Role of Aquatic Plant Nutrients in Causing Sediment Oxygen Demand Part II – Sediment Oxygen Demand[1]

G. Fred Lee, PhD, PE, DEE and Anne Jones-Lee, PhD
G. Fred Lee & Associates
El Macero, CA 95618
gfredlee@aol.com www.gfredlee.com
June 2007

Part II of this report on the role of sediments as a source of oxygen demand for waterbodies. Part I, discussed the responsibility of inorganic oxygen demand reactions, involving ferrous iron and sulfides, for the rapid oxygen demand exerted when sediments are suspended into a watercolumn. As discussed therein, many aquatic sediments have a considerable reservoir of inorganic oxygen demand, which, under certain conditions – such as associated with stormwater runoff events – can lead to significant dissolved oxygen (DO) depletion when suspended in a watercolumn.

Biochemical oxygen demand (BOD) is a characteristic of a material (such as a sediment or wastewater) that represents the amount of oxygen utilized, primarily by bacteria, in the decomposition of the carbonaceous and nitrogenous substrates in that material under test conditions. The "Standard Methods" procedure for BOD determination is provided by APHA et al. (latest edition). Typically the BOD test does not include a reliable assessment of the inorganic (abiotic) rapid oxygen demand of the material, as that is initially removed in the execution of the test. The rate at which biotic (biochemical) reactions occur is slow (taking days) compared with the rate of the abiotic reactions largely responsible for the rapid DO depletion associated with suspension of sediments in a watercolumn. The BOD measurement is, therefore, of limited use in assessing the rapid DO depletion in urban streams associated with stormwater runoff situations.

Traditionally, DO depletion issues in streams and rivers have focused on domestic and some industrial wastewater discharges of BOD. Through water pollution control efforts, those types of problems have been largely controlled; an exception is combined sewer overflows. However, there are still situations in which other sources of oxygen demand can lead to significant DO depletion in waterbodies. Of particular importance, and the focus of this Part II of the Newsletter, is the role of dead algae as a source of oxygen demand for certain waterbodies.

There are two major types of situations for which nutrients discharged to waterbodies from point and non-point sources – including stormwater runoff from urban and agricultural areas – lead to sufficient algal populations to significantly adversely impact the DO concentrations in a waterbody. One occurs in unstratified waterbodies where the rate of exertion of dead-algal BOD is sufficient to overwhelm oxygen added to the system from photosynthesis and surface atmospheric aeration. Examples of such

---

[1] Reference as Lee, G. F., and Jones-Lee, A., "Role of Aquatic Plant Nutrients in Causing Sediment Oxygen Demand Part II – Sediment Oxygen Demand," Report of G. Fred Lee & Associates, El Macero, CA, June (2007).

situations are discussed herein for the San Joaquin River (SJR) Deep Water Ship Channel (DWSC) near the Port of Stockton, CA, and some South Delta channels in the Sacramento/San Joaquin Delta. The second situation is where nutrients from stormwater runoff from urban and agricultural sources and, in some instances, from wastewater discharges, lead to sufficient growths of algae to severely impact DO resources in a waterbody. This typically occurs in stratified eutrophic waterbodies. Lake Mendota in Madison, WI provides an example of this situation in this discussion.

This Newsletter also provides information on the relationship developed in the US part of the OECD International Eutrophication studies, between nutrient loads to lakes/reservoirs and hypolimnetic oxygen depletion rate.

Nomenclature

In this report the word “diffusion” is used to describe the migration of oxygen demand/oxygen into or out of sediments. It is important to understand that the use of this term does not imply that Fickian chemical concentration gradient diffusion is the cause of this “diffusion.” Fickian diffusion is a very slow process compared to the rate of exchange of materials between water and sediments. As discussed by Lee (1970) in a review of factors influencing the transfer of chemicals between bedded sediment and overlying waters, sediment/water exchange is governed by physical mixing processes caused by organism activity, bubbles of dissolved gas such as methane rising through the sediments, and water currents at the sediment/water interface that cause mixing of sediments with significant suspension of the bedded sediments into the watercolumn.

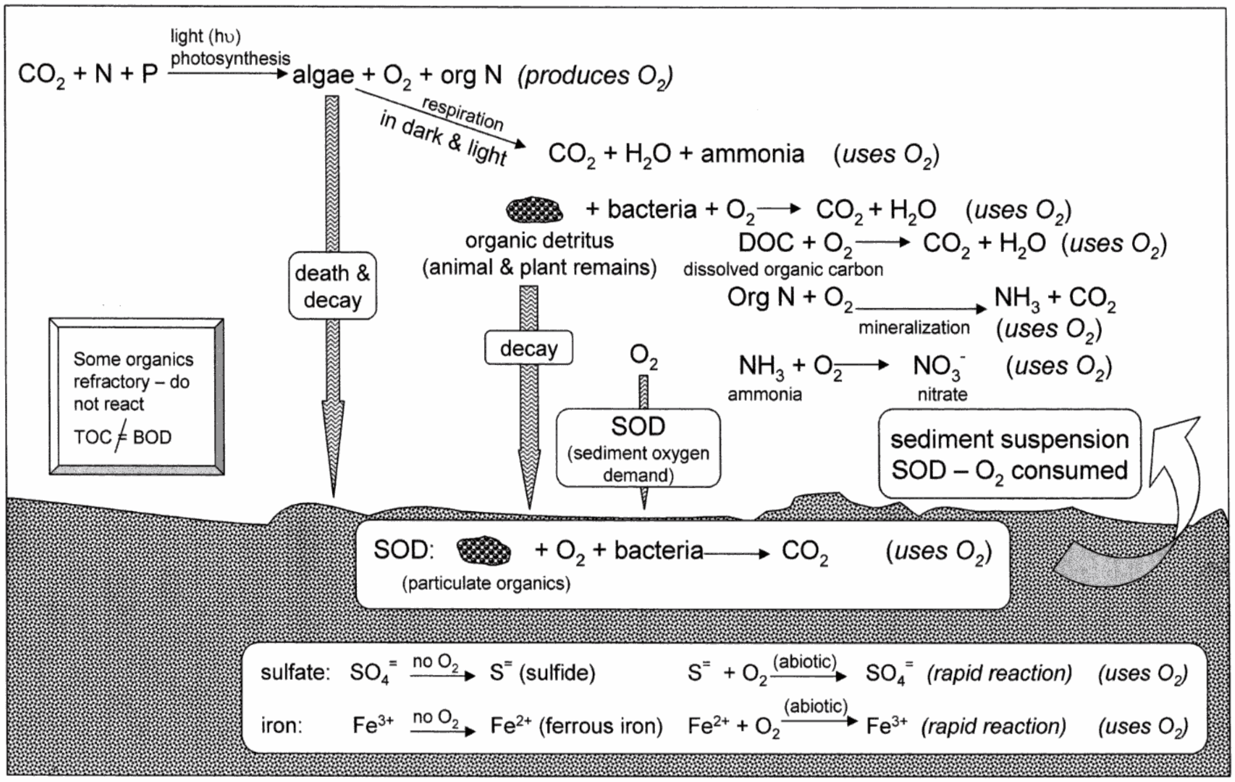
The chemical symbols used in this Newsletter with Roman numerals, such as Fe(III), S(-II) designate the element and its oxidation state; the Roman numeral indicates the number of electrons gained or lost from the elemental state. This approach does not indicate the chemical species present in a water or sediment.

