On-site Evaluation Report

of the

California Department of Public Health
Drinking Water and Radiation Lab
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Safe Drinking Water Program
Chemistry Section

By

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INTRODUCTION

On December 3 - 6, 2019, Christopher Cagurangan and Cynthia Williams, U.S. Environmental Protection Agency (U.S. EPA) Laboratory Certification Officers (LCOs), conducted an on-site evaluation of the State of California Department of Public Health (CDPH) Drinking Water and Radiation Laboratory (DWRL) in Richmond, California. The purpose of the on-site evaluation was to certify the Laboratory for analysis of chemistry parameters in drinking water samples under the U.S. EPA's Safe Drinking Water Program. Criteria for certification are set forth in the Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition (January 2005); hereafter referred to as the Manual.

The CDPH DWRL is designated as California's Primary State Laboratory (PSL) under the Safe Drinking Water Act (SDWA). The lab provides technical assistance to municipal and privately-owned laboratories, and training to state sampling technicians and engineers. Although minimal, the lab has analyzed drinking water compliance samples for the Division of Drinking Water (DDW) of the State Water Resources Control Board (SWRCB) and emergency response entities. Since the last on-site evaluation, CDPH DWRL has analyzed 117, 213, and 410 drinking water compliance samples in 2017-2019, respectively. The increase in samples analyzed is largely due to the responses of the Paradise Fire in 2018 and the Kincaid fire in 2019.

The 2019 on-site evaluation of the CDPH DWRL for chemistry parameters included interviews with supervisors, analysts, and technicians. U.S. EPA LCOs also evaluated the lab's adherence to approved methods, reviewed the quality assurance project plan (QAPP), reviewed the standard operating procedures (SOPs), and assessed and verified equipment and personnel capability. U.S. EPA LCOs also reviewed initial demonstrations of capability (IDCs), method detection limit (MDL) studies, proficiency testing (PT) samples and data, sample receipt and storage, sample analysis data, analyst logbooks, temperature logs, thermometer certifications, and balance logs.

CDPH DWRL plans to obtain certification from The National Environmental Laboratory Accreditation Conference (NELAC) Institute (TNI) within 1- 1 ½ years. If this is achieved prior to the next scheduled on-site audit in 2023, a TNI accrediting body (AB) would conduct subsequent on-site evaluations and have oversight over CDPH DWRL.

ORGANIZATION AND PERSONNEL

Responsibility for the CDPH DWRL lies with the Branch Chief, Dr. William Draper. Dr. Shiyamalie Ruberu serves as the Chemistry and Radiation Section Chief. Dr. Syrago-Styliani Petropoulou serves as the Chemistry Unit Supervisor and during the vacancy of the Quality Assurance Officer (QAO), she assumed the duties after the 2017 DW audit. Wayne Tseng recently filled the QAO position on December 4, 2019.

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There has been almost 100% turnover in analytical and supervisory staff since the last DW Chemistry audit was performed in 2017. The only individuals who were present during the last audit are the Branch Chief, Dr. Draper, and the Sample Technician, Leah Pels. However, the DWRL is in the process of hiring new analysts over the next few months.

Following is a list of the analytical personnel and their assigned methods of responsibility at the time of the audit. All were interviewed about their respective duties and knowledge of their assigned methods.

Rajashree Ravi -	EPA 200.7, EPA 200.8, EPA 245.1, EPA 300.1, QuickChem 10-204-00-1-X
Nova Tasnima -	EPA 504.1, EPA 524.2, EPA 548.1,
Zheng Miao -	EPA 508, EPA 508A, EPA 508.1, EPA 515.4, EPA 531.2, EPA 547, EPA 549.2, EPA 552.3
Fatemeh Fouladkou -	EPA 525.2, EPA 531.2

LABORATORY FACILITIES, EQUIPMENT AND INSTRUMENTATION

The general laboratory facilities encompass multiple rooms on two floors of the CDPH Richmond campus building. The rooms allow sufficient space for future analytical expansion and are more than adequate for the analysis of compliance samples. Security measures are in place to ensure that the integrity of the samples is not compromised. The facilities are clean and well maintained.

