





ATTACHMENT 1.

SAMPLE COLLECTION AND QUALITY CONTROL PROCEDURES FOR WATER AND SEDIMENT SAMPLES

The following sections present recommended sample collection and field and laboratory quality control (QC) procedures for collection and analysis of water (including surface and groundwater) and sediment samples for the Mendota Pool monitoring program. Following these procedures will ensure data quality and data usability.

SAMPLE COLLECTION PROCEDURES

Surface water, groundwater, and sediment samples will be collected and analyzed for various constituents as described in this Appendix and summarized in Tables B-4, B-6, and B-7. Analytical methods and required detection limits are summarized in Tables B-5 and B-8.

SURFACE WATER AND SEDIMENT SAMPLING

Sampling equipment for surface water sample collection includes a non-disposable bailer or bucket for purposes of collecting grab samples. The surface water sampling equipment is rinsed between locations with laboratory-quality water (i.e., potable water that is chemically characterized to ensure the rinse water does not effect the results of trace level analyses for such constituents as selenium; this water is not chlorinated).

Sediment samples are collected from a boat using an Ekman dredge. Sediment for analysis is collected from the top 2 cm of the sediment collected by the dredge. Multiple deployments of the dredge may be necessary to obtain sufficient samples for each replicate. Sampling equipment is washed and rinsed with laboratory-quality water between each replicate.

GROUNDWATER PURGING AND SAMPLING

Groundwater samples are most often collected from water supply wells that are equipped with permanent pumping equipment. Some wells in the water quality monitoring program have been constructed specifically for monitoring purposes and are small-diameter wells completed to varying depths, ranging from near or at the water table to below the Corcoran Clay. These wells are sampled with portable submersible pumping equipment, except for the Spreckels Sugar Co. monitoring wells, which are equipped with permanent submersible pumps.

Prior to sampling a well, the well is purged to remove groundwater that has been in the casing. While there is a gradient that moves groundwater through the well structure where the well is perforated, the quality of the water in the casing is subject to changes in composition due to atmospheric exposure and other factors. Purging typically includes the removal of three casing volumes of water prior to sample collection, but there are many additional factors that can be considered when determining whether sufficient purging has occurred. The best approach to making this determination is by monitoring the stabilization

of a few simple water quality parameters during purging operations. Typically, at least three indicator parameters are measured including electrical conductivity (EC), pH, and temperature. Discharge water is collected in a beaker (with a volume of about 0.5 liter) to allow measurement with a portable field meter. Depending upon the field instrumentation, all three parameters (EC, pH and temperature) can be measured simultaneously. The field instrument is calibrated daily in accordance with the procedures specified in the instrument's manual.

When wells are sampled on behalf of the MPG, the indicator readings and field observations are recorded on a field data sheet. In addition to indicator parameter measurements, other measurements are periodically recorded, including measurement time and pumping rate (primarily to track the volume of water removed during purging operations); pumping water level measurements are sometimes recorded, but are not necessary for the purposes of this project. The field observations include turbidity (particulate matter) measurements, which are particularly useful when evaluating trends in total metals concentrations because samples collected from supply wells or monitoring wells that have variable turbidity depending upon well construction, use, or other factors may influence the observed total metals/trace elements concentrations. In the absence of a field meter to quantify turbidity, visual observation and field notations are helpful for identifying atypical groundwater conditions. The sampler will note whether the water is clear or cloudy (turbid) at the outset of purging operations and whether the water clears during purging operations (the degree of clarity when purging operations are complete should be noted).

As indicated above, portable submersible pumps are used to sample many of the monitoring wells. Because the focus of the sampling program is primarily on salinity and associated constituents and selected trace elements, purging operations are sufficient to remove residual water from the pump and tubing that remained from the previously sampled well. No other special cleaning operations are required.

