San Joaquin Valley Drainage Authority
ERP-02D-P63

Interim Report

Task 8: Linking the San Joaquin River to the Stockton Deep Water Ship Channel

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Objectives

The goal of the project is to quantitatively determine the cause of the decrease in chlorophyll and other organic matter between Vernalis and the DWSC. The following objectives are proposed to meet this goal:

- Quantify oxygen demands entering the DWSC.
- Characterize the growth and decay of algae from Vernalis to the DWSC.
- Quantify losses of organic matter associated with settling and agricultural diversions.
- Estimate BOD decay and nitrification rates.
- Provide a comprehensive data set for model development and calibration from Vernalis to the DWSC.

While this work seeks to develop a mechanistic understanding of algal processes between Vernalis and the DWSC, utilization of a water quality model may prove necessary to fully explain the generated data. As such, development of a comprehensive data set for model algorithm development and calibration is included as one of the objectives.

Task 9 augments Task 8 by assessing algae grazing and changes in algal populations between Vernalis and the DWSC. A separate interim report has been prepared by Dr. Mark Brunell for Task 9.

Background

The growth and decay dynamics of algae in the SJR reach between Vernalis and the DWSC is poorly characterized despite 2 years of intensive study performed during 2000 and 2001. Contradictory data exist for algal growth and decay between Vernalis and the DWSC (Jones & Stokes 1998; Lehman 2001; Foe, Gowdy, and McCarthy 2002). However, the data do strongly indicate a significant loss of algal biomass downstream of Vernalis and Mossdale (Jones & Stokes 2002; Lehman 2001). Extant DWSC models rely on input data generated at Mossdale, but this model over predicts the chlorophyll entering the DWSC by approximately 3 times and under predicts the DO by 2 mg/L for 2001 (Jones & Stokes 2002).

The existing monitoring program has been incapable of explaining apparent losses of algal biomass between Mossdale and the DWSC. Estimates were made in 2001 of inflows and diversions to this SJR reach (Quinn and Tullock 2002). However, this work was based on scanty historic information and a boat survey – insufficient to properly characterize the algal dynamics or other mechanisms responsible for the algal decline. The SJR reach between Vernalis and the DWSC is of critical importance since it dictates the loading of live or decaying algae that directly affect oxygen removal from the water column. Tidal effects complicate the dynamics of this reach also and slow the transport of biological material to the DWSC and its passage through the DWSC.

This study will also yield critical input parameters for developing an accurate water quality model of the SJR and DWSC. Continuous monitoring performed over weeklong periods provides information on the diurnal fluctuations in algal loads as well as providing more accurate insight into data noise than has been possible in the past. Previous sampling in this reach has been limited to grab sampling supplemented with continuous monitoring at Mossdale.

Approach and Methods

Location of Project

This component of the 2003 SJR low DO project is located in the SJR downstream of Vernalis and upstream of Channel Point at the DWSC as shown in Figure 1.

Approach Overview

The loss of chl-*a* may be associated with agricultural diversions, diminished exposure to light as the SJR deepens in the tidal prism of the Delta, dilution (dispersion) of the SJR during flood tides with water from the DWSC that exhibits much lower chl-*a* concentrations, or settling out of the water column. Dye measurements will provide evidence of mass balance and losses and would indicate diversions from the SJR, when used in combination with current and planned flow and water quality monitoring in this reach. Additional self-contained, continuous, monitoring stations will capture additional data including chl-*a,* DO, pH, and water temperature. Light-dark bottle field tests are proposed to quantify algal DO productivity. Long-term BOD bottle tests will quantify DO decay and nitrification rates.

This task is proposed for three years of investigation. The approach is flexible to permit adaptive monitoring within the SJR between Vernalis and the DWSC. During the first year, four monitoring runs will be conducted during each of month from June to September. Only two trials are scheduled for the second year, and one run is proposed for the last year of this study. The monitoring runs are designed to address extant questions about the SJR, but the emphasis on certain study elements will be modified to attempt to resolve new questions that arise as more information becomes available.

Each monitoring run will involve four specific tasks:

Task 8.1: Deploy four continuous monitoring sondes at selected locations for approximately 4-5 days while Task 8.2 tasks are performed. The sondes measure water temperature, dissolved oxygen, electrical conductivity, pH, turbidity, chlorophyll *a*, and instrument depth. This subtask will provide a data set for modeling and provide a means for interpreting the results of Task 8.2. The positioning of the monitoring sondes in the SJR is flexible in order to optimize the utility of the data collected. As new data become available, the positioning of the sondes will be tailored to answer specific questions.

Task 8.2: Perform Lagrangian monitoring to assess mass losses of a conservative tracer and reactive substances (i.e., chl-*a*, pha-*a*, BOD, ammonia). Rhodamine WT tracer is released at Vernalis and then followed as this parcel of water flows to the DWSC. In situ measurements of water temperature, dissolved oxygen, electrical conductivity, pH, turbidity, chlorophyll *a,* and rhodamine WT, instrument depth, water depth are collected every 2 seconds and stamped with time and coordinate location. Water samples are collected periodically and analyzed for nitrogen species (NH_3, NO_2^-, NO_3^-, TKN) , chlorophyll *a*, pheophytin *a,* total suspended solids (TSS), volatile suspended solids (VSS), and long-term biochemical oxygen demand (BOD), carbonaceous BOD, and nitrogenous BOD.