Oxygen Depletion in the San Joaquin River/Stockton Deep Water Ship Channel

As discussed in Newsletter 10-1 (http://www.members.aol.com/annejlee/swnews101.pdf) at times the San Joaquin River Deep Water Ship Channel near the Port of Stockton (CA) exhibits severe DO depletion problems, with DO concentrations frequently several mg/L below saturation. On some occasions the DO decreases to zero or near zero, and causes fish kills. Newsletter 10-1 summarized the SJR DWSC low-DO issues; this Newsletter provides additional details on the role of nutrients/algae and other factors in the development of low DO in the DWSC. It includes a summary of the role of DWSC sediments as a source of oxygen demand; Lee and Jones-Lee (2003, 2004a,b) provided detailed information on this situation. Additional papers and reports on the DO depletion problem in the SJR DWSC are available at http://www.gfredlee.com/psjriv2.htm.

Figure 1 is a diagrammatic representation of the processes that govern the DO depletion in the DWSC. Over $4-million over an approximately 4-yr period have been devoted to investigating this issue; about half of the funds were derived from CALFED (the CA Bay-Delta Authority). One of the primary causes of depletion of DO in the SJR DWSC is the decomposition of algae in the DWSC. The algae develop in the comparatively shallow (8- to 10-ft deep) San Joaquin River upstream of the DWSC, from nutrients derived from agricultural stormwater runoff, irrigation tailwater, and subsurface drainwater discharges. The SJR is sufficiently well-mixed upstream of the DWSC that the algae in the river are sufficiently exposed to sunlight to live and reproduce, amassing to 50 to 100 µg/L planktonic algal chlorophyll during the summer and early fall. As the SJR water enters the 35-ft-deep DWSC, it slows, and the algae settle out of the photic (light penetration) zone. They die and become a source of oxygen demand.

Figure 1
Conceptual Model of DO Depletion Reactions
in the SJR DWSC



Algal decomposition (mineralization to CO_2 and water) can be an important source of oxygen demand in waterbodies. The normal atomic stoichiometric composition of algae, 106 C, 16 N and 1 P, means that a small amount of algal-available N and P can produce a large amount of organic carbon. Richards (1965) pointed out that 276 oxygen atoms are used in mineralization for each P atom incorporated into an algal cell. Fitzgerald (1964) found that, per unit mass, dead algal cells have a BOD about equivalent to that of organic matter in domestic wastewaters. He also found that the rate of BOD exertion by dead algae is about the same as it is for domestic wastewaters.

Another source of oxygen demand in the DWSC is the ammonia that is discharged by the city of Stockton to the SJR just upstream of the Channel. Through nitrification reactions bacteria oxidize the ammonia to nitrate, consuming oxygen in the process. At times, the city's wastewater effluent contains ammonia concentrations of 25 to 30 mg/L N. The biological conversion of one gram of ammonia to nitrate consumes 4.6 grams of oxygen. Organic nitrogen in the city of Stockton's wastewaters can be converted, through ammonification reactions, to ammonia, which, in turn, can also be nitrified to nitrate.

As discussed by Lee and Jones-Lee (2003), the significance of organic N and ammonia in domestic wastewater from the city of Stockton, compared with algae, as a source of oxygen demand in the DWSC during the summer and early fall, depends on the flow of the SJR through the DWSC. When the SJR flow through the DWSC is low, the city's ammonia load to the DWSC is the primary cause of low DO in the DWSC. The city of Stockton is in the process of modifying its domestic wastewater treatment to nitrify its wastewater before discharge to the SJR. If the ammonia concentration in the effluent is reduced to a few mg N/L, the contribution of ammonia to the low-DO problem in the DWSC can be significantly reduced. That notwithstanding, under certain SJR flow conditions there will still be sufficient algae-derived oxygen demand to cause significant DO depletion in the DWSC.

