

Assessing Algal Available Phosphorus¹

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At the US EPA Science Symposium on “Sources, Transport, and Fate of Nutrients in the Mississippi and Atchafalaya River Basins,” held in Minneapolis, Minnesota, in November 2006, there were several presentations on phosphorus sources and dynamics in the Mississippi River watershed. One of these was by William James of the US Army Corps of Engineers, “Phosphorus Forms, Fluxes, and Transformations in the Upper Mississippi River,” in which he stated that the phosphorus that he measured in the lower Minnesota River was bioavailable, implying that it would support algal growth. James’ presentation at the symposium was based on James (2006), which provides additional information on his studies. A review of his data showed that a substantial amount of this phosphorus was in particulate form.

The issue of the forms of phosphorus that support algal growth is a topic that was intensively researched in the 1960s and 1970s in connection with developing management programs for excessive fertilization of waterbodies in Wisconsin and in the Great Lakes states. It was found in several studies, as summarized below, that particulate P in agricultural erosion and urban stormwater runoff was largely unavailable to support algal growth and did not convert to algal available forms under conditions that typically exist in aquatic systems.

In my comments on Mr. James’ presentation at the meeting I indicated that there is substantial literature based on algal assays, appropriately conducted leaching tests and studies on whole waterbody algal responses to particulate P loads relative to soluble P loads that most of the particulate phosphorus associated with soil erosion is not available to support algal growth. As I indicated in my comments on Mr. James’ presentation, the problem with his assessment of bioavailable P is with the methods he used to assess available P. He used a procedure based on chemical methods which selectively sequentially extracts phosphorus from particulate P in the Minnesota River samples that he examined. It is important to understand the limitations of the chemical leaching tests, such as those that he used for assessing “algal available” phosphorus.

This approach was first developed by soil scientists to estimate terrestrial soil P that would be available to support terrestrial plants through root uptake. The soil near roots is a significantly different environment from the aquatic environment where algae must extract phosphorus from particulates. The chemical extraction procedures, which involve an acid, a base and the use of complexing agents, etc., represent different conditions than those in which algae in aquatic systems must extract P from particulates. While there were (and still are) some investigators who, without careful evaluation, claim that the chemical extraction method for soil phosphorus would measure algal available P in water, studies conducted in the 1960s and 1970s showed that

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the soil P extraction procedures are not necessarily reliable to estimate algal available P. Subsequent studies using algal assays demonstrated that labeling some of the fractions extracted in the soil leaching tests as algal available P can be unreliable.

When I made these comments at the meeting, Mr. James indicated that he agreed with my statement. However, he added that his definition of available P considered the possible reactions that particulate P could undergo in the aquatic environment. Of particular concern is the conversion of iron P associated with particles to soluble ortho P. I further commented at the meeting that the conversion of particulate P to soluble ortho P in aquatic systems is an area in which I and others have conducted extensive research. It is well established that the thermally stratified conditions that promote the release of phosphorus from aquatic sediments under anoxic conditions also typically promote the release of ferrous iron to the water column. With few exceptions algal growth occurs in the euphotic zone above the thermocline/pycnocline where there is sufficient light to support algal growth. In many waterbodies when the hypolimnetic waters are mixed into the euphotic zone, the ferrous iron is oxidized to ferric iron which in turn co-precipitates the phosphorus in the iron hydroxide precipitate where it is not available to support algal growth.

Release of Phosphorus from Sediments

In the early 1970s I became involved in the US Army Corps of Engineers Dredged Materials Research Program (DMRP). The DMRP was a \$30-million, five-year research effort devoted to evaluating the potential water quality impacts of open-water disposal of contaminated dredged sediments. At that time, various Corps districts faced the problem of some regulatory agency staff claiming that open-water disposal of contaminated dredged sediments was having a significant adverse impact on the nation's water quality.

Under contract with the Corps, I developed a comprehensive literature review on this issue. I also served as a member of the DMRP Steering Committee, which oversaw the development, implementation and reporting of these studies. Also, I was responsible for conducting about one million dollars of DMRP research devoted to developing dredged sediment disposal criteria, focusing on evaluating the reliability of the elutriate test as a means of assessing the potential release of chemical contaminants from dredged sediments when suspended in a water column associated with open-water disposal of the sediments. These studies involved collecting US waterway sediments from approximately 20 sites across the US, performing chemical analyses on these sediments, and conducting leaching tests on the release of contaminants from the sediments to simulate open-water disposal of hydraulically dredged sediments.

