**San Joaquin Valley Drainage Authority**
**ERP-02D-P63**

**San Joaquin River**
**Up-Stream DO TMDL Project**

***Interim Report No. 1***
***January 6, 2006***

# Task 7: Biological Oxygen Demand (BOD) Isotope Study

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## Objectives

The main objectives of task #7 of the Upstream DO TMDL Project are to characterize BOD isotopic composition in the SJR and tributaries, and then to use these data to better understand the temporal and spatial variations in BOD in the San Joaquin River and tributaries. In specific, we will identify correlations among the following over the seasonal and spatial variations sampled: (1) the isotopic compositions of nutrients (many nitrate and DOC, but some data for ammonium and phosphate) and particulate organic matter (POM), (2) water chemistry (concentrations), and (3) BOD. This will allow us to link specific nutrient sources in the sub-watersheds with the characteristic types of organic matter formed there and the resulting influence on BOD.

## Scope of work

Obtain split water samples and particulate organic matter (POM) samples from LBNL sampling team for samples collected from the SJR, tributaries, and sub-watersheds during the 3 years of the project. Freeze-dry, homogenize, and acidify all the POM samples (up to 704 per year) and analyze them for $\delta^{15}N$, $\delta^{13}C$, and C:N. Further analyze selected samples (approximately 20%) for $\delta^{34}S$ and C:S. A few POM samples will be analyzed for 14C to quantify contributions of old detrital carbon. Different size fractions of POM will also be isolated from a few samples (using centrifugation and Ludox separations) and analyzed separately for $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ to better characterize pure, undegraded phytoplankton when the rivers contain significant amounts of non-algal POM (i.e., during storms).

Selected water samples (approximately 20% of the 704 total) will also be analyzed for: (1) concentration and $\delta^{13}C$ of dissolved organic carbon (DOC), (2) concentration and $\delta^{13}C$ of dissolved inorganic carbon (DIC), (3) optical properties (specific UV absorbance), and (4) $\delta^{18}O$ of water (for water mass budgets). Key water samples, identified by an adaptive management plan, will also be analyzed for nitrate $\delta^{18}O$ and $\delta^{15}N$.

The results for the 20% of samples analyzed for various constituents will be used to decide which analytes (including $\delta^{34}S$ of POM) appear to provide the most useful characterization of the BOD and the source of the BOD. Using an adaptive management strategy, additional samples will then be selected and analyzed, up to the limits of the budget. Splits of all the water and POM samples received will be archived for later analysis as part of PIN 700 or if additional funds become available.

Isotopic characterization methods will be integrated to provide a fingerprint comparison among sites in the watersheds and in the mainstem SJR. Isotopic analysis will be used to link specific nutrient (ammonium, nitrate, and phosphate) and organic matter sources in the sub-watersheds with the specific types of activities (e.g., wastewater treatment plant

effluent, agricultural drains with only tailwater, agricultural drains with only tile drainage, dairy waste, native soil nitrates, fertilizer). All water samples collected by LBNL from sub-watershed locations will be analyzed for nitrate $\delta^{15}N$ and $\delta^{18}O$. If concentrations permit, selected samples will be analyzed for ammonium $\delta^{15}N$ and DON $\delta^{15}N$. Dissolved and particulate phosphate from a few selected samples will be analyzed for $\delta^{18}O$ of phosphate to provide information on the source of P incorporated in algal material in areas where phosphate limitation is suspected. Algae from P-limited sites will show a different isotope fractionation than algae from sites with excess P.

Identify correlations among the following over the seasonal and spatial variations sampled: (1) the isotopic compositions of nutrients (nitrate, ammonium, phosphate) and organic matter (POM, DOM), (2) water chemistry (concentrations), and (3) BOD. This will allow us to link specific nutrient sources in the sub-watersheds with the characteristic types of organic matter formed there and the resulting influence on BOD.

Deliverables: Electronic and hard copy record of all data collected; Interim Task Report; draft Final Task Report; Final Task Report.

