories: (1) the removal of phosphorus associated with suspended sediment as well as other particulate forms of phosphorus through physical settling; or (2) the removal of dissolved inorganic phosphorus (phosphate) by adsorption to flocculents formed by the addition of certain metal salts (Fe or Al). These two treatment methods for impounded inflow may be combined. Also, the treatment of impounded inflow may be a precursor to treatment by a fixed system, particularly where the removal of suspended solids is important.

The second part of this report is a separate laboratory evaluation conducted by the Wisconsin Department of Natural Resources, Water Resources Research Section. This study analyzed two techniques using the affinity of aluminum hydroxide for phosphate by various adsorption/ precipitation reactions. Data are provided for both the impounded water and fixed system treatment strategies discussed in the literature review.

The third section, based on results of other studies and data reviewed in the first two sections, evaluates the efficacy and application of treatment of inflow as a lake management technique for phosphorus control.

LITERATURE REVIEW OF TREATMENT TECHNIQUES

Sediment/Phosphorus Relationships

The simplest method for the removal of phosphorus from water with suspended sediment and other particulate matter is by the physical settling of the material in sedimentation basins or other structures for impounding water. Phosphorus adsorbs readily to certain types of sediment or may be incorporated in particulate organic matter. Consequently, techniques designed to reduce the amount of suspended material passing through a water course can also be applied to remove phosphorus.

The settling of sediment under quiescent conditions is described by Stoke's Law (Vanoni 1975). The settling velocity is a function of four variables: the diameter of the particle (value squared), the kinematic viscosity of the liquid, the specific weight of the sediment, and the specific weight of the liquid. Theoretical settling velocities for various diameter particulates of a uniform specific gravity are summarized in Table 1.

TABLE 1. Settling velocities for various spherical particle sizes under quiescent conditions--20C and specific gravity of 2.65*.

Sediment Class	Sand	Coarse Silt	Medium Silt	Fine Silt	Very Fine Silt	Coarse Clay
Size (microns)	62 ←→ 31	31 ←→ 16	16 ←→ 8	8 ←→ 4	4 ←→ 2	
Settling Velocity (m/hr)	12	3.1	.79	.19	.050	.012

*Computed from data in Vanoni (1975).

Settling velocities are increased at higher water temperatures but decreased by greater kinematic viscosities and liquid specific weights as a result of large amounts of sediment in suspension. Also, particulate organic matter may have significantly less specific gravities than inorganic material, thereby having slower settling velocities. Coagulants (such as used in sewage treatment plants), which effectively increase particle diameters, can greatly increase settling velocities as evidenced from Table 1.

Clay particles, due to their small size, have very slow settling velocities. In addition, electrostatic charges on clay surfaces prevent any settling within reasonable time periods. Clay particles range in size from 4 microns (upper limit of coarse clay) to 0.24 microns (lower limit of very fine clay), near the operational definition of dissolved (0.45 microns). Except for large reservoirs or other detention structures with long water residence times where clay particles are acted upon by other factors removing them from the water (such as zooplankton ingestion and agglomeration), clay will not generally be removed by sedimentation basins unless coagulants are used. Trap efficiencies are consequently biased toward larger-sized particles.

Phosphorus associations to various size particles are not easily simplified. Adsorption of phosphorus on clay surfaces is significant. Presence of clay surface charges, Al^{+3} ions on clay plate edges, and phosphate/silicate structural substitution can determine the amount of phosphorus associated with clay particles (Stumm and Morgan 1970). Data are variable, but certainly less phosphorus is associated with coarse grain inorganic materials (sand) than with clay per unit weight of material (Browman et al. 1975).

The amount of phosphorus associated with silt-size fractions can be similar to the amounts associated with clay, particularly during the initial flush and

high flow periods of storm events. When flow is dropping during the latter stages of a runoff event, most of the particulate phosphorus is associated with sediment particles with slow settling velocities.

Data on sediment and phosphorus losses from watersheds further reveal the need for site-specific data in order to evaluate the efficacy of sedimentation basins for phosphorus removal. Monk (1975), studying particulate nutrient losses from four watersheds in the southern Appalachians, determined that sediment eroded from coppice hardwood, old field, and pine plantation watersheds was approximately 75% sand, and 50% sand from the mature hardwood watershed. The rest of the material in all watersheds was more or less evenly divided between silt and clay-size fractions. Organic material, and inorganic material less than 2 microns, each represented about 10% of the watershed export of inorganic material greater than 2 microns. Particulate phosphorus losses were about 7-10 $\mu\text{g P/g}$ sediment for particles less than 2 mm in size. However, this represented less than 1% of the dissolved phosphorus fraction exported.

Extensive research as part of the International Biological Program study of Lake Wingra, near Madison, Wisconsin revealed numerous runoff phosphorus characteristics for two urban drainage basins (Browman et al. 1975). Dissolved inorganic phosphorus comprised more than 80% of the total dissolved phosphorus in runoff. On an annual basis, the dissolved inorganic phosphorus was about 45% of the total phosphorus exported by the storm sewers. Dissolved inorganic phosphorus concentrations were considerably higher in fall and spring, coinciding with leaf and fruit fall, respectively. Total loading was highest during late winter and early spring due to greater runoff resulting from snow melt and early spring rains.

Although Browman et al. (1975) emphasized the importance of dissolved inorganic phosphorus, particulate phosphorus was a significant source of phosphorus to Lake Wingra during periods of runoff. Suspended sediment or related particulates were suggested to continuously release inorganic phosphorus into surrounding waters even if initially deposited to the sediments, although iron surface-bound inorganic P as compared to apatite inorganic P would have a greater effect on the phosphorus status of the receiving lake. The actual settling characteristics of the particulate phosphorus (in runoff samples) indicated 35-50% of the phosphorus had settling velocities slower than 0.06 m/hour, which was similar to the theoretical upper limit clay settling velocity given in Table 1. Greater than 70% of the particulate phosphorus in the runoff had settling velocities slower than 0.6 m/hour, which corresponded to the medium silt/fine silt separation. The authors speculated that only about 25-33% of the particulate phosphorus, because of its settling characteristics and chemical form, would be potentially available for algae growth in the lake. However, the unused particulate phosphorus could represent a long-term input to the phosphorus budget of the lake.

Data collected for numerous urban and rural watersheds in Dane County, Wisconsin (Lathrop and Johnson 1979) supported the findings of the Lake Wingra study. Because of the large number of runoff water samples collected and the difficulty in filtering the water for dissolved phosphorus analyses, water was

taken from the top of the sample container after being allowed to settle overnight. The reactive phosphorus test was run on these surface aliquots which have an indication of the nonsettleable inorganic phosphorus in runoff. Total and reactive phosphorus tests were also run on a number of filtered samples which indicated that most of the dissolved fraction was inorganic.

A comparison was made between the dissolved reactive and "settled" reactive phosphorus tests on over 160 samples collected on the Dane County streams during both baseflow and runoff conditions, representing phosphorus concentrations from near analytical detection limits to over 2.00 mg/l. A good relationship existed between the two analyses ($R^2 = .95$) with the dissolved reactive concentration representing about 75% of the reactive concentration. On an annual basis for both the urban and rural watersheds, approximately one-half of the total phosphorus export from the watersheds was in a particulate form that could potentially settle in quiescent conditions.

Sedimentation Basins

The amount of sediments removed by sedimentation basins or small reservoirs has been studied extensively by investigators attempting to determine trap efficiency for various impoundment designs. In general, trap efficiency for sedimentation basins has been found to be higher when detention times are greater than 10 hours; resuspension is negligible if the sedimentation basin depth is greater than 1 m (Nawrocki 1978). However, a recent evaluation of the sediment trap efficiency of a small detention basin in southwestern Wisconsin (Trout Creek) indicated a poor retention of settled material as the receding stream eroded and resuspended the deposited material (Graczyk et al. 1982). For small reservoirs, to attain a trap efficiency of 80%, the water residence time was found to be 0.1 years (36 days); trap efficiency was only 40% for 0.01 years (3-4 days) residence time (Heinemann 1981). The data are again variable due to the conflict between designs for water storage detention (trap little sediment) vs. sediment trap efficiency (clean water downstream) needs.