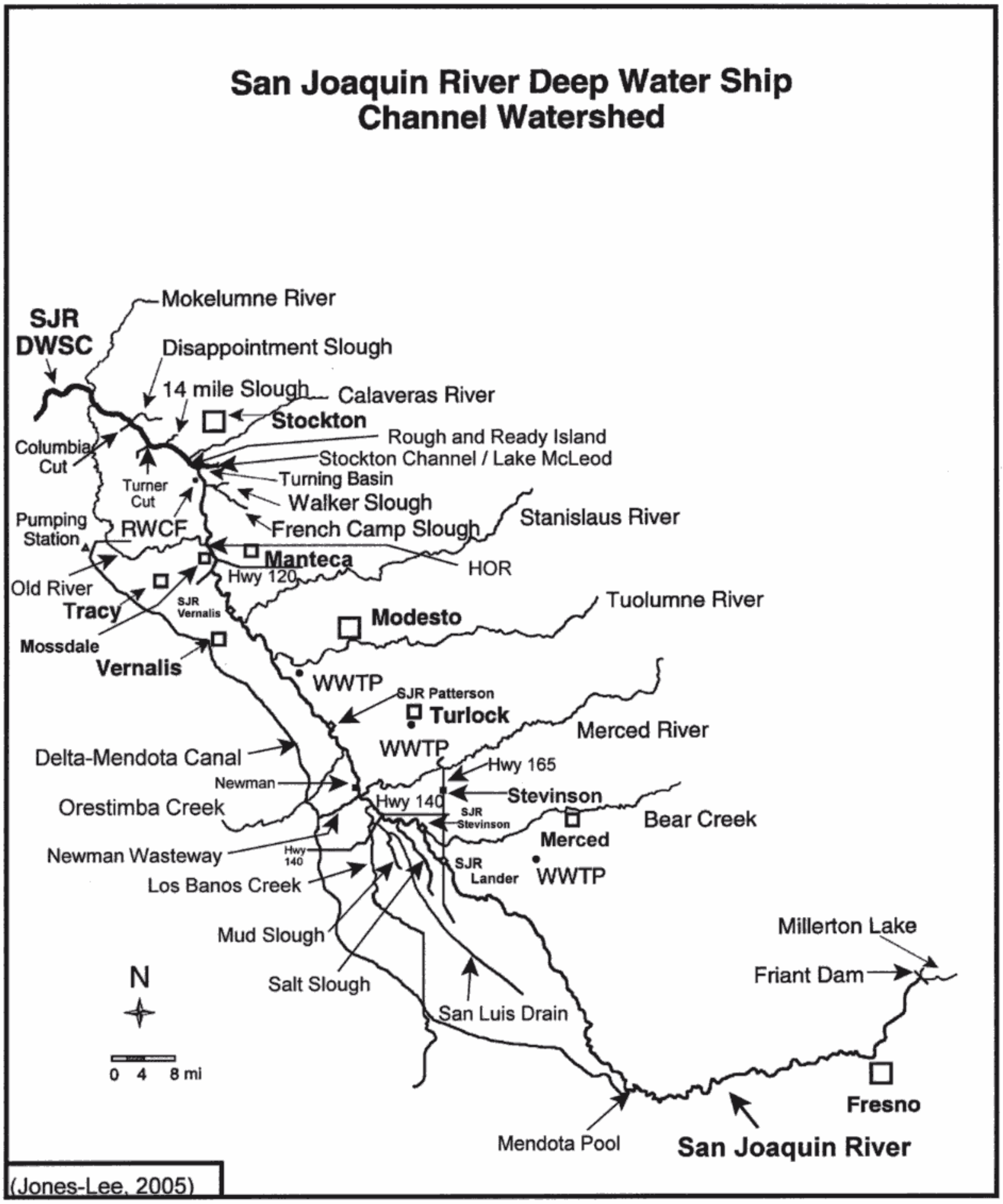
Figure 2 is a map of the Delta and its SJR watershed showing the locations of the areas mentioned in this Newsletter. The California Department of Water Resources (DWR, 2007) has published an updated "Overview" of the characteristics of the Delta. As discussed by Lee and Jones-Lee (2003), diversions of SJR water upstream of the DWSC largely control the flow of the SJR through the DWSC. Of particular significance is the diversion that occurs at the Head of Old River where the US Bureau of Reclamation and the CA Department of Water Resources draw SJR water into the South Delta for export to the San Francisco Bay area, and central and southern California, via the Federal and State Projects. At times, these projects reduce the summer/fall flow of the SJR through the DWSC from the typical 1000—2000 cfs to about 50 cfs. This reduction changes the residence time of oxygen-demanding materials in the critical reach of the DWSC (first 7 mi) from a few days to a few weeks. This allows much greater exertion of the oxygen demand within this reach of the DWSC, before the SJR water mixes with Sacramento River water that is drawn down Turner Cut into the Central Delta.

Overall, it is concluded that since there is no low-DO problem in the SJR upstream of the DWSC (even though the algal concentrations/loads are the same as the water that enters the DWSC) the development of the DWSC to enable ocean-going vessels to reach the Port of Stockton is a primary factor responsible for the low-DO problem in the DWSC.

The CA Central Valley Regional Water Quality Control Board (CVRWQCB) is proposing to control the low-DO problem in the DWSC by establishing a Total Maximum Daily Load (TMDL) for oxygen-demanding materials, and assigning a joint responsibility for controlling the low-DO problem to: those discharging oxygen-demanding materials to the DWSC; to those water diverters who alter the SJR flow through the DWSC; and to the Port of Stockton owing to its interest in maintaining the DWSC as a navigation channel. (Information on this TMDL is available at http://www.waterboards.ca.gov/centralvalley/programs/tmdl/sjr_do/index.html.)

The CVRWQCB is requiring that the responsible parties work together to solve the low-DO problem in the DWSC. It is likely that that problem will be at least partly solved by the aeration of the DWSC that is being developed and for which the responsible parties

Figure 2



(Jones-Lee, 2005)

will pay. The state of California legislature has made about $30-million available for the initial development of solutions for the low-DO problem. At this time, funding beyond that amount will have to be supplied by the responsible parties.

SJR DWSC SOD Issues. One of the issues of interest in assessing the low-DO in the DWSC is the role played by sediment oxygen demand (SOD) in the channel. The SJR Deep Water Ship Channel does not exhibit persistent thermal stratification. While there is temporary thermal stratification of the nearshore waters of the DWSC, there is complete mixing of the watercolumn from the surface to the 35-ft-deep bottom of the channel each night. Therefore sediment oxygen demand would contribute to the overall oxygen depletion that occurs in the channel.

G. Litton of the University of the Pacific in Stockton, CA conducted studies to examine the sediment oxygen demand in the SJR DWSC (Litton, (2003) available at, http://sjrdotmdl.org/library_folder/litton_final_report.pdf). His studies were summarized by Lee and Jones-Lee (2003) in their synthesis report on the SJR DO TMDL studies. Litton found that the bedded-sediment oxygen demand of the Ship Channel was on order of 2,000 lb/day of dissolved oxygen. On a per-unit-area basis, the DWSC SOD is on the low end of oxygen demand typical of bedded sediments in rivers. Litton's studies revealed that the high tide-induced currents in the channel kept the dead algae and other oxygen-demanding materials suspended in the channel watercolumn a few meters above the sediment/water interface. Typically, in other waterbodies, the particulates, including oxygen-demanding particulates such as dead algae, settle to the sediments and become part of the bedded (deposited) sediments and thereby contribute to the bedded-sediment SOD. This may account for the finding of lower measured SOD in the DWSC system.

Bowman and Delfino (1980) reported on the characteristics, strengths, and weaknesses of various methods used to measure sediment oxygen demand. Hatcher (1986) organized an SOD conference wherein a number of papers discussed what was known then about aquatic sediments as sources of oxygen demand. As far as has been determined, the conference proceedings are not available on the Internet or from their publisher; they may be available in some university libraries.

