Accumulation of Phosphates in Water

Robert F. Holt, Donald R. Timmons, and Joseph J. Latterell[1]

Natural and agricultural sources of phosphorus to surface waters include precipitation, animal wastes, fertilizers, and land runoff. The actual contribution from these sources is shown to be quite low. However, the concentration of phosphorus required to support profuse algal blooms is so low that the limited amounts supplied are sufficient to exceed this requirement. Eroded soil delivers appreciable amounts of phosphorus to surface waters, but the soil materials capacity to sorb phosphorus results in little tendency for release of this source into the water. Bottom sediments appear to be a sink for dissolved orthophosphate that is supplied to surface waters. Leaching of vegetation can supply relatively large amounts of phosphorus to lakes and streams. Deep incorporation of phosphatic fertilizers materially reduces the concentration of phosphorus in runoff waters as compared to shallow incorporation.

Recently there has been increasing public concern about the deterioration of our environment, particularly the pollution of water supplies. This concern is based, to a large extent, on the intended use of a given water supply. Considerations of the quality of water in a lake or stream will depend on the myriad of potential uses for that water, including municipal, industrial, agricultural, navigational, recreational, and power uses.

The concentration of phosphate in water may be less than 0.001 ppm. This is because of the low solubility of the phosphate compounds formed by reaction of the phosphate ions with cations commonly associated with surface water, the strong affinity of phosphate for the suspended material in surface water, and the rapid biological tieup of the phosphate. Certain use conditions will be adversely affected by small increases at relatively low phosphate concentrations.

The phosphorus content of surface waters is frequently the limiting factor for the growth of algae and aquatic weeds. Hutchinson (1957) states that most relatively uncontaminated lake districts have surface waters containing 0.01 to 0.03 ppm. Sawyer (1952) found that inorganic phosphorus concentrations above 0.01 ppm and inorganic nitrogen concentrations of 0.30 ppm at spring overturn could produce dense algal blooms. Apparently a very small increase in soluble phosphorus can create conditions suitable for abundant algae production, decreasing recreational values. If the main recreational value rests in the fishing potential, the phosphorus levels quoted are apparently too low. Moyle (1956) has estimated fish production in Minnesota waters to be 90, 150, and 370 lb of fish per acre, respectively, for waters with 0.03, 0.06, and 0.13 ppm total phosphorus content.

The nature of phosphorus and its reactions with soil preclude its leaching to any appreciable depth. This immobility has been well demonstrated by studies of Scarseth and Chandler (1938), Russell (1963), and Taylor (1967). Because of the limited amounts of phosphorus that enter the ground water as a result of phosphorus immobility in the soil, the present discussion will be limited to phosphorus accumulation in surface waters.

North Central Soil Conservation Research Center, SWC, ARS, USDA, Morris, Minn. 56267

[1] Present address: Department of Science and Mathematics, University of Minnesota, Morris, Minn. 56267

PHOSPHORUS LEVELS IN SURFACE WATERS

Total phosphorus content in surface water may be divided into soluble phosphorus and suspended insoluble phosphorus. The soluble phosphorus is composed of soluble inorganic orthophosphate, hydrolyzable polyphosphates, and organic phosphorus. The suspended insoluble phosphorus includes insoluble inorganic phosphorus compounds, sorbed or fixed phosphorus, and phosphorus in microorganisms.

The reported values for phosphorus concentrations in lakes and streams are extremely variable, largely because of the difficulty encountered in obtaining a representative sample. Studies of surface waters taken from lakes and ponds in Minnesota (Water Resources Coordinating Committee, 1969) reported the total soluble phosphorus content as ranging from 0.002 to 1.6 ppm. Thermal stratification results in considerable accumulation of soluble phosphorus below the thermocline on hard-water lakes of high fertility. For example, in Lake Minnetonka at Wayzata, Minn., during early June, the mean total soluble phosphorus content of 17 surface samples was 0.05 ppm and the mean of 13 deep samples was 0.20 ppm. A greater contrast is observed as the thermocline fully develops. The soluble orthophosphate concentration of surface water samples of lakes will vary considerably throughout the season, presumably due to the rapid biological uptake of the inorganic phosphate. In 1967, the soluble orthophosphate in Big Stone Lake (1967) ranged from 0.009 to 0.16 ppm from mid-May to early September, probably due to the rapid turnover of orthophosphate.