Where practical, instrumentation is dedicated for a specific method. Log books are routinely used to document analysts' activities and show that standards and reagents are adequately tracked. It is a concern, however, that maintenance of the instruments was not documented with specific logbooks to help determine if new IDCs should be performed should a major change in parameters or repair of the instrument require it. This concern is further detailed later in this report.

GENERAL LABORATORY PRACTICES AND ANALYTICAL METHODS

General laboratory practices of the CDPH DWRL adhere to the requirements of the Manual. The analytical methods used are approved for the analysis of drinking water samples. Internally developed SOPs are used and kept current through periodic reviews.

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QUALITY CONTROL

The QAPP outlines the quality assurance and quality control (QC) procedures required for EPA drinking water methods. It is comprehensive and well written.

RECORDS REVIEW

PT records and the Laboratory's SOPs were reviewed, and discrepancies are detailed in this report. U.S. EPA LCOs reviewed analytical logbooks, check weights' calibration, thermometer records and raw data files associated with PT and sample analysis.

SAMPLE COLLECTION, HANDLING AND PRESERVATIVES

It is the laboratory's responsibility to provide the appropriate sample containers with the appropriate preservatives (when applicable) to samplers. Samples are accompanied by a chain of custody (COC) form and checked for preservation and condition upon receipt at the laboratory.

FINDINGS

1. **EPA Method 300.1 (Part B):** Section 8.3 details the preservation requirements for the inorganic disinfection by-products (DBP) detailed in Part B of the Method. "Addition of ethylenediamine (EDA) is required to preserve the integrity and prevent the degradation of bromate and chlorite in the samples" (EPA Method Section 8.6).

   The sample technician follows instructions sent via email on how to prepare sample bottles prior to being sent out in the field. Upon review, the EPA LCOs found this process to be flawed. Records review of batch 19-2030 data showed that samples were received at the lab on February 1, 2019 for trihalomethanes (THMs), volatile organic compounds (VOCs), metals, anions, and mercury analyses. The original COC did not list any analyses for DBP by 300.1 (Part B) which would require the addition of EDA to the sample bottles prior to shipment to the field. DBP analysis was requested after February 1st.

   As a result, sample bottles that were sent out could not have the proper preservation (EDA) because this analysis was not requested by the customer before the sampling process, and not communicated to the sample technician. The request from the customer should have been rejected as the sample bottles used were not compliant

with the method preservation requirements for the analysis being requested.

Appendix E of CDPH DWLR's QAPP details preservation, temperatures, container type, volumes required, and holding times for each analyte by method. This short table in Appendix E is a great resource for, not only, the sample technician, but also, the staff and samplers. To ensure that the sample technician is given the proper preservation instructions and to minimize errors in the future, the notification email should detail the necessary method-specific preservation requirements and be verified against the QAPP prior to the containers being shipped. Also, during the next training for samplers, these new procedures should be discussed along with clarification that samplers cannot use sample containers designated for specific analyses for other analyses that have different preservation requirements.

2. **EPA Method 300.1 (Part B):** When conducting analysis for 300.1 Part B, EDA must also be added to the laboratory reagent blank (LRB), laboratory fortified blank (LFB), laboratory fortified matrix (LFM), and calibration standards. "The addition of EDA to all reagent water used to prepare calibration and quality control samples is required not as a preservative but rather as a means to normalize any bias attributed by the presence of EDA in the field samples." (EPA Method 300.1 Sections 8.2.2, 9.3.1.1, 9.3.2.1, 10.3.1)

   Although it was discovered that EDA was not added to the sample containers prior to shipment to the field, the analyst and supervisor stated that EDA was added to all the QC and calibration standards as specified in the method. The EPA LCOs were not able to find any documentation to support the addition of EDA. This should be documented in the analyst's logbook. Also, there is obvious bias between the QC and field samples for this analytical batch, since EDA was added to QC samples and not the field samples.