A number of examples illustrating phosphorus removal efficiencies by sedimentation basins/impoundments in high flow situations are given below. Whereas data on sediment removal efficiencies have been collected for years, research has only recently been initiated to evaluate the potential of removing particulate pollutants from flowing waters by sedimentation basins. According to Whipple and Hunter (1981), the EPA has at least 13 ongoing studies to evaluate this question. In a few years much more data should be available.

Whipple and Hunter (1981), from preliminary data on four separate New Jersey urban runoff detention basins, found that 40-60% of the suspended solids were removed within 8 hours and 60-70% removed with 32 hours of detention in basins that were 6 ft deep. However, in the four basins only 15-55% and 25-65% of the phosphorus was removed with 8 and 32 hours of detention, respectively. They concluded that pollutants do not settle out in amounts proportional to their respective particulate concentrations.

Gill, et al. (1976) evaluated the efficiency of small agricultural reservoirs for phosphorus retention. In this study, sediment and phosphorus losses from watersheds were based on particle size and phosphorus analyses of the soil, but with amounts eroded estimated by the Universal Soil Loss Equation and delivery factors. Material trapped in the reservoirs was measured. Calculated retentions of organic phosphorus were low (20%-25% of eroded material), but the inorganic phosphorus retentions were much higher (30%-60%) with 2-5 times as much inorganic phosphorus initially available in the soil for transport. However, the authors concluded that reservoirs were more effective in retaining soil particles than soil phosphorus.

For five years, Brown et al. (1981) monitored the sediment and phosphorus removal efficiencies of a sedimentation pond receiving surface water runoff from irrigated land in Idaho. For the five years, annual removals varied from 65-76% and 25-33% for sediment and phosphorus, respectively. The average retention time of the pond was 2.7 hours. Phosphorus passing through the pond was either soluble or attached to soil particles too small for rapid settling. Sediment removal efficiencies were greater than 50% when inflow sediment concentrations exceeded 100 mg/l.

McCuen (1980) attempted to model the trap efficiency of a Maryland stormwater management basin for various water quality constituents. The model predicted that the median instantaneous outflow loading of orthophosphates from the basin (lb/sec) was 93% of the median instantaneous inflow loading. The median instantaneous total phosphorus loading was reduced by 99%. However, due to the relatively long stormwater detention time of the basin, modeled trap efficiencies for a wide range of storm return periods (frequency of occurrence) and storm durations were not as impressive. Orthophosphates had predicted trap efficiencies varying between 0.69 and 0.22 for a 2-year, 0.5-hour storm, and a 100-year, 6.0-hour storm, respectively. Predicted trap efficiencies were much poorer for total phosphorus, with efficiencies varying between 0.22 and 0.02 using the same storm return frequency and duration data. It would appear that the detention time for the 2-year, 0.5-hour storm should have been quite long with the basin acting as a small lake, thereby improving the trap efficiency. Data on the amount of suspended sediment in the storm events were insufficient for drawing further conclusions on the basin's ability to remove sediment-associated phosphorus.

In another study, two impoundments were built in urbanizing areas near Toronto, Canada (Brydges and Robinson 1980). Each lake had a sedimentation basin placed at the inflow. Table 2 summarizes the relevant study data. Lake Wabukayne and the sedimentation basin to Lake Aquataine each had relatively short water retention times of about 2 weeks; sediment removal efficiencies were low and phosphorus removal efficiencies were especially low. The Lake Aquataine removal efficiencies for both sediment and phosphorus were high, as the lake retention time was almost one year. However, the input sediment and nutrient concentrations were so low that very little coarse particulate associated phosphorus was present to settle out. It is likely that almost all the phosphorus was in a biologically available form and consequently used and retained in the lake system.

TABLE 2. Sediment and phosphorus retentions in two separate urban sedimentation basin-impoundment systems near Toronto, Canada.*

Characteristic	Lake Aquataine		Lake Wabukayne	
	Lake	Sed. Basin	Lake	Sed. Basin
Water Retention Time (days)	330	17	13	0.55
Avg. Annual Inflow Sediment Concentration (mg/l)	10-57		13-16	
Avg. Annual Inflow Phosphorus Concentration (mg/l)	.10-.20		.05-.09	
Sediment Reduction (%)	69-90	4-25	29-33	
Phosphorus Reduction (%)	78-81	0	0-27	

*From Brydges and Robinson (1980).

Chemical Addition

Chemical addition systems refer to the addition of flocculators such as lime, iron or aluminum salts, polyelectrolytes, or other agents for the removal of phosphorus. Clarification is achieved by settling or filtration.

In one innovative experiment in Maryland, chemical flocculents were added upstream of a sedimentation basin to decrease the amount of suspended sediment entering Lake Needwood (Young 1970). In theory, the basin trap efficiency was to be improved by flocculation of the finer silts and clay-size particles which normally passed through the basin and entered the lake. Although the basin's phosphorus removal efficiency was not studied, improved turbidity levels in the lake water would have also meant a significant reduction in the particulate phosphorus loading.

However, a follow-up to the Lake Needwood sediment flocculation project revealed unsatisfactory results (Anthony Janda, Maryland National Capital Park and Planning Comm., pers. comm. 1982). In 1979, the flocculating equipment was removed because the equipment had worked well only twice during the previous five years. Equipment failures, erratic distribution and need to occasionally stir the heavy viscous liquid flocculents while not being used

were major problems. At times when runoff was excessively large and the water residence time of the basin short, flocculent was not meant to be added, but in fact, large doses of flocculents actually entered the lake itself. In addition, the main problem of the system was that fine particles that had settled out in the forebay (sedimentation basin) were resuspended after every major storm event and carried into the lake. Although no data was ever collected, it was the opinion of the Maryland lake managers that after the flocculation was discontinued, the lake water turbidity improved. They felt that the sedimentation basin alone was effective at controlling sediment entering the lake.

Chemical addition systems have been used mainly for applying iron or aluminum salts which adsorb/precipitate dissolved inorganic phosphorus by forming insoluble hydrous iron or aluminum oxides, $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$. Iron has advantages over aluminum for this purpose, in that Fe^{+3} has a stronger affinity for phosphate and a stronger hydrolyzing power than Al^{+3} (Hsu 1976). Iron salts are also much cheaper than aluminum salts.

The use of iron and aluminum have been extensively applied for the removal of phosphorus in sewage treatment plants (U.S. EPA 1976). In more recent years, aluminum sulphate (alum) and sodium aluminate have been applied to lakes for the reduction of in-lake concentrations and/or the restriction of internal recycling of phosphorus from the lake sediments (Cooke and Kennedy 1980; Knauer and Garrison 1980; Narf 1982; Peterson et al. 1973). Iron has not been used extensively for lake treatments due to the dissolution of the flocculent in anaerobic situations; Fe^{+3} is converted to soluble Fe^{+2} under low redox environments, thereby liberating the adsorbed phosphorus.

Bjork (1974) reported the use of aluminum sulphate to reduce the phosphorus concentration in water returning to a Swedish lake (Lake Trumman) from dredge spoil settling ponds. Concentrations in the return water were reduced from 0.6 mg/l total phosphorus to 0.03 mg/l. The system consisted of an automatic dosage device adding alum to the return channel. The water was then mixed in a small pond by a compressed air hose, and the treated water then entered a sedimentation basin for floc settling. This technique proved effective because return water flows and phosphorus concentrations were relatively stable and therefore treatment designs were simplified.

One of the most ambitious and effective large-scale phosphorus inflow treatment programs has been the treatment of the Wahnbach River with iron salts before the river enters the Wahnbach Reservoir in West Germany (Bernhardt 1980; Bernhardt et al. 1971). This reservoir is an important regional public water supply. The eutrophication of the reservoir has exacerbated algal blooms such that water treatment became more difficult and expensive. It was felt that if the reservoir would revert to a more oligo/mesotrophic state, algal blooms would be less severe and water purification problems would decrease. A nutrient budget analysis for the reservoir revealed that 90% of the annual phosphorus loading (and water) came from the Wahnbach River, the main tributary input.

