A Review the Role of Phosphorus in the Eutrophication of Receiving Waters

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Abstract

Phosphorus (P) is an essential element for all life forms. It is a mineral nutrient. Orthophosphate is the only form of P that autotrophs can assimilate. Extracellular enzymes hydrolyze organic forms of P to phosphate. Eutrophication is the overenrichment of receiving waters with mineral nutrients. The results are excessive production of autotrophs, especially algae and cyanobacteria. This high productivity leads to high bacterial populations and high respiration rates, leading to hypoxia or anoxia in poorly mixed bottom waters and at night in surface waters during calm, warm conditions. Low dissolved oxygen causes the loss of aquatic animals and release of many materials normally bound to bottom sediments including various forms of P. This release of P reinforces the eutrophication. Excessive concentrations of P are the most common cause of eutrophication in freshwater lakes, reservoirs, streams, and headwaters of estuarine systems. In the ocean, N becomes the key mineral nutrient controlling primary production. Estuaries and continental shelf waters are a transition zone, where excessive P and N create problems. It is best to measure and regulate total P inputs to whole aquatic ecosystems, but for an easy assay it is best to measure total P concentrations, including paniculate P, in surface waters or N/P atomic ratios in phytoplankton. SOCIETY normally wishes to maintain a reasonable level of productivity in our lakes, rivers, and estuaries and this requires the presence of modest levels of mineral nutrients. Historically, many of these water bodies have progressed from low productivity or oligotro-phic settings to productive mesotrophic conditions to over enriched hypertrophic or eutroph condition The results are often algal orcyanobacterial mats, anoxia, and fish kills leading to greatly reduced biodiversity (e.g., Carpenter et al., 1969; Jaworski, 1981; Likens, 1972). The relationships among P input, primary production, dissolved oxygen, biodiversity and trophic status are shown conceptually in Fig. 1. From the human perspective it is desirable to prevent or minimize eutro-phication of receiving waters for aesthetics and to maintain the productivity of animal species preferred for recreation and commercial fisheries. Examples of the over enrichment of receiving waters with nutrients have occurred frequently all over the world. Questions that most often arise with respect to eutrophic conditions include: (i) Which nutrients are the most frequent cause of this eutrophication?, (ii) What nutrient concentra-tions are acceptable to society?, and (iii) Can we control eutrophication by limiting a key nutrient?The causes and affects of eutrophication are very complex. The causes also vary somewhat for different aquatic systems. Thus, lakes and reservoirs behave somewhat differently than streams and rivers, while all of these differ from estuaries and other coastal waters. Any one system will also exhibit high variation in behav-ior both seasonally and interannually. These facts make it difficult to assess the eutrophication impacts of human interventions on the watershed and receiving waters and the mechanisms of these impacts. Changes over time due to human activities must be extricated from those due to variations in weather and, sometimes, due to natural successional processeDespite these complexities, there are some general-izations that can be made regarding eutrophication, based on the large body of scientific literature on this topic. It is my goal to summarize our knowledge of the role of P in the eutrophication of lakes, reservoirs, streams, rivers, and estuaries.

CHARACTERISTICS OF PHOSPHORUS

Phosphorus is an essential component of nucleic acids and many intermediary metabolites, such as sugar phosphates and adenosine phosphates, which are an integral part of the metab-olism of all life forms. With the exception of trace emissions of phosphines from volcanoes, the P compounds found on the surface of the Earth are not volatile and transport through the atmosphere is primarily in dust or aerosols. Atmosphericflux rates are slow compared with those in surface waters(Hutchinson, 1957). With few exceptions surface waters receive most of their P in surface flows rather than in groundwater,since phosphates bind to most soils and sediments. The exceptions are where watersheds are of volcanic origin or where soils are water-logged and anoxic. Phosphoruso nly occurs in the pentavalent form in aquatic systems. Examples are orthophosphate, pyrophosphate, longer-chain polyphosphates, organic