3. **EPA Method 300.1 (Part B):** The SOP must be revised to include and highlight the addition of EDA to the sample containers, calibration and QC samples when analyzing for DBP by Method 300.1 Part B.

4. **EPA Method 300.1 (Part B):** The SOP needs to be revised to state that the lowest calibration standard must be used to verify the initial calibration and not the midrange standard. The requirement to use the lowest standard for calibration verification is for Part B only. (EPA Method 300.1, Section 10.5.2). Currently the SOP states that the validity of the imported calibration is checked by the analysis of the mid-range standard (Section 9.3 of SOP).

5. **EPA Method 300.1 Parts A and B:** PGF must be analyzed and must fall between 0.80 and 1.15 in order to demonstrate proper instrument performance (Section 9.3.3). It was not stated in the SOP for 300.1 Part A and the analyst stated it was not being

monitored for either Part A or B.

6. **EPA Method 300.1 Part A:** When analyzing for nitrate and nitrite by EPA Method 300.1 Part A, samples must be analyzed within 48 hours after collection. Samples (19-2030-01, -03 and -04) were received February 1, 2019 and analyzed February 4, 2019. Data was not qualified and it was not stated that samples did not meet the holding time requirements.

   During the exit interview, the supervisor stated that because the analysis was for total nitrate and nitrite as N, samples were acidified with sulfuric acid and therefore, the holding time increases from 48 hours to 28 days. The EPA LCOs found this to be incorrect. The laboratory reported nitrate and nitrite results separately. EPA Method 300.0, which CDPH DWRL is not certified for, allows for total nitrate/nitrite analysis within 28 days after acidication with sulfuric acid. EPA Method 300.1 does not allow the analysis of total nitrate and nitrite. The hold time must not exceed 48 hours and must not be acidified when analyzing and reporting nitrate and nitrite separately by EPA Method 300.1. EPA Methods 300.0 and 352.2 allows for the analysis and reporting of total nitrate and nitrite as N. If the lab would like to request certification for total nitrate/nitrite by N, then it must provide an SOP, IDC, and PTs to EPA for review.

7. **EPA Method 200.8:** DW compliance samples were analyzed and reported without a complete initial demonstration of performance (IDP) (missing MDLs). A complete IDP requires an established linear calibration range (LCR), analysis of a quality control sample (QCS), and MDLs for all analytes. (EPA Method Section 9.2) Until the IDC is completed, CDPH DWRL must not analyze any DW compliance samples.

8. **EPA Method 525.2:** The lab's reporting limits (RLs) for benzo(a)pyrene, heptachlor, heptachlor epoxide, and lindane were above the maximum contaminant level (MCL). This was discovered upon review of data for the PT reporting of benzo(a)pyrene. When questioned about the unacceptable result, CDPH DWRL stated that the result they achieved (0.198) was below their MDL of 0.2. The assigned PT value was 0.226 and the MCL for benzo(a)pyrene is 0.2. The RL must be below the MCL (The Manual Chapter 4, Section 7.2.12). It is strongly recommended that a master list of MDLs, MCLs, and RLs by Method be created and regularly reviewed. Reporting limits should be controlled and not arbitrarily changed without proper documentation and approval. The lab has decided to report down to the MDL for these compounds (MDL=RL). The lab will need to show that the instrument can detect/report down to the MDL by running a check standard at the new RL since the current calibration curve's lowest level is above the MCL. Any reported data must be qualified if QC

criteria is not met. If the instrument cannot achieve the required sensitivity, then the instrument must be repaired or replaced.

9. **EPA Method 531.2:** CDPH DWRL's SOP incorrectly states the LFM criteria within ±35%. The method requires the LFM within ±30%.