Samples collected from water supply wells in the network that have been idle prior to a sampling event have similar purging requirements to those described above. Sampling events for water supply wells are preferably coordinated with the pumping period, so purging becomes less necessary and sampling can be expedited. It is important that the well identification be noted (well clusters have in the past resulted in questionable data sources). It is also important that the samples be collected at the wellhead to the extent possible. If the sampling point is located away from the wellhead, care should be taken to ensure that the sampling point (spigot, tubing, pipe, etc.) has been flushed with the water to be sampled and that field parameters are measured and turbidity measured and/or noted.

Purging is conducted until field parameters stabilize. Stabilization is defined as three consecutive readings at 5-minute intervals where parameters do not vary by more than 5 percent. If parameters have not sufficiently stabilized, purging should continue. The sampling and purging data collected as part of the project provide a useful indication of purging requirements for future sampling events. Unless extraordinary circumstances are encountered, not more than ten casing volumes will be purged. Monitoring well samples will be collected while pumping at a slow rate (less than 0.1 gpm).

CONTAINERS AND PRESERVATION

Sample containers and preservation for metals analyses (including selenium and molybdenum) are summarized in Table 1. Due to the potential of contaminating the samples with boron from borosilicate glass, at no time should water or sediment samples contact glass, glass wool, or filter materials containing glass.

Table 1. Required Sample Containers, Preservation, and Holding Times for Water and Sediment Samples

| ANALYTE | SAMPLE MATRIX | CONTAINER | PRESERVATIVE | HOLDING TIME ^a |
|---------------------------------|---------------|-----------|--------------------------------|--------------------------------|
| Metals, Total | Water | P/G | Add HNO3 to pH<2 | 6 months |
| Cations | Water | P/G(B) | Refrigerate | 24 hours (regulatory: 14 days) |
| Anions | Water | P | None or refrigerate at 4°C | 28 days |
| Electrical Conductivity | Water | P/G | Refrigerate | 28 days |
| Total Dissolved Solids (TDS) | Water | P/G | Refrigerate | 7 days (regulatory: 2 days) |
| pН | Water | P/G | Analyze immediately | 24 hours |
| Hydroxide | Water | | | |
| Nitrite as N | Water | P/G | Analyze as soon as possible or | None (regulatory: 48 hours) |
| Total hardness | Water | P/G | Add HNO3 to pH<2 | 6 months |
| Metals, Total | Sediment | P/G | Cool, 4°C | 6 months |
| Grain Size | Sediment | P/G | Cool, 4°C | 6 months |
| Electrical Conductivity | Sediment | P/G | Refrigerate | 28 days |
| Cation Exchange Capacity | Sediment | | | |
| Total Organic Carbon (TOC) | Sediment | P/G | Cool, 4°C | 28 days |

Notes:

- 1. P = Polyethylene
- 2. G = Glass
- 3. G(B) = Glass/borosilicate

QUALITY CONTROL PROCEDURES

The following sections present recommended field and laboratory QC checks for the sampling and analysis activities. A discussion of field QC samples, frequency of collection, and acceptance criteria is included. A discussion of laboratory QC samples and analyses follows.

FIELD QC SAMPLES

The recommended type and frequency of field QC samples to be collected are summarized in Table 2 and described below.

FIELD (SOURCE WATER) BLANKS

Field blanks are samples of the water source (laboratory-quality water) used for decontamination. This blank is used to monitor for potential contaminants introduced from the water source used to rinse equipment during field sampling activities. Due to the low level target values established as Refuge Water Quality Objectives by CDFG, these blanks are considered important for evaluation of the surface water quality results in order to ensure that the rinse water does not contain levels of the target compounds that would result in nonrepresentative grab samples and apparent exceedance of established target concentrations. Field blanks will not be collected for groundwater quality samples.

Typically, at least one sample for each source of water or one field blank per lot number of laboratory-quality water for a specified event will be collected and analyzed for the same parameters as the corresponding field environmental samples.