In addition, I conducted detailed field monitoring studies of actual open-water disposal operations in the Atlantic Ocean at the New York Bight; in Elliot Bay, Puget Sound, Washington; the upper Mississippi River near Minneapolis-St. Paul; the James River near Hopewell, VA; the Gulf of Mexico near Galveston, Texas; Mobile Bay, Alabama; and Apalachicola Bay, Florida. These studies involved taking approximately 500 to 1,000 water samples just prior to, during and just following an open-water dredged sediment disposal operation. My DMRP studies were based on about 50,000 data points for 30 chemical parameters (heavy metals, pesticides, PCBs, nutrients, etc.). The studies included toxicity testing of the water and sediments as a means of integrating the effects of the different chemical and

physical factors that could influence water quality. My DMRP studies generated about 1,500 pages of reports, including Jones and Lee (1978) and Lee et al. (1978).

One of the parameters that received intensive study was phosphorus. Dr. Anne Jones-Lee (then, Anne Jones) conducted her PhD dissertation on the release of phosphorus upon suspension of US waterway sediments into the water column, under laboratory and field conditions. The complete data for these studies are presented in the above-referenced DMRP reports. Jones and Lee (1981) summarized the results of the release of phosphorus from the US waterway sediments investigated. These sediments were primarily estuarine/marine, with a few from fresh waters.

Overall, while the sediments contained significantly elevated concentrations of phosphorus, little or none of this phosphorus was released to the water column under conditions where it would be available to support algal growth – i.e., in the euphotic zone. A number of the sediments removed phosphorus from the water column that was present in the disposal site waters in which the elutriate tests were conducted. The sediments were typically anoxic at the time of collection and, therefore, had the potential to release phosphorus to the water column when suspended in it. They also released ferrous iron under anoxic conditions. However, when contacted by dissolved oxygen in the water column, the ferrous iron was rapidly converted to ferric iron, which co-precipitated the phosphate, taking it back to the sediments.

The interaction between iron and phosphorus is a topic area that I have extensively researched. Recently Jones-Lee and Lee (2005) have published a summary of the “Role of Iron Chemistry in Controlling the Release of Pollutants from Resuspended Sediments.” Based on the work of several investigators, including myself, it should not be assumed that the aquatic chemistry of phosphate is such that particulate P will be converted to soluble ortho P and remain in that form to support algal growth. Also, it should not be assumed that chemically extracted phosphate associated with iron (iron phosphate fraction of the soil leaching test) is a reliable measure of phosphorus that can lead to algal growth.

As mentioned above, the impetus for the DMRP studies was assertions that open-water disposal of contaminated dredged sediments was significantly degrading the quality of US surface waters. Studies conducted during the DMRP and subsequently have shown that such assertions were inaccurate and, in fact, the alternative approach for dredged sediment management (i.e., upland disposal) may cause greater adverse impacts on the environment, including the aquatic environment, than open-water disposal of dredged sediments. These issues have been reviewed by Lee and Jones-Lee (2000). As they discuss, the chemistry of aqueous iron associated with open-water disposal of dredged sediments is the primary reason why chemicals present in anoxic sediments (with the exception of ammonia) do not remain in the water column at the open-water disposal site and therefore do not have an adverse impact on water quality. This same situation will occur in waterbodies where deposited sediments become anoxic and then are suspended in the water column during elevated flow, storm conditions, etc.

Further review of Mr. James’ presentation at the symposium shows that the lower Minnesota River where he conducted his studies is dominated by domestic wastewater discharges of a variety of pollutants, including phosphorus. According to Gunderson and Klang (2004) of the Minnesota Pollution Control Agency,

“Wastewater treatment facilities contribute approximately two-thirds of the phosphorus to the lower Minnesota River during low flows. One step toward implementing the TMDL is the Minnesota River Basin General Phosphorus Permit – Phase I. The permit regulates phosphorus discharge from over 150 wastewater treatment facilities in the basin.”

Examination of the characteristics of the lower Minnesota River upon which Mr. James based his studies shows that the flow-weighted mean concentrations of viable chlorophyll-a in the Minnesota River near Jordan were 60 µg/L annual, 80 µg/L summer, and 50 µg/L winter during the period 1976-1996 (MCES 2002). The Minnesota River upstream and in the reach that was studied by Mr. James is a domestic-wastewater-dominated system, which is not typical of Mississippi River watershed streams and rivers that primarily derive their phosphorus from transport of erosional particulate P in runoff from agricultural lands. It is inappropriate to assume that the results obtained by Mr. James are representative of algal available P that would be present in upper Mississippi River watershed rivers and streams, where the phosphorus is derived from agricultural runoff sources.

