QAPP Amendment Form

PROGRAM:	Delta Regional Monitoring Program (DRMP)
PROJECT:	Constituents of Emerging Concern (CEC)
QAPP VERSION:	Version 2.0
PREPARED BY:	MLJ Environmental
DATE SUBMITTED:	May 12, 2022

Title: Amendment to the Isotope Dilution Analogue reporting requirements and PPCP MDLs

Section of QAPP affected:

- Table 7-2. Purposes of field and laboratory QC sample types and data quality indicators applicable to the Delta RMP;
- Table 7-3. Method detection limits for chemical analytes;
- Table 9-1. Standard Operating Procedures (SOPs) referenced in this QAPP;
- Table 12-1. Storage and hold time requirements for each parameter group;
- Section 14.2.1 – Measurement Quality Metrics; and Table 14-2. Measurement quality objectives for laboratory measurements.

Reason for Changes:

A total of 13 Pharmaceutical and Personal Care Product (PPCP) constituents are analyzed in water samples by Weck Laboratories. This analysis is done by a modified version of EPA 1694, which uses an isotope dilution method to quantify the analytical results. Though the isotopically labeled standards used for this quantification are added at the beginning of the extraction process, the previous methodology by which Weck processed and analyzed the samples did not allow for the calculation of the percent recovery results of the isotope dilution analogues (IDAs) in the extraction standards.

Given recent CEDEN guidance regarding the reporting of isotope dilution methods, the recoveries of each IDA associated with a sample result should be reported with the result concentration. Moving forward, Weck will be providing these percent recoveries with each analysis performed with EPA 1694M. For previous data with which Weck does not have the ability to directly report the IDA recoveries, Weck staff will be providing the relative recoveries with the caveat that though some results may fall below the laboratory control limits, all data were reviewed by an analyst and accepted based on the signal to noise ratio. This process was discussed on March 22, 2022 with representatives from Weck, MLJ Environmental, the Regional Water Board Quality Assurance (QA) Representative, and the State Water Resources Control Board (SWRCB) QA Officer. The updated Standard Operating Procedure (SOP, ORG111.R5.0) allowing for the

provision of the IDA recoveries has been provided directly to the SWRCB QA Officer for review and approval; this documentation is confidential and not available for external review (Table 9-1).

As an additional outcome to the updated methodology for EPA 1694M, Weck has also reduced the sample collection size requirements, which has been updated in Table 12-1.

The other laboratory using an isotope dilution method for water samples, Vista Analytical Laboratories, has already been providing the IDA recoveries with their data reporting; however, the requirement is being clarified for analysis performed by Vista with EPA 537M in Table 14-2.

In addition to the clarification updates regarding IDA sample recoveries, Weck staff notified the Delta RMP in February that they had completed a method detection limit (MDL) study for their PPCP analysis and that the detection limits for all 13 analytes under this project were therefore updated from the original values provided in the QAPP (Table 7-3).

- Seven of the 13 updated MDLs were decreased from the previous values. The associated analytes include estrone, 17-beta-estradiol, ibuprofen, triclosan, 17-alpha-ethynylestradiol, progesterone, and testosterone.
- Six of the 13 updated MDLs were increased from previous values, including diclofenac, bisphenol A, gemfibrozil, iopromide, naproxen, and salicylic acid.
    - Of these analytes, only diclofenac and bisphenol A are required analytes. Both MDLs and RLs are still below the target RL range identified in the CEC Pilot Study Workplan and are therefore sufficient to meet the project objectives.
    - The remaining four analytes are additional analytes and are not explicitly required by the Workplan; the elevated MDLs therefore do not affect the project objectives.

Finally, Weck noted that due to an oversight in the original QAPP, the reporting limit (RL) for triclosan is being updated. The RL for triclosan has been elevated from 10 to 20 ng/L and is still below the targeted RL and monitoring trigger limit (MTL) identified in the CEC Pilot Study Workplan.

Detail of Changes:

Changes have been made to the following tables and sections of the CEC QAPP to include references to reporting IDA recoveries. Updates have also been made to the MDLs for the PPCPs analyzed by Weck Laboratories and the sample collection volume requirements.

Table 7-2. Purposes of field and laboratory QC sample types and data quality indicators applicable to the Delta RMP.