Several investigators have reported on the phosphorus concentration of lakes and streams. A listing of some of these analyses is given in Table I. If the figure of 0.01 ppm soluble inorganic phosphorus is taken as the point above which algae growth can flourish, one would expect all of the bodies of water where soluble orthophosphate was determined to be capable of supporting abundant algal blooms. Unfortunately, the relationship between total dissolved phosphorus (presumably soluble organic phosphorus + inorganic phosphorus) and inorganic phosphorus is not well defined; however, for the values obtained, the inorganic fraction has ranged from 38 to 67% of the total soluble phosphorus. Perhaps a value of 50% for streams in agricultural or forested areas that do not receive inputs from industrial or municipal sources is a reasonable estimate. If this is true, most of the water analyses recorded in the table would either have equaled

Table I. Phosphorus Concentration of Some Lakes and Streams

Source	Concentration of phosphorus in ppm: Dissolved inorganic P	Total dissolved P
Illinois River basin streams (Engelbrecht and Morgan, 1959)	0.18	0.29
Unpolluted streams in Maine (Mackenthun and Ingram, 1967)	...	0.020
St. Louis River (Lake Superior)	0.018	0.048
Black River (Lake Superior)	0.062	0.093
Lake Superior, Minn. (Putnam and Olson, 1958–1959)	...	0.015
Avg. of 18 streams in Pa., Ohio, West Va., Ky., Ill.	...	0.080
Avg. of 28 streams in Wash. (President's Science Advisory Comm., 1965)	...	0.030
Lake Washington, Seattle, Wash.[a] (1950)	0.023	...
(Anderson, 1961) (1957)	0.089	...
(1958)	0.074	...
Average of 479 N.E. Wis. lakes (Juday and Birge, 1931)	...	0.023
Linsley Pond, Conn. (Hutchinson, 1941)	...	0.021
Lake Zoar, Conn. (Curry and Wilson, 1955)	...	0.025
Lake Minnetonka, Minn., Epiliminion		0.050
Lake Minnetonka, Minn., Hypoliminion		0.20
Lake Crystal, Minn., Epiliminion		0.10
Lake Crystal, Minn., Hypoliminion (Water Resources Coordinating Comm., 1969)		1.40
Big Stone Lake, Minn. (Big Stone Lake Study, 1967)	0.09	0.18

[a] Hypoliminion samples.

or exceeded the 0.01 ppm value for soluble orthophosphate. These values tend to emphasize the precarious position of many of our surface waters in terms of their potential for supporting undesirable growths.

SOURCES OF PHOSPHORUS FOR SURFACE WATERS

The sources of the phosphorus in surface waters are frequently divided into those coming from industrial, municipal, and agricultural endeavors. We will consider only natural and agricultural sources. These are arbitrarily broken down into precipitation, animal wastes, land runoff, and fertilizers.

PRECIPITATION

Precipitation contains small but finite amounts of dissolved phosphorus, probably attributable to the slight solubility of particulate matter in the atmosphere. Voight (1960) measured 0.01 ppm soluble phosphorus in rainwater collected in an open area surrounded by forests. Chalupa (1960) found 1.65 lb of inorganic phosphorus (P_2O_5) fell on an 88.4 acre reservoir in 7 months and considered it an important source for stimulating primary production of organisms during periods of thermal stratification. Analysis of rainwater collected monthly for 3 yr at Taita, New Zealand, averaged 0.3 lb of phosphorus per acre per year. This is a low value in terms of phosphorus needs of an agricultural crop, but it becomes appreciable in terms of the level of phosphorus in runoff water from agricultural lands. Tamm (1951) found 0.03 ppm phosphorus in rainwater collected in an open area.

While the actual contribution of phosphorus to surface waters by rainfall is small, the extremely low levels of phosphorus required to produce nuisance blooms of algae in surface waters makes this source one to be considered.