An issue that needs to be better understood is the conversion of organic phosphorus to algal available forms. Generally it has been found that phosphorus in algal cells is largely, although not completely, mineralized to soluble orthophosphate. Whether this phosphate is available to support algal growth, however, depends on whether it is transported to the euphotic zone of a waterbody at a time when algal growth in the waterbody is limited by available P. As discussed by Lee et al. (1975), there are some sources of phosphorus, such as wetlands, that are refractory and therefore do not appear to convert to algal available P.

Assessing Algal Available P

During the 1960s and 1970s there was considerable interest in developing phosphorus management strategies for Lake Erie. Lake Erie was experiencing excessive growths of algae that led to impaired water quality and low dissolved oxygen in the lake. The predecessor organization to the US EPA, and its Ontario (Canadian) counterpart, proposed a phosphorus management strategy involving treatment of the domestic wastewaters discharged to the lake as a means of reducing phosphorus loads. At that time there was opposition to this approach by some who claimed that treating domestic wastewaters for phosphorus control would not reduce the phosphorus in the lake waters because of the large reservoir of phosphorus in the lake sediments. This led to interest in algal available phosphorus that is present in Lake Erie sediments and Lake Erie shoreline bluff erosion as a source of phosphorus for the lake. As part of this interest, the International Joint Commission for the Great Lakes organized a conference devoted to phosphorus management strategies for lakes in which I was invited to present a summary of the work that my graduate students and I had been doing on algal available forms of phosphorus. This led to the publication of “Availability of Phosphorus to Phytoplankton and its Implications for Phosphorus Management Strategies” (Lee et al. 1980).

This paper presented an integrated summary of the previous work that my graduate students and I had done on this issue in the 1960s and 1970s, as well as the subsequent work of others. The key finding from this work was that the algal available phosphorus in a water sample was equal

to the soluble orthophosphate plus about 20 percent of the particulate phosphorus. These results were based on algal assay studies, in which water samples were incubated under conditions where the only source of phosphorus for algal growth was that originally present in the sample at the time of collection.

Current Studies on Nutrient-Caused Water Quality Problems in the San Joaquin River Watershed and Delta

At this time I am involved in providing technical information that can help shape policy in regulating P in runoff/discharges from irrigated agriculture in the Central Valley of California. This situation is a miniature version of the Gulf of Mexico hypoxia, where the San Joaquin River (SJR) Deep Water Ship Channel (DWSC) near Stockton, California, experiences low dissolved oxygen (DO) concentrations each summer/fall and sometimes in the winter. In addition to the low DO being harmful to aquatic life in the channel, during the fall the SJR DWSC is a migratory route for Chinook salmon returning to their home stream waters for spawning. The low DO has been found to inhibit Chinook salmon migration. The state of California legislature has made available \$30 million to develop a program to implement a TMDL to solve this problem. Additional information on the SJR DWSC low-DO problem is available in Lee and Jones-Lee (2003, 2004a) and at <http://www.gfredlee.com/psjriv2.htm>.

The low DO in the SJR DWSC is the result of irrigated agriculture discharge of nutrients (N and P compounds) that develop into planktonic algae in the San Joaquin River. While there are no low-DO problems in the SJR upstream of the DWSC where the river depth is eight to 10 ft, upon entering the DWSC (35 ft deep) the algae die (due to being unable to gain sufficient light – euphotic zone is less than 6 ft), decompose and are a source of oxygen demand. The Central Valley Regional Water Quality Control Board (CVRWQCB) has designated the SJR DWSC as a Clean Water Act (CWA) section 303(d) impaired waterbody and is developing a TMDL to control the DO water quality standards violations. Lee and Jones-Lee served as the coordinating PIs for a two-million-dollar, two-year CALFED-supported study designed to develop information that can serve as the technical base for formulating a management program for eliminating the low-DO problem. Lee and Jones-Lee (2003) developed a synthesis report of the studies on the low-DO problem in the SJR DWSC. Much like the Mississippi River, the SJR has a large surplus of algal available N and P. The growth of algae in the SJR is light-limited due to self-shading and inorganic turbidity derived from erosion of agricultural lands.