QC Sample Type	Data Quality Indicator/Purpose
Field Sampling QA	
Field Blanks	Identify contamination resulting from field conditions (bias from field conditions)
Field Duplicates	Document the precision of the sampling and analysis process
Trip Blank	"A trip blank (usually only used for VOCs) is designed to measure cross-contamination that may occur during sample handling and transport (e.g., from a broken bottle in the sample ice chest)" (Baylor et al. 2014)
Laboratory QA	
Laboratory Blanks	Assess potential sample contamination, confirm the absence of analytes introduced throughout the sample preparation and analysis process.

QC Sample Type	Data Quality Indicator/Purpose
	Also sometimes referred to as "Method Blanks." Bias from laboratory procedures.
Laboratory Duplicates or Laboratory Replicates	Assess analytical precision, through replicate sub-samples of field samples (preferred), taken through the full analytical procedure including all lab processes combined. Although certified reference materials, lab reference materials, matrix spike samples, or laboratory control samples can also be analyzed in duplicate, they are referred to prefaced with their sample type, e.g., "matrix spike duplicate"
Laboratory Control Samples	Assess analytical accuracy, in samples containing known amounts of target analytes, analyzed much like an ordinary field sample. Primarily used for lab created clean or null matrix samples spiked with target analytes. See "lab reference material" for natural matrix samples
Laboratory Reference Materials	Assess accuracy within an analytical batch and precision across analytical batches in natural matrix samples. "Lab Reference Material" is used for natural matrix recovery samples without certified values, but with known expected values (e.g., archived homogenized collected material previously analyzed, diluted CRMs).
Certified Reference Materials	Assess accuracy within an analytical batch and precision across analytical batches in natural matrix samples. Certified reference materials (CRMs) have externally validated expected "certified" concentrations of analytes of interest, and are obtained from commercial or government vendors (e.g., NIST, which calls them "SRMs" (standard reference materials)).
Matrix Spikes (MS)/Matrix Spike Duplicates (MSD)	Accuracy and precision/evaluate the effect of the sample matrix on the recovery of the compound(s) of interest and providing an estimate of analytical precision when measured in duplicate (laboratory chemical analysis).
Surrogate Spikes	Accuracy of analytical method/assess the efficiency of the extraction method for organic analytes (laboratory chemical analysis).
Internal Standards	Accuracy of analytical method/enable optimal quantitation, particularly of complex extracts subject to retention time shifts or instrument interferences relative to the analysis of standards. Internal standards can also be used to detect and correct for problems in the injection port or other parts of the instrument (laboratory chemical analysis).
Isotope Dilution Analogues (IDAs)	Accuracy of analytical method/uncertainty in quantitation of results analyzed using an isotope dilution method. For analytes using these methods, the response of the associated isotopically labeled version of the same or similar analyte (the analogue) is used for both the performance of the extraction/analytical methods and the quantitation of the final results.

Table 7-3. Method detection limits for chemical analytes.

Matrix / Analyte Type	Analyte	CEDEN Matrix Code	Mon Trigger Level (MTL)	Target RL (1/2 MTL)	MDL	RL	Units	Lab	Method
			Water						
Required	Estrone	samplewater	6.0	3.0	~~10~~ 4	10	ng/L	Weck	~~Hormones by LCMSMS-APCI+~~ List B by EPA 1694M-APCI
Required	17-beta-estradiol	samplewater	2.0	1.0	~~10~~ 4	10	ng/L	Weck	~~Hormones by LCMSMS-APCI+~~ List C by EPA 1694M-APCI
Required	Ibuprofen	samplewater	100	50	~~5~~ 4	10	ng/L	Weck	~~Pharmaceuticals by LCMSMS-ESI-~~ List C by EPA 1694M-ESI-
Required	Diclofenac	samplewater	100	50	~~0.26~~ 4	10	ng/L	Weck	~~Pharmaceuticals by LCMSMS-ESI~~-List B by EPA 1694M-ESI-
Required	Galaxolide (HHCB)	samplewater	700	350	0.1	1	ng/L	Physis	EPA 625.1M
Required	Triclosan	samplewater	250	125	~~10~~ 8	~~10~~ 20	ng/L	Weck	~~Pharmaceuticals by LCMSMS-ESI-~~ List B by EPA 1694M-ESI-
Required	Triclocarban	samplewater	-	-	TBD[1]	TBD[1]	ng/L	Physis	EPA 625.1M
Required	Bisphenol A	samplewater	60	30	~~2~~ 4	10	ng/L	Weck	~~Pharmaceuticals by LCMSMS-ESI-~~ List B by EPA 1694M-ESI-
Ancillary	Suspended Sediment Concentration	samplewater	n/a	n/a	3.1	5	mg/L	Weck	ASTM D3977-97
Required	Perfluorooctanesulfonic acid	samplewater	none listed	n/a	NA[2]	2	ng/L	Vista	Modified EPA 537M
Required	Perfluorooctanoic acid	samplewater	none listed	1	NA[2]	2	ng/L	Vista	Modified EPA 537M
Additional	Ethynylestradiol, 17alpha-	samplewater	-	-	~~10~~ 4	10	ng/L	Weck	~~Hormones by LCMSMS-APCI+~~ List B by EPA 1694M-APCI