## Activities and Tasks Performed and/or Completed

Since March 2005, we have been receiving splits of all the water samples collected by the LBNL team. These samples arrive in coolers which contain a chain of custody form, a frozen glass fiber filter in a centrifuge tube, a frozen 250cc filtered water sample, and an unfiltered 250 cc water sample. We note any discrepancies on the form and return it to LBNL. There have been very few breakages or missing samples. At a later time, we receive an electronic copy of the file to enter directly into our data management system. A copy of the 3 page chain of custody form sent to us in September for samples collected 8/18/05 is attached in Appendix 1, as an example.

We have logged in all the samples collected 3/10/05 to 10/27/05 into our various laboratory databases, along with the nitrate and DOC concentrations and other relevant data sent to us from LBNL.

Analysis of POM samples for $\delta^{13}C/\delta^{15}N$ and nitrate samples for $\delta^{15}N/\delta^{18}O$ are proceeding smoothly , and we will start analyzing the DOC and water isotope samples in January.

When we poured off splits from the filtered water samples for nitrate, water, DOC, and DON isotopes, we also put splits into bottles for some other analyses that we think will ultimately enhance our ability to interpret the rest of isotope and chemical data, namely for SUVA, chloride, sulfate, and silica concentrations. We hope to do these mostly unfunded analyses sometime this spring or summer, when our workforce is complete again.

## List and record of milestones accomplished and/or completed

All samples received (collected March 10 thru September 27, 2005) have been logged into our laboratory databases (353 samples), and split into the various bottles for subsequent analyses.

We have no QA/\QC'd data to report at this time.

## Problems Encountered

1) The LBNL team decided that the field team did not have time to collect water samples for DIC-$\delta^{13}C$; hence, we will be unable to make these measurements on samples collected thus far. We have discussed some alternative (simpler) methods with Will Stringfellow that could be used to collect us DIC samples in the future; alternatively, we have discussed the possibility of collecting DIC samples for only a few trips each year. We will explore these ideas further in the spring. From our earlier work on the SJR, DIC-$\delta^{13}C$ was not overwhelmingly useful except in locations with algal blooms; in these places, the $\delta^{13}C$ provided invaluable information about the interplay of photosynthesis and respiration in controlling DO levels.

2) We had originally asked for 1 L of water to be filtered to isolate the POM samples for isotopic analysis, because from our SJR experience this would always give us enough POM for isotopic analysis. The LBNL people have had problems with clogging filters since the water volumes filtered to produce our POM samples averages 400 cc, with a range of about 200-700 cc. Our visual inspection of the POM filters suggested that most of these samples appear to be plenty big for at least one $\delta^{13}C/\delta^{15}N$ analysis; we were not sure if all would give enough material for repeats or for $\delta^{34}S$. However, if we find that we are having trouble analyzing these samples in the next month because of sample size, we will ask for larger samples to be filtered in the future since it is a lot more work for us if the samples are too small.

3) Analysis of the samples has been delayed because this project and the overlapping PIN700 project did not get contracted until late July, and it was late September before we had Calfed (Josh Grover) approval of the QAPP and Monitoring Plan for the PIN 700 project. One might ask, what does this have to do with the DO project? Well, Grover felt that although the samples collected under the DO project had approved QAPP and Monitoring Plans for their collection and analysis, these plans were not sufficient for these samples to be analyzed by the PIN700 project. To eliminate any possible future problems related to this issue, we postponed starting the processing and analysis of the DO project samples until we had approval to analyze everything collected by the DO project, for the complete suite of possible isotopes covered by both projects. The PIN 700 QAPP and Monitoring Plans were approved in September.