Typically, the SJR during the summer months has a planktonic algal chlorophyll of 20 to as much as 80 $\mu\text{g/L}$. Total P is about 0.5 mg/L, and soluble ortho P, a few tenths of a mg/L. Nitrate typically occurs at 5 to 10 mg/L N. As discussed by Lee and Jones-Lee (2004b; 2006a,b) the nutrients in the SJR upstream of the DWSC not only lead to the growths of algae that lead to the low-DO problem in the DWSC, they also lead to excessive growths of macrophytes (water hyacinth and egeria) in the Sacramento-San Joaquin Delta. The Delta is the largest estuary on the west coast. It is a largely freshwater tidal system that is the source of domestic water supply for over 22 million in California. The water utilities that use Delta water as a raw water source experience sufficient growths of algae in their water supply storage reservoirs to cause severe tastes and odors in the treated waters, which have to be controlled by additional water treatment. These problems are related to the nutrients derived from irrigated agriculture in the SJR watershed, as well as other sources. As discussed by Lee and Jones-Lee (2006c,d) in their

presentation on “Agriculture-Related Water Quality Problems in the San Joaquin River” at the International Conference on the Future of Agriculture, in time, as nutrient criteria are developed for the SJR, DWSC, Delta and downstream water supply reservoirs, TMDLs will need to be developed to control the input of excessive N and P from irrigated agriculture in the SJR watershed.

While the south Delta and part of the eastern Delta contain excessive nutrients and severe water quality problems caused by these nutrients, the northern and central Delta have low nutrient concentrations as a result of the federal (US Bureau of Reclamation) and state (Department of Water Resources) water export projects drawing from about 10,000 to 13,000 cfs of predominantly low-nutrient Sacramento River water from the southwestern Delta.

One of the major issues that will need to be addressed is whether there is need to control the winter runoff particulate P from agricultural runoff in the SJR watershed. The precipitation patterns in the Central Valley are such that rainfall only occurs in the winter and spring; the summer and fall are generally dry, without precipitation. During this time irrigated agriculture generates tailwater and subsurface drain discharges. If the particulate P that is present in the high-volume stormwater runoff during the winter is not available to support algal growth and does not become available in downstream waters, then there would be no need to construct large detention basins to remove the particulate P in the winter runoff. This situation could potentially save irrigated agricultural interests considerable funds in treating field runoff. As part of exploring this situation, I recently prepared a proposal (Lee, 2006) for support of research that would be devoted to determining the algal available P in the SJR watershed winter stormwater runoff. The key components of this proposal are available at <http://www.members.aol.com/annejlee/AlgalAssayAvailP.pdf>

This proposal includes information on the type of testing that needs to be done to conduct assays of algal available P. Basically, the procedures are a modification of US EPA algal toxicity testing. Testing laboratories that conduct effluent and/or ambient water toxicity testing using *Selenastrum capricornutum* can readily conduct algal available P assays. This proposal also contains an updated discussion of algal available P literature.

Developing Phosphorus Control Programs in the Mississippi River Watershed

The issue of the role of particulate P in influencing nutrient management policy for controlling the size of the hypoxic zone in the Gulf of Mexico is important to agricultural interests in the Mississippi River watershed. While the primary driver for the hypoxia in the Gulf of Mexico is nitrate discharged to the Gulf, there is some evidence that algal growth in the Louisiana nearshore waters of the Gulf is limited by algal available P. The US EPA Region 4 (2004) issued a report which states in the Abstract, that “...*the Mississippi River system appears to be phosphorus limited.*” The eastern portion of the hypoxic zone also appears to be phosphorus limited.

This report stimulated considerable controversy regarding the approach that should be followed in managing the Gulf of Mexico hypoxia. The US EPA (2005) conducted an independent peer review of the role of phosphorus and nitrogen in influencing/controlling the hypoxic zone in the Gulf. There are some who assert that the phosphorus management strategy for various sources

of phosphorus in the Mississippi River watershed should be based on total phosphorus, implying that all of the particulate phosphorus is algal available or is converted to algal available forms in the Gulf. However, such claims are not in accord with the literature on the aquatic chemistry of phosphorus in marine systems (see Reviewer 3's discussion of this issue in US EPA 2005). Reviewer 3 in US EPA (2005) states,

“While the inclusion of P reduction goals should be thoroughly evaluated in the Reassessment, it is premature to add P goals without much more careful analysis. Based on the examples provided in 10.b.iv there may actually be a credible risk in increasing the size or severity of hypoxia by reducing P loading without also reducing N loading.”

Additional Information

I have been involved in developing phosphorus-based excessive fertilization management programs in the US and other countries since the mid 1960s. Listed below, under “Additional References,” are some of my publications on this issue. They provide additional information on issues that should be considered in formulation of a phosphorus management strategy to control excessive fertilization of waterbodies.

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