

## **Comments on Definitions for the San Joaquin River Low DO Control TMDL**

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July 1999

Presented below are comments on the definitions that Tom King compiled from the literature that are pertinent to terms used in the San Joaquin River Deepwater Channel Low DO Control TMDL project. Tom's list of definitions was sent to you by email several weeks ago. As discussed, several of the definitions that Tom obtained from the literature, especially from the US EPA TMDL report (4), are not necessarily correct or adequate. Others need additional information to work toward improving their appropriate use in the project activities. The definitions provided in Tom's e-mail are presented below in italics, with my comments following.

If there are questions or comments on these definitions and my comments on them, please contact me. Fred

***Aerobic*** - *environmental conditions characterized by the presence of dissolved oxygen; describes biological or chemical processes that occur in the presence of oxygen. (4)*

***Anaerobic or Anoxic*** - *environmental condition characterized by the absence of oxygen; describes biological and chemical processes that occur in the absence of oxygen. (4)*

The US EPA staff member(s)/contractor who developed the definitions of aerobic, anaerobic, anoxic, and while not listed, oxic, is not familiar with the proper use of these terms. Aerobic and anaerobic refer to biochemical processes. While typically they refer to processes that take place in the presence or absence of oxygen, oxygen can be absent and still have an aerobic process where other constituents serve as electron acceptors. Oxic and anoxic refer to the presence and absence of oxygen, irrespective of the biochemical processes governing an organism's metabolism.

***Ammonia*** - *inorganic form of nitrogen; product of hydrolysis of organic nitrogen and denitrification. Ammonia is preferentially used by phytoplankton over nitrate for uptake of inorganic nitrogen. (4)*

The US EPA staff member(s)/contractor who developed this definition is not familiar with denitrification. Denitrification does not lead to ammonia production. Denitrification typically leads to N<sub>2</sub> gas and normally small amounts of several gaseous oxides of nitrogen. Further, ammonia does not always originate from hydrolysis of organic nitrogen. Much of the ammonia that is used as a fertilizer has a different origin. The fact that ammonia is preferred by phytoplankton over nitrate is not a significant factor in excessive fertilization of a waterbody. If either of these forms of nitrogen is available in a waterbody, algae will use them to the extent needed. The specific algae that will develop may be different, however, depending on the form present. The proper definition of ammonia is that it is an inorganic form of nitrogen

with the formula  $\text{NH}_3$ . Ammonia can also be present as the cation  $\text{NH}_4^+$ . pH determines the distribution between these two forms of ammonia.

**Algal Bloom** - *rapidly occurring growth and accumulation of algae within a body of water. It usually results from excessive nutrient loading and/or a sluggish circulation regime (long residence time). The decay associated with seasonal die-off of algal blooms result in water column and sediment oxygen demand. (4)*

The US EPA staff/contractor's definition of algal bloom is not accurate. An algal bloom is large biomass of algae. It does not have to occur due to rapid growth. It can occur as a result of slow growth. The key issue is accumulation of a large biomass. The incorporation of a long residence time is incorrect. Also, algal bloom does not have to be associated with a "seasonal die-off."

**Algal Settling** - *algal cells are lost from the water column by physical sedimentation of the cell particles. Algal biomass lost from the water column is then incorporated as sediment organic matter and undergoes bacterial and biochemical reactions releasing nutrients and consuming dissolved oxygen. (4)*

The phrase "undergoes bacterial and biochemical reactions" should be changed to "undergoes biochemical reactions." Biochemical reactions are carried out principally by bacteria, and generally are not separate from bacteria.

**Assimilative Capacity** - *the amount of contaminant load (expressed as mass per unit time) that can be discharged to a specific stream or river without exceeding water quality standards or criteria. Assimilative capacity is used to define the ability of a waterbody to naturally absorb and use waste matter and organic materials without impairing water quality or harming aquatic life. (4)*

Assimilative capacity applies to all waterbodies and not just streams and rivers. Also, it is not restricted to meeting water quality standards or criteria. Assimilative capacity is the ability of a waterbody to assimilate constituent loads without adverse impacts on its beneficial uses, which include ecosystem functioning.