A treatment method was designed and tested by a pilot plant in the early 1970's, and then expanded to a full-scale treatment plant that began operating

in 1977. The treatment process included passing the river through a pre-reservoir that acted both as a sedimentation basin and a flow regulator for the treatment plant by providing a water storage reservoir for periods of high river discharge. Water was pumped from the pre-reservoir to the phosphorus elimination plant where treatment consisted of phosphorus precipitation and flocculation by the addition of 4-10 mg/l of ferric iron, agglomeration, and subsequent filtration through a 3-layer bed of active carbon, hydro anthracite, and quartz sand of various granulations and densities. The total bed filtration area was 1,100 m². The average river water inflow total phosphorus concentration of 100 µg/l (range 60-180 µg/l) was reduced to 4 µg/l. The treatment design was for a maximum flow of 5 m³/sec, but the long-term average flow was only 1 m³/sec. An effective treatment of up to 8 m³/sec of river discharge could be maintained for short periods because of the water storage capability of the pre-reservoir.

The river treatment has reduced the total phosphorus loading to the reservoir from all sources to the point where the Vollenweider (1976) model predicted the reservoir total phosphorus concentrations to be 10 µg/l, the theoretical separation between oligotrophy and mesotrophy. Actual reservoir water quality measurements (expressed as annual means) have showed dramatic improvements in just two years of treatment plant operation: total phosphorus decreased from 25 µg/l to less than 9 µg/l, chlorophyll a concentrations decreased from a range of 11-25 µg/l to 5 µg/l and Secchi transparency increased from 3-6 m. A shift in algal species of blue-greens to greens has resulted.

Wetlands

Wetlands have been proposed as an important natural filtration/purification system for phosphorus reduction. Wetlands, due to their ability to reduce runoff water velocity, are sometimes excellent filters of suspended sediment, given that the wetland system is not short-circuited by defined stream channels. Other factors such as size of the wetland relative to the drainage basin can also be important.

In recent years, much attention has focused on the use of wetlands for sewage effluent disposal sites (see numerous papers presented in the following research symposia and review articles: Brennan 1981; Tilton et al. 1976; Tourbier and Pierson 1976). Wide ranges in phosphorus removal efficiencies were reported with removal efficiency being inversely proportional to wetland areal phosphorus loading rate (Brennan 1981). Efficiencies varied between 20% and 95% for loading rates of 60 and 1.8 g P/m²/yr, respectively. Spangler et al. (1977) found ranges between 0% and 64%, with a common range of 35% for artificial and natural marsh systems in Wisconsin.

Wetlands have also been identified as important for the control of nonpoint pollution. Hickok (1979) reported that a 7-acre wetland adjacent to Lake Minnetonka near Minneapolis, Minnesota removed 94% of the suspended solids and 77% of the phosphorus from runoff entering the lake from a 70-acre urbanizing watershed. Four mechanisms of phosphorus detention in the wetland were identified: physical entrapment, microbial utilization, plant uptake, and adsorption. Microbial utilization was felt to be the most important for removing phosphorus (presumably dissolved phosphorus since physical entrapment would have removed the particulate phosphorus).

Hickok also reviewed briefly five other wetland projects for stormwater management around Minneapolis. Further, a wetland in the Lake Josephine watershed near Minneapolis has recently been used for diversion of urban stormwater runoff to remove phosphorus before the water enters the lake (Peter Willenbring, E. A. Hickok and Assoc., pers. comm. 1982). Preliminary data indicates that over 50% of both the total and ortho-phosphorus loading from the stormwater has been reduced, although the long-term effectiveness of the wetland has not been evaluated as of yet.

The hydrologic cycle greatly affects phosphorus retention in wetlands. Dissolved inorganic phosphorus retentions are highest during late spring and summer when plant assimilation rates are high, but accumulated phosphorus may be exported as a result of plant leaching during the winter snowmelt/spring rain period when the marsh is saturated and often partly flooded (Browman et al. 1975; Lee et al. 1971; Loucks et al. 1977; Spangler et al. 1977). Annual retention of dissolved inorganic phosphorus is therefore minimal in many cases.

Research on the Lake Wingra wetland (Madison, Wisconsin) between August 1975, and August 1976, provided extensive data on the amount of phosphorus removed from urban runoff by a natural wetland system (Loucks et al. 1977; Perry et al. 1981). The importance of the hydrologic cycle on phosphorus retention was obvious. Because of a very wet spring and a dry summer of 1976 (Lathrop and Johnson 1979), the dissolved inorganic phosphorus retention for the year was low, 10-14%, due to the lack of infiltration by the wetlands and by leaching from the dead vegetation (Loucks et al. 1977; Perry et al. 1981). However, the particulate phosphorus retention for the year was 82% as a result of sedimentation, with the winter having the lowest retention (50%) for the year; the retention during the period of high spring runoff was 76% (Perry et al. 1981). The total phosphorus retention for the year was 49%.

The establishment of artificial wetlands for stormwater phosphorus control is being implemented as a management program. On Clear Lake near Waseca, Minnesota, \$717,000 was spent on creating a wetland system of dikes, peat, and canary grass, where runoff water is filtered through the peat and collected at a lower level in ditches (Douglas R. Knauer, Wis. Dept. Nat. Resour. pers. comm. 1982). The water is then pumped to the lake. A 78% reduction in phosphorus loading has been reported with a subsequent reduction in blue-green algae blooms in the lake. The success of this study and other research has encouraged the Wisconsin Department of Natural Resources, Office of Inland Lake Renewal, to propose an artificial wetland system to reduce rural runoff sediment and phosphorus loadings to Lake Redstone in southcentral Wisconsin (Douglas R. Knauer, pers. comm. 1982).

Fixed Bed Systems

The use of filter beds that have direct adsorption capabilities for dissolved inorganic phosphorus removal from flowing waters has also been attempted. Clasen (1980) reviewed two small, experimental systems in West Germany -- seepage trenches and aluminum oxide (aluminum) columns. In the first system, seepage trenches were designed to remove phosphate ions through adsorption and ion exchange reactions with clay minerals. The filtration speed was found to be quite slow, 1-2 m/day, and in three separate trenches phosphate reductions

were from 17 to 7, 25 to 13, and 19 to 12 $\mu\text{g P/l}$. In the second system, aluminum oxide columns were placed on small tributaries (not affected by runoff) that contained the effluent from trout hatcheries. The phosphorus was reduced from 0.37 to 0.02 mg/P/l.

A pilot-scale filtration bed system was implemented on the major nutrient inflow to Fountain Lake, near Albert Lea, Minnesota (Kadwell 1977), but a follow-up study indicated the lack of success in this system (National Biocentric 1979; William Regan, Water Qual. Div. Minn. Poll. Cont. Agency, pers. comm. 1982; Steve Tuveson, Sanitarian Freeborn Co., Minn., pers. comm. 1982). The basic design consisted of an initial sedimentation basin for removing much of the coarser sediments and associated phosphorus. The water then entered a dike system where it was filtered through a bed to remove the finer particulate phosphorus and the dissolved phosphorus before being collected by a tile drainage system and pumped to the lake. Laboratory studies initially determined that a marshland type of soil filter had too slow a filtration rate. A bed of 50% sand and 50% clay that was installed in the pilot system had mixed effects. The finer particulate phosphorus increased. Further laboratory studies with various sizes of crushed limestone also indicated a good, fine particulate phosphorus removal but little dissolved inorganic phosphorus removal. Consequently, the pilot study was discontinued.

Other

Other techniques that have been tried with some success to reduce phosphorus in urban runoff have been adapted from sewage treatment plant technology. Physical treatment methods employed, other than sedimentation basins previously described, include high rate filtration, screening, dissolved air flotation, swirl regulators/separators and magnetic separation (Oberts 1977; Traver 1980). These techniques are more effective at removing sediment (and hence particulate phosphorus) than dissolved nutrients. The following biological treatment systems have been suggested as possible methods for removing phosphorus from inflowing waters: (1) contact stabilization modification of activated sludge; (2) high rate trickling filtration; (3) bioadsorption using rotating biological contractors; and (4) treatment lagoons. Major drawbacks to biological systems are the problems associated with keeping the system alive during dry periods and washout which can occur as a result of large storm events.