ANIMAL WASTES

The potential contribution of phosphorus to surface waters in the United States by animal waste is enormous. Its magnitude can be illustrated by a comparison with the amounts attributable to human waste and commercial fertilizer use. Animal waste contains about four times the

Source	Total P (Billion lb/yr)
Human[a]	0.83
Animal[b]	3.2
Fertilizer[b]	3.7

[a] Calculated at 4.5 lb per person for population of 185 million.
[b] Based on Agricultural Statistics—1968.

amount of phosphorus found in human waste and about the same amount as that applied as fertilizer. The actual contribution from animal waste is, in most instances, quite limited. However, under some conditions there is evidence of appreciable movement of phosphorus into surface water from animal waste. A study of the nutrient sources for Lake Mendota at Madison, Wis. (Nutrient Sources Subcommittee, 1966) has estimated that about 40% of the total annual phosphorus load to the lake comes from rural land runoff and 75% of this is estimated to come from manure that is spread on frozen ground. Concern over the nutrient enrichment of Big Stone Lake on the border between Minnesota and South Dakota has resulted in a joint commission to investigate the nutrient sources. A report of this commission (Big Stone Lake Study, 1967) indicated that about 20 to 25% of the phosphorus entering Big Stone Lake each year comes from cattle feeder lots immediately adjacent to the lake or its tributaries. Soluble orthophosphate concentrations ranging from 20 to 30 ppm have been found in cattle feedlot runoff that continued for a period of over 2 hr as a result of a 1.74-in. rain (Loehr, 1967). An average value of 50 ppm phosphate was found in runoff from feedlots with concrete surfaces (Miner *et al.*, 1966).

Current trends in livestock production with increasing numbers of animal units per production unit create highly concentrated sources under confined conditions. This will necessitate the development of systems that will minimize the movement of phosphorus from these concentrated wastes into surface waters.

RURAL LAND RUNOFF

Surface runoff water will contain small amounts of dissolved phosphorus and small or large sediment loads, depending on the topography, soil type, vegetation, and the way in which precipitation reaches the surface. The sediment may contain 500 to 2000 ppm of perchloric acid-oxidizable phosphorus, but the contribution that this source makes to the soluble phosphorus level in surface waters is not well known.

PHOSPHORUS IN ERODED SOIL

Phosphorus is tightly held to soil particles, and when a phosphate fertilizer is applied to the soil, there is little movement downward. Consequently, continued applications of fertilizer phosphorus will result in higher concentrations in the surface soil, where it is extremely vulnerable to loss by erosion. Scarseth and Chandler (1938) concluded that 60% of the phosphate applied over a 26-yr period was lost by erosion from a nearly level Norfolk loamy sand in a cotton, corn, oat, legume rotation. Ensminger (1952) reported that 63% of the phosphorus applied was lost from a Hartsell fine sandy loam under a corn and cotton rotation. Taylor (1967) estimated that fertilizer and soil phosphorus contained in eroded soil may contribute from 1 to 5 lb per acre per yr of readily available phosphorus to surface waters. He assumed that 10% of the total phosphorus in eroded soil would be available for aquatic plant growth.

The annual average ammonium fluoride-extractable phosphorus in sediment losses from a Barnes soil in western Minnesota is given below.

Cropping treatment	Phosphorus loss (Lb/acre/yr)
Fallow	0.9
Continuous corn	0.5
Corn-oats-hay rotation	0.02

These values are based on the average measured soil losses for the different cropping system, and the analyses of these sediments during a 2-yr period. The quantity that actually reaches the surface water supplies and the availability of this source when it does enter a lake or stream is not known. Keup (1968), quoting studies by Gessner on the soluble phosphorus concentration of the turbid Amazon River, indicates that when the soluble phosphorus exceeds 0.01 ppm, it is sorbed on finely divided inorganic suspended material. Results from Latterell *et al.* (1969) indicated that lake bottom sediments have a high capacity to remove orthophosphate from solution. Equilibration of undried lake bottom sediments with calcium phosphate solutions containing up to 42 ppm orthophosphate resulted in equilibrium phosphate concentrations of only a few hundreds of a part per million. The disposition of phosphorus in natural lakes has been the subject of numerous investigations (Mackenthum, 1965). Quantitatively, considerable variation has been reported as to the role of sediment in the dissolved phosphorus content of lake waters. Qualitatively, however, there is general agreement that bottom sediments do remove soluble phosphorus from the water. Hayes *et al.* (1952), in a study of the kinetics of phosphorus exchange in lakes, demonstrated that bottom mud showed a strong uptake of radioactive phosphorus applied in solution to the surface of a lake.