10. **General Finding--Documentation:** During the on-site evaluation, the U.S. EPA LCOs had difficulty retrieving and reviewing IDC or sample data and confirming method procedures were followed. Many transcription errors were found. Below are several examples.

    a. CDPH DWRL analysts do not have separate maintenance logbooks. It was stated by the supervisor that, at times, maintenance was listed in the same logbook as sample preparation. During review of logbooks, U.S. EPA LCOs did not find any documentation of maintenance or service. It was found that there was a software change in 2018 for EPA Method 504.1. This was not noted in any logbook and LCOs were not able to retrieve raw data on the instrument computer. Although it was stated that there was a backup of data on a shared drive, it did not seem that it was easily accessible. Excel sheets that were reviewed for IDC did not contain analyst name, sequence run, dates, or time. Each instrument should have dedicated maintenance logs to document any repairs or changes to the instrument to help analysts determine when a new IDC and/or MDL study is required. Also, the Manual states that the laboratory should maintain easily accessible records for five years or until the next certification data audit is complete, whichever is longer (Chapter 4, Section 8.2).

    b. From 2016-2019, several PT results have been reported under the wrong method. In each year, analytes for EPA Method 508.1 were reported as either Methods 508A or 508. Transcription errors were also noted during review of raw PT analytical data. For example, during review of PT WS 19-2 raw data for EPA Method 508.1, the analyst made several transcription errors on the standard and QC results for heptachlor epoxide in the Excel sheet submitted. QC results were not listed in the lab's LIMS system, however, the result for heptachlor epoxide was submitted for PT reporting. It is strongly recommended that CDPH DWRL add a second or third level of review prior to submitting results to the supervisor and standardize required documentation to be submitted for review. This would greatly reduce transcription errors and ensure that records are complete.

    c. It was found during the on-site that new instrumentation was acquired and used for Methods 515.4 and 524.2 without notification. EPA must be notified within thirty days of any change in instrument or personnel (The Manual, Chapter III, Section 14.1).

d. Overall, records and any data submitted, whether paper or electronic, should be traceable. It should be clear who analyzed the samples, the date the samples were run, who conducted a temperature check, when the temperature check occurred, when a standard or reagent expires, etc. If raw data is transcribed to an Excel sheet, it should be complete, and the document should be controlled.

11. **General Finding--Thermometers:** There are no annual calibration checks of the thermometers in the lab. Thermometers in the lab must be verified with a NIST traceable thermometer. Two NIST traceable thermometers are available but were not used to perform calibration checks. The NIST thermometers were certified annually which meets and exceeds the U.S. EPA recommendation of every 5 years.

    Hot block heaters used in several methods do not have calibrated thermometers. The analysts rely solely on the digital readout of the heaters. The following methods use thermometers during sample preparation and require calibration: 200.7 and 200.8 (when digestion is required); 245.1, QuickChem 508A, 531.2, 548.1, and 552.3. Many of these methods have specific temperature ranges that must be adhered to during the sample preparation process. Refrigerators and freezers used to store standards and/or samples for methods also need to be monitored using calibrated thermometers. The date the thermometer was calibrated and the correction factors, if applicable, should be on the thermometer or in documentation readily available for inspection. (The Manual Chapter 4 Section 7.1.5). Note that liquid thermometers need to be calibrated annually and digital thermometers recommended quarterly.

    When selecting a company for calibration/verification of thermometers traceable to NIST, the lab should check traceability by ensuring the following:

    - Documentation of their calibration methods and procedures.
    - Clearly stated calibration uncertainties.
    - Traceability records which should be both public and non-proprietary.
    - Laboratory accreditation with assurance that qualified assessors have looked at a laboratory's traceability procedures.

RECOMMENDATIONS

1. The sample technician is very organized and properly prepared sample containers prior to sending them out to the field. Upon receipt of the samples, temperatures were checked but were only noted on the COC for microbiology samples. EPA recommends that

temperature be documented on all COCs so the analysts can verify proper shipping conditions and qualify data, if necessary.