Matrix / Analyte Type	Analyte	CEDEN Matrix Code	Mon Trigger Level (MTL)	Target RL (1/2 MTL)	MDL	RL	Units	Lab	Method
Additional	Progesterone	samplewater	-	-	~~10~~ 4	10	ng/L	Weck	~~Hormones by LCMSMS-APCI+~~ List B by EPA 1694M-APCI
Additional	Testosterone	samplewater	-	-	~~10~~ 4	10	ng/L	Weck	~~Hormones by LCMSMS-APCI+~~ List B by EPA 1694M-APCI
Additional	Gemfibrozil	sample water	-	-	~~0.08~~ 4	10	ng/L	Weck	~~Pharmaceuticals by LCMSMS-ESI-~~ List B by EPA 1694M-ESI-
Additional	Iopromide	samplewater	-	-	~~1.8~~ 4	50	ng/L	Weck	~~Pharmaceuticals by LCMSMS-ESI-~~ List B by EPA 1694M-ESI-
Additional	Naproxen	samplewater	-	-	~~2~~ 4	10	ng/L	Weck	~~Pharmaceuticals by LCMSMS-ESI-~~ List B by EPA 1694M-ESI-
Additional	Salicylic Acid	samplewater	-	-	~~0.86~~ 100	500	ng/L	Weck	~~Pharmaceuticals by LCMSMS-ESI-~~ List B by EPA 1694M-ESI-

Table 9-1. Standard Operating Procedures (SOPs) referenced in this QAPP.

Originator	Title	Notes	Document Reference
Applied Marine Sciences (AMS)			
	Sampling and Analysis Plan for Delta CECs Pilot Study		Water Collection SAP
Marine Pollution Studies Laboratory (MPSL-DFW)			
	Tissue collection		MPSL-102a v 5, 2021
	Tissue preparation		MPSL-105 v 5, 2021
Weck Laboratories			
	Pharmaceuticals and personal care products	~~Weck asserts that its~~ SOPs are proprietary and confidential; provided directly to the SWRCB QA Officer for review and approval.	~~N/A~~ ORG111.R5.0
	TOC		~~N/A~~ ORG132.R2.1
	SSC		~~N/A~~ WET116.R1.0
Vista Laboratory			
	PFAS	confidential information redacted	Vista-49
Physis Labs			
	EPA Method 625.1 (m)		Physis SOP for EPA Method 625.1 (m)
SGS-AXYS			
	BDE and BFR	Confidential, available for review upon request	MSU-033 R10
	PFAS in aqueous solids, tissues	Confidential, available for review upon request	MSU-110 R23
	Moisture Determination	Confidential, available for review upon request	SLA-015 R12
	Gravimetric Lipid Determination by Weight of Extract	Confidential, available for review upon request	SLA-020 R07
	Procedures for Homogenization of Solids and Tissues	Confidential, available for review upon request	SLA-013 R10

Table 12-1. Storage and hold time requirements for each parameter group.