Rigler (1956), however, estimated that only 3% of the P^{32} added to the surface of a lake with 11.8 acres surface area was lost to the bottom sediments in 4 weeks. It should be pointed out that it is difficult to separate that phosphorus adsorbed or precipitated by the lake sediments and that which is added through the bio-system. The turnover rate of soluble inorganic phosphate to organic forms in lake water is rapid, having been reported to be less than 10 min for a number of hard- and soft-water lakes in Canada (Rigler, 1964).

The removal of dissolved phosphate from lake waters by bottom deposits has been investigated by Holden (1961), who has calculated that 0.4 in. depth of mud could remove all the phosphate from a body of water 33 ft deep containing 0.14 ppm, phosphate-phosphorus. Most of the phosphate removed by the mud would thus remain in the aerobic zone of the bottom deposit which normally extends to 0.8 in. Only about 6% of this phosphorus was extractable by 0.1 N hydrochloric acid, indicating a rather stable form of phosphorus.

Because of the rapid turnover of inorganic phosphorus due primarily to the rapid incorporation of phosphate into the bio-system of lakes, it is difficult to assess the contribution that sediment makes to the phosphate levels of surface waters. In general, the eroded soil material might have considerable potential to remove dissolved phosphorus from waters, but at the same time might act as a reservoir of phosphorus when the concentration in the water is sufficiently low and equilibrium between water and sediment is attained.

DISSOLVED PHOSPHORUS IN RUNOFF WATERS

The concentration of dissolved phosphorus that is carried off the land surface and into the surface water supply is quite low. In order to adequately assess the contribution from this source, it is necessary to know not only the concentration of dissolved phosphorus, but also the total amount of water involved. Keup (1968) reviewed the sources of phosphorus in flowing waters based on the contributing watershed area, and found the areal contribution to vary between 0.03 and 0.8 lb per acre per yr. In general, contributions from the sparsely settled forested areas of the north-central and northeastern portions of the United States were lowest and those from the more densely populated agricultural areas of the Midwest were highest.

Timmons *et al.* (1968) have investigated the phosphorus content in runoff waters from small plots as influenced by different cropping practices. The annual average dissolved inorganic phosphorus in this surface runoff for a 2-yr period is given below.

Crop	Phosphorus loss (Lb/acre/yr)
Fallow	0.05
Corn—continuous	0.06
Corn—rotation	0.06
Oats—rotation	0.01
Hay—rotation	0.21

The pattern of phosphate removal from the cropping sequence is of interest. Crops planted to corn and fertilized annually with about 26 lb of P per acre lost about 0.06 lb of soluble inorganic phosphorus per acre per yr. Fallow plots which received no fertilizer for the previous 6 yr lost soluble inorganic phosphorus at the rate of 0.5 lb per acre per yr, while hay plots which were not fertilized the year of sampling lost 0.21 lb per acre per yr. Virtually all of the phosphorus was removed from the hay plots with the snowmelt in the spring. Laboratory leaching studies of fresh frozen hay (alfalfa) samples by Timmons (1969) have demonstrated that virtually all the plant phosphorus can be leached with water and over 70% is in the inorganic (orthophosphate) form. From a practical standpoint, it appears that hay land may make an appreciable contribution to the dissolved phosphorus in surface waters. The average loss of dissolved orthophosphate from land that is in 50% corn, 25% oats, and 25% hay was about 0.08 lb per acre per yr (Timmons *et al.*, 1968).