4) Analysis of the samples has also been delayed by instrument problems and lack of technical staff. In October we started the "official" login and sample processing (freeze-drying, grinding, weighing, acidifying) of the POM samples (the main samples funded by the DO project) for isotopes, and have been stockpiling them to run them all together. However, we have not made much progress because we our USGS project was short 3 technicians most of the fall and we did not get permission to replace them until recently. So far, we have only found the equivalent of 1 new technician, and we probably will not be able to hire the 2 other new technicians for another month or two (we need to do an official civil service announcement). As for the other isotope samples (nitrate isotopes, water isotopes, etc), they have been sitting in limbo as we suffered an amazing series of lab problems over the last 2+ months. In specific, we have had multitudes of instrument problems with 3 of our 4 mass specs this fall (including a month of trouble with the one normally used for POM samples), about a month of wasted time with bad microbial cultures (used to prepare nitrate isotope samples for analysis), and have been short on technical staff to do the analyses when one or more of the mass specs were operational anyway. But the good news is that in the last month, we have finally gotten the last of the 3 mass specs operating again, the other mass specs have undergone various tests to get them running OK again, and we are back on track again with sample analyses.

5) We have identified some potential problems with the LBNL database structure. Dan Doctor made the following suggestion (in an email to Sharon Borglin and Will Stringfellow, in mid December) that might make handling the data smoother in the future. If these problems can be addressed now, all of us will have an easier time dealing with the database.

a) The Master File is currently set up to be sorted on two parameters: the site number, and then the sample ID. We suggest that we use only the sample ID for sorting. The reason is that it will be easier for us to share and handle data between our respective databases, because in our databases we have unique lab IDs that we link to the unique sample IDs.

b) A potential problem with sorting on the sample IDs as they are in the Master File sent to us is that some of the site numbers are individual digits (eg, DO-4-031005) and some are two-digit numbers (DO-10-031005). In Excel, the two digit number would be sorted above the single digit, in spite of the fact that 4 comes before 10. This is because Excel thinks of it as text, and sorts 1 before 4. This can be overcome by inserting a zero in front of the single digit entries (eg, DO-04-031005). This is a preferred format for the sample IDs, and is how the sample IDs are reported in the individual spreadsheets submitted with he samples. It would be best to update the Master File to this format to be consistent and for ease of sorting the data. Stringfellow responded that this problem will be fixed.

c) Also, it would be easiest for data interpretation if, when sorted on sample ID, the samples are arranged chronologically by site. The last six digits should therefore start with the year code (eg, 050310 for Mar 10, 2005). This is because once we get into 2006, the samples as they are will be sorted by month regardless of the year of collection (eg, 031005 then 03##06, etc) and would need to be resorted again on another parameter (i.e.,

serial date). Although we cannot go back and change the field IDs for those samples already collected, we might be able to address this problem now by adding a sequential number code to sample IDs in the Master File (eg, **0001**- DO-04 -031005). Once the rows are properly sorted, this is easily accomplished in Excel using the CONCATENATE function.

d) The Master File (sent to us in December) does not contain separate rows for the trip blanks and the field duplicates. This makes handling the data more difficult, for these samples are treated like any other in the lab and yet there is no place to report the data into this Master File. We can understand the desire to have a file that contains only the data that will be used for interpretation, but first we need to have a file that will contain all of the data, including the QA/QC data. We suggest compiling a separate Master File for this purpose based on a compilation of the sample submission sheets, into which we can add our data as it come in. However, Stringfellow responded that he would prefer to keep the duplicates and blanks in a separate file.

## List of proposed activities and tasks for the following quarter.

1) We plan to see if we can get >90% of the POM samples and >80% of the nitrate samples collected from 3/05 through 10/05 analyzed by mid February. If we no not have instrument problems, we will also try to analyze some of these for water $\delta^{18}O$, water $\delta^{2}H$, and/or DOC-$\delta^{13}C$. If time permits, we will analyze more recently collected samples too.

We think we can accomplish our analytical goals if 3 of the 4 mass specs give us little or no problems AND if almost everyone in my group drops whatever they were doing and concentrates on getting the Calfed-funded samples analyzed during the month of January. And by "all" I mean all the samples collected by the DO project, whether they were funded by the DO project or the overlapping PIN 700 project. It certainly makes sense to us to use all the data we have to write the best and most complete interim report we can. But, if we have more mass spec problems, we can run the POM samples (the main analyte funded by the DO project) on any of 3 mass specs, so we certainly will be able to analyze them even if we have problems running some of the other analyses.