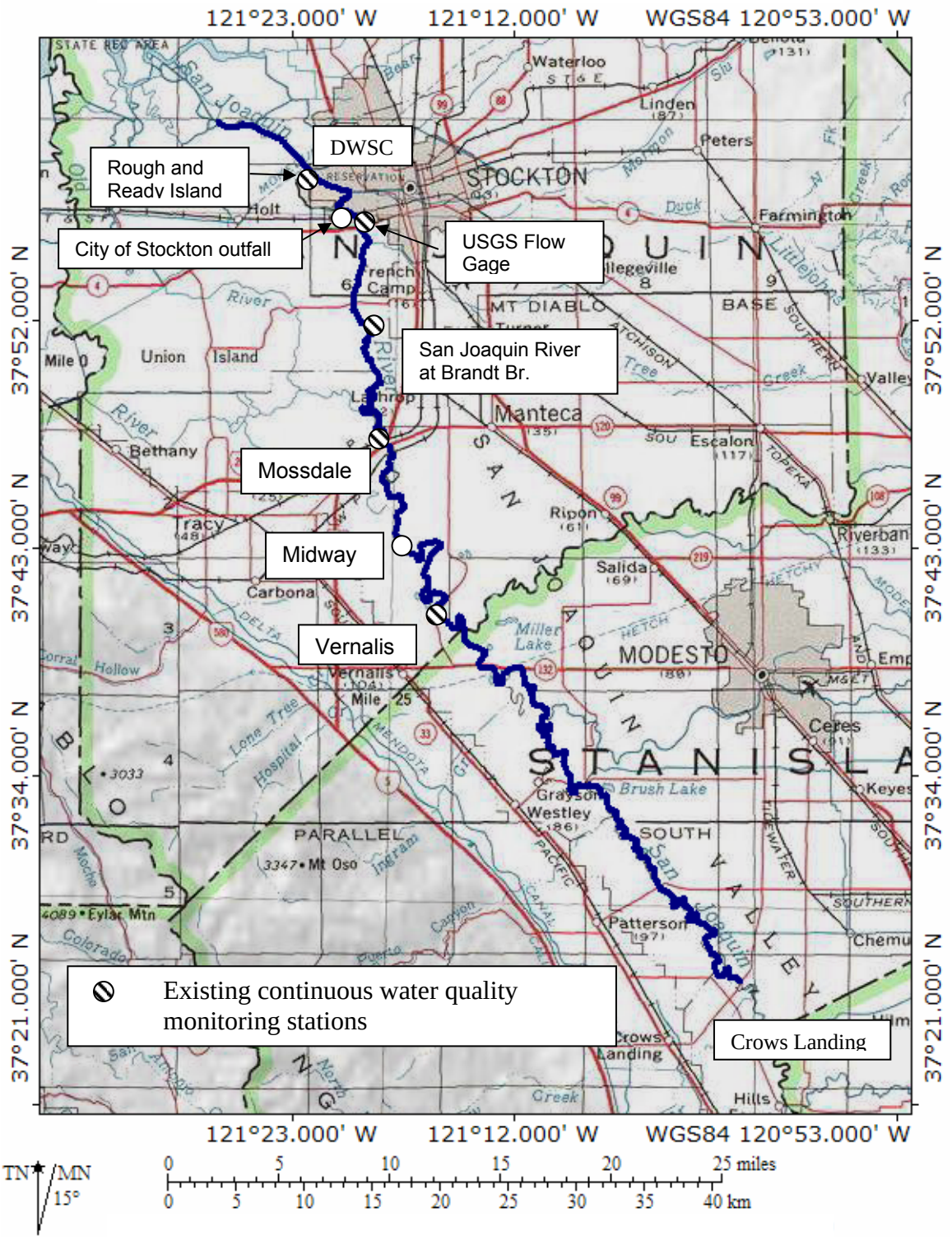

Figure 1: The San Joaquin River between Vernalis and the Stockton Deep Water Ship Channel.

Task 8.2 facilitates Tasks 8.3 and 8.4 since these subtasks use water samples collected during this subtask.

Task 8.3: Augment fieldwork with laboratory assessment of BOD decay and nitrification kinetics. Long-term BOD laboratory trials are performed in a dark, temperature controlled environment.

Task 8.4: Field light/dark bottle experiments. Light and dark bottles are suspended at various depths to measure chlorophyll a and dissolved oxygen production as a function of light. Light intensity is measured as a function of depth during the deployment of the bottles.

Water Quality Measurements

Continuous Water Quality Measurements

Tasks 8.1 and 8.2 were performed with multiparameter sondes manufactured by Hydrolab, Inc. These instruments were previously described in Task 4: Monitoring. Calibration will be performed per standard methods (APHA 1998) or manufacturer's specifications and checked periodically in the field. The data acquisition frequency was set to 15 minutes. Continuous measurements performed from the monitoring boat utilized a YSI 600 XL sonde with separate SCUFA fluorometers for chlorophyll *a* and rhodamine WT.

Discrete Water Sample Collection and Analysis

All the tasks will require the collection of water samples for constituent quantification. Sampling will be performed by manual grab methods or peristaltic pumps. Analysis will be performed in accordance with standard methods (AHPA 1998). TSS and VSS will be performed by SMs 2540 D and E, respectively. However, trials will be performed with filters required for chl-*a* (SM 10200H) instead of filters required by SMs 2540 D and E to obtain better correlations among VSS, chl-*a,* and BOD. Filter pore sizes for TSS and VSS can be significantly larger than pores sizes of filters specified for chl-*a* analysis. Chl-*a* and pha-*a* will be extracted using an acetone/water solution and UV absorption in accord with SM 10200H. Biochemical oxygen tests will be of a long-term nature (SM 5210 C) to facilitate determination of decay rate constants.

Detailed Task Descriptions

Task 8.1: Deployment of Continuous Recording Sensors

Four additional monitoring sites on the SJR were instrumented between Vernalis and the DWSC. These locations are flexible and will be changed as new information becomes available. Continuous water quality sondes (Hydrolab 5SDX, Hach Inc., Boulder, CO), measuring chl-*a,* turbidity, EC, pH, DO, and water temperature were deployed at four locations for approximately 1 week once a month from May to October. The deployment coincides with the Lagrangian dye tracking measurements. These sondes capture the diurnal patterns of algal growth and decay allowing advective transport of algae to be

separated from tidal transport and more careful mass accounting of algal loading in this SJR reach. These stations also yield important data sets for model calibration.

Task 8.2: Lagrangian Monitoring

In addition to the in-river, continuous sensors, a slug of rhodamine WT dye will be dispersed uniformly across the SJR and tracked downstream by boat. Monthly injections of dye and deployment of the light-dark bottle experiments are proposed from May to October. In situ measurements of dye concentration, chl-*a,* pH, DO, turbidity, water temperature, water depth, and instrument depth will be captured electronically with their GPS coordinate location. Figure 2 presents a photograph of the monitoring boat and a schematic diagram of the equipment required for this task. This system permits the simultaneous collection of all data from five different instruments every second. These data are processed in real-time and displayed graphically using MATLAB (MathWorks, Natick, MA). This system permits accurate accounting of dye mass in the SJR and precise characterization of chl-*a,* DO, and other parameters in the SJR. For example, bathymetry measurements will yield water depth information that may be correlated to the growth and decay of chl-*a* in the reach between Vernalis and the DWSC.

To augment the continuous monitoring, discrete water quality samples were also collected for quantification of chl-*a,* pha-*a,* VSS, TSS, BOD, CBOD, and verification of in situ turbidity, DO, pH, chl-*a* measurements. As shown on Figure 2, discrete water samples can be collected at a prescribed water depth using 5/16-inch-inner-diameter tubing attached to a peristaltic pump (MasterFlex, Cole-Parmer Instrument Company, Vernon Hills, IL). Mass balance applied to the longitudinal measurements of inorganic solids will be used to assess net losses associated with settling. Sediment deposition traps may also be deployed if significant sediment losses are detected with the initial water quality measurements.

These monitoring efforts will be coordinated with other water tracking studies proposed in the river above Vernalis so the same water parcel and associated changes in water quality and algal populations can be followed from the upper San Joaquin River to the DWSC. It is anticipated that each full river dye tracking study will require 4 to 5 continuous days of extensive field work. Water samples collected during these trials will be periodically transported to the laboratory and processed or preserved as appropriate.

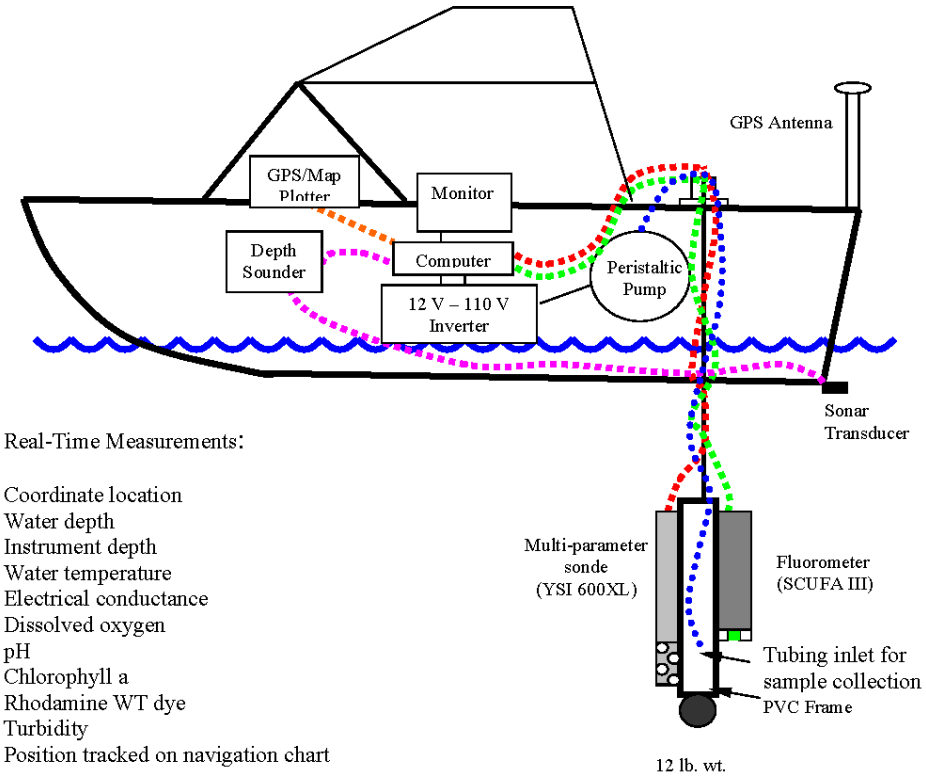

Figure 2: Monitoring boat and data acquisition system.