Big Stone Lake, on the border between Minnesota and South Dakota, is fed by a 735,000-acre watershed. Estimates of phosphorus (based on analyses and total flow volumes) being supplied to the lake from various sources attribute 57,000 lb per yr to agricultural land runoff or 0.077 lb per acre per yr for the watershed. This amount of phosphorus added to the volume of water in Big Stone Lake would give a concentration of about 0.15 parts per million—well above the threshold level for profuse algae growth. The best estimate for the acreage receiving fertilizer on this watershed is about 10% of the land. It is evident, therefore, that the rather natural conditions which exist surrounding this lake supply an abundant source of soluble phosphorus for algae and weeds. Sediment samples from the lake have indicated an equilibrium phosphate concentration of about 0.03 ppm orthophosphate. In this case, the sediment might be expected to remove phosphorus from the lake water.

Engelbrecht and Morgan (1961) have reported the mean lb of P_2O_5 per day per sq mile of drainage area in the Kaskiskia River in Illinois as being 1.4. This calculates to about 0.15 lb per acre per season (April through September) of total soluble P (ortho + hydrolyzable) a figure that agrees quite well with the results of Timmons *et al.* (1968) if one assumes about 50% of the total phosphorus to be orthophosphate.

FERTILIZER

Discussion up to this point has not considered the influence of commercial fertilizer applications on agricultural lands as a source of phosphorus for surface waters. It has been shown that runoff from farm land can contribute appreciable phosphorus to waters under conditions where fertilizer cannot be considered to be a major factor. With present trends in fertilizer usage in the United States (increase from 0.97 million tons P in 1950–54 to 1.88 million tons P in 1966) one can only assume that more of the applied phosphorus will eventually find its way into surface waters. In southwestern Wisconsin, three watersheds that were fertilized at the average rate of 4.8 lb of P per acre lost phosphorus at the average rate of 0.6 lb of P per acre under normal runoff rates (Witzel *et al.*, 1969). However, nearly all of the runoff resulted from rain on frozen ground and melting snow, a condition that was shown to contribute relatively large supplies of soluble phosphorus from areas where no fertilizer was applied.

The immobility of phosphorus in soil would lead one to expect that the method of incorporation of phosphate fertilizer into the surface soil could have an appreciable effect on the content of dissolved phosphorus in runoff waters. Timmons (1969) investigated three methods of incorporation of superphosphate into surface soils with respect to the concentration of dissolved phosphorus in runoff water. The concentrations of soluble inorganic phosphorus as orthophosphate in runoff water are given below. Deeper incorporation of phosphate

Fertilizer application	Phosphorus (ppm)
Control	0.08
Broadcast and plowed under	0.09
Broadcast and disked in	0.16
Broadcast (no incorporation)	0.30

fertilizers into the surface soil resulted in substantially lower concentration of dissolved phosphorus in runoff waters. This is in agreement with the work of Bauer and Kucera (1969) who showed substantially lower bicarbonate-soluble phosphorus in the 0- to 3-in. layer of soils when the broadcast fertilizer application was moldboard plowed than when it was disked into the surface. Since the most common practice of broadcast fertilizer application in the Midwest presently involves spreading the fertilizer on a plowed surface and disking in about 3 in., it seems likely that, in the interest of water quality, consideration should be given to methods that incorporate the fertilizer deeper into the soil.

The total phosphorus uptake by a crop is directly related to the amount of phosphorus available to it. Krantz *et al.* (1949) showed that phosphorus fertilizer applications and/or increasing levels of soil phosphorus increased the total phosphorus uptake by crops. Therefore, one might conclude that the phosphorus in runoff waters can be increased by the indirect effect of fertilizer due to subsequent leaching of the vegetation by precipitation.