DUPLICATE (BLIND) FIELD SAMPLES

Blind duplicate field samples are collected to monitor the precision of the field sampling process. Duplicates will be collected for surface water and groundwater samples; they will not be collected for sediment samples because the inherent variability of those samples precludes obtaining a true duplicate. The true identity of the duplicate sample is not noted on the chain of custody form, rather a unique identifier is provided. It is recommended that blind duplicates be collected from at least 5 percent of the total number of sample locations (i.e., a duplicate sample would be collected from one of the thirteen surface water sampling stations during each event and approximately four samples would be collected in duplicate from the wells sampled by the MPG during any one sampling year). It is best to choose locations that are known or suspected to contain moderate levels of the analytes of interest so that detected levels can be compared for precision.

The identities of the duplicate samples are recorded in the field-sampling logbook, and this information is forwarded to the data quality evaluation team to aid in reviewing the data quality. The sources (locations) of the blind field duplicates will not be revealed to the laboratory. Each blind field duplicate sample will have a unique sample identification number on the chain of custody form sent to the laboratory such that the laboratory cannot determine its source.

Table 2. Field QC Samples For Precision and Accuracy

| Type of QC Sample | Frequency |
|--|---|
| Equipment rinsate blank – Total metals | 1 per surface water sampling event |
| Field (rinse water source) blank | 1 per rinse water source |
| Field "blind" duplicate | 5 percent of samples collected per event (i.e., 1 for each sw sampling event and about 4% for the groundwater sampling conducted during the year by the MPG |

Note: Duplicates to be collected from surface water and groundwater samples only. The inherent variability of sediment samples precludes obtaining a true duplicate sample for assessment of precision.

LABORATORY QUALITY CONTROL REQUIREMENTS

Laboratory Responsibilities

The laboratory should report quality control data with each analytical batch or sample delivery group, which is not to exceed 20 samples. At a minimum, the laboratory should analyze and report results for a method or procedural blank, a laboratory duplicate, a laboratory control spike for selected analytes (particularly for trace elements with low-level detection limits), and each sample delivery group. These results should be reported with the sample results, and the QC data sheets or the report narrative should include the acceptance criteria for these analyses. Before the laboratory releases each data package, the laboratory must carefully review the sample and laboratory performance QC data to verify sample identity and also the completeness and accuracy of the sample and QC data. An explanation of any QC data that do not meet acceptance criteria and any corrective actions taken by the laboratory should be included in the data report.

Review of Laboratory Data Reports

Data validation should include a data completeness check of each data package and a thorough review of all laboratory reporting forms. Specifically, this review should include:

- Review of data package completeness;
- Review of the required reporting summary forms to determine if the QC requirements were met and to determine the effect of exceeded QC requirements on the precision, accuracy, and sensitivity of the data;
- Review of the overall data package to determine if contractual requirements were met;

- Review of additional quality assurance (QA) and QC parameters, such as field blank contamination, to determine technical usability of the data; and
- Application of standard data quality qualifiers to the data.

In addition, each data validation should include a comprehensive review of the following QA/QC parameters as indicated in the National Functional Guidelines:

- Holding times (to assess potential for degradation that would affect accuracy);
- Blanks (to assess contamination for all compounds);
- Internal Standards (to assess method accuracy and sensitivity);
- Target Compound Identification;
- Compound Reporting Limits and Method Detection Limits (to assess sensitivity as compared to project-specific requirements).

Data validation is partially based on best professional judgment. In order to achieve consistent data validation, data worksheets should be completed for each data validation effort. A data review worksheet is a summary form on which the data reviewer records data validation notes and conclusions specific to each analytical method. The worksheets will help the reviewer to track and summarize the overall quality of the data. Sample results will then be qualified as appropriate, following EPA protocols. Samples that do not meet the acceptance limit criteria will be indicated with a qualifying flag, which is a one or two-letter abbreviation that indicates a problem with the data (Table 3).

Table 3. Data Validation Qualifiers

| Qualifier | Explanation of Qualifier |
|-----------|---|
| U | The compound was analyzed for, but was not detected above, the reported method detection limit. |
| J | The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample. |
| R | The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified. |
| UJ | The analyte was not detected above the reported method detection limit. However, the reported limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample. |
| В | The analyte was positively identified; the reported concentration is greater than the instrument detection limit but less than the QA Project Plan specified Reporting Limit. |