Task 8.3: BOD Decay and Nitrification Rates

The BOD and CBOD tests were performed over 20 days to determine kinetic decay rate constants of BOD, CBOD, and NBOD. The rate of NBOD decay will also be evaluated by monitoring the ammonia and nitrate concentrations when ammonia concentrations exceed 0.5 mg/L. Direct measurements will be made of ammonia oxidation rates as a function of time will be made using Clark-type electrodes. The data from these experiments will be used to determine more accurately the liability of the soluble ammonia in this SJR reach. Understanding and predicting how fast ammonia is oxidized in this region is important to assigning the oxygen demand allocation between algal biomass and ammonia. These tests are scheduled for each of the Lagrangian dye tracking investigations.

Task 8.4: Light-Dark Bottle Experiments

As part of the Lagrangian studies, light-dark bottle experiments were also performed to assess whether the apparent decay of algal biomass from Mossdale to the DWSC may be associated with reduced exposure to light as the river channel depth increase within the tidal prism. Previous studies have shown that algae collected in the SJR 1 mile above the DWSC decay extremely rapidly when kept in darkness (Litton 2002). To assess the impact of light reductions, light-dark bottles were suspended from a buoy at various depths while following the dye slug. Light intensity will be measured at each depth periodically. The pH, DO, chl-*a,* and pha-*a* concentrations will be quantified for the light-dark bottle experiments. These tests assess whether light limitation is a significant cause of the chl-*a* decay between Mossdale and the DWSC. These data also yield algal productivity and DO response curves as a function of light intensity, data critical for modeling this SJR reach.

Results and Discussion

Status of Work

The following elements of Task 8 have been completed.

- Establishment of the QAPP, laboratory standard operating procedures (SOP), and student training to carry out monitoring tasks.
- Bathymetric survey of the reach from Vernalis to the DWSC.
- Improvements to electrical and data collection system required for extended Lagrangian monitoring.
- A test rhodamine WT release for testing of dispersion system and data collection system on the San Joaquin River near Vernalis.
- Lagrangian and fixed-location sonde water quality monitoring was performed in July and August. More trials are scheduled for September and October of 2005 and later years.
- Light-dark bottle experiments were deployment in July and August. The analysis of the July trial is complete.
- Long-term BOD experiments for July are complete. August tests are in progress.

Task 8 work was originally scheduled to start in May, 2005. However, extremely high flows in the San Joaquin River yield short travel times and yield data sets that would not be representative of the river during periods of critical DO levels in the DWSC. A comparison of the 2004 and 2005 flows at Vernalis is presented in Figure 3. As shown in Figure 3, May and June flows were in excess of 10,000 cfs. The flow during these time periods is often between 1000 and 2000 cfs. Therefore, field work was postponed until July to allow the flows to subside and conserve resources for more intensive monitoring at times when more representative data will be collected. As such, this interim report only contains data for July, 2005. A second trial was conducted in August, but laboratory analyses are still being conducted.

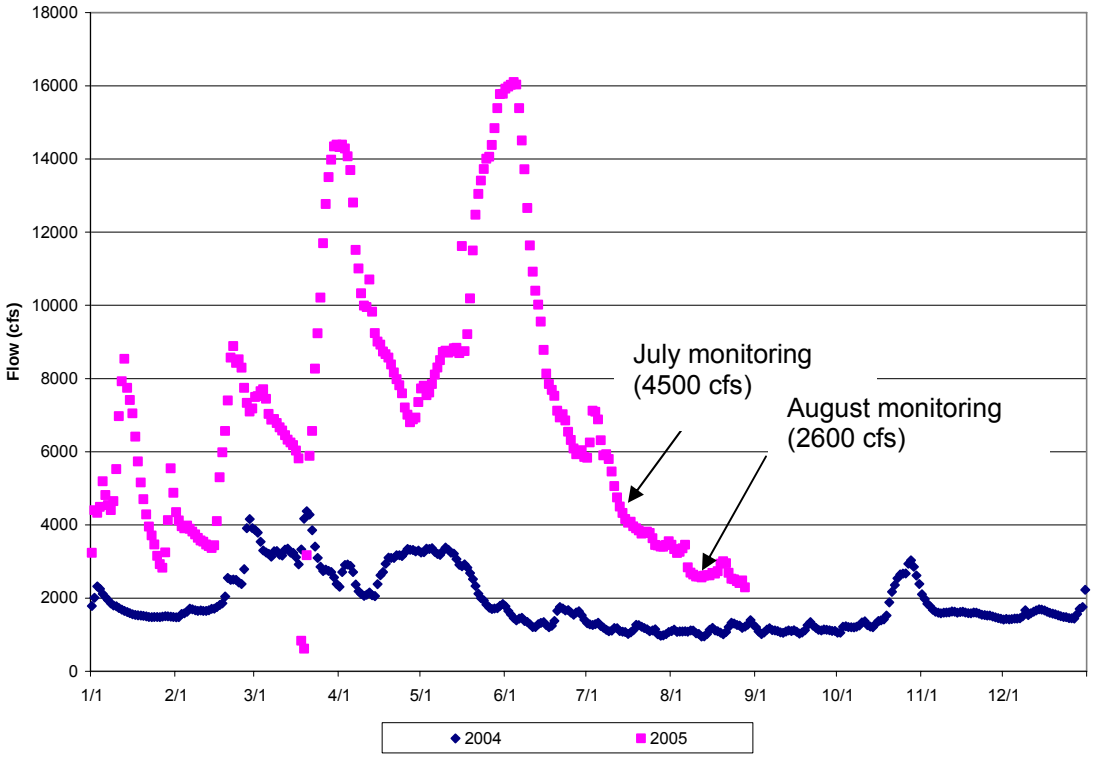

Figure 3: San Joaquin River Flow at Vernalis for 2004 and 2005.

Water quality measurements from Vernalis to the DWSC.