LITERATURE CITED

"Agricultural Statistics," U.S. Dept. of Agriculture, 1968.
Anderson, G. C., "Algae and Metropolitan Wastes," U.S. Public Health Service, SEC TR W61-3, pp. 27–33, 1961.
Bauer, A., Kucera, H. L., *N. Dak. Agr. Exp. Sta. Farm Res.*, **26,** 4–6 (1969).
Big Stone Lake Study, A joint report by Minnesota and South Dakota, Nov., 1967.
Chalupa, J., *Sb. Ved. Pr. Vys. Sk. Chemickotechnol. Pardubice* (Prague), Fac. Technol. Fuel. Wat. Vol. 4, Pt. 1, 295–308 (1960). (English summary, *Water Pollution Abstract*, Vol. 35, No. 5, Abs. No. 660).
Curry, J. J., Wilson, S. L., *Sewage Ind. Wastes*, **27** (11) 1262–1266 (1955).
Engelbrecht, R. S., Morgan, J. J., *Sewage Ind. Wastes* **31** (4) 458–478 (1959).
Engelbrecht, R. S., Morgan, J. J., U.S. Public Health Service, SEC TR W61-3, 74–79 (1961).
Ensminger, L. E., *Soil Sci. Soc. Amer. Proc.* **16,** 338–342 (1952).
Hayes, F. R., McCarter, J. A., Cameron, M. L., Livingston, D. A., *Ecology* **40,** 202–216 (1952).
Holden, A. V., *Verk. Interat. Verein. Limnol.* **XIV,** 247–251 (1961).
Hutchinson, G. E., "Ecological Monographs," Vol. 11, 21 (1941).
Hutchinson, G. E., "A Treatise on Limnology," Wiley, New York, N.Y., 1957.
Juday, C., Birge, E. A., *Trans. Wis. Acad. Sci., Arts Lett.* **26,** 353–382 (1931).
Keup, L. E., "Water Research," Vol. 2, 373–386, Pergamon Press, Great Britain, 1968.
Krantz, B. A., Nelson, W. L., Welch, C. D., Hall, N. S., *Soil Sci.* **68,** 171–177 (1949).
Latterell, J. J., Holt, R. F., Timmons, D. R., unpublished data (1969).
Loehr, R. C., Annual Progress Report, FWPCA Demonstration Grant WPD-123-01-66, July 1967.
Mackenthun, K. M., "Nitrogen and Phosphorus in Water. An Annotated Bibliography," U.S. Dept. Health, Ed., and Welfare, PHS. Div. Water Supply and Pollution Control, 1965.
Mackenthun, K. M., Ingram, W. M., "Biological Associated Problems in Freshwater Environments," U.S. Dept. Int., FWPCA, 1967.
Miner, J. R., Lipper, R. I., Fine, L. R., Funk, J. W., *J. Water Pollut. Contr. Fed.* **38,** 1582–1591 (1966).
Moyle, J. B., *Wild. Man.* Vol. 20, No. 3, 302–320 (1956).
Nutrient Sources Subcommittee of the Technical Committee of the Lake Mendota Problem Committee, "Report on the Nutrient Sources of Lake Mendota," Jan. 3, 1966.
President's Science Advisory Committee, "Report of the Environmental Pollution Panel," Nov., 1965.
Putnam, H. D., Olson, T. A., "A Preliminary Investigation of Nutrients in Western Lake Superior, 1958–1959," School of Public Health, Univ. of Minnesota.
Rigler, F. H., *Ecology* **37,** 550–562 (1956).
Rigler, F. H., *Limnol. Oceanogr.* 9 (4) 511–518 (1964).
Russell, E. W., "Soil Conditions and Plant Growth," 9th ed., Wiley, New York, N.Y., 1963.
Sawyer, C. N., *Sewage Ind. Wastes* **24,** 768–776 (1952).
Scarseth, G. D., Chandler, W. V., *J. Amer. Soc. Agron.* **30,** 361–374 (1938).
Tamm, C. O., *Physiol. Plant.* **4,** 184–188 (1951).
Taylor, A. W., *J. Soil Water Conserv.* **22,** 228–231 (1967).
Timmons, D. R., unpublished data, 1969.
Timmons, D. R., Burwell, R. E., Holt, R. F., *Minn. Sci.* **24,** 16–18 (1968).
Voigt, G. K., *Amer. Midl. Natur.* **63,** 321–326 (1960).
Water Resources Coordinating Committee, State Planning Agency, Tech. Bull. No. 2, 1969.
Witzel, S. A., Minshall, N., Nichols, M. S., Wilke, J., *Trans. ASAE* **12,** 338–341 (1969).

Received for review January 16, 1970. Accepted April 17, 1970. Presented at the Division of Fertilizer and Soil Chemistry, 158th Meeting, ACS, New York, N.Y., September 1969.