Stringfellow suggested that we analyze one set per month first, and then analyze the rest – so that we will have a moderately comprehensive dataset for the March report, even if we have more mass spec problems. This is a good idea and we will do so POM samples. However, for nitrate and DOC samples we get more accurate data if we analyze samples and standards with similar concentrations at the same time.

2) We will ensure that the data meet our QA/QC standards prior to reporting the data.

3) We will provide the data in electronic form for inclusion in the LBNL master database.

4) We will write a second interim report, due in March.

# Appendix 1a. POM samples

**Chain of Custody Record - DO TMDL Project**

**Date Samples Collected** 8/18/2005 **Sampled by** LBNL

**Ship From:**

Sharon Borglin
Lawrence Berkeley National Lab
1 Cyclotron Rd, MS 70A-3317
Berkeley, CA 94720
510-486-7515

**Ship to:**

Carol Kendall
United States Geologic Survey
345 Middlefield Road, MS 434
Menlo Park, CA 94025
650-329-4576

| DO Site Number | Sample Site | Sample code | Date | Time | Sample Matrix | Number of Containers | Preservation/Container |
|---|---|---|---|---|---|---|---|
| 12 | Stanislaus River at Caswell Park | DO-12-081805 | 8/18/2005 | 8:06 | Filter | 1 | 50 ml PP centrifuge tube |
| 13 | Stanislaus River at Ripon | DO-13-081805 | 8/18/2005 | 8:57 | Filter | 1 | 50 ml PP centrifuge tube |
| 14 | Tuolumne River at Shiloh | DO-14-081805 | 8/18/2005 | 10:05 | Filter | 1 | 50 ml PP centrifuge tube |
| 16 | Merced River at River Rd | DO-16-081805 | 8/18/2005 | 12:01 | Filter | 1 | 50 ml PP centrifuge tube |
| 17 | Merced River near Stevinson | DO-17-081805 | 8/18/2005 | 13:15 | Filter | 1 | 50 ml PP centrifuge tube |
| 19 | Salt Slough at Lander Ave | DO-19-081805 | 8/18/2005 | 10:24 | Filter | 1 | 50 ml PP centrifuge tube |
| 20 | Los Banos Creek at Hwy 40 | DO-20-081805 | 8/18/2005 | 11:01 | Filter | 1 | 50 ml PP centrifuge tube |
| 23 | MID Lat 5 to Tuolumne River | DO-23-081805 | 8/18/2005 | 10:33 | Filter | 1 | 50 ml PP centrifuge tube |
| 24 | MID Lat 6 to Stanislaus River | DO-24-081805 | 8/18/2005 | 9:22 | Filter | 1 | 50 ml PP centrifuge tube |
| 26 | TID Highline Spill | DO-26-081805 | 8/18/2005 | 12:52 | Filter | 1 | 50 ml PP centrifuge tube |
| 33 | Hospital Creek | DO-33-081805 | 8/18/2005 | 11:01 | Filter | 1 | 50 ml PP centrifuge tube |
| 34 | Ingram Creek | DO-34-081805 | 8/18/2005 | 11:17 | Filter | 1 | 50 ml PP centrifuge tube |
| 35 | Westley Wasteway | DO-35-081805 | 8/18/2005 | 11:40 | Filter | 1 | 50 ml PP centrifuge tube |
| 36 | Del Puerto Creek | DO-36-081805 | 8/18/2005 | 12:08 | Filter | 1 | 50 ml PP centrifuge tube |
| 52 | Salt Slough at Sand Dam | DO-52-081805 | 8/18/2005 | 9:13 | Filter | 1 | 50 ml PP centrifuge tube |
| 53 | Salt Slough at Wolfsen Road | DO-53-081805 | 8/18/2005 | 9:57 | Filter | 1 | 50 ml PP centrifuge tube |
| 26D | TID Highline Spill | DO-4D-081805 | 8/18/2005 | 12:52 | Filter | 1 | 50 ml PP centrifuge tube |
| Trip Blank | Trip Blank | DO-TB-081805 | 8/18/2005 | n/a | Filter | 1 | 50 ml PP centrifuge tube |