LABORATORY TESTS ON THE USE OF ALUMINUM HYDROXIDE FOR THE REMOVAL OF PHOSPHATE FROM FLOWING WATERS

Introduction

In the first part of this report, the use of aluminum salts for the removal of phosphorus in sewage treatment plant effluents as well as more recent applications to in-lake treatments for phosphorus control was briefly discussed. The second section provides experimental data on the use of aluminum for removing phosphorus via the impounded water and the fixed bed treatment strategies reviewed in the first section. Both strategies involve the same adsorption/precipitation reactions between phosphate ions in solution

and hydrous aluminum oxides. These oxides are formed when Al^{+3} ions in an acidic medium take on OH^- radicals as the pH is raised to ranges found in natural waters. For Al^{+3} concentrations greater than 0.3 mg/l and pH's higher than 4-5, insoluble $Al(OH)_3$ is formed (see Fig. 1, Eisenreich et al. 1977).

The literature contains much information on the effectiveness of Al^{+3} to remove high dissolved inorganic phosphorus (DIP) concentrations in sewage effluents, but the lower concentrations in lake waters and runoff waters change the chemistry somewhat (Browman et al. 1977). The Al^{+3} ion has a strong affinity for both OH^- and PO_4 radicals. Precipitation reactions are favored under lower pH's and lower $Al:PO_4$ ratios. Coprecipitation is favored by simultaneous combination of Al , OH , and PO_4 , while adsorption requires that the combination of Al and OH be made prior to exposure with PO_4 . In general, precipitation yields a higher P/Al ratio than does adsorption, but the difference between precipitation and adsorption decreases with lower initial Al and PO_4 concentrations.

The rate of reaction of the DIP with the aluminum floc is a function of the floc particle size which determines the surface area available for the adsorption/precipitation reactions (Browman et al. 1977). Adequate mixing of the aluminum salts will ensure prolonged contact time for the removal of the DIP. Experience has shown that alum applied to a lake without adequate mixing will form a thick, large globular floc which settles rapidly to the bottom while removing very little DIP from the lake water itself (Narf, in press).

One technique which we tested was developed by researchers at the Dept. of Soil Science, University of Wisconsin-Madison, and involved a cation exchange resin affixed with the hydroxy-aluminum complex (R. B. Corey, University of Wisconsin Soil Science Dept., pers. comm. 1978, Robarge 1975; Wendt et al. 1978). This resin system was made selective for phosphate (and arsenate) anions by first saturating the cation exchange resin with Al^{+3} , then hydroxylating the resin by rinsing with a weak base ($NaHCO_3$). The resin then acts in a similar fashion to the $Al(OH)_3$ adsorption/precipitation chemistry, except that the $OH:Al$ ratio is approximately 2:1. Thus, the problem of anion exchange resins taking up all anions including PO_4 is avoided. The cation exchange resin acts as a solid matrix which can potentially be regenerated after all phosphorus adsorption sites on the Al -hydroxy complex are saturated.

Methods

All phosphorus test water solutions were made from Nevin Hatchery spring water with natural levels of 0.02 mg/l DIP and 0.04 mg/l total phosphorus, and pH and total alkalinity of approximately 7.6-8.0 and 260 mg/l $CaCO_3$, respectively. Final DIP concentrations needed for the experiments were made by spiking the hatchery spring water with prepared standardized phosphate solutions (all chemical reagents were prepared using distilled water). The spring water was used instead of deionized water in order to have a natural buffering system to the pH changes that would result from the formation of the $Al(OH)_3$ floc. Phosphate test solutions were prepared in 5-gallon carboys or 100-gallon tanks depending on the volume needed for the experiments.

The pH was measured by a Beckman Zeromatic pH meter. Reactive phosphorus (inorganic) was analyzed colorimetrically by the ascorbic acid/molybdenum blue procedure (Eisenreich et al. 1975). Low range sensitivity of the analytical procedure was about 4 µg P/l. Aluminum concentrations were prepared using reagent grade $AlCl_3$.

To simulate the removal of phosphorus from impounded water by the addition of aluminum salts, test solutions of varying Al^{+3} concentrations were prepared in beakers containing 1 liter of water. NaOH was added when the solution fell below pH 6. Contact time between the $Al(OH)_3$ flocculent and the phosphorus test water was maintained by a slow speed paddle stirrer. The flocculent was then allowed to settle 10-15 minutes or longer, or centrifuged for 2 minutes (depending on the experiment), and phosphorus analyses were run on the resultant "supernatant". Reexposure experiments were conducted by: (1) decanting the supernatant (generally 600-800 mls); (2) adding new phosphorus test water to the floc to bring the solution back to the original 1-liter volume, (3) stirring; and (4) repeating the procedure. The effective Al concentration was computed using the total volume of water that was in contact with the Al. Actually, since most of the Al remained in the beaker as flocculent, the Al concentration was similar for each reexposure. Experiments were run testing percent inorganic phosphorus removal by varying the amount of initial Al added, contact time, and number of reexposures of the Al to the phosphorus test water.

To simulate the fixed bed system for the removal of DIP by the hydroxy-aluminum resin complex, laboratory column experiments using spiked hatchery water were run. Two resins were evaluated: Dowex 50WX2 (20-50 mesh) and Dowex MSC-1 (20-50 mesh). Resin specifications and handling procedures were provided in Dow Chemical Company's 1971 manual "A Laboratory Manual on Ion Exchange" (40 pages).

Maximum flow rates for various resin column heights were tested using prepared 66-mm diameter plexiglass columns. The columns had a fine mesh fiberglass screen near the bottom covered with a small amount of glass wool upon which the resin was filled to the desired height. Care was taken to adequately compact the resin in filling the columns. Powdered alumina (Al_2O_3) was also tested to compare maximum flow rates with those obtained with the resins. Smaller columns (17 mm diameter) of resin were also prepared to determine if flow rate per unit surface area of resin column was independent of column size (lack of column wall effect). Hydraulic heads of 29 and 44 cm were used for the flow rate experiments to give an indication of head effect.

The resin affixed hydroxy-Al was prepared by the following procedure (from Robarge 1975 and Wendt et al. 1978) for 500 ml of resin:

1. Rinsed the resin in the 66 mm column with 10 liters of 5% HCl for 1 hour; flow rate about 4.5 ml/cm²/min.
2. Rinsed with 10 liters of deionized water for one hour.

3. Saturated the resin with Al^{+3} by rinsing with 10 liters 0.3 M $AlCl_3$ solution for 1 hour (5 times calculated cation exchange capacity to ensure saturation).
4. Rinsed with 12 liters deionized water.
5. Removed resin and added to large beaker. Stirred resin with 3.5 liters of 0.2 N $NaHCO_3$ solution, decanted water, then repeated with 2 liters $NaHCO_3$ solution, repeated again with another 2 liters of solution.
6. Returned resin to column, rinsed with 12 liters of 0.05 M $AlCl_3$ solution for one hour.
7. Rinsed with 5 liters deionized water.

The cation exchange capacity for each resin was experimentally determined by directions given by Dow Chemical Company.

Tests for the amount of phosphorus retained by the resin columns were made by regulating the flow rate through the resin at the bottom of the column, collecting all the water which passed through the columns, and at various time intervals taking inflow and outflow water samples for phosphorus analyses.

Results and Discussion

Impounded Water Treatment. The minimum contact time needed for DIP removal for various concentrations of Al^{+3} was determined. For concentrations of Al^{+3} equal to or greater than 10 mg/l, DIP removal was rapid, with less than 1 minute of exposure needed; for concentrations of Al^{+3} less than 10 mg/l (as evidenced by the 5 mg/l data), increased contact time between the DIP and $Al(OH)_3$ flocculent was needed (Fig. 1). For the Al^{+3} concentrations studied, 10 minutes was adequate for settling most of the flocculent, such that the "treated" supernatant could be drawn off. Eisenreich et al. (1977) also found that DIP was removed within 1 minute of exposure to the flocculent formed from 10 mg Al/l .