**Benthic Denitrification** - *Under anaerobic or low oxygen conditions, denitrifying bacteria synthesize cellular material by reducing nitrate to ammonia and nitrogen gas. Denitrification is a component of the overall nitrogen cycle and has been shown to account for a significant portion of the "new" nitrogen loading to freshwater and estuarine ecosystems. (4)*

Again, there are severe problems with the US EPA staff member/contractor's definition of denitrification leading to the production of ammonia. The statement, "Denitrification is a component of the overall nitrogen cycle and has been shown to account for a significant portion of the 'new' nitrogen loading to freshwater and estuarine ecosystems" is incorrect. Denitrification is the principal mechanism used to

remove algal-available nitrogen from wastewaters and from some waterbodies. Denitrification is the biochemical reduction of nitrate to produce nitrite and nitrogen gas, as well as some oxides of nitrogen. It occurs under anoxic conditions which may be localized within clusters of cells, where the overall waterbody still has low levels of measurable dissolved oxygen.

**Chemical Oxygen Demand (COD)**- *a measurement of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. (1)*

In a strict sense, COD is the analytical result expressed as O<sub>2</sub> equivalents of the reduction of organic matter by chromic acid under boiling conditions. COD is sometimes correlatable to BOD (biochemical oxygen demand), especially for conventional domestic wastewaters. COD does not measure all organics or even all organics that are oxidizable by bacteria in normal domestic wastewater treatment plant influent and effluent, and ambient waters. COD is not an appropriate procedure for measuring inorganic oxygen demand; COD measurements are largely uninterpretable in terms of measuring a definable quantity of substances when made on ambient waters such as a river or lake. COD is being replaced by the measurement of TOC (total organic carbon) and DOC (dissolved organic carbon).

**Carbonaceous Biochemical Oxygen Demand (CBOD)** - *a measurement of BOD derived from the oxidation of organic matter in a sample. A nitrification inhibitor is added to a sample prior to incubation that minimizes the oxygen lost from a sample as a result of nitrification. (1)*

CBOD is due to biochemical oxidation of organic matter. The word “lost” should be changed to “consumed.”

**Dissolved Oxygen Sag** - *longitudinal variation of dissolved oxygen representing the oxygen depletion and recovery following a waste load discharge. (4)*

While the definition is correct and in accord with tradition when applied to river situations, there would be some who argue that the low DO that occurs in the deepwater channel of the San Joaquin River is not a DO sag but a DO depression. As far as is known now, there is no well-defined source of oxygen demanding materials that are principally responsible for this depression. The deepwater channel of the San Joaquin River appears to have the characteristics more of that of a lake than a river channel.

**Eutrophication** - *the enrichment of an aquatic ecosystem with nutrients (nitrates and phosphates) that accelerate biological productivity (growth of algae and aquatic macrophytes). Eutrophication results in an accumulation of algal biomass that typically dies off and contributes to both a water column and sediment oxygen demand during its decay. (4)*

Eutrophication is not, necessarily, an accelerated growth of algae. From a water quality perspective it is an enrichment of a waterbody that results in an increased aquatic plant biomass. It is rare that eutrophication results in significantly depressed dissolved oxygen levels in surface waters. DO

depletion due to excessive fertilization is typically manifested in deeper waters where there is density stratification which inhibits mixing of the water column.

It is inappropriate to use the plural “nitrates” and “phosphates”. The correct terminology is nitrate and phosphate, these are plural terms. It is no more appropriate to use nitrates, phosphates, and chlorides than it is to use sodiums, calciums, etc.