phosphate esters and phosphodiesters, and organic phosphonates. Phosphorus is delivered to aquatic systems as a mixture of dissolved and particulate inputs, each of whichi s a complexmixture of these different molecular forms of pentavalent P. However P, is a very dynamic,b iologically active element. After these P inputs arrive in a receiving water, the particulatesmay release phosphate and organic phosphates to solution in the water columna nd various P compoundms ayb e chemicallyor enzymatically hydrolyzedto orthophosphate, which is the only form of P that can be assimilated by bacteria, algae, and plants. Particulates may be deposited in the bottom sediments, where microbial communities gradually use many of the organic constituents of the sediments, ultimately releasing much of their P contents back to the water column as orthophosphate (Fig. 2). Hence, one should not

assume that particulate P or dissolved organic P are inert in these aquatic systems because under appropriate conditions these forms of P can be converted to dissolved orthophosphate. Once delivered to a lake, reservoir, or estuary, P is usually retained fairly efficiently by a combinatioonf biological assimilation and the deposition of sediments and biota to the bottom sediments (Fig. 2). This efficient trapping of P inputs makes these systems sensitive to pollution with excessive amounts

THE PHOSPHATE BUFFER

It has often been claimed or assumed that particulate P inputs to receiving waters have relatively little effect on algal growth(e.g., Sonzogniet al., 1982), but this is not true. It has been widely observed that the patterns of dissolved orthophos-phate concentrations in receiving waters can only be explained if dynamicinteractions with both suspended

Fig. 1. Conceptualization of freshwater eutrophication.

particulate P and bottom sediments are taken into consideration (Hutchinson, 1957; Edmondet al., 1981; Boynton and Kemp. 1985: Jordanet al., 1991). For suspended sediments these dynamicequilibria between particulate and dissolved P became known as the phosphate buffer mechanism (Carritt and Goodgal, 1954; Froelich, 1988). Kinetically, there are two populations of par-ticulate P, rapidly and slowly equilibrating populations. The rapid population equilibrates within a few minutes, while the slower population takes a few days. The rapid reaction is believed to be due to reactions at the surface of particulates, while the slow reaction involves solid-state diffusion within the particulates. Whena river bearing suspended sediments discharges into a lake or estuary, the particulate P in the suspended sediments begins to re-equilibrate with the receiv-ing water's dissolved P. If the concentration of dissolved P is low, P is released from the suspendedsediments and vice versa. Once the particulates have settled to the bottom of the receiving water the situation becomes more complex. Biologi-cal activity gradually mineralizes organic P and releases P into the pore water surrounding the particles in the bottom sediments. This dissolved P may diffuse into the overlying water, but the phosphate may become bound to the surfaces of particulates before it can reach this overlying water. Binding to alumiiaum and ferric hydroxides is particularly strong. If the pore water becomesanoxic, due to respiratory activity in the sediments, the ferric ions are reduced to ferrous and bind-ing is weakened, allowing phosphate to diffuse more freely (Chen et al., 1973: Crosby et al.. 1984: Hutchinson. 1957: Wau-chope and McDowell.1984). Thus. the exchange of P between the water columnand bottom sediments often occurs at differ-ent rates seasonally or may only occur during such events as the spring turnover of lakes.

WHAT CONCENTRATION OF PHOSPHORUS IS ACCEPTABLE?