Task 8.1 Deployment of Continuous Recording Sensors

Water quality sondes were deployed at the Vernalis, Midway, Mossdale, and Brandt Bridge stations shown in Figure 1. Examples of the dissolved oxygen, pH, and chlorophyll *a* results are shown in Figures 4 and 5 for the Midway and Brandt Bridge stations, respectively. Algal productivity is clearly shown in the diel variations of chlorophyll *a*. During daylight hours chlorophyll *a* levels increase until approximately 4:00 PM and then decrease during the night. The dissolved oxygen and pH also respond to this algal production and respiration. As show in the chemical representation below, the production of algae will yield higher DO and pH levels in the water.

$$106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 122\ H_2O + 18\ H^+ \rightarrow \underset{\text{(algae)}}{C_{106}H_{263}O_{110}N_{16}P} + 138\ O_2$$

The pH increases due to the consumption of 18 hydronium ions for each algal cell produced. A quantitative analysis of the production of algae and dissolved oxygen and the consumption of carbonate minerals will be performed once data sets for August, September, and October become available. An approach similar

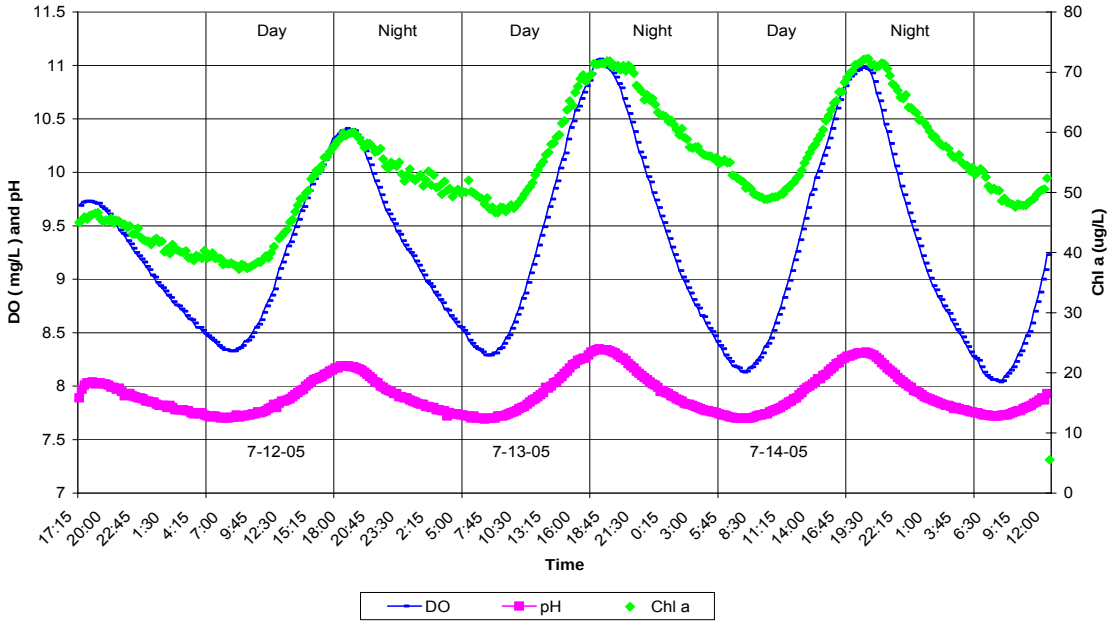

Figure 4: Dissolved oxygen, pH, and Chl a measured midway between Vernalis and Mossdale on the San Joaquin River, July 11-15, 2005.

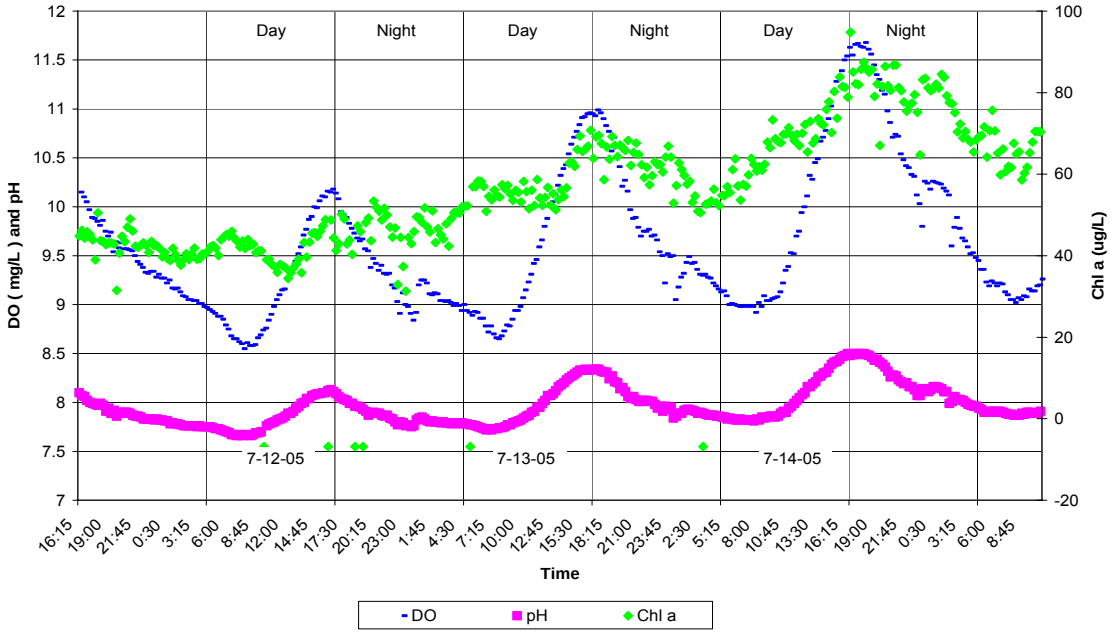

Figure 5: Dissolved oxygen, pH, and Chl a measured at Brandt Bridge on the San Joaquin River, July 11-15, 2005.

to that presented later in this report for light-dark bottle data analysis will be used to determine whether the dissolved oxygen production and carbonate mineral consumption can be predicted from chl *a* and light intensity measurements.

Task 8.2 Lagrangian monitoring

Four liters of rhodamine WT dye was dispersed into the San Joaquin River on July 13, 2003 at 12:30 PM and tracked to the DWSC. The travel time to the DWSC was approximately 32 hours. During this period, the flow at Vernalis was approximately 4500 cfs. The San Joaquin River flow splits at the Head of Old River, with approximately 1800 cfs continuing to the DWSC as measured at the Garwood Bridge USGS station (station code SJG at cdec.water.ca.gov). These flows are much higher than flows observed during drier water years and yield a relatively fast travel times. Figure 6 presents the river reaches in which continuous in situ measurements were made and the locations where grab samples were collected for laboratory analysis. The river mile associated with the sample locations and collection time are presented in Table 1.

Table 1: The San Joaquin River Mile associated with sampling location and time.

Station	Date	Sample time	River mile
SJR 1	7/13/05	13:00	68.37
SJR 2	7/13/05	15:20	65.77
SJR 3	7/13/05	17:48	61.43
SJR 4	7/13/05	19:55	58.90
SJR 5	7/13/05	23:45	55.60
SJR 6	7/14/05	3:00	53.07
SJR 7	7/14/05	4:55	51.06
SJR 8	7/14/05	8:00	51.06
SJR 9	7/14/05	10:05	46.65
SJR 10	7/14/05	14:05	44.08
SJR 11	7/14/05	16:00	42.94
SJR 12	7/14/05	18:30	40.62

Dispersion attenuates the peak tracer concentration as the dyed water moves downstream. In addition, approximately 60 percent of the water dyed at Vernalis flowed down Old River and never reached the DWSC. As such, the tracer plume was replenished below the Head of Old River at 2:30 AM on July 14, 2005 with another 4.00 L of rhodamine WT. During the tracking of the tracer, the concentration profile was periodically measured from the boat at a fixed location.

These data provide a means of measuring the mass of the tracer in the water and also provide estimates of the dispersion. An example of a tracer profile measured during the July trial is shown in Figure 7 for the tracer passing river mile 53.07. The dispersion coefficient, E, was determined by fitting an analytical model to the data as also presented in Figure 7 (Chapra, 1997). The tailing appearing in the measured profile appears to be associated with tracer that becomes temporarily trapped in eddy currents or pools common to sinuous rivers. Parameter fitting was performed by eye, yielding a dispersion coefficient of 0.5 m^2s^{-1}.