**Load, Loading, Loading rate** - *the total amount of material (pollutants) entering an aquatic system from one or multiple sources; measured as a rate in weight per unit time such as pounds per day. (4)*

Load, loading, and loading rate are not restricted to pollutants. They can refer to the amount of any constituent added to a waterbody per unit time, independent of whether the constituent is a pollutant (i.e., a substance that impairs water quality - beneficial uses of a waterbody).

**Mathematical Model** - *a system of mathematical expressions that describe the spatial and temporal distribution of water quality constituents resulting from the fluid transport and the one, or more, individual processes and interactions within some prototype aquatic ecosystem. A mathematical water quality model is used as the basis for waste load allocation evaluations. (4)*

The word “prototype” should be deleted. It should be understood that what is described as a mathematical model is a deterministic model where there is an attempt to develop differential equations that describe the rate processes and transport that govern the distribution of constituents within an aquatic system of interest. There are also stochastic and empirical models that are useful for describing load response relationships in TMDL development. The most important of these is the Vollenweider OECD eutrophication model relating phosphorus loads to lakes and reservoirs and the planktonic algal biomass that develops in the waterbody. The database for this model evolved out of a \$50 million, 5-year, 22-country study effort that was conducted on 200 waterbodies located in Western Europe, North America, Japan, and Australia during the 1970s. This model is only applicable to waterbodies where phosphorus is the only nutrient governing planktonic algal biomass development. Subsequently Dr. Jones-Lee and I have expanded this database to over 750 waterbodies located throughout the world. Information on the Vollenweider model and its predictive capability is available from my wife and my website at [www.gfredlee.com](http://www.gfredlee.com) in

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* 11:67-174, 118 (1986) and

Lee, G. F. and Jones, R. A., "Effects of Eutrophication on Fisheries," *Reviews in Aquatic Sciences*, 5:287-305, CRC Press, Boca Raton, FL (1991).

**N/P ratio** - *the ratio of nitrogen to phosphorus The ratio may be used as an indicator of the nutrient limiting conditions for algal growth in aquatic systems; also used as indicator for the analysis of trophic levels of receiving waters. (4)*

Contrary to popular belief, N/P ratios or Redfield numbers are not necessarily reliable for estimating nutrient limiting conditions. They are never a reliable indicator of the trophic level of receiving waters. N/P ratios relate to algal composition stoichiometry (100 C: 16 N: 1 P). This is the average composition of algae on an atomic basis.

The basic problem with the way that many of those who attempt to use N/P ratios in estimating nutrient limitation is that they ignore the aqueous environmental chemistry of nitrogen and phosphorus in aquatic systems. As discussed by Lee, G.F. and Jones-Lee, A., "Determination of Nutrient Limiting Maximum Algal Biomass in Waterbodies," (1998) available from [www.gfredlee.com](http://www.gfredlee.com), a limiting nutrient is one which is present in algal-available forms at concentrations which limit algal biomass. While there are some who attempt to extrapolate limiting nutrient measured at one time to other times, such an approach can readily be in significant error. This approach assumes that the conditions (rates of supply of chemical constituents and chemical reactions) that lead to the limiting nutrient at one time do not change; this is rarely the case.

At this time the only reliable way to determine whether a nutrient is limiting algal biomass is to assess whether algal-available forms of that nutrient are available at growth rate limiting concentrations for planktonic algae. For algal growth that is phosphorus-limited, the concentration of soluble ortho P must be less than about 5 : g/L P. For nitrate plus ammonia the total N concentration for these two species must be about 20 : g/L N to have growth rate limiting nitrogen conditions. By examining the nitrate plus ammonia and soluble ortho P concentrations at peak algal biomass, it is possible to determine whether N or P are limiting algal growth. It is doubtful that N or P ever occur at growth rate limiting conditions in the San Joaquin River. The issue that needs to be addressed in our studies is whether it will be possible, through nutrient control programs, to reduce the nitrogen and/or phosphorus loads to the river to growth rate limiting concentrations.