More extensive data on the minimum amount of aluminum needed to effect good DIP removal efficiencies were developed. A contact time of 15 minutes was used to ensure a reasonable amount of exposure between the flocculent and the DIP. A comparison was also made between centrifuged and settled samples to determine how much flocculent was still left in suspension after the allotted 10 minutes of settling time. DIP removal efficiencies were generally poor for Al^{+3} concentrations of 2 mg/l or less (Fig. 2). Also, a dramatic improvement in removal efficiencies resulted in the centrifuged samples of Al^{+3} concentrations between 4 and 20 mg/l. The flocculents formed in these concentration ranges were more of a pin-floc which had slower settling times than the heavier flocs formed from higher Al^{+3} concentrations. Pin-floc formation would have provided a larger surface area of flocculent for DIP adsorption per amount of Al added. However, removal efficiencies did increase slightly with increased Al^{+3} concentrations above 10 mg/l (Fig. 1, 2).

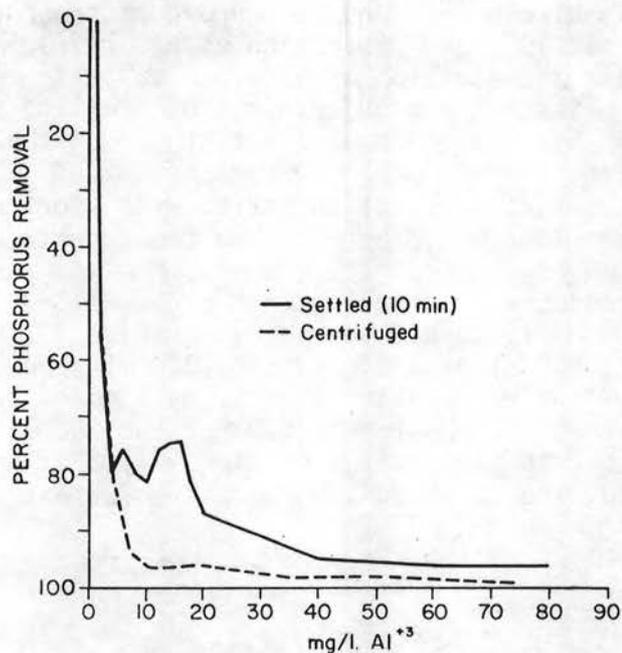


FIGURE 1. Removal of reactive phosphorus by Al(OH)₃ (P concentration=90 ug/l, contact time=15 min).

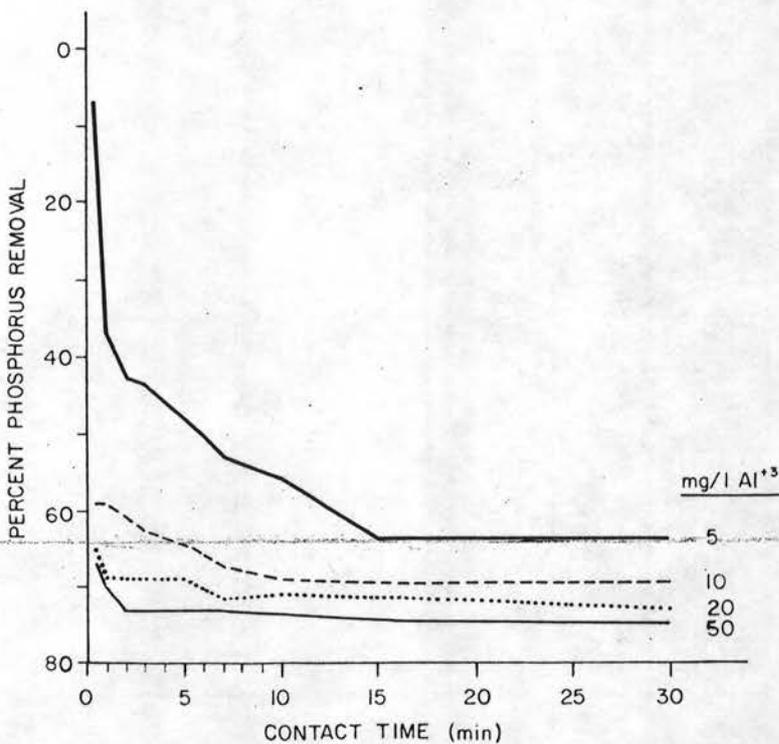


FIGURE 2. The effect of contact time for phosphorus removal by Al(OH)₃ (P concentration=74 ug/l, floc centrifuged).

Increased settling time has also been found to improve phosphorus removal efficiencies, (Browman et al. 1977 and Eisenreich et al. 1977). Our experiments were to evaluate the addition of aluminum salts to impounded water from high flow situations with the imposed criteria of treating the water rapidly; therefore, longer settling times were not studied. The difference between the removal efficiencies determined by centrifugation and settling (Fig. 2) obviously indicates that in settling basins with short residence times, both DIP and aluminum floc would be entering the downstream lake.

One final experiment was conducted reexposing much higher Al^{+3} concentrations (100 and 200 mg/l) to DIP source water (Fig. 3). For the 100 mg/l reexposure experiment, 800 ml of the original 1000 ml were decanted off for each reexposure to new test water after a settling time of 30 minutes. The remaining 200 ml contained the settled floc. For the 200 mg/l experiment, only 600 ml were decanted off indicating the greater volume of the remaining flocculent. For comparison, the decanted supernatant solutions (treated

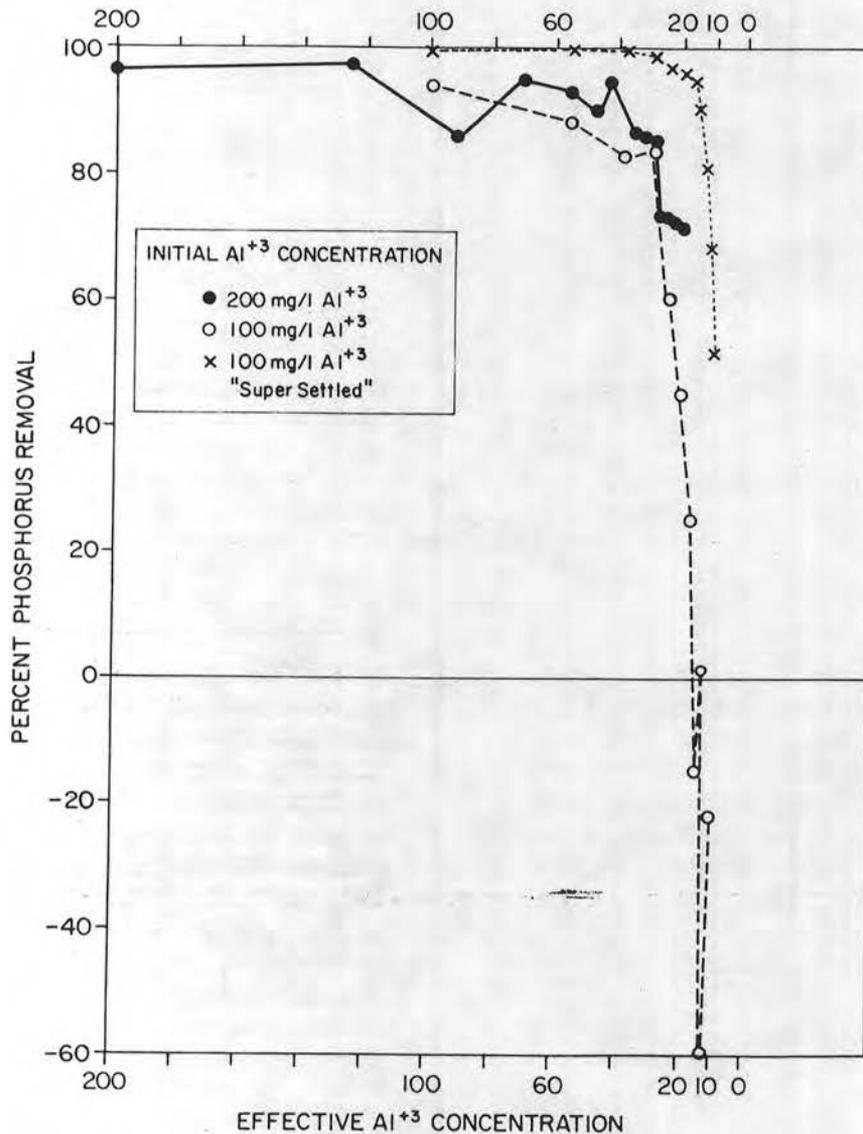


FIGURE 3. Reexposure of $Al(OH)_3$ floc to phosphorus source water (P concentration=94 ug/l, contact time = 15 min. x settling time = 30 min.).

water) from the various reexposure experiments were allowed to settle for an additional week ("super settled") to determine how much pin-floc settling and concomitant DIP removal resulted.