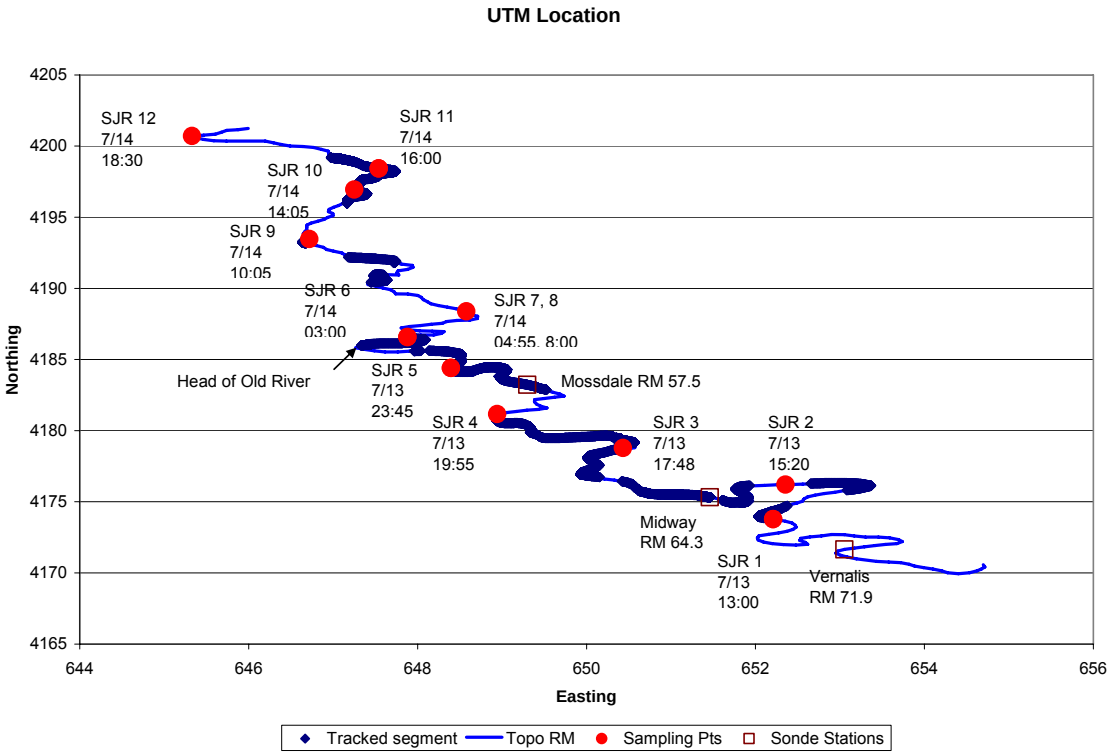

Figure 6: Sampling locations and tracked segments on July 13-14, 2005. dispersion.

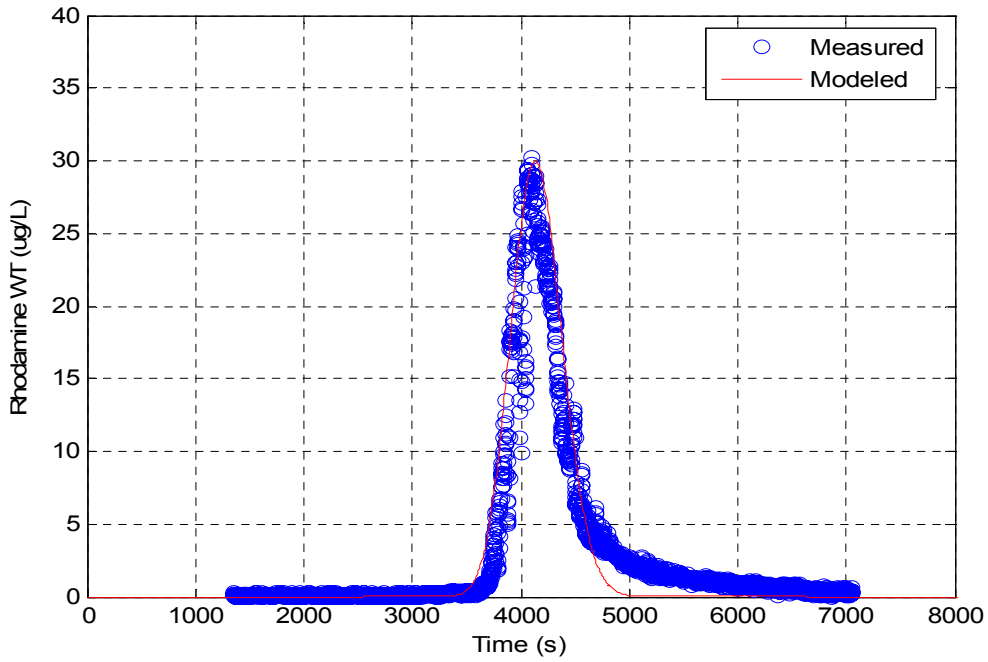

Figure 7: Measured and modeled rhodamine WT concentrations in the San Joaquin River at river mile 53.07. The release of tracer occurred at river mile 53.77 (just downstream from the Head of Old River) at 2:30 AM on July 14, 2005.

The response of chlorophyll *a* in the dyed parcel of water that flowed to the DWSC is shown in Figure 8. Similar to the chlorophyll a data measured by the fixed sondes, these data also exhibit a diel pattern were chlorophyll a increases during the day and decreases by night. Figure 8 also contains chlorophyll *a* data measured in the laboratory from discrete water samples. The pH and DO data are also consistent with the chlorophyll results as shown in Figure 9. The pH and DO increase or decrease with chlorophyll production or respiration. As with the fixed sonde data, additional analyses will be performed to evaluate whether chemical stoichiometry and light intensity can be used to simulate these responses in DO and pH.

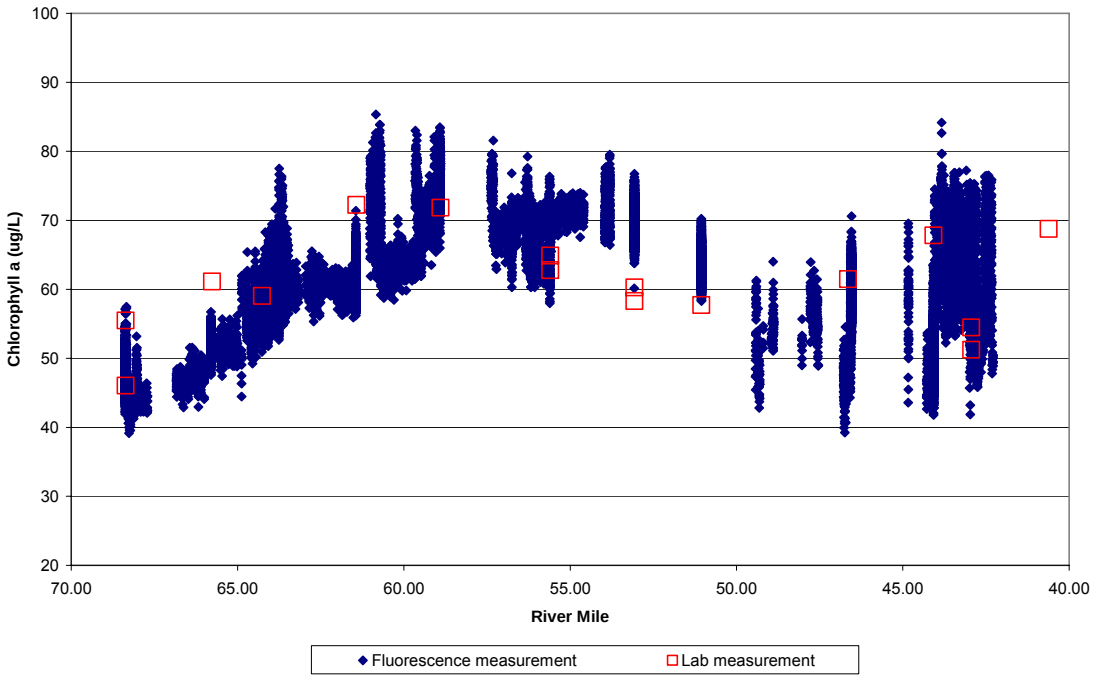

Figure 8: Chlorophyll a concentrations within the rhodamine WT plume flowing from Vernalis to the DWSC, July 13-14, 2005.