**Nitrification** - *a two-step process mediated by a group of chemoautotrophic bacteria that oxidize ammonia. The first step converts ammonia and oxygen to nitrite, hydrogen ion and water ( $NH_4^+ + 1/2O_2 \rightarrow NO_2^- + 2H^+ + H_2O$ ); the second step converts nitrite and oxygen to nitrate, the fully oxidized form of nitrogen ( $NO_2^- + 1/2O_2 \rightarrow NO_3^-$ ). This process can contribute to conditions of low dissolved oxygen. (2, 4)*

The equations set forth in this definition do not have the appropriate charges on the chemical species. This is a significant omission since there are chemical species of nitrogen which do not have charges on them with the same formula.

**Organic Nitrogen** - *the organic fraction that includes plant and animal residue at various stages of decomposition, cells, tissues, and substances synthesized by the soil population. Commonly determined as the amount of organic material contained in a soil or water sample. (4)*

Organic nitrogen is not restricted to development by soil populations. It is also developed by aquatic life.

**Orthophosphate** - *Form of phosphate available for biological metabolism without further breakdown. (4)*

The correct definition for algal available P is soluble orthophosphate. There are some forms of orthophosphate that are not available to algae.

**Phytoplankton** - *a group of generally unicellular microscopic plants characterized by passive drifting within the water column. See Algae. (4)*

Phytoplankton and zooplankton do not passively drift with the water. They have limited locomotion ability but can change their position in the water column to a considerable extent under low mixing conditions.

**Residence time** - *length of time that a pollutant remains within a section of a stream or river. The residence time is determined by the streamflow and the volume of the river reach or the average stream velocity and the length of the river reach. (4)*

The term “pollutant” should be changed to “constituent” and the term “residence time” should be changed to “hydraulic resident time.” Residence time is not restricted to rivers but applies equally well to lakes and reservoirs, etc. The hydraulic residence time of a waterbody is the volume of the waterbody divided by the amount of water added per unit time. There are also chemical residence times which are useful in estimating the fate of nutrients and other constituents in waterbodies. The chemical residence time of a particular constituent is the total mass of the constituent in the waterbody divided by its loading rate.

**Sediment Oxygen Demand (SOD)** - *a combination of the chemical and biochemical oxygen consuming processes that occurs at or just below the sediment/water interface. Most of the SOD at the surface of the sediment is due to the biological decomposition of organic material and nitrification while the SOD several centimeters into the sediment is often dominated by the chemical oxidation of species such as iron, manganese and sulfide. (3)*

This definition of SOD refers to bedded sediments and does not consider the SOD that occurs when these sediments are suspended into the water column due to mixing. The suspension process can be a significant source of sediment oxygen demand, due to the inorganic reactions between ferrous iron, sulfide - polysulfides, and dissolved oxygen. At neutral to alkaline pH conditions, these inorganic reactions are much faster than the biochemical reactions involving bacterial action on dissolved and particulate organics. Manganese is rarely an important factor in controlling SOD.

**Total Maximum Daily Load (TMDL)** - *the sum of the individual waste load allocations and load allocations. A margin of safety is included with the two types of allocations so that any additional loading, regardless of source, would not produce a violation of water quality standards. (4)*

I do not understand the first sentence of this definition. The TMDL is the total amount of a constituent that can be added to the waterbody to achieve the TMDL goal which is typically the water quality standard for the waterbody for the constituent of concern.

### **Diel and Diurnal**

Many individuals incorrectly use the term diurnal for diel. Diel refers to the 24-hour cycle of night and day. Webster's New Collegiate Dictionary defines diel as "involving a 24-hour period that usually includes a day and the adjoining night." While Webster defines diurnal as "a. recurring everyday," "b. having a daily cycle, i.e., tides."