Both Bowman and Delfino (1980) and several of the authors in the Hatcher (1986) conference proceedings discussed the use of submerged chambers for assessing SOD. This approach involves placing a chamber on the bedded sediment and measuring the oxygen concentration in the chamber over time. Sonzogni et al. (1977) used large submerged chambers to measure sediment-water release of phosphorus from Lake Shagawa, Minnesota. Those studies included DO uptake which they measured to be 0.17 g/m^2/day.

According to Bowie et al. (1985) in the US EPA report, "Rates, Constants, and Kinetic Formulations in Surface Water Modeling," the typical SOD of bedded river sediment is on the order of 0.1 to about 10 g O_2/m^2/day. Chapra (1997) reported that the typical range of bedded SOD is about 0.05 to 2 g O_2/m^2/day. Those values, many of which were based on a submerged chamber SOD measurement approach, are the ones typically used in Streeter-Phelps-type modeling of oxygen demand reactions in rivers downstream from oxygen-demand sources. While submerged chamber and Streeter-Phelps modeling approaches are widely used, they do not provide a reliable assessment of the SOD of bedded sediments under environmental conditions. The SOD so-measured is due to BOD of organic matter in the sediments and the inorganic oxygen demand due to ferrous iron and sulfides which, through slower, “diffusion”-controlled processes, interact with DO that enters the sediments. It largely ignores the rapid oxygen demand associated with sediment-associated ferrous iron and sulfides that become suspended into the watercolumn. As discussed in Newsletter 10-4, short-term, episodic events, such as storms, that stir bedded sediment into the watercolumn can have a significant adverse impact on the DO and aquatic life in a waterbody. Exertion of sediment oxygen demand in that manner is not typically addressed in Streeter-Phelps-type oxygen-demand modeling of rivers.

South Delta Low-DO Problems. The DO depletion situation in the Sacramento/San Joaquin Delta occurs not only in the DWSC but also in several of the South Delta channels, including Old River near the Tracy Blvd. bridge. That channel has become essentially stagnant with respect to flow of water as a result of the US Bureau of Reclamation (USBR) and California Department of Water Resources’ (DWR) export of water from the South Delta in the Federal and State water export Projects. This export-pumping of water from the South Delta can be sufficiently rapid to lower the water level in some of the South Delta channels and thereby prevent irrigation pumps from obtaining water from the affected channels. The lowering of the water level also impairs the navigability of the channel by small recreational boats. In an effort to maintain water levels in the South Delta channels, DWR constructs temporary rock barriers on several channels to limit movement of water out of those channels. Algae grow in those channels and cause a potential for low-DO conditions to develop, especially at night. On August 5, 2004 a large fish kill occurred in the Old River channel near the Tracy Blvd. bridge near the location at which DWR operates a continuously recording DO monitoring station (Lee et al., 2004). On the night before that fish kill, the DO in the channel was recorded at zero. By mid-morning after the fish kill, the DO at that location was several mg/L, apparently due to algal photosynthesis. Based on the DWR monitoring stations’ data, low-DO that is significantly adverse to fish and other aquatic life occurs periodically in several of the South Delta channels. The diurnal photosynthesis/respiration cycle and the decomposition of algae are likely to be the primary cause of that low DO.

Oxygen Depletion in Stratified Lakes

Lakes and reservoirs in temperate regions tend to thermally stratify during late spring, a condition maintained through summer and early fall. This stratification divides the waterbody into the warmer upper (epilimnetic) water, and the somewhat cooler lower (hypolimnetic) water. The transition between the epilimnion and hypolimnion is called the thermocline; in this transition area there is a sharp change in temperature with depth. In many waterbodies, the temperature-induced density difference that exists across the thermocline is an effective barrier to the mixing of surface with bottom waters. The establishment of stratification is due to solar heating of the surface waters which causes them to be less dense than the waterbody as a whole at the time of spring mixing, and causes them to remain at the surface. In a lake or reservoir typical of temperate areas, the thermocline occurs at about 8 to 12 m below the surface. Its position is determined to a considerable extent by the degree of wind-mixing. Algae grow in the photic zone, typically the upper few meters of the waterbody wherein there is sufficient light penetration to support algal growth. As the algae that grow in the photic zone die, they settle through the thermocline and begin to undergo bacterial decomposition with the attendant utilization of dissolved oxygen. This leads to a depletion of the dissolved oxygen in the hypolimnetic waters. In a waterbody whose hypolimnion is of small volume compared to the waterbody surface area, all of the hypolimnetic oxygen can be depleted by early summer. In waterbodies with comparatively large hypolimnetic volumes, the oxygen demand of the descending phytoplankton may not be sufficient to exhaust the DO in the bottom waters. (Additional information on the limnological processes that take place in lakes and reservoirs is available from Goldman and Horne, 1983).

Role of Sediment Oxygen Demand in Depletion of Hypolimnetic DO. Lee and Jones-Lee (1995) summarized the mechanism of deoxygenation of the hypolimnia of lakes. In her MS thesis, Conway (1973) (with the assistance G. Veith of the Water Chemistry Program at the University of Wisconsin, Madison) developed a model that describes the role of Lake Mendota sediments in hypolimnetic DO depletion. That model was based on the earlier work of Hutchinson (1938, 1957) who proposed that DO depletion in the hypolimnia of lakes is the result of the decomposition of phytoplankton that develop in the upper waters (epilimnia) and settle through the thermocline where they die and decompose.

In the Conway-Veith work it was found that the primary cause of the oxygen demand in the hypolimnion of Lake Mendota was the decomposition in the hypolimnion of algae produced in the epilimnion. Even though the Lake Mendota sediments had a very high inorganic oxygen demand (discussed below), that demand was not a major factor controlling the DO depletion in the hypolimnion. The influence of the sediment oxygen demand extended only a meter or so above the sediment/water interface. This is another example of the control of the exertion of high inorganic sediment oxygen demand by the degree of mixing/suspension of the sediment into the watercolumn (discussed in Newsletter 10-4). The sediments in the deeper water of Lake Mendota are fairly cohesive and not readily suspended.