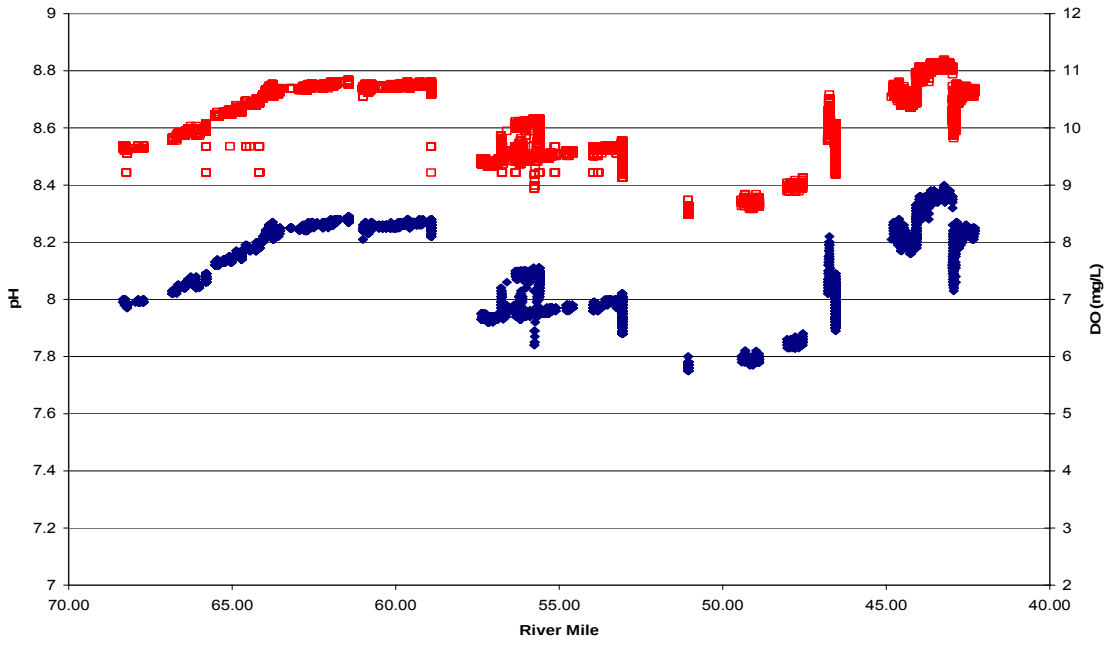

Figure 9: Dissolved oxygen concentrations and pH within the rhodamine WT plume flowing from Vernalis to the DWSC, July 13-14, 2005.

Task 8.3: BOD Decay and Nitrification Rates

During the tracer transport to the DWSC samples were also collected to assess the biochemical oxygen demand of the water. Nitrification rate kinetic experiments were also scheduled if ammonia concentrations exceeded 0.5 mg/L as N. All ammonia concentrations were measured below the detection limit of 0.05 mg/L, and thus, nitrification rate tests were not performed with the samples collected in July.

Long-term BOD experiments were performed at selected sample stations between Vernalis and the DWSC. For the July monitoring, all BOD tests were performed in duplicate. The carbonaceous component of the BOD was measured by inhibiting nitrifying bacteria with 2-chloro-6-(trichloro methyl) pyridine (TCMP). The nitrogenous BOD was determined by subtracting the CBOD from the BOD.

An example of the BOD tests is shown in Figure 10.

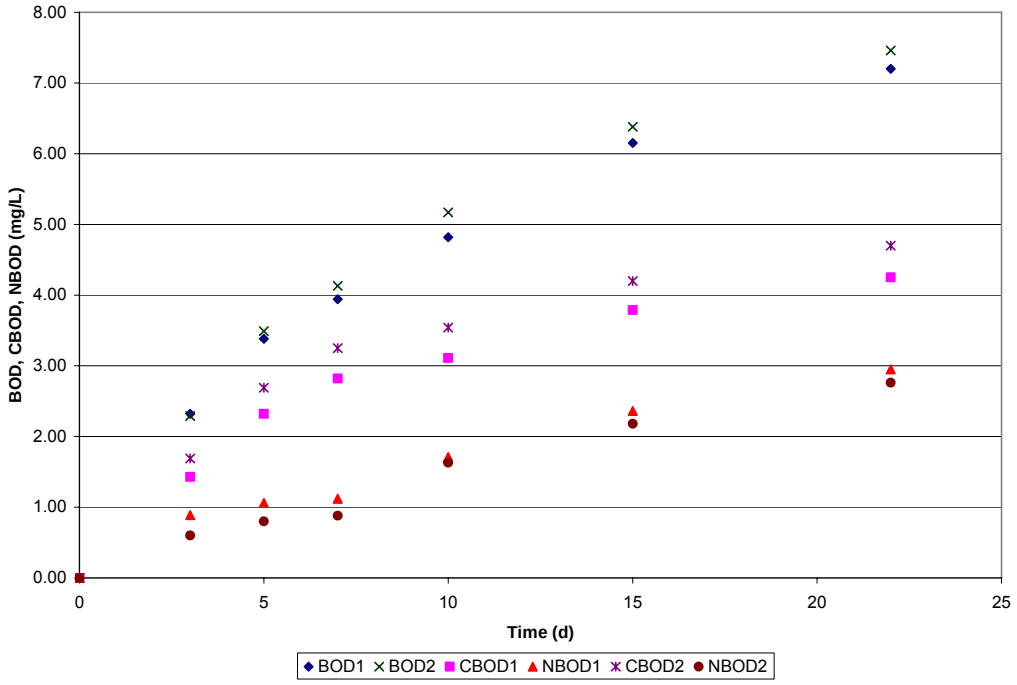

Figure 10: BOD, CBOD and NBOD measured for San Joaquin River water collected at SJR 3.

The BOD results for the six sample locations are presented in Table 2. These results vary little with location in the San Joaquin River, suggesting that inputs of oxygen demanding substances was insignificant during July 13 and 14 in the study reach. The relatively high flows and the timing of the tracer plume entering the DWSC may best explain the uniformity of the BOD results.

The data also suggest that about 30 percent of the BOD is nitrogenous. However, total ammonia was undetected during the transport to the DWSC as shown in Table 3. The NBOD may originate from the algae that decay during the BOD test. A common chemical expression of algae decomposition provides estimates of its associated CBOD and NBOD:

$$C_{106}H_{263}O_{110}N_{16}P + 138\ O_2 \rightarrow 106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 122\ H_2O + 18\ H^+.$$
(algae)

Thus, each mg/L of algae will yield a theoretical oxygen demand of 1.2 mg/L. Of this 1.2 mg/L, approximately 25 percent is nitrogenous.

Table 2: BOD results for July 13-14, 2005 along the San Joaquin River.