### **Overall Comments**

It is evident that the authors of reference (4), the US EPA publication "Technical Guidance Manual for Developing Total Maximum Daily Loads; Part 1: Biochemical Oxygen Demand/Dissolved Oxygen and Nutrients/Eutrophication" were not familiar with the terminology in the field in which they were writing. While in the 1960s and 70s, the US EPA and its predecessor organizations had a strong group of staff who were familiar with eutrophication-related issues, this group was disbanded by the US EPA administration in order to chase priority pollutant rodent carcinogens in the late 1970s/early 80s.

This deficiency in knowledge of eutrophication-related issues is reflected in the US EPA's currently proposed approach for developing chemically-based water quality criteria for nutrients (nitrogen and phosphorus compounds). As part of developing the Clean Water Action Plan, the US EPA in June 1998 released an interim final "Water Quality Criteria and Standards Plan – Priorities for the Future," EPA 822-R-98-003. This is available from the US EPA website. One of the priority areas in this Plan is to develop nutrient criteria. As proposed, these criteria are to be regionally adjusted and as stated in the Clean Water Action Plan,

*"By the end of 2000, EPA will publish nutrient guidance documents explaining methodologies that can be used to calculate nutrient criteria by waterbody type (lakes, reservoirs, streams and rivers, wetlands and estuaries) and ecoregions of the country, and nutrient criteria (expressed as target ranges) for use by the States and Tribes."*

*"Between 2000 and 2003, EPA will work with the States and Tribes as they adopt and implement numerical nutrient criteria into water quality standards by developing their own criteria or using default EPA nutrient ranges applicable to their ecoregion(s)."*

Many of those who have worked on nutrient load eutrophication response relationships, including myself, find that the US EPA's proposed approach for developing nutrient criteria is not technically valid. Rather

than trying to develop a single numeric value for the nitrate, ammonia, and phosphate concentrations that can be present in a waterbody or its tributaries and not cause excessive fertilization of a waterbody, it is necessary to examine the characteristics of each of the waterbodies and determine the appropriate load of available forms of nutrients to protect the eutrophication-related designated beneficial uses of the waterbody to the desired degree. This protection can include the prevention of low DO conditions.

The US EPA's current efforts in developing chemically based nutrient criteria will certainly impact the SJR low DO control TMDL development. For further information on the deficiencies on the US EPA's approach in developing nutrient-based water quality criteria, consult Dr. Jones-Lee at my website, [www.gfredlee.com](http://www.gfredlee.com), in the Excessive Fertilization/Eutrophication section.

### **Additional Water Quality Definitions**

In connection with developing a paper "Assessing the Degree of Appropriate Treatment of Shipyard and Drydock Wastewater Discharges and Stormwater Runoff" that is to be presented at Oceans '99 MTS/IEEE Conference proceeding session, "Treatment of Regulated Discharges from Shipyards and Drydocks," to be held Seattle, WA, September 13-16, 1999, Dr. Jones-Lee and I have developed a set of definitions of commonly misused terms in the water quality field. A prepublication copy of this paper/list of terms is available at our website and is presented below.

### **Definitions - Terminology**

One of the major problems within the water quality management field is a lack of common understanding of water quality-related terminology relative to regulatory requirements and appropriate evaluation of water quality. This lack of understanding, especially as it relates to developing technically valid, cost-effective water pollution control programs, leads to over-regulation of wastewater discharges and stormwater runoff-associated constituents for which there are water quality criteria/standards. It also leads to under-regulation of real significant water quality use impairments caused by the unregulated constituents for which there are no water quality criteria/standards. It is important to use such terms as "pollutant," "pollution," "water quality," "water chemistry," etc., in accord with legal and technically correct usage to eliminate the inappropriate characterization of a water quality evaluation situation. I have observed where regulatory boards and the courts have issued rulings which affect the expenditure of large amounts of public and private funds to control inert chemical constituents which were incorrectly called pollutants. The adoption of the following terminology would significantly improve the technical quality and cost-effectiveness of managing water pollution.