Conway (1973) also examined the history of DO depletion in the hypolimnion of Lake Mendota with particular emphasis on the role of hypolimnetic oxygen depletion in the demise of Cisco (*Leucichthys* *artedi)* in this lake. Cisco are a cold-water salmonids fish that cannot survive in the epilimnion of lakes like Lake Mendota because of their low tolerance for warm temperatures and diminished DO; they require temperatures of less than about 20 C and DO concentrations of at least 3 mg/L. Lake Mendota had a native population of Cisco; there were a number of Cisco die offs during the summer in the period 1930 to the 1950s until its demise from the lake. The hypolimnion of Lake Mendota has become anoxic since measurements were first made in 1906. DO depletion rates in the hypolimnion of this lake as measured at 15 m depth (a meter or so below the thermocline) has increased from about -0.15 mgO_2/L/day in 1906 and -0.18 mgO_2/L/day in 1907 to -0.2 mgO_2/L/day to -0.25 mgO_2/L/day in the 1960s and 1970s. The DO depletion just below the thermocline is a first-order process with respect to oxygen concentration; the rate is proportional to the amount of oxygen present. During that period the oxygen depletion rate at 21 m depth (about 1-2 meters above the sediment/water interface) was on the order of -0.04 mgO_2/L/day with no apparent increase in the rate depletion between 1906/7 and the 1960s. Oxygen depletion near the sediment/water interface is a zero-order process with respect to oxygen concentration; the rate is independent of DO and is controlled "diffusion" processes. These results are in accord with what is expected for sediment oxygen demand near the bottom and planktonic algal decay just under the thermocline.

During the period 1900s to the 1960s the Lake Mendota watershed became increasingly urbanized. That urbanization likely contributed the increased load of phosphorus to the lake that has resulted in increased phytoplankton growth. The increased phytoplankton production has resulted in the observed increased rate of hypolimnetic oxygen depletion. It is estimated that in the early 1900s the Cisco survived in the anoxic hypolimnion by inhabiting a limited niche just under the thermocline where the water temperature was sufficient low to allow the fish to survive and the DO sufficiently high, as a result of "diffusion"/mixing of oxygenated epilimnetic waters through the thermocline. With increased phytoplankton production, the oxygen levels just below the thermocline became too low for the Cisco to survive. The temperature of the surface waters of Lake Mendota, which would have sufficient DO, can reach about 25 C during the summer, too high for Cisco to survive. As illustrated by the Lake Mendota Cisco die-off, the oxygen demand associated with the decomposition of planktonic algae can be of comparatively greater significance to oxygen resources of the hypolimnion of a stratified lake, than SOD.

Oxygen Demand of Lake Mendota Sediments. Gardner and Lee (1965) studied the rate of reaction of Lake Mendota sediments and DO using a monometric technique, measuring the decrease in the amount of gas-phase oxygen over time as it reacts with sediments shaken in water. (This approach is described by Baird and Smith (2002) and Standard Methods (APHA et al., latest edition).) Lake Mendota's sediments contain high concentrations of iron- and sulfide/polysulfide precipitates. The sediment samples investigated by Gardner and Lee contained about 20,000 mg/kg (dry weight) iron and about 2,000 mg/kg (dry weight) "sulfides". The oxidation of the iron and "sulfides" (as discussed in Newsletter 10-4) in the Gardner and Lee (1965) investigation is similar to that which occurs in urban and rural streams when a stormwater runoff event suspends the stream/waterway sediments into the watercolumn. (The Lake Mendota sediments contained about 30% $CaCO_3$ (calcium carbonate) and were therefore well-buffer at a pH of about 8. This buffering prevents change in pH normally associated with oxidation/reduction reactions.) Gardner and Lee found that the initial DO consumption reaction by these sediments was extremely rapid for a period of about 3 days; this was followed by a much slower reaction that took place over months. The slower reaction appeared to be zero-order and controlled by the rate of diffusion of DO into the ferric hydroxide coating that had formed on the iron sulfide/polysulfide precipitates [S(-II)/S(-

I), H_2S, and HS^-]. In oxic waters, the stable sulfur species is sulfate. In anoxic waters all the oxidized forms of sulfur, such as sulfate, are reduced to "sulfides" which can precipitate with ferrous iron.

As discussed by Bortleson and Lee (1972), deeper water sediments of Lake Mendota are covered with a half-meter-thick layer of gyttja ("sludge"), which is underlain by gray marl. The Bortleson and Lee studies of Lake Mendota sediments included collecting an approximately 10-meter long piston core of the lake sediment at the 84-foot-deep "deep hole" of the lake. This core penetrated through all of the post-glacial sediments that had accumulated in the lake since the glacier ice retreated from this area about 10,000 years ago. Their results indicated that stable conditions existed in Lake Mendota and its watershed prior to settlement of the Lake Mendota watershed in the mid to late-1800s. Since that time, there has been a significant increase in the amounts of P, Fe, Mn, Al, and K in the upper sediments. The organic carbon content of the sediments has fluctuated several times in the past with slightly higher values in the more recent sediments.

The black color of the gyttja is sometimes incorrectly attributed to organics in the sediments. It is, in fact, caused by iron sulfides and polysulfides which are black in color. Under conditions of limited mixing such as in the laboratory environment, a brown ferric hydroxide oxidized layer occurs on the surface of the gyttja. This is the result of the interaction of DO with ferrous iron, which precipitates on the surface of the sediment as brown-colored ferric hydroxide. However, in the lake environment, mixing within the sediment caused by hypolimnetic currents, benthic organism bioturbation, fish foraging, and gas evolution, tends to destroy stratification layering within the gyttja so that the sludge layer is fairly homogeneous in composition. Lee (1970) discussed the factors influencing the transfer of chemicals between sediments and the overlying waters. As he discussed, the rate of transfer is controlled primarily by the rate of mixing of the sediments with the overlying waters. More recently, Thibodeaux (2005) confirmed the earlier finding of Lee; he reported that the primary mechanism for sediment-water exchange reactions is physical mixing.

Manganese as a Source of Sediment Oxygen Demand. Manganese exists in aquatic systems in the dissolved manganous (Mn II) form and in the solid manganic (Mn IV) form as the MnO_2 precipitate. In aquatic systems, manganese undergoes oxidation/reduction and precipitation reactions in much the same way as iron (see Newsletter 10-4). Mn (II) reacts with dissolved oxygen to form MnO_2. In the absence of dissolved oxygen, MnO_2 is reduced to Mn (II) which can be present as a soluble form in the watercolumn or as manganese carbonate ($MnCaCO_3$) or manganese sulfide (MnS) precipitate in the sediment. Thus, reduced forms of manganese in a waterbody sediment can potentially contribute to the inorganic sediment oxygen demand. Stumm and Morgan (1996) discuss more details of the chemistry of manganese in aquatic systems.