Location River Mile	Sample No.	20 day results		
		BOD	CBOD	NBOD
68.4	SJR 1	6.0	4.0	2.0 / 33%
61.4	SJR 3	7.0	4.5	2.5 / 36%
55.6	SJR 5	7.0	4.5	2.0 / 29%
53.1	SJR 6	7.0	4.8	2.2 / 31%
46.7	SJR 9	6.2	4.3	1.9 / 31%
42.9	SJR 11	7.0	4.6	2.4 / 34%

Table 3: Nitrogen species concentrations in the San Joaquin River, July 13-14, 2005

Location River Mile	Sample No.	NH_3 (mg/L-N)	NO_2^- (mg/L-N)	NO_3^- (mg/L-N)	TKN* (mg/L-N)
68.4	SJR 1	<0.05	<0.05	0.24	1.0
61.4	SJR 3	<0.05	<0.05	0.22	0.8
55.6	SJR 5	<0.05	<0.05	0.26	0.9
53.1	SJR 6	<0.05	<0.05	0.27	0.9
46.7	SJR 9	<0.05	<0.05	0.24	0.7
42.9	SJR 11	<0.05	<0.05	0.27	0.5

* Total Kjeldahl Nitrogen (NH_3 + Organic nitrogen)

Task 8.4: Light-Dark Bottle Experiments

Light-dark bottle trials were performed by suspending 2-L BOD bottles at depths of 1, 2, and 3 ft from a buoy. A dark bottle was also suspended to evaluate algal respiration. Data collected in July for an experiment performed below Vernalis is presented in Table 4. The bottles were incubated for approximately 4.5 hours during midday. Chlorophyll *a* concentrations increased from 54 to 88 ug/L for the bottle placed at a depth of 1 ft. Photosynthesis occurring in this bottle increased the dissolved oxygen from 8.6 to 14.3 mg/L. Consumption of carbonate minerals increased the pH over 1 unit. In contrast the bottle maintained in darkness exhibited a decrease in chlorophyll *a*, DO and pH due to algae respiration and decay.

Table 4: Initial and final DO, pH, and chlorophyll a July light-dark bottle experiment results.

Depth (ft)	Elapsed Time (hr)	DO (mg/L)		pH		Chlorophyll *a (ug/L)*	
		Start	End	Start	End	Start	End
1	4:45	8.63	14.32	7.92	9.05	54.1	88.0
2	4:40	8.60	13.38	7.92	8.94	54.1	85.4
3	4:30	8.59	10.5	7.97	8.43	54.1	70.9
dark	4:55	8.50	8.03	7.94	7.91	54.1	51.9

The light intensity was also measured as a function of depth. Combining the light intensity measurements with the data presented in Table 4 yields a productivity-intensity (PI) curve that can be used to estimate DO production. Figure 11 presents the PI curve generated for the July light-dark bottle trial.

The production of chl a can also be estimated from the chemical representation for the growth of algae.

$$106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 122\ H_2O + 18\ H^+ \rightarrow \underset{\text{(algae)}}{C_{106}H_{263}O_{110}N_{16}P} + 138\ O_2$$

The production of algae will yield an increase in dissolved oxygen and pH, and a decrease in the total carbonate species concentration. Total carbonates, $C_{T,CO3}$, is the sum of dissolved carbon dioxide gas (CO_2), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). The total carbonate concentration was calculated from the total alkalinity and the pH of the solution.

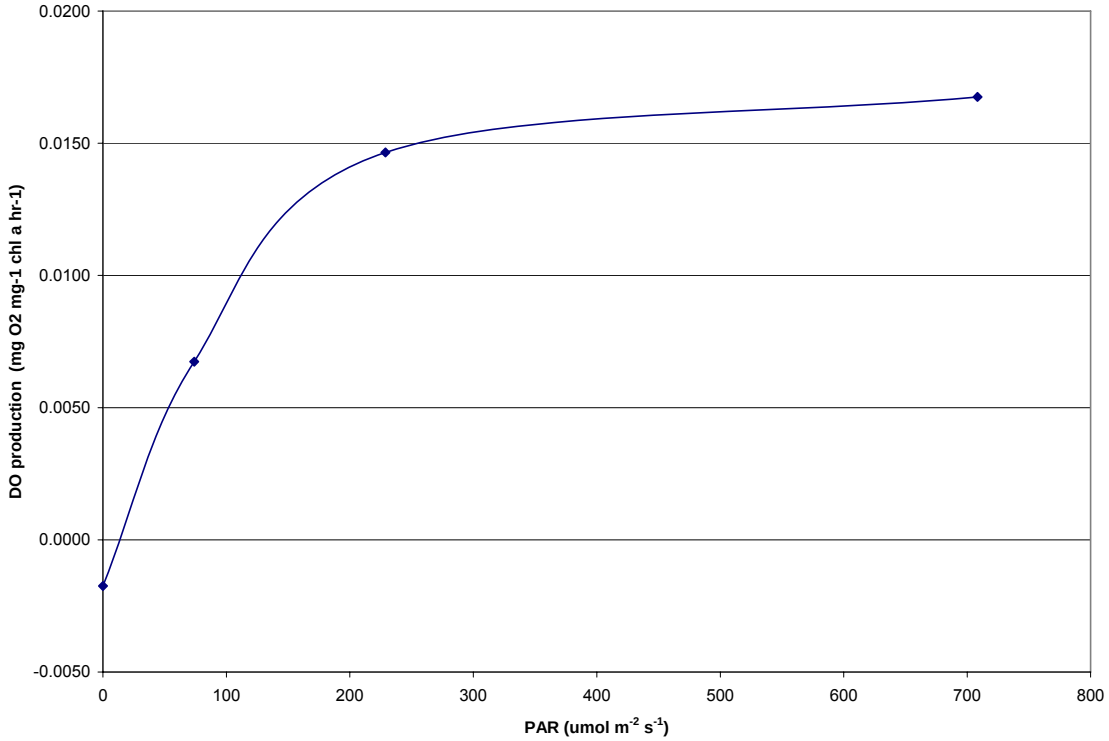

Figure 11: Dissolved oxygen production for measured light intensity at depths of 1, 2, and 3 feet.

The change of the pH is also regulated by the following carbonate species that serve to buffer the pH of water when acids or bases are added. The sum of these species concentration is the total carbonate concentration, C_T.

$$C_T = [CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] - [CO_3^{2-}]$$

Since $CO_{2(aq)}$ is approximately 1000 times greater than H_2CO_3 it is common to combine these species as $H_2CO_3^*$ yielding the following chemical equilibrium.

$$H_2CO_3^* \Leftrightarrow H^+ + HCO_3^- \qquad K_{a1}=10^{-6.35} \text{ at } 25^oC$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \qquad K_{a2}=10^{-10.33} \text{ at } 25^oC$$

When alkalinity is dominated by the presence of carbonate species, the initial alkalinity and pH of the water can be used to calculate the initial total carbon concentration.

$$alkalinity = C_T(\alpha_1 + 2\alpha_2) + [OH^-] - [H^+] \qquad (2),$$

where, α_1 and α_2 are the ionization fractions for HCO_3^- and CO_3^{2-}:

$$\alpha_1 = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}},$$

$$\alpha_2 = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}.$$

The equilibrium constants, K_{a1} and K_{a2}, are dependent on the ionic strength and temperature of the water. Temperature correction for the equilibrium constants were performed with Van't Hoff's equation.

$$\ln \frac{K_{25}}{K_i} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_i} - \frac{1}{T_{25}}\right)$$

Where, ΔH° is the standard change of enthalpy for the specific chemical reaction, R is the universal gas constant, T_i and T_{25} are the absolute temperatures at temperature i and 25ºC, and K_{25} and K_i are the equilibrium constants at 25ºC and temperature i.