**Pollution.** Pollution is defined in the Clean Water Act as an impairment of the beneficial use(s) of a waterbody. Finding chemical constituents in elevated concentrations in the water column or sediments is not pollution unless these constituents are impairing the beneficial uses of the waterbody.

**Water Quality.** Water quality should be assessed based on the characteristics of the water relative to the beneficial uses of the water. Water quality is not, as frequently used, a list of chemical constituent

concentrations. In order to reliably assess whether the concentration of a constituent impairs the water quality - beneficial uses of a waterbody, it is necessary to evaluate on a site-specific basis whether the constituent is present in toxic/available forms at a critical concentration for a sufficient duration to be significantly adverse to aquatic life that is important to the beneficial uses of the waterbody.

***Water Quality Assessment.*** A water quality assessment is an evaluation of the beneficial use impairment that is occurring, or could potentially occur, due to the presence of a particular chemical(s) or other constituent. It is not an assessment of the frequency of exceedance of a water quality standard.

***Water Quality Standard Compliance.*** Water quality standard compliance is based on an assessment of the frequency of exceedance of a water quality standard in ambient waters receiving the discharge/runoff. Such compliance does not ensure that the beneficial uses of the waterbody are being protected or that significant over-regulation is not occurring.

***Administrative Exceedance.*** An administrative exceedance of a water quality standard occurs when concentrations of a constituent are present in waters above the standard without adverse impacts to aquatic life and other beneficial uses. An example is a situation where non-toxic forms of copper are present in a waterbody above a water quality standard that is based on copper toxicity.

***Excessive Bioaccumulation.*** Excessive bioaccumulation of chemicals occurs when the tissue residue-body burden within edible aquatic organisms exceeds US EPA or FDA regulatory guidelines. It is not an elevated concentration of a chemical constituent relative to background or so-called “NAS” guidelines. As whole organism tissue residue guidelines are developed to protect higher trophic-level fish/shellfish-eating birds and animals, such guidelines may be used to evaluate excessive bioaccumulation.

***Aquatic Life Adverse Impact.*** In order for a chemical constituent to be adverse to the beneficial uses of a waterbody, and therefore be a pollutant, it is necessary that the chemical constituent cause altered numbers and/or types/characteristics of desirable forms of aquatic life.

***Cause of Aquatic Life Adverse Impacts.*** The association of elevated concentrations of a constituent in water and/or sediments with aquatic life toxicity or altered organism assemblages is not a valid basis for assessing the cause of adverse impacts. Site-specific studies involving assessing cause and effect must be used to determine if chemical constituents in water or sediments are responsible for aquatic life-related adverse impacts.

***Aquatic Chemistry.*** Aquatic chemistry involves the physical, chemical factors/reactions that control the distribution of chemical species that impact how a chemical affects water quality-beneficial uses. It includes the transport (advection and mixing) and transformations-reactions (kinetics and thermodynamics) that control the concentrations of chemical species in a waterbody.

Aquatic chemistry is not a list of the concentrations of chemical constituents found in a water or sediment sample. Such a list is a compilation of chemical characteristic, not chemistry.

***Toxic Hot Spot.*** A toxic hot spot should be defined as an area in which there is aquatic life toxicity that is significantly adverse to the beneficial uses of a waterbody. Further, a toxic hot spot is an area which serves as a significant source of a bioaccumulatable chemical that is present in edible organisms at hazardous levels. A toxic hot spot should not be defined based on exceedance of a water quality standard or sediment quality guideline.

One of the designation criteria that is used in the California Water Resources Control Board's BPTCP Policy is the finding that the concentrations of constituents in a water or sediments exceed a water quality criterion/standard. With few exceptions, the water quality criteria/standards are based on worst-case assumptions. Using exceedance of a water quality criterion/standard as the basis for designating a toxic hot spot is obviously technically invalid and can lead to over-regulation.