2. Since the pH of samples are checked by each assigned analyst, it is strongly recommended that is noted on the COC or in the lab instrument logbook. Otherwise, there is no documentation or confirmation that samples have been properly preserved in the field.

3. The sample technician plays an integral part in the sampling process. Different methods have very specific container and preservation requirements that must be met prior to being sent out in the field for sample collection. Since the sample technician is reliant on the instructions from their supervisor, it is recommended that a detailed list (e.g. Appendix E in QAPP) of the preservation requirements for each method being requested is included in the instructions.

4. **EPA Method 300.1:** Samples batch 19-2030 analyzed for nitrite (Part A) and chlorite (Part B) did not meet the criteria listed in the lab's SOPs. Sections 9.3 of each SOP (300.1 Part A &B), states that if at the end of the batch the results for the instrument performance check (IPC) or QCS fail the 100 ±15% criterion, the whole batch must be repeated. The ending QCS was outside the criteria for this batch. This is not a method requirement; therefore, it is recommended that either the analyst follow the SOP, or the SOP be revised to remove the requirement. The method does require an ending CCV. If the QCS serves as the CCV, then this should be made clear in the SOP and the criteria changed accordingly.

5. Due to the infrequency with which drinking water compliance samples are analyzed for some of the methods, it is highly recommended that analysts review the Methods in addition to the SOPs prior to running analyses. There are often important steps, procedures, and requirements that have to be met for samples that are often optional or not applicable when analyzing PTs. It is also highly recommended that these specific sample procedures which are not performed for PTs be highlighted in the SOPs.

6. **Sample Receiving:** Thermometer that is used for sample login (IR thermometer S/N 89495-968) does not match the serial number listed in SOP.

7. **EPA Method 245.1:** Spiking PT samples in order to have an LFM in the analytical run batch is not necessary. The Lab can remove this from their SOP unless it is found to be useful.

8. **EPA Methods 200.7 and 200.8:** It is recommended that turbidity checks and pH results are documented.

9. The QAPP states that MDLs are analyzed on multiple days but U.S. EPA LCOs found MDLs for many methods were analyzed on one day. Also, some of the MDLs reviewed incorporated the methods blanks in addition to the spiked samples to calculate an MDL as described in the new MDL procedures. The SOPs only state that MDLs are either performed annually, as part of a analysts' IDC, or if changes are made to the instrument. MDL procedures should be clearly defined.

10. Due to the recent findings, the U.S. EPA LCOs strongly recommend that all SOPs include preservation requirements for all samples and analysts should be trained to verify preservation requirements have been met prior to analysis.

11. **EPA Method 549.2:** Revise SOP to specify that 3 mL of methanol is added to, not only, the samples, but also, to QC and calibration samples for better extraction. Also, the Method states the samples must be between 7-9 pH prior to analysis but the SOP does not mention this step. During review, the analyst was aware of this step and did state the pH is checked before analysis. It is recommended that this step be documented.

12. **EPA Method 552.3:** During the next SOP revision, it is recommended that the correct reference method is listed (SOP refers to Method 515.3 but should be 515.4) and that acetone is removed from Section 7 since it is not used in the procedure.

13. **EPA Method 524.2:** The total THM MCL of 80 µg/L is not listed in the SOP. Also, the ion abundance criteria for 4-bromofluorobenzene (BFB) criteria in the SOP must match the Method. The mass (m/z) of 177 should be 5-9% of mass 176. The SOP and the instrument lists that mass 177 is 5-10% of mass 176. During the on-site evaluation, it was found that the proper criteria was followed up until recently. CDPH DWRL should correct the SOP during the next revision and ensure that the instrument criteria are corrected for BFB. Lastly, pH should be checked following analysis to ensure proper preservation during sample collection. Results should be qualified if samples were not acidified during collection.