For the 200 mg/l and 100 mg/l reexposure experiments, effective phosphorus removal resulted with repeated reexposures up to a concentration of at least 20 mg/l of Al^{+3} (based on total exposed volume). However, a continuation of the 100 mg/l test indicated that after 7 reexposures of the $Al(OH)_3$ flocculent, phosphorus was actually being desorbed from the flocculent and added to the "treated" effluent. After 14 reexposures of the 200 mg/l test, DIP removal efficiencies were still greater than 70%, but further reexposures were not made to verify the desorption phenomenon found in the 100 mg/l experiment. The "super settled" test indicated some minor improvement in the DIP removal efficiencies.

One problem encountered when creating elevated Al^{+3} concentrations was a dramatic drop in pH in the treated water. Using the natural buffering capacity of the hatchery water (total alkalinity of 260 mg/l $CaCO_3$), neutralization (with NaOH) of the test water solutions was necessary for Al^{+3} concentrations greater than 20 mg/l to maintain a pH above 6.

Fixed Bed Treatment. The results of the resin affixed hydroxy-aluminum column experiments were disappointing, although interesting. Maximum flow rates through various column heights of both resins (DOWEX MSC-1 and DOWEX 50WX2) and powdered alumina indicated a rapid decrease in flow rate as column height increased. However, when larger column heights were used, flow rate decreases were more gradual (Fig. 4). As expected, increases in water head (pressure) increased flow rates. Flow rates were similar through both resins, but were considerably less for powdered alumina.

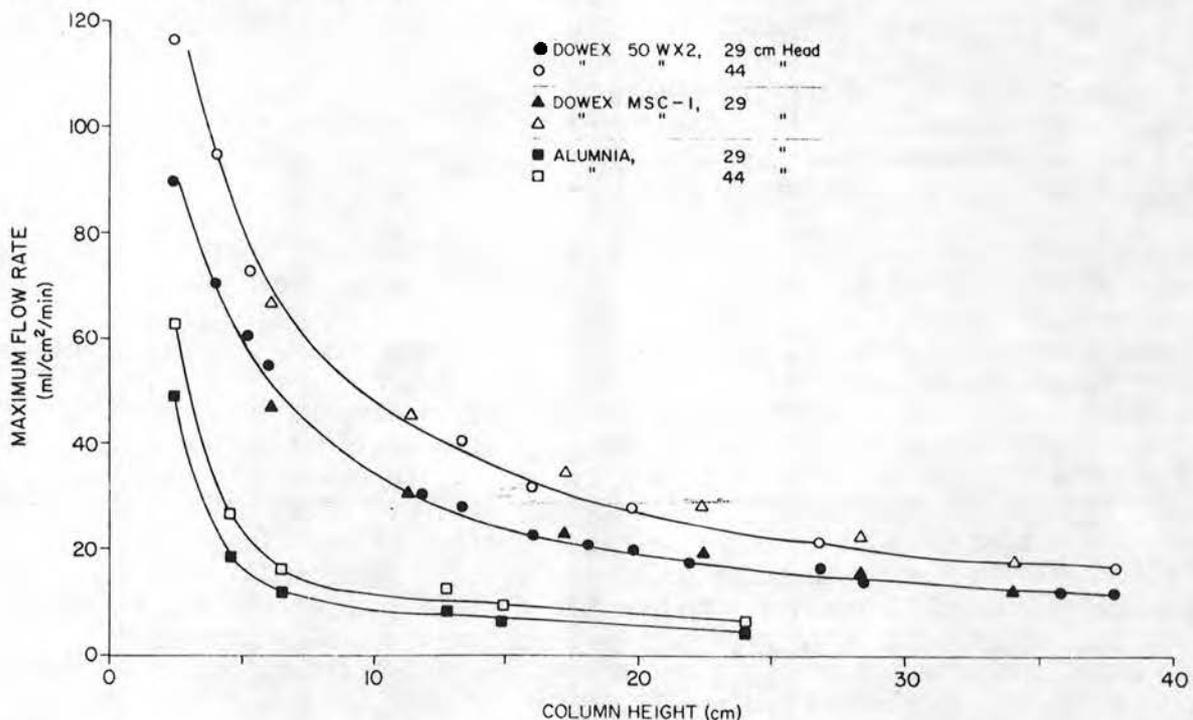


FIGURE 4. Maximum flow rates through various column heights of resin and alumina.

Relative DIP removal efficiencies of the DOWEX 50WX2 resin column were different for the 10, 1, and 0.1 mg P/l test solutions, depending on how long the column experiments were run (Fig. 5-7). For the first 30 minutes, removal efficiencies were approximately 90%, 60%, and 35% for the 10, 1, and 0.1 solutions, respectively (Fig. 5). However, as the resin column experiments were extended in duration up to 50 hours, with reduction in both the amount of resin and the flow rate, early trends in relative removal efficiencies were reversed with the 10 mg/l DIP water having the lowest removal efficiency and the 0.1 mg/l water having the highest efficiency (Fig. 7). The reason that the 10 mg/l DIP water removal efficiency probably decreased was due to saturation of all adsorption sites in the hydroxy-aluminum complex by the high phosphorus water. Reasons for the increase in the removal efficiency for the 0.1 mg/l water by the end of the 50 hours were not known, but better contact between the test water and the resin complex must have occurred.

One last experiment using the DOWEX 50WX2 resin was set up to test removal of 10 mg/l DIP water for over a week until resin saturation was achieved. However, the basic problem with this system was that after about two days of testing, an apparent bacterial slime began to grow in the resin columns and test water could not flow through the column. Phosphorus saturation of the resin was never achieved. Similar problems with bacterial growths also occurred in the experiments at the Dept. of Soil Science, University of Wisconsin-Madison (Richard B. Corey, pers. comm. 1982). Based on the results of the test with the 10 mg/l DIP water and 50-hour duration treatment (Fig. 7), approximately 140 mg of phosphorus were removed per square centimeter of resin column area during the 50 hours. Extrapolation of the test results to a square meter of resin column would remove 1.4 kg of phosphorus.

TREATMENT OF INFLOW FOR PHOSPHORUS REMOVAL: MANAGEMENT IMPLICATIONS

The treatment of inflow certainly cannot be described as a panacea for phosphorus management of lakes. However, in certain situations, treatment of inflow may be cost-effective and desirable, but only after extensive site-specific analyses determine the best system design.

Experience with sedimentation basins indicates that sediment control should be the main function of these basins, with some reduction in particulate phosphorus loading also being achieved as a minor benefit. Much of the phosphorus removed may not be readily biologically available, but could enter into the long-term phosphorus budget of the lake. However, since a significant proportion of storm runoff phosphorus loading is dissolved or associated with fine particulates (having very slow settling velocities), sedimentation basins with a short retention time would have little success in reducing this phosphorus loading. Also, frequent cleaning of the sedimentation basin may be necessary as resuspension of the finer particulates (which contain the largest proportion of the settled phosphorus) from subsequent storms would seriously reduce the basin's trap efficiency for phosphorus. In situations of high suspended sediment loading (from rural or urban runoff), sedimentation basin phosphorus removal efficiencies should be as much as 30-50%, given the basin was adequately designed and cleaning was carried out regularly.