Comments:

| Sample reliquished by (signature): | Date/Time | Print Name |
|---|---|---|
| | | |
| **Sample received by (signature):** | **Date/Time** | **Print Name** |
| | | |

# Appendix 1b. Filtered water samples

**Chain of Custody Record - DO TMDL Project**

**Date Samples Collected** **8/18/2005** **Sampled by** **LBNL**

**Ship From:**

Sharon Borglin
Lawrence Berkeley National Lab
1 Cyclotron Rd, MS 70A-3317
Berkeley, CA 94720
510-486-7515

**Ship to:**

Carol Kendall
United States Geologic Survey
345 Middlefield Road, MS 434
Menlo Park, CA 94025
650-329-4576

| DO Site Number | Sample Site | Sample code | Date | Time | Sample Matrix | Number of Containers | Preservation/Container |
|---|---|---|---|---|---|---|---|
| **12** | Stanislaus River at Caswell Park | DO-12-081805 | 8/18/2005 | 8:06 | Filtered Water | 1 | -20o/250mL HDPE |
| **13** | Stanislaus River at Ripon | DO-13-081805 | 8/18/2005 | 8:57 | Filtered Water | 1 | -20o/250mL HDPE |
| **14** | Tuolumne River at Shiloh | DO-14-081805 | 8/18/2005 | 10:05 | Filtered Water | 1 | -20o/250mL HDPE |
| **16** | Merced River at River Rd | DO-16-081805 | 8/18/2005 | 12:01 | Filtered Water | 1 | -20o/250mL HDPE |
| **17** | Merced River near Stevinson | DO-17-081805 | 8/18/2005 | 13:15 | Filtered Water | 1 | -20o/250mL HDPE |
| **19** | Salt Slough at Lander Ave | DO-19-081805 | 8/18/2005 | 10:24 | Filtered Water | 1 | -20o/250mL HDPE |
| **20** | Los Banos Creek at Hwy 40 | DO-20-081805 | 8/18/2005 | 11:01 | Filtered Water | 1 | -20o/250mL HDPE |
| **23** | MID Lat 5 to Tuolumne River | DO-23-081805 | 8/18/2005 | 10:33 | Filtered Water | 1 | -20o/250mL HDPE |
| **24** | MID Lat 6 to Stanislaus River | DO-24-081805 | 8/18/2005 | 9:22 | Filtered Water | 1 | -20o/250mL HDPE |
| **26** | TID Highline Spill | DO-26-081805 | 8/18/2005 | 12:52 | Filtered Water | 1 | -20o/250mL HDPE |
| **33** | Hospital Creek | DO-33-081805 | 8/18/2005 | 11:01 | Filtered Water | 1 | -20o/250mL HDPE |
| **34** | Ingram Creek | DO-34-081805 | 8/18/2005 | 11:17 | Filtered Water | 1 | -20o/250mL HDPE |
| **35** | Westley Wasteway | DO-35-081805 | 8/18/2005 | 11:40 | Filtered Water | 1 | -20o/250mL HDPE |
| **36** | Del Puerto Creek | DO-36-081805 | 8/18/2005 | 12:08 | Filtered Water | 1 | -20o/250mL HDPE |
| **52** | Salt Slough at Sand Dam | DO-52-081805 | 8/18/2005 | 9:13 | Filtered Water | 1 | -20o/250mL HDPE |
| **53** | Salt Slough at Wolfsen Road | DO-53-081805 | 8/18/2005 | 9:57 | Filtered Water | 1 | -20o/250mL HDPE |
| **26D** | TID Highline Spill | DO-4D-081805 | 8/18/2005 | 12:52 | Filtered Water | 1 | -20o/250mL HDPE |
| **Trip Blank** | Trip Blank | DO-TB-081805 | 8/18/2005 | n/a | Filtered Water | 1 | -20o/250mL HDPE |