Contingent for Certification

EPA Methods 508, 508A, 508.1, 515.4, and 531.2: Since the assigned analyst, Mario Estrada, retired in November 2019, it has not been definitively decided which analyst(s) will be assigned to the Methods above. As a result, certification for these Methods are contingent upon receiving IDCs from each assigned analyst by **June 30, 2020**. Compliance samples cannot be analyzed until IDC requirements detailed in each Method are completed and submitted to EPA for review. **If these requirements are not met by the due date, then certification for these methods will be rescinded.**

Comments

Although, there are a number of findings and recommendations, the U.S. EPA LCOs would like to highlight the progress that has been made since the 2017 audit. CDPH DWRL has hired a new supervisor, QA officer, and are working to fill analyst vacancies. During the time period that the lab had no QA officer, Dr. Petropoulou completed QC review of all Chemistry methods, ordered and submitted PT results, qualified data and ensured comments were listed on laboratory data reports and reviewed and approved corrective action reports (CARs). During emergency DW analyses, Dr. Peptropoulou had another analyst review sample preparation and analysis data to ensure that QC and Method criteria were met. When QC and Method criteria failed, it was noted on the laboratory report that results should not be used for regulatory purposes. Dr. Petropoulou also took necessary steps to protect the health of her staff when issues with the chemical methyl tert-butyl ether (MTBE) was brought to her attention. MTBE, extraction solvent for EPA Method 552.3, has been found to cause adverse effects upon skin contact or inhalation of vapors for susceptible individuals. Building engineers were contacted to ensure proper air ventilation and applicable instrumentation was moved to the fume hood. Also, samples for haloacetic acids (HAA5) analysis by Method 552.3 have not been accepted at the lab until the issue with MTBE is resolved for the assigned analysts. The lab also properly rejected samples due to improper preservation in the field and every document that the U.S. EPA LCOs requested for review was provided before the end of the on-site evaluation.

CERTIFICATION STATUS

Certification is contingent upon U.S. EPA's receipt and acceptance of corrective actions and a corrective action plan from CDPH DWRL. Corrective actions and a corrective action plan must be submitted by **January 30, 2020**. The CDPH DWRL is requesting certification for the following regulated drinking water parameters determined by the listed methods:

Inorganic Parameters

EPA 200.7	sodium
EPA 200.8	antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, nickel, selenium, thallium
EPA 245.1	mercury
EPA 300.1	fluoride, nitrite, nitrate, chlorite, bromate
QuickChem 10-204-00-1-X	cyanide

Organic Parameters

EPA 504.1	ethylene dibromide (EDB), dibromochloropropane (DBCP)
EPA 508	PCBs as aroclors (screening)
EPA 508A	PCB as decachlorobiphenyl (quantitation)
EPA 508.1	endrin, lindane, heptachlor, heptachlor epoxide, hexachlorobenzene, hexachlorocylcopentadiene, chlordane (total), methoxychlor, toxaphene (total)
EPA 515.4	2,4-D, pentachlorophenol, picloram, dinoseb, dalapon, and 2,4,5-TP (silvex)
EPA 524.2	benzene, carbon tetrachloride, chlorobenzene, p-dichlorobenzene, o-dichlorobenzene, 1,2-dichloroethane, 1,1-dichloroethylene, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, dichloromethane, 1,2-dichloropropane, ethyl benzene, styrene, tetrachloroethylene, toluene, 1,2,4-trichlorobenzene, 1,1,1,-trichloroethane, 1,1,2-trichloroethane, trichloroethylene, vinyl chloride, xylenes (total), total trihalomethanes (THMs): bromoform, chloroform, bromodichloromethane, and dibromochloromethane
EPA 525.2	alachlor, atrazine, benzo(a)pyrene, di(2-ethylhexyl)adipate, di(2-ethylhexyl)phthalate, endrin, heptachlor, heptachlor epoxide, hexachlorobenzene, hexachloropentadiene, lindane, methoxychlor, simazine
EPA 531.2	carbofuran, oxamyl
EPA 547	glyphosate
EPA 548.1	endothall
EPA 549.2	diquat
EPA 552.3	total haloacetic acids (HAA-5)