

Updates to Chemical Analysis and Data Quality Assurance Procedures Under the DMMP

Prepared by the DMMP Agencies

Introduction/Problem

Several data analysis and quality assurance protocols in the DMMP User Manual are being updated to acknowledge analytical method updates and to better align with regional guidance. The updates include recommended methods for conventionals and organics analysis, CRM/SRM analysis requirements, recommended validation stage for dioxin analysis, data flagging guidelines for dioxin data, and removal of the 2010 dioxin QAPP preparation guidance.

The justification and explanation for the updates are explained below:

1. **Recommended Methods for Conventionals Analysis** – Standard Methods SM4500-S2 for total sulfides and SM4500-NH3 for ammonia will be added to the recommended analytical methods list. This update was made because many labs have blended the PSEP/Plumb methods and Standard Methods for sediment analysis. While the preparation steps in the PSEP/Plumb methods are still relevant, the finishing steps do not acknowledge automated instrumentation which provides more consistent and streamlined analysis of samples.
2. **Recommended Methods for Metals/Organics Analysis** – Specific analytical method versions will be removed from the Recommended Analytical Methods Table in the User Manual. Instead, a footnote stating that a recent version should be used was added. This update is being made because SW-846 methods are routinely updated.
3. **Reference Material Analysis Requirements** - Currently, analysis of a CRM/SRM is required for TOC, metals, PCBs, pesticides, SVOCs and dioxin. For PCBs and dioxin, the Puget Sound SRM must be used (DMMP 2018). The 2010 dioxin QAPP guidance states that the Puget Sound SRM must be analyzed with every analytical batch (DMMP 2010a, DMMP 2010b). DMMP agencies have reconsidered the CRM/SRM requirement and determined that it is unnecessary for most DMMP projects. CRM/SRMs are not required by other programs that manage sediment and dredged material in the Pacific Northwest and are considered on a project-by-project basis within cleanup programs. In addition, it is a financial burden for small projects to pay for the additional SRM/CRM analysis as well as the required MS/MSD samples. CRM/SRMs are no longer required for standard DMMP projects for TOC, metals, SVOCs, pesticides, PCBs and dioxin. There may be some instances when an SRM/CRM is required (e.g., non-routine method being used, non-NELAP certified laboratories, larger projects, etc.).
4. **Validation Stage for Dioxin** – In 2010 the DMMP agencies adopted disposal site management guidelines for dioxin and QAPP guidance for dioxin analysis, which stated that an EPA Stage 4 data validation for dioxins was highly recommended for DMMP projects. Since that time dioxin analysis has become much more common and more analytical labs are accredited for dioxin analysis. Data validation with EPA Stage 2B plus EMPC qualifier assessment and confirmation of GC column resolution of 2,3,7,8-TCDD is sufficient for DMMP decision making. Therefore, there is no longer a need for expensive Stage 4 data validation for most DMMP projects. EPA Stage 2B validation (plus EMPC and GC column resolution assessment) for dioxins will be required, and projects may elect to do Stage 4 validation. Additionally, Stage 4 validation may be recommended for complex projects.

5. **Validation qualifiers for EMPC-flagged dioxin data** – In 2010 the DMMP agencies established data flagging guidelines for EMPC-flagged dioxin congeners in the dioxin QAPP guidance (DMMP, 2010c), which states “For the purposes of TEQ summation, estimated maximum potential concentrations (EMPCs) shall be reported as nondetects (U) at the EMPC value”. EPA Region 10 has published updated guidance on validating dioxin data (EPA, 2014) and this is the appropriate guidance document to follow for instructions on validating and qualifying EMPC-flagged dioxin data.
6. **Status of 2010 DMMP Revised Supplemental Information on PCDD/F for use in Preparing a QAPP** – The information provided in the 2010 dioxin QAPP guidance (DMMP, 2010c) is superseded by the information in this clarification paper. The 2010 dioxin QAPP guidance will no longer be used. Users should follow the EPA Region 10’s dioxin validation guidance (EPA, 2014) and the DMMP User Manual. Labs should follow their own Standard Operating Procedures (SOPs).
7. **Measurement Performance Criteria** – Measurement performance criteria were inadvertently removed from previous versions of the User Manual. A table of recommended measurement performance criteria will be added to the 2021 User Manual. Measurement performance criteria should be provided for each analytical method in the SAP for a project.