Comments:

| **Sample reliquished by (signature):** | **Date/Time** | **Print Name** |
|---|---|---|
| | | |
| **Sample received by (signature):** | **Date/Time** | **Print Name** |
| | | |

# Appendix 1c. Unfiltered water samples

**Chain of Custody Record - DO TMDL Project**

**Date Samples Collected** 8/18/2005 **Sampled by** LBNL

**Ship From:**

Sharon Borglin
Lawrence Berkeley National Lab
1 Cyclotron Rd, MS 70A-3317
Berkeley, CA 94720
510-486-7515

**Ship to:**

Carol Kendall
United States Geologic Survey
345 Middlefield Road, MS 434
Menlo Park, CA 94025
650-329-4576

| DO Site Number | Sample Site | Sample code | Date | Time | Sample Matrix | Number of Containers | Preservation/Container |
|---|---|---|---|---|---|---|---|
| 12 | Stanislaus River at Caswell Park | DO-12-081805 | 8/18/2005 | 8:06 | Water | 1 | -20o/250mL HDPE |
| 13 | Stanislaus River at Ripon | DO-13-081805 | 8/18/2005 | 8:57 | Water | 1 | -20o/250mL HDPE |
| 14 | Tuolumne River at Shiloh | DO-14-081805 | 8/18/2005 | 10:05 | Water | 1 | -20o/250mL HDPE |
| 16 | Merced River at River Rd | DO-16-081805 | 8/18/2005 | 12:01 | Water | 1 | -20o/250mL HDPE |
| 17 | Merced River near Stevinson | DO-17-081805 | 8/18/2005 | 13:15 | Water | 1 | -20o/250mL HDPE |
| 19 | Salt Slough at Lander Ave | DO-19-081805 | 8/18/2005 | 10:24 | Water | 1 | -20o/250mL HDPE |
| 20 | Los Banos Creek at Hwy 40 | DO-20-081805 | 8/18/2005 | 11:01 | Water | 1 | -20o/250mL HDPE |
| 23 | MID Lat 5 to Tuolumne River | DO-23-081805 | 8/18/2005 | 10:33 | Water | 1 | -20o/250mL HDPE |
| 24 | MID Lat 6 to Stanislaus River | DO-24-081805 | 8/18/2005 | 9:22 | Water | 1 | -20o/250mL HDPE |
| 26 | TID Highline Spill | DO-26-081805 | 8/18/2005 | 12:52 | Water | 1 | -20o/250mL HDPE |
| 33 | Hospital Creek | DO-33-081805 | 8/18/2005 | 11:01 | Water | 1 | -20o/250mL HDPE |
| 34 | Ingram Creek | DO-34-081805 | 8/18/2005 | 11:17 | Water | 1 | -20o/250mL HDPE |
| 35 | Westley Wasteway | DO-35-081805 | 8/18/2005 | 11:40 | Water | 1 | -20o/250mL HDPE |
| 36 | Del Puerto Creek | DO-36-081805 | 8/18/2005 | 12:08 | Water | 1 | -20o/250mL HDPE |
| 52 | Salt Slough at Sand Dam | DO-52-081805 | 8/18/2005 | 9:13 | Water | 1 | -20o/250mL HDPE |
| 53 | Salt Slough at Wolfsen Road | DO-53-081805 | 8/18/2005 | 9:57 | Water | 1 | -20o/250mL HDPE |
| 26D | TID Highline Spill | DO-4D-081805 | 8/18/2005 | 12:52 | Water | 1 | -20o/250mL HDPE |
| Trip Blank | Trip Blank | DO-TB-081805 | 8/18/2005 | n/a | Water | 1 | -20o/250mL HDPE |

Comments:

| Sample reliquished by (signature): | Date/Time | Print Name |
|---|---|---|
| | | |
| **Sample received by (signature):** | **Date/Time** | **Print Name** |
| | | |

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