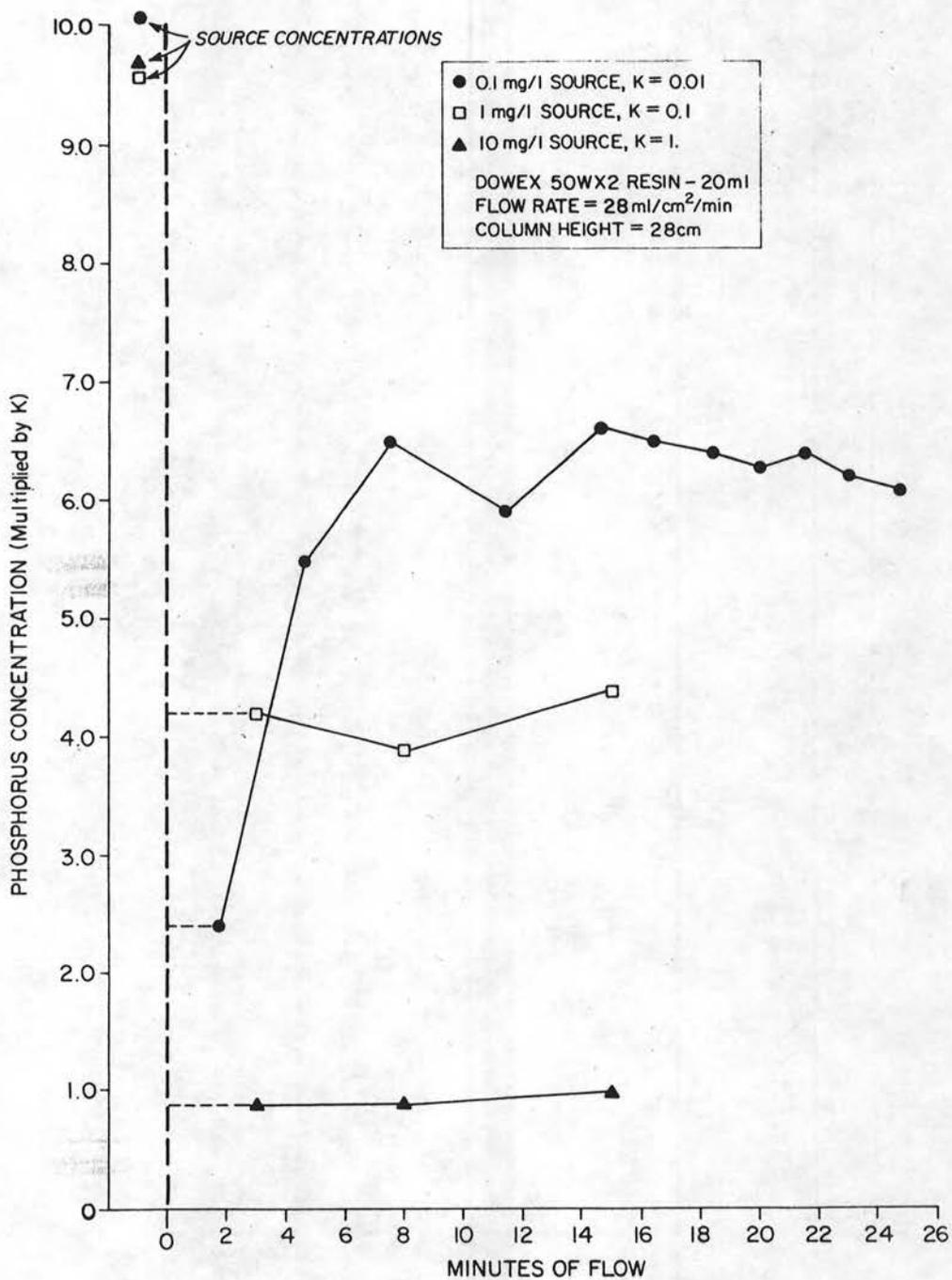


FIGURE 5. Phosphorus removed by resin-affixed hydroxy-aluminum, short duration exposure.

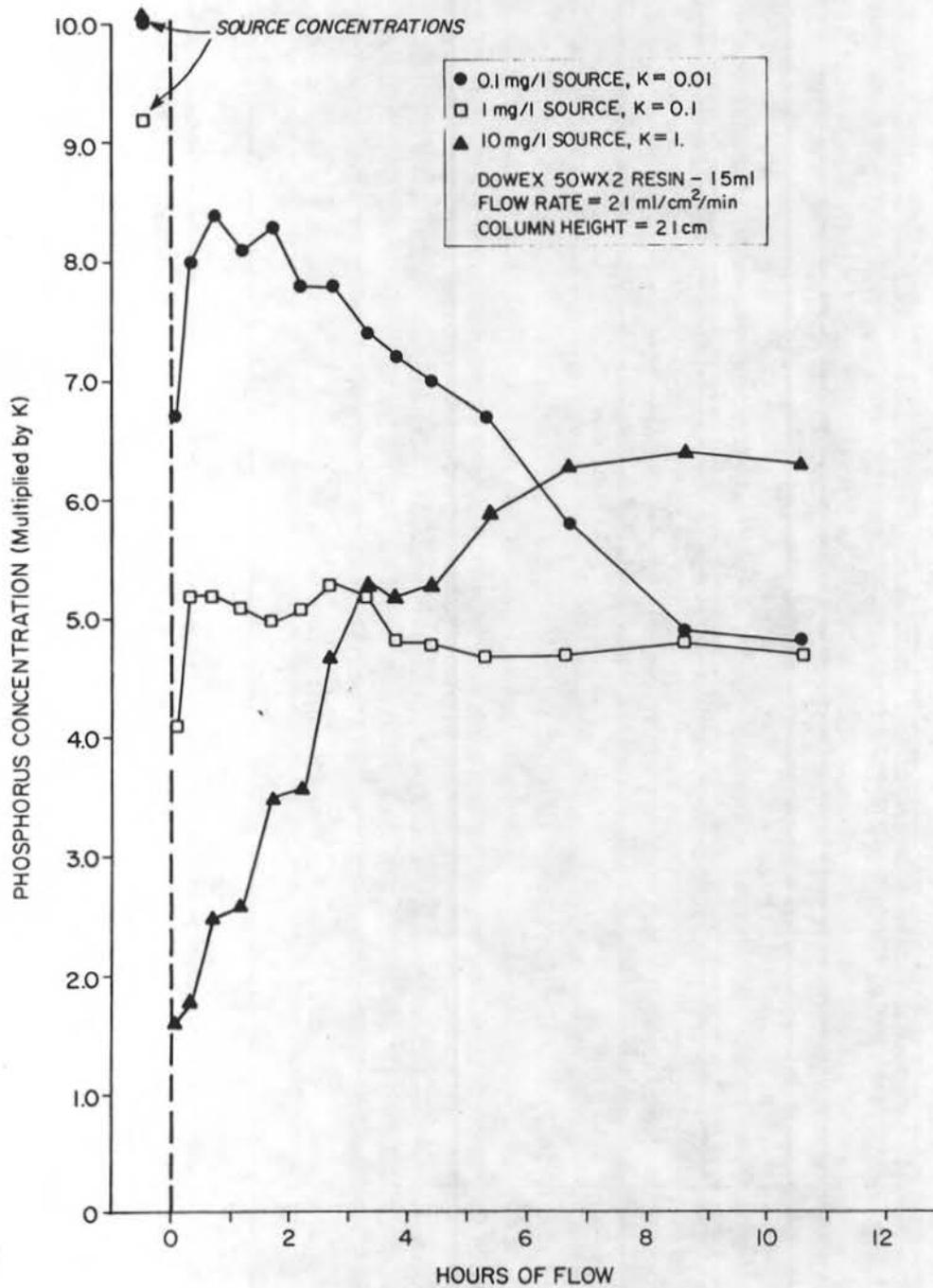


FIGURE 6. Phosphorus removed by resin-affixed hydroxy-aluminum, medium duration exposure.