The salinity of water will also affect chemical equilibrium. The ionic strength, μ, of water can be estimated from the specific conductance or total dissolved solids (SC; Russell, 1976; Lind, 1970).

$$\mu = 1.6\times10^{-5} \times \text{SC (μmho/cm)}$$

$$\mu = 2.5\times10^{-5} \times \text{TDS (mg/L)}$$

The SC of the San Joaquin River typically ranges from 600 to 900 μmho/cm and the TDS varies from approximately 250 to 650 mg/L. A value of 600 μmho/cm yields an ionic strength of approximately 0.01, a level at which the equilibrium constants should be adjusted. The adjustment is achieved with the activity coefficient of each species in the solution. For example, a pH electrode measures the hydronium ion activity in water:

$$\{H_3O^+\} \equiv \{H^+\} = \gamma_{H+}[H^+],$$

where, $\{H^+\}$ is a shorthand notation for the hydronium activity, $[H^+]$ is the molar hydrogen ion concentration, and γ_{H+} is the activity coefficient for the hydrogen ion.

For ionic strengths less than 0.1, the Güntelberg approximation provides reasonable estimates for the activity coefficient,

$$-\log \gamma_i = \frac{0.5 Z_i^2 \mu^{1/2}}{1+\mu^{1/2}},$$

where Z_i is the valance of ion i. Ionic strength effects can be incorporated into chemical equilibrium calculations by developing a corrected equilibrium constant. As an example, consider the dissociation of water at 25ºC.

$$H_2O \Leftrightarrow H^+ + OH^- \qquad K_w=10^{-14} \text{ at } 25ºC$$

$$K_w=\{H^+\}\{OH^-\} = \gamma_{H+}[H^+]\,\gamma_{OH-}[OH^-]$$

Thus the corrected equilibration constant, K_w^c, is computed from the activity constants and K_w:

$$K_w^c = \frac{K_w}{\gamma_{H^+}\gamma_{OH^-}} = [H^+][OH^-].$$

Similar adjustments were also performed for the other equilibrium equations.

Aqueous solutions are electrically neutral. This balance of positive and negative charges yields the following equation for the San Joaquin River:

$$\text{alkalinity} + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-],$$

and after substitution, the concentration of carbonate minerals, $C_{T,CO3}$, before and after the light-dark bottle incubation period is computed from:

$$\text{alkalinity} + [H^+] = \alpha_1 C_{T,CO3} + 2\alpha_2 C_{T,CO3} + [H^+]/K_w^c$$

These chemical equations and calculations were used to estimate chl *a* production based on increases in DO and pH. The alkalinity was also measured before and after the light exposure. Chlorophyll *a* was assumed represent 1% of the total algal biomass. The predictions for the each of the bottles are shown in Figure xx. Estimations of chlorophyll *a* production from DO or pH data are reasonably good and exhibit the same trend as the measured values as the light decreases with depth in the water column. These analyses suggests that common chemical representations of algae and equilibrium calculations may be adequate to describe algal productivity and decay in the San Joaquin River. However, direct application to the river data over a wider environmental condition remains to be performed.

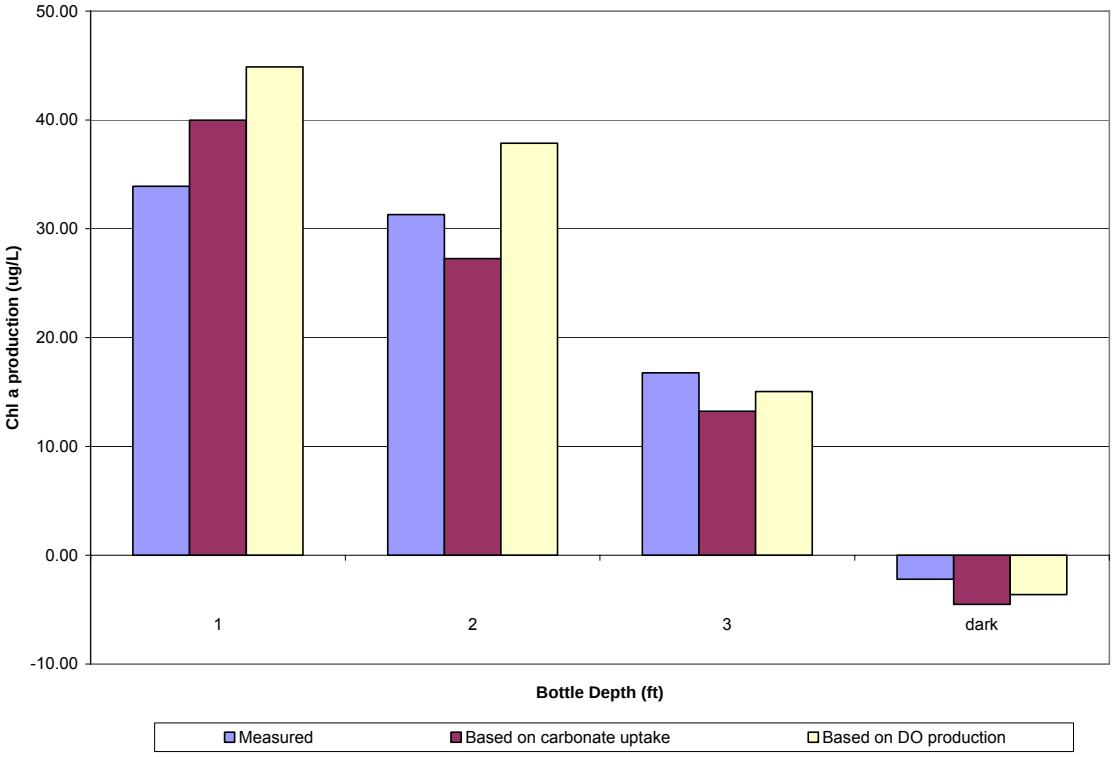

Figure 12: Measured and calculated chlorophyll a production in light-dark bottles deployed below Vernalis (River Mile 72 to 69)

Summary and Conclusions

A three-year study has been initiated to evaluate algal productivity and decay between Vernalis and the Stockton DWSC. A monitoring approach that relies on measuring parameters at fixed locations while simultaneously tracking water quality and algal changes in a dyed parcel of water during transport to the DWSC has been employed. Oxygen demands and algal productivity were also characterized with isolated batch microcosm experiments. Task 9 augments this work by identifying and enumerating phytoplankton populations for assessing changes in species composition within the study reach. In addition, Task 9 identifies and quantifies zooplankton and bi-valve populations to evaluate the impacts of grazing on algae flowing to the DWSC and South Delta

High flows in the San Joaquin River during May and June delayed the start of major field components until July. The resources originally assigned for May and June have been rescheduled to later months or years when low flow exist as these conditions have a greater impact on dissolved oxygen in the DWSC. The most important results of the July investigations are presented here. Monitoring will continue through October and then resume in May of 2006 after the Vernalis Adaptive Management Plan (VAMP) flows subside.

The July monitoring was performed at relatively high flows in the San Joaquin River; approximately 4500 cfs at Vernalis and 1800 cfs below the Head of Old River. Under these conditions, the travel time for a tracer dispersed in the River was only 32 hours. Chlorophyll a concentrations exhibited a strong diel signal with dramatic increases observed during daylight hours followed by significant declines at night. A highly correlated response was observed in pH and dissolved oxygen data. Light-dark bottle experiments further suggest that algal productivity can be predicted with either pH or dissolved oxygen measurements using chemical stoichiometry and equilibrium calculations. This approach will be applied directly to river data and combined with light intensity measurements to simulate the algal productivity and respiration between Vernalis and the DWSC once data sets become available for the lower flow conditions expected in later this year. These data and elucidation of the mechanisms driving algal productivity or decay and associated oxygen demands entering the DWSC should prove valuable to on-going modeling efforts.

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