Proposed Clarification

The DMMP is proposing the following clarifications:

1. **Recommended Methods for Conventional Analysis** – Standard Methods SM4500-S2 for total sulfides and SM4500-NH3 for ammonia will be added to the recommended analytical methods list in the 2021 version of the DMMP User Manual.
2. **Recommended Methods for Metals/Organics Analysis** – A recent version of the recommended analytical method should be used.
3. **Reference Material Analysis Requirements** – CRM/SRMs are no longer required for standard DMMP projects for TOC, metals, SVOCs, pesticides, PCBs and dioxins. This requirement will be removed from the DMMP User Manual.
4. **Validation Stage for Dioxin** – EPA Stage 4 is no longer “highly recommended” for all projects. A minimum of EPA Stage 2B plus EMPC qualifier assessment and confirmation of GC column resolution of 2,3,7,8-TCDD is required. EPA Stage 4 validation may be recommended for complex projects.
5. **Validation qualifiers for EMPC-flagged dioxin data** – EMPCs should be qualified consistent with Region 10 data validation guidelines (EPA, 2014). In general, the data validation guidance states that if EMPC is <RL but >EDL, qualify data as non-detect “U” reported at the level the analyte was detected. If the EMPC is >RL, check the chromatogram for interferences. If interferences can be minimized or removed by further extract clean-up, request additional clean-up from the laboratory. If the peak cannot be isolated from the interferences, flag the result estimated “J”.
6. **2010 DMMP Revised Supplemental Information on PCDD/F for use in Preparing a QAPP**. This document (DMMP, 2010c) will no longer be used by the DMMP and will be removed from the DMMP website. Users should follow the dioxin guidance provided by EPA Region 10 and the DMMP User Manual. Labs should follow their own SOPs.
7. **Measurement Performance Criteria** – Measurement performance criteria should be provided for each analytical method in the project SAP. The following table will be added to the 2021 User Manual:

Table 8-1. Recommended Measurement Performance Criteria

Analysis Type	Precision	Accuracy	Surrogate Limits	Completeness	CRM/SRM ²
Semivolatiles	±35% RPD	50%-150% R	Lab Limits	95%	Certified limits
Pesticides	±35% RPD	50%-150% R	Lab Limits	95%	Certified limits
PCBs	±35% RPD	50%-150% R	Lab Limits	95%	PS-SRM Advisory limits
Metals	±20% RPD	75%-125% R	NA	95%	Certified limits
Ammonia	±20% RSD	75%-125% R	NA	95%	NA
Total Sulfides	±20% RSD	75%-125% R	NA	95%	NA
Total Organic Carbon	±20% RSD	75%-125% R	NA	95%	Certified limits
Total Solids	±20% RSD	NA	NA	95%	NA
Total Volatile Solids	±20% RSD	NA	NA	95%	NA
Grain Size	±20% RSD	NA	NA	95%	NA
Tributyltin	±35% RPD	50%-150% R	Lab Limits	95%	NA
Dioxins/Furans	±30% RPD	R10 Validation Limits ¹	R10 Validation Limits ¹	95%	PS-SRM Advisory limits

Notes:

CRM = certified reference material

NA = not applicable

PS-SRM = Puget Sound Sediment Reference Material

RPD = relative percent difference

RSD = relative standard deviation

R = recovery

SRM = standard Reference material

¹ EPA Region 10 Data Validation and Review Guidelines for PCDD/PCDF Data Using Method 1613B and SW846 Method 8290A (EPA, 2014).

² when CRM/SRM analysis is required.

References

DMMP, 2010a. New Interim Guidelines for Dioxins. Dredged Material Management Program. December 6, 2010.

DMMP, 2010b. DMMP Clarification Paper: Polychlorinated Dioxins and Furans (PCDD/F): Revisions to the Supplemental Quality Assurance Project Plan. Prepared by Erika Hoffman (EPA Region 10) and David Fox (U.S. Army Corps of Engineers) for the DMMP agencies

DMMP, 2010c. Revised Supplemental Information on Polychlorinated Dioxins and Furans (PCDD/F) for use in Preparing a Quality Assurance Project Plan (QAPP). November 8, 2010.

DMMP, 2018. Dredged Material Evaluation and Disposal Procedures: User Manual. Prepared by the DMMP Agencies. December 2018.

EPA, 2014. R10 Data Validation Review Guidelines for Polychlorinated Dibenzo-p-Dioxin and Polychlorinated Dibenzofuran Data (PCDD/PCDF) Using Method 1613B, and SW846 Method 8290. EPA-910-R-14-003. May 2014.

Acronyms

CRM/SRM – Certified Reference Material/Standard Reference Material

DMMP – Dredged Material Management Program

DMMO – Dredged Material Management Office

EDL – Estimated Detection Limit

EMPC – Estimated Maximum Possible Concentration

EPA – Environmental Protection Agency

GC – Gas Chromatography

MS/MSD – Matrix Spike/Matrix Spike Duplicate

NELAP – National Environmental Laboratory Accreditation Program

PCB – Polychlorinated Biphenyl

PCDD/F – Polychlorinated dibenzo-p-dioxins and furans

PSEP – Puget Sound Estuary Program

RL – Reporting Limit

QAPP – Quality Assurance Project Plan

SOP – Standard Operating Procedure

SVOC – Semi-Volatile Organic Compound

TEQ – Toxicity Equivalent

TOC – Total Organic Carbon