Parameter group	Lab	Sample Container	Initial Preservation/Storage	Extraction/ Preparation Hold Time	Analysis Hold Time[1]	Notes
Fish and Bivalve Tissue						
PBDEs	SGS-AXYS	4 oz amber glass jar, Teflon lined.	< -10°C dark	365 days	40 days	
PFAS	SGS-AXYS	4 oz HDPE jar, unlined.	< -10°C dark	NA	365 days	
Sediment						
PBDEs	SGS-AXYS	4 oz amber glass jar, Teflon lined.	< -10°C dark	365 days	40 days (not to exceed 365 days from sample collection)	
PFAS	SGS-AXYS	4 oz HDPE jar, unlined.	< -10°C dark	NA	365 days	
Total Organic Carbon	Weck	4 oz clear glass jar, Teflon lined.	< 6°C dark	NA	28 days	
Water						
PPCPs	Weck	2 x ~~250~~ 40 mL amber glass	Preserve with sodium azide (~~200~~ 8 mg) and Ascorbic acid (~~100~~ 4 mg); store at <6°C	28 days	40 days	2 bottles are needed for particular QAQC samples; preserved with Sodium azide, Ascorbic acid
PPCPs (galaxolide and triclocarban)	Physis	2 x 1.0 L amber glass (clear glass may be used if samples are protected from light)	<6°C	7 days	40 days	Recommend to ship w/in 48-72hrs. Lab will preserve with sodium thiosulfate only if residual chlorine is present.
PFAS	Vista	HDPE or polypropylene bottle or jar	<10°C	28 days	30 days	
Suspended Sediment Concentration	Weck	1.0 L polycarbonate bottle	<6°C	NA	14 days	

[1]Analysis hold time requirements begin from the initiation of the sample extraction/preparation process.

14.2.1. Measurement Quality Metrics

Laboratory Performance Measurements for Laboratory Analyses

Laboratory performance measurements are included in the QA data review to check if measurement quality objectives are met. Results of analyses of QC samples are to be reported with results of field samples. Minimum frequencies and target performance requirements for QC measures of reported analytes are specified in **Table 14-2**. Laboratories are free to perform additional QC in accordance with their standard practices.

QC measures typically used for evaluation of laboratory and field sampling performance include the following (not all are possible/available for all matrices; required types for each analysis are listed in **Table 14-2**):

1. **Laboratory method blanks**: samples of a clean or null (e.g., empty container) matrix taken through the entire analytical procedure, including preservatives, reagents, and equipment used in preparation and quantitation of analytes in samples, to assess contamination introduced in laboratory processes.
2. **Field blanks**: samples of a clean or null matrix taken through the sampling procedure, then analyzed much like an ordinary field sample to assess contamination introduced in the field superimposed on any existing laboratory method blank contamination.
3. **Laboratory duplicates**: replicate sub-samples of field samples, taken through the full analytical procedure including all laboratory processes combined, to measure analytical precision. Although standard reference materials, laboratory reference materials, matrix spike samples, or laboratory control samples can also be analyzed in replicate, references to those are prefaced by their sample type name, e.g., “matrix spike duplicates”.
4. **Field duplicates**: samples collected identically to the primary field samples at a site, used to assess spatial or temporal heterogeneity in the sampled matrix, superimposed on any existing laboratory analytical variation.
5. **Surrogate standards**: analytes introduced to samples prior to sample extraction to monitor sample extraction method recoveries.
6. **Laboratory control samples:** samples of a clean or null matrix spiked with target analytes, then analyzed much like an ordinary field sample, used to assess accuracy of the analytical method.
7. **Matrix spike samples/duplicates**: field samples to which known amounts of target analytes are added, indicating potential analytical interferences present in field samples, and errors or losses in analyses not accounted for by surrogate correction.
8. **Certified Reference Materials:** natural matrix samples with externally validated "certified" concentrations of analytes of interest, usually obtained from commercial or government vendors (e.g., NIST, which calls them "SRMs" (standard reference

materials)). Often analyzed across multiple analytical batches, to track drift or shifts in analytical accuracy and precision.

9. **Laboratory reference materials**: materials collected, bought, or created by a laboratory as internal reference samples, to track performance across batches.
10. **Isotope Dilution Analogues (IDAs)**: standards containing isotopically labeled versions of the target analytes (or chemicals similar to the target analytes) that are added to each environmental and QC sample prior to extraction and are used to quantify the result concentrations of the unlabeled analytes present in the sample matrix. For samples analyzed using an isotope dilution method, the recovery of the IDA associated must be reported with each result to monitor analytical performance.