As discussed above, the response of lakes to P can be pre-dicted with the Vollenweider model from the rates of total P input to the lake. However, it is often desireable to predict whether a system will have excessive productivity based on water column concentrations of P. For one thing, it is a lot easier to measure concentrations in the water than fluxes into a system. If we elect to use this approach to assessing eutrophi-cation status, it is important to measure total P (including paniculate P) in the surface waters. Dissolved orthophosphate in eutrophic surface waters is often turning over every few minutes (e.g., Correll et a!., 1975). In such cases, the turnover rate of the available phosphate is so rapid, that the pool size is often misleading. Thus, total P is usually more meaning
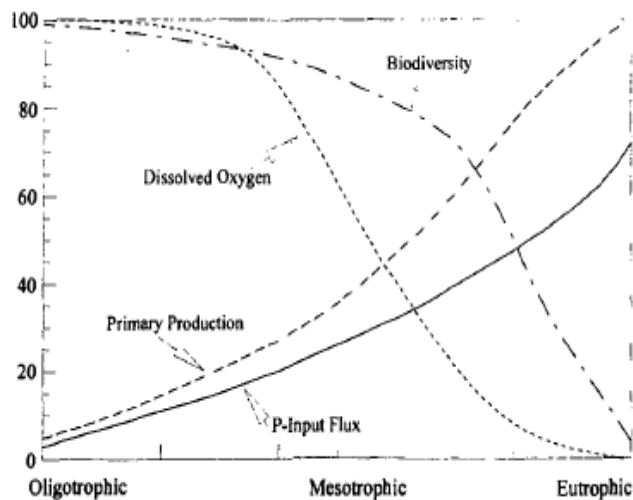
For example, in Chesapeake Bay during a period of increasing eutrophication in the 1970s, total P in surface waters during the summer and fall increased in a period of 8 yr from 20 to 50 (jig/L to 150 to 200 (ig/L, but dissolved orthophosphate-P was only 5 to 8 |Ag/L and hardly changed at all (Correll, 1981). If one had only monitored dissolved phosphate concentration, no change would have been apparent. In a laboratory study of 11 species of freshwater algae the concentration of phosphate- P needed to maintain equilibrium algal growth rates varied from 0.003 to 0.8 (xg/L (Grover, 1989). If phosphate-P levels were maintained at 15 u,g/L in mesocosms of Lake Michigan plankton, chlorophyll concentration increases and photosynthetic C fixation were maximized.Phosphate-P levels of 5 jJLg/L had almost as great an effect in these mesocosms (Shelske et al., 1974). These studies all lead one to believe that a pool size of a few micrograms per liter of phosphate-P is sufficient to saturate algal growth in most systems. How-ever, the recycling rate must be sufficient to maintain this pool size. This fact makes monitoring of dissolved phosphate a technique of limited value, if the goal is to measure eutrophi-cation potentials. A study by Morris and Lewis (1988) com-pared nine nutrient limitation indices for eight mountain lakes in Colorado. They conducted microcosm nutrient enrichments in situ in 10-L bottles to assess the actual nutrient limitations. They found that the ratio of dissolved inorganic N to total P was the best predictor of chlorophyll responses in the meso-cosms followed by paniculate N to particulate P ratios. Some investigators now use a combination of tests to infer whether P or N is most limiting. For example, Fisher et al. (1992) used phosphate and ammonium turnover times, alkaline phospha-tase activity, nutrient enrichment bioassays, and ratios of dissolved total N to total P in studies of Chesapeake Bay. It is best to measure P inputs to the whole system, hut for an easy assay it is best to measure total P concentrations in surface waters or N/P ratios in phytoplankton.What concentration of total P is acceptable? There is no clear, widely accepted answer to this question. Certainly, for most lakes, streams, reservoirs, and estuaries concentrations of 100 (xg total P/L are unacceptably high and concentrations of 20 n.g/L are often a problem.

is transported primarily by surface waters. In most aquatic ecosystems P is naturally present in more limiting amounts than the other essential elements. Human activities often result in large fluxes of P to receiving waters. Since P tends to be retained efficiently in these aquatic systems, this leads to higher primary production, especially in the summer and fall. High primary production, in turn, leads to high rates of decomposition and depletion of dissolved oxygen in bottom waters and surface waters at night in calm weather. These eutrophic conditions can result in fish kills and major shifts in the species composition at all trophic levels (Fig. 1). Lake primary production can be accurately predicted from data on input fluxes of P, but research and data synthesis are needed to establish reasonable standards for total P concentration in various types of receiving waters. Much of the dissolved organic P and particulate P inputs to receiving waters become available to the phytoplankton and bacteria as the result of phosphate buffering equilibrium between the particulates and dissolved phases, the action of phosphatases, and biological activity in the bottom sediments. When receiving waters have limiting amounts of P the phytoplankton biomass has N/P atomic ratios significantly above the Redfield ratio of 15 to 16. When N is limiting the Redfield ratio is much lower. If one needs to assess the P status of receiving water based only on P concentrations in the water column, it is better to measure the sum of dissolved and particulate total P than to rely on dissolved orthophosphate concentrations

CONCLUSIONS

Phosphorus plays a unique and important role in the eutrophication of receiving waters, especially lakes, reservoirs, streams, and the upper reaches of estuaries. While N and C can be obtained from the atmosphere,P

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