The Lake Mendota deep water sediments contain about 1,000 mg Mn(II)/kg dry wt. of sediment (Delfino et al. 1969). The studies of Delfino (1968) (as part of his Ph.D. dissertation in the Water Chemistry program at the University of Wisconsin, Madison) as published by Delfino and Lee (1968, 1971) on the chemistry of manganese in Lake

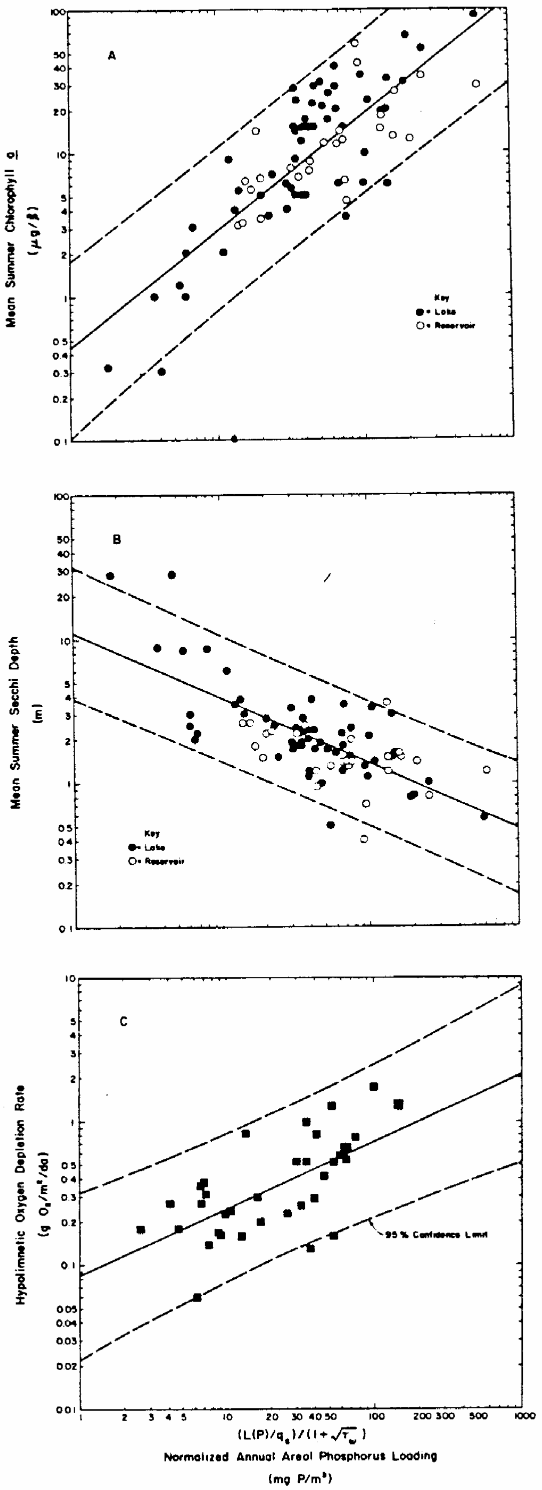
Mendota provide insight into the role of manganese in surface sediments as a source of oxygen demand for the Lake Mendota. Delfino has published several other papers on the chemistry of manganese in aquatic systems. They are listed on his website at http://www.ees.ufl.edu/homepp/delfino/pubs.htm.

As part of his Ph.D. dissertation in Environmental Engineering at Harvard University, Morgan conducted studies on the reactions of Mn (II) with dissolved oxygen (published by Morgan and Stumm (1965) and in Stumm and Morgan (1996)). His studies were similar to those of Stumm and Lee (1961) on the reactions between iron II and dissolved oxygen. The results of the Morgan and Stumm (1965) studies were also similar to those of Stumm and Lee in that the Morgan studies showed that in pure solution, manganese oxidation by dissolved oxygen (like ferrous iron oxidation), was highly pH-dependent. One significant difference between the oxidation of iron and the oxidation of Mn, however, was that the Mn (II) was autocatalytic, i.e., the rate of reaction increased as the reaction proceeded. The autocatalytic nature was believed to be due to the oxidation of Mn (II) that had sorbed onto MnO_2.

Another difference was that Morgan found that pH's above about 9 were necessary to achieve a rapid oxidation of manganese by dissolved oxygen. (Recall that Stumm and Lee (1971) had found rapid oxidation of ferrous iron at pH's near or above about 7.) The finding that a higher pH was necessary to achieve rapid oxidation of Mn (II) by DO has important implications regarding the role of the Mn (II) in a waterbody sediment in the rapid exertion of sediment oxygen demand upon suspension of the sediment in the watercolumn. Ordinarily, pH in waterbodies is less than 9. Thus, the manganese present in Lake Mendota sediments, and likely those of other waterbodies, may not be a major factor in rapid DO depletion upon suspension of the sediments in the watercolumn. It could, however, be a factor in the slower exertion of oxygen demand associated with aquatic sediments.

OECD Eutrophication Studies. As part of the Organization for Economic Cooperation and Development (OECD) eutrophication studies, Vollenweider (1968, 1976) developed empirical relationships between the phosphorus load to a waterbody (lake or reservoir), as normalized by waterbody mean depth and hydraulic residence time (filling time), and average annual chlorophyll concentration in the waterbody. G. F. Lee had the US EPA contract to develop the synthesis report for the US portion of the OECD eutrophication study. As part of that work, Rast and Lee (1978) and Lee et al. (1978) expanded Vollenweider's modeling approach in various aspects, including defining a similar relationship between the normalized phosphorus load and Secchi depth (water clarity) and between normalized P load and hypolimnetic oxygen depletion rate, based on data for the US OECD waterbodies. These relationships are shown in Figure 1.

The abscissa for these three plots is the phosphorus load to the lake/reservoir normalized by the waterbody's mean depth and hydraulic residence time; that value for a waterbody is approximately equal to the waterbody's average in-lake P concentration. As shown in Figure 1, using the US OECD data, a correlation can be defined between the normalized P loads and the measures of planktonic algal biomass — chlorophyll (A), Secchi depth



KEY

L(P) = Areal Annual Phosphorus Load (mg P/m²/yr)

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

τ_ω = Hydraulic Residence Time (yr)

Figure 1. US Waterbody P Load -- Eutrophication Response Relationships (After Jones and Lee[6])

After Jones and Lee (1982, 1986).