Table 14-2. Measurement quality objectives for laboratory measurements.

Method	Sample type	Matrix	Frequency	Acceptable limits (MQO)
PPCP – ~~Hormones~~ List B				
LCMSMS-APCI and EPA 1694M-APCI	Field Blank	Water	1 per 20 samples (with one coming from each field collection crew)	Less than the MDL for target analytes
LCMSMS-APCI and EPA 1694M-APCI	Field Duplicate	Water	1 per 20 samples (with one coming from each field collection crew)	RPD ≤ 35%; n/a if concentration of either sample < MDL
LCMSMS-APCI and EPA 1694M-APCI	Laboratory Blank	Water	1 per batch	Less than the MDL for target analytes
LCMSMS-APCI and EPA 1694M-APCI	Laboratory Control Sample/Duplicate	Water	1 per batch	70-130% recovery if certified; otherwise, 50-150% recovery; RPD ≤25%.
LCMSMS-APCI and EPA 1694M-APCI	Isotope Dilution Analogue standards	Water	Every sample	50-200%
PPCP – ~~Pharmaceuticals~~ List C				
LCMSMS-ESI and EPA 1694M-ESI-	Field Blank	Water	1 per 20 samples (with one coming from each field collection crew)	Less than the MDL for target analytes
LCMSMS-ESI and EPA 1694M-ESI-	Field Duplicate	Water	1 per 20 samples (with one coming from each field collection crew)	RPD ≤ 35%; n/a if concentration of either sample < MDL
LCMSMS-ESI and EPA 1694M-ESI-	Laboratory Blank	Water	1 per batch	Less than the MDL for target analytes
LCMSMS-ESI and EPA 1694M-ESI-	Laboratory Control Sample/Duplicate	Water	1 per batch	70-130% recovery if certified; otherwise, 50-150% recovery; RPD ≤25%.
LCMSMS-ESI and EPA 1694M-ESI-	Isotope Dilution Analogue standards	Water	Every sample	50-200%
Perfluoranate – PFOS and PFOA				

Method	Sample type	Matrix	Frequency	Acceptable limits (MQO)
EPA 537M	Field Blank	Water	1 per 20 samples (with one coming from each field collection crew)	Less than the MDL for target analytes
EPA 537M	Field Duplicate	Water	1 per 20 samples (with one coming from each field collection crew)	RPD ≤ 35%; n/a if concentration of either sample < MDL
EPA 537M	Laboratory Blank	Water	1 per batch	Less than the MDL for target analytes
EPA 537M	Lab Duplicate	Water	none	NA
EPA 537M	Laboratory Control Sample/Duplicate	Water	1 per batch	70-130% recovery if certified; otherwise, 50-150% recovery; RPD≤30%.
EPA 537M	Matrix Spikes/Duplicates	Water	none	NA
EPA 537M	Isotope Dilution Analogue standards	Water	Every sample	25-150% recovery.

Approval:

The amendment(s) detailed within this document shall be effective upon signature completion of all parties listed below. By signing this amendment, all parties listed below acknowledge and accept these changes. A copy of this document shall be distributed to all parties within the QAPP distribution list and shall be included and/or attached to all distributed copies of the original QAPP.

CEC Program Manager:	DocuSigned by: Melissa Turner 9796DD915C44446... Melissa Turner	Date: 5/27/2022
CEC Quality Assurance Officer:	DocuSigned by: Will Hagan A1D771E8E56040F... Will Hagan	Date: 5/27/2022
Quality Assurance Officer, Weck Laboratories:	DocuSigned by: Alan Ching 4DC2BDF31A43426... Alan Ching	Date: 5/27/2022
Quality Assurance Officer, Vista Analytical Laboratories:	DocuSigned by: Teresa Morrison 3B7BB1D27DC2410... Teresa Morrison	Date: 5/27/2022
Quality Assurance Representative, CVRWQCB:	DocuSigned by: Selina Cole F3102A0E248746B... Selina Cole	Date: 6/2/2022
Quality Assurance Officer, SWRCB:	DocuSigned by: Andrew Hamilton 7CBAC1C276074C6... Andrew Hamilton	Date: 5/31/2022