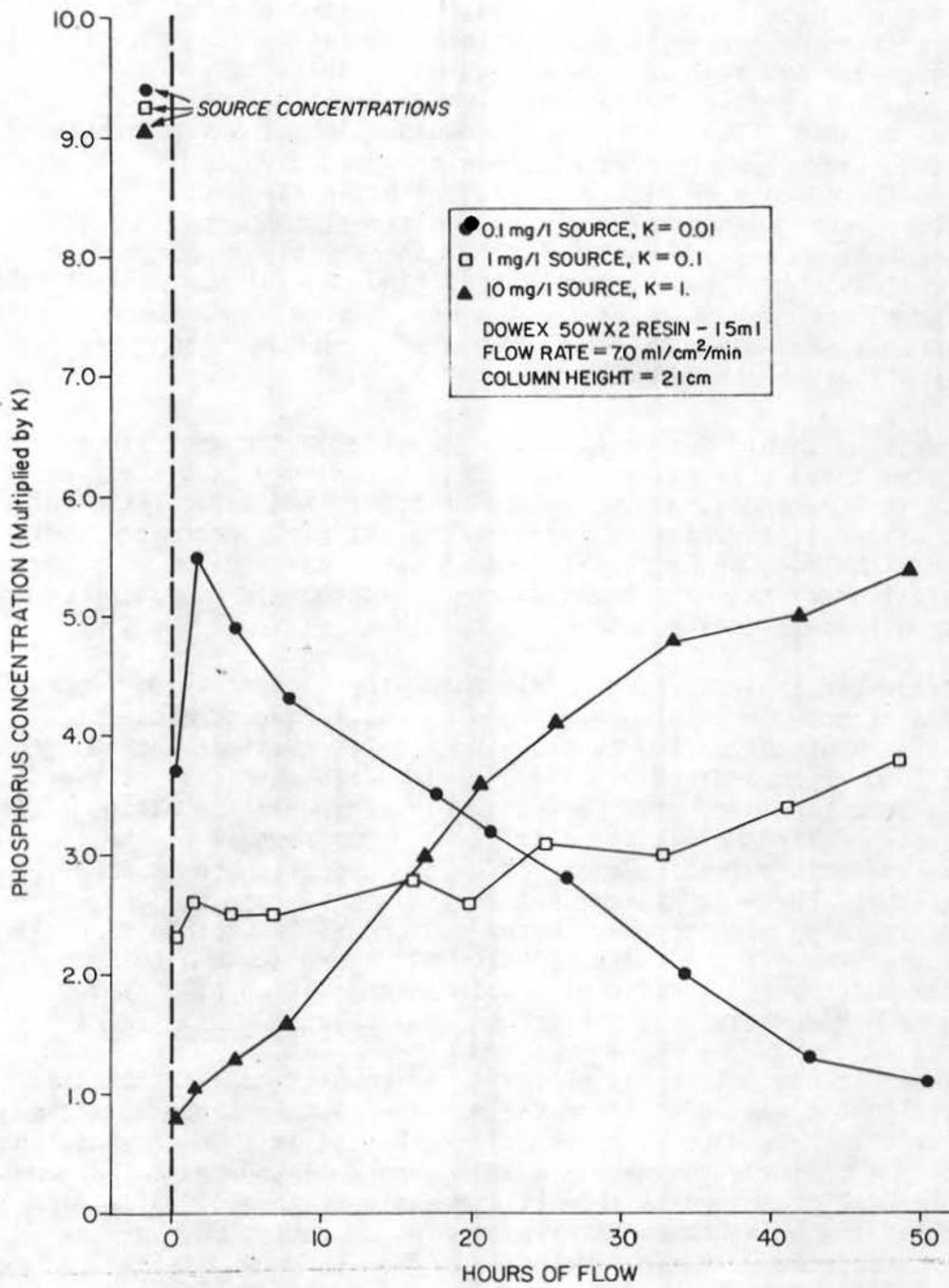


FIGURE 7. Phosphorus removal by resin-affixed hydroxy-aluminum, long duration exposure.

Chemical addition systems can greatly increase phosphorus trap efficiencies of sedimentation basins by removing a large portion of the fine particulate and dissolved inorganic phosphorus components of runoff or other high flow waters. However, experience has shown that automated chemical dosing systems are often unreliable, thereby necessitating frequent monitoring. Relatively constant doses are satisfactory when flows are stable, but in runoff situations, dosing needs to be variable, which greatly complicates treatment procedures. Because of the problems of resuspension of the phosphorus-laden flocculents during later storm events, basins would have to be designed for reuse of the flocculents or else for frequent basin cleaning. The use of chemical flocculents such as alum create additional concerns. Best settling of the flocculent occurs under higher Al^{+3} concentrations, but higher doses create an unacceptably low pH, thereby requiring careful neutralization for the water to be environmentally safe. The use of alum would appear best suited for lake inflows with moderate flow and higher phosphorus concentrations, such as dredge spoil water return channels.

Fixed bed systems should generally not be considered for use, since limited data indicates these systems are ineffective. Although laboratory experiments demonstrate the tremendous precipitation or adsorption capabilities of various chemical substances, the lack of adequate contact time, restricted water flow rates through the bed, or bacterial slime growths fouling the beds could make field application of this treatment system a nightmare. Operation costs would be high as well as initial construction costs.

However, fixed bed systems, if properly maintained, can provide impressive loading reductions. An excellent example is the large, sophisticated treatment system of the inflow to the Wahnbach Reservoir in West Germany (Bernhardt 1980; Bernhardt et al. 1971) reviewed in the first section. The treatment system consisted of a pre-reservoir sedimentation basin, a chemical addition system (using Fe^{+3}), and a filter bed for removal of the phosphorus-laden flocculent. Construction and operation costs would be high for similar type treatment plants, but in the West German project, reservoir water was being used as a drinking water source, so less algae meant lower purification costs. If the eutrophication of a downstream lake by a major river inflow was a very significant problem, application of a system similar to the Wahnbach Reservoir system might be desirable.

One case where it was originally believed the results of this investigation might be applicable was in treating the outflow of Lake Mendota, the major loading source to Lake Monona, near Madison, Wisconsin. On an annual basis, approximately 40% of the phosphorus loading from all sources to Lake Monona is dissolved inorganic phosphorus from Lake Mendota (Lathrop 1979). A treatment system similar to the Wahnbach River system would remove much of the phosphorus associated with algae washed out from Lake Mendota and reduce phosphorus loading to Lake Monona by 50-60%. The treatment system could also be used during the summer (when outlet discharges were low) to remove dissolved inorganic phosphorus from water pumped from the hypolimnion of Lake Mendota.

Although the cost-benefit ratio for such a system is not known, the design characteristics between the West German system and what would be needed for the Lake Mendota outlet are similar. Fall and spring DIP concentrations, when Lake Mendota outlet discharges are highest, are 0.10-0.12 mg/l. Maximum

sustained river discharges are only slightly greater for the Lake Mendota outlet. Obviously, the installation of such a system would depend on a major public effort to make the Madison lakes less eutrophic for improved recreation. It is doubtful that such interest could be generated, since the Madison lakes are not generally perceived as excessively eutrophic. Therefore, a great deal more study and analyses would be needed before any specific recommendations could be made.

One final management technique for the removal of phosphorus from flowing waters is the use of wetlands as natural filtration systems. In some cases, wetlands have been found to remove significant amounts of particulate phosphorus by physical entrapment due to reduced flow velocities. Also, wetlands sometimes reduce dissolved inorganic phosphorus and other biologically available phosphorus sources through uptake by the wetland plants during the growing season. Reported low phosphorus retention by some wetlands on an annual basis results from spring runoff flushes removing a large amount of leached phosphorus from decaying plants. Channelization of wetlands is also a problem, such that the phosphorus retention in many existing wetlands might be improved by altering the existing channel designs.

Although no ideal treatment system with low construction and operation costs exists, a system combining a sedimentation basin and an adequately sized wetland might be effective in certain cases for removing phosphorus from stream runoff waters. The system should be constructed such that spring flushing of the wetland would be prevented. The sedimentation basin would act as a pre-filter for large storm events only (through various engineering designs) before the water entered the wetland. During the winter and early spring when the wetland was to remain inactive, the sedimentation basin would be the sole nutrient removal system, albeit just for particulate phosphorus. By restricting the basin design to only major storm events, the settled material could be air-dried and removed by earth-moving machines before the next major runoff event. Water from minor runoff events (which would contain relatively little particulate phosphorus) would enter the wetland directly. As the phosphorus retained in the wetland would eventually leach out due to elevated concentrations, periodic harvesting of certain wetland plants should be considered. If a combined sedimentation basin/wetland system were properly designed and operated, annual phosphorus removal efficiencies should be at least 50% or even greater.

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