(B) and hypolimnetic oxygen depletion rate (C). The relationship shown in Figure 1A is essentially the same as that described by Vollenweider on the basis of non-US OECD waterbodies. (Jones and Lee (1982, 1986) provide additional discussion of the development of the relationships shown in Figure 1.) Jones and Lee (1986) discussed the continuing development and expansion of the relationship between normalized P load and chlorophyll (Figure 1A) as additional data were obtained. Presently, the empirical relationship is defined from data on more than 750 waterbodies from many parts of the world and covering waterbodies with a wide range of trophic, geographic, and climatologic conditions. The reliability of using these relationships for predicting the impact of changing the P load to a waterbody on its planktonic algal chlorophyll levels was evaluated by Rast et al. (1983) using actual data for waterbodies before and after major alterations to their P loads. They found the approach to be highly reliable for water quality management.

The middle plot in Figure 1 shows the relationship between normalized P load and water clarity as measured by Secchi depth. This relationship is defined by the role of planktonic algae in reducing light penetration into a waterbody. It does not apply to waterbodies whose turbidity arises largely from erosional input of turbidity from the watershed or the stirring of the waterbody's sediments into the watercolumn.

The third plot in Figure 1 shows the empirical relationship between the normalized P load and the rate of DO depletion in the main part of the hypolimnion several meters above the sediments, normalized by hypolimnion surface area. This relationship is a logical extension of the Vollenweider (1976), Rast and Lee (1978), and Lee et al. (1978) relationships since, as discussed in this Newsletter, the primary mechanism for the depletion of hypolimnetic DO is the decomposition of the phytoplankton produced in the surface waters during the period of its thermal stratification. While there is considerable scatter about the line of best fit for hypolimnetic DO depletion rate (Figure 1C) there is a sufficiently well-defined relationship to enable the estimation of the rate of hypolimnetic oxygen depletion in thermally stratified waterbodies. This relationship has been successfully used, for example, to predict whether a new reservoir would be expected to maintain DO in its hypolimnion Lee and Jones (1984a,b). The findings of such an analysis would be of importance especially for those reservoirs that are to be used for domestic water supply, for reservoirs from which there may be a hypolimnetic discharge of water at the reservoir dam, or for waterbodies in which there is concern about maintaining cold water species in the hypolimnion.

Overall, the OECD Eutrophication Study relationships provide a readily usable approach that can be implemented for many waterbodies to evaluate the eutrophication-related water quality as impacted by phosphorus loads. Jones and Lee (1982, 1986) provide guidance on the application of these relationships to waterbodies.

References

APHA, AWWA, and WEF, "Standard Methods for the Examination of Water and Wastewater," (American Public Health Association, American Waterworks Association, and Water Environment Federation), American Public Health Association, Washington, D. C., (latest edition).

Baird, R, B., and Smith, Roy-Keith, “**Third Century of Biochemical Oxygen Demand,**” Water Environment Foundation, Alexandria, VA (2002).

Bortleson, G. C., and Lee, G. F., "Recent Sedimentary History of Lake Mendota, Wisconsin," Environ. Sci. & Technol. **6**:799-808 (1972).
http://www.members.aol.com/LFandWQ/BortlesonSedHistMendota.pdf

Bowie, G. L., Mills, W. B., Porcella, D. B., Campbell, C. L., Pagenkopf, J. R., Rupp, G. L., Johnson, K. M., Chan, P. W., and Gherini, S. A., “Rates, Constants, and Kinetic Formulations in Surface Water Modeling,” 2nd edition, US EPA EPA/600/3-85/040, US EPA, Athens, GA, June (1985).

Bowman, G. T., and Delfino, J. J., " Sediment Oxygen Demand Techniques: “A Review and Comparison of Laboratory and in Situ Systems," Water Research **14**:491-499 (1980).

Chapra, S., **Surface Water Quality Modeling**, McGraw-Hill, New York (1997).

Conway, C., **Oxygen Depletion in the Hypolimnion**, MS thesis Water Chemistry Program, University of Wisconsin Madison, Madison, WI (1973)

Delfino, J., “**Aqueous Environmental Chemistry of Manganese**,” PhD dissertation, Water Chemistry Program, University of Wisconsin Madison, Madison, WI (1968).

Delfino, J., and Lee, G. F., "Chemistry of Manganese in Lake Mendota, Wisconsin," Environ. Sci. & Technol. **2**(12):1094-1100 (1968).
http://www.members.aol.com/LFandWQ/DelfinoChemistryMn.pdf

Delfino, J., and Lee, G. F., "Variation of Manganese, Dissolved Oxygen and Related Chemical Parameters in the Bottom Waters of Lake Mendota, Wisconsin," Journ. Water Res. **5**:1207-1217 (1971).
http://www.members.aol.com/LFandWQ/DelfinoVariationMendota.pdf

Delfino, J. J., Bortleson, G.C. and Lee, G. F., “Distribution of Mn, Fe, P, Mg, K, Na and Ca in the Surface Sediments of Lake Mendota,” Environ. Sci & Technol. **3**:1189-1192 (1969). http://www.members.aol.com/LFandWQ/DelfinoDistributionMn.pdf

DWR, “Sacramento San Joaquin Delta Overview,” California Department of Water Resources, Sacramento, CA (2007). Available at
http://baydeltaoffice.water.ca.gov/sdb/tbp/deltaoverview/index.cfm

Fitzgerald, G. P., “The Effect of Algae on BOD Measurements,” J. Wat. Pollut. Control Fed. **36**:1524 (1964).

Gardner, W. S. and Lee, G. F., "Oxygenation of Lake Sediments," Air & Water Pollut. **9**:553-564 (1965). http://www.members.aol.com/annelhome/GardnerOxSediments.pdf

Goldman, C. R., and Horne, A. J., **Limnology**, McGraw-Hill, New York (1983).

Hatcher, K.J. (ed), **Sediment Oxygen Demand, Processes, Modeling and Measurement**, Institute of Natural Resources, University of Georgia, Athens, GA (1986).

Hutchinson, G. E., "On the Relation Between Oxygen Deficit and the Productivity and Typology of Lakes," Int. Rev. Gesamten Hydrobiol. Hydrogr. **36**:336 (1938).

Hutchinson, G. E., **A Treatise on Limnology**, Vol. I., Wiley, New York (1957).

Jones-Lee, A., Map prepared by Anne Jones-Lee, G. Fred Lee & Associates, El Macero, CA (2005).

Jones, R. A. and Lee, G. F., "Recent Advances in Assessing the Impact of Phosphorus Loads in Eutrophication-Related Water Quality," *J. Water Res.* 16:503-515 (1982). http://www.members.aol.com/annejlee/RecentAdvWaterRes.pdf

Jones, R. A. and Lee, G. F., "Eutrophication Modeling for Water Quality Management: An Update of the Vollenweider-OECD Model," World Health Organization's Water Quality Bulletin **11**(2):67-74, 118 (1986). http://www.gfredlee.com/voll_oecd.html

Lee, G. F., "Factors Affecting the Transfer of Materials between Water and Sediments," University of Wisconsin Eutrophication Information Program, Literature Review No. 1, 50 pp (1970). http://www.members.aol.com/duklee2307/NewFactors-Affecting-Paper-Revised.pdf

Lee, G. F. and Jones, R. A., "Predicting Domestic Water Supply Raw Water Quality in Proposed Impoundments," IN: Proc. American Water Works Association 1984 Annual Conference Proceedings, pp 1611-1630 (1984a). http://www.members.aol.com/annejlee/RawWQProposedImp84.pdf

Lee, G. F. and R. A. Jones, "Prediction of Water Quality in Proposed Hydropower Impoundments," Proc. Internat. Conf. on Hydropower, Vol. III, University of Tennessee, pp. 1254-1273 (1984b).

Lee, G. F. and Jones-Lee, A., "Mechanisms of the Deoxygenation of the Hypolimnia of Lakes," Report of G. Fred Lee & Associates, El Macero, CA (1995). Available from gfredlee@aol.com as EF 010.

Lee, G. F., and Jones-Lee, A., "Synthesis and Discussion of Findings on the Causes and Factors Influencing Low DO in the San Joaquin River Deep Water Ship Channel near Stockton, CA: Including 2002 Data," Report Submitted to SJR DO TMDL Steering

Committee and CALFED Bay-Delta Program, G. Fred Lee & Associates, El Macero, CA, March (2003). http://www.gfredlee.com/SynthesisRpt3-21-03.pdf

Lee, G. F., and Jones-Lee, A., “San Joaquin River Deep Water Ship Channel Low DO Problem and Its Control,” PowerPoint slides presented at SETAC World Congress Portland, OR, November 2004. Updated December (2004a). http://www.members.aol.com/GFLEnviroQual/LowDOSummaryDec2004.pdf

Lee, G. F., and Jones-Lee, A., “Supplement to Synthesis Report on the Low-DO Problem in the SJR DWSC,” Report of G. Fred Lee & Associates, El Macero, CA, June (2004b). http://www.members.aol.com/duklee2307/SynthRptSupp.pdf

Lee, G. F., Rast, W., and Jones, R. A., "Eutrophication of Water Bodies: Insights for an Age-Old Problem," Environ. Sci. & Technol. **12**:900-908 (1978). http://www.members.aol.com/apple27298/Eutrophication-EST.pdf

Lee, G. F., Jones-Lee, A., and Burr, K., “Results of the August 5, 2003, Tour of the South Delta Channels,” Report of G. Fred Lee & Associates, El Macero, CA (2004). http://www.members.aol.com/duklee2307/South-Delta-Tour.pdf

Litton, G. M., “Sediment Oxygen Demand, Sediment Deposition Rates and Biochemical Oxygen Demand Kinetics in the San Joaquin River near Stockton, California, Fall 1999 (Final),” Report prepared for City of Stockton and San Joaquin River Dissolved Oxygen TMDL Technical Committee, June 25 (2003). http://www.sjrdotmdl.org/library_folder/litton_final_report.pdf

Morgan, J, J., and Stumm, W., “The Role of Multivalent Metal Oxides in Limnological Transformations as Exemplified by Iron and Manganese,” Proc. 2nd Int. Conference on Water Pollution Research, pp. 103-131, Pergamon Press, New York (1965).

Rast, W. and G. F. Lee, “Summary Analysis of the North American (US Portion) OECD Eutrophication Project: Nutrient Loading-Lake Response Relationships and Trophic State Indices,” Report to US EPA, EPA 600/3-78-008, US EPA, Corvallis, OR (1978).

Rast, W., Jones, R. A., and Lee, G. F., “Predictive Capability of US OECD Phosphorus Loading-Eutrophication Response Models,” Journ. Water Pollut. Control Fed. **55**:990-1003 (1983). http://www.members.aol.com/annelhome/PredictiveCapabilityOECD.pdf

Richards, F. A., “Anoxic Basins and Fjords,” IN: **Chemical Oceanography**, Vol I, Riley and Skirrow (eds.), Academic Press, London (1965).

Sonzogni, W. C., Larsen, D. P., Malueg, K. W., and Schuldt, M. D., “Use of Large Submerged Chambers to Measure Sediment-Water Interactions,” Water Res. **11**:(5)421-464 (1977).

Stumm, W., and Lee, G. F., "Oxygenation of Ferrous Iron," Ind. Eng. Chem. **53**:143-146 (1961). http://www.members.aol.com/annejlee/StummOxygenFerrous.pdf

Stumm, W., and Morgan, J. J., **Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters**, 3rd Ed, Wiley-Interscience, New York (1996).

Thibodeaux, T. J., "Recent Advances in Our Understanding of Sediment-to-Water Contaminant Fluxes: The Soluble Release Fraction," Aquatic Ecosystem Health and Management **8**(1):1-9 (2005).
http://www.che.lsu.edu/faculty/thibodeaux/AEHMS.KEYNOTE.CHICAGO.02.ppt

Vollenweider, R. A., "Scientific Fundamentals of the Eutrophication of Lakes and Flowing Waters with Particular Reference to Nitrogen and Phosphorus as Factors in Eutrophication," Technical Report DAS/CSI/68.27, Organization for Economic Cooperation and Development, Paris, 250pp (1968).

Vollenweider, R. A., "Advances in Defining Critical Loading Levels for Phosphorus in Lake Eutrophication," Mem. 1st. Ital. Idrobio. **33**:53-83 (1976).