

Draft Joint DMMP-Ecology TCP Clarification Paper
Extension of Holding Time for Total Mercury

April 6, 2021

Prepared by Joy Dunay (U.S. Army Corps of Engineers, Seattle District) for the DMMP Agencies and Chance Asher (WA Department of Ecology) for the Toxics Cleanup Program (TCP).

Introduction and Problem Identification

Due to the frequent overlap between DMMP and TCP procedures, and that data generated by DMMP must comply with the Sediment Management Standards (SMS), scientifically defensible consistency between the agencies is desirable when proposing changes to established QA/QC requirements. This is a joint clarification paper between DMMP and TCP. Additionally, we are coordinating with the Regional Sediment Evaluation Team (RSET) to advance this issue on a more expansive regional basis.

Both DMMP and TCP allow a phased analytical approach where sediment can be held for additional analysis to ensure accurate and defensible data are used for decision making and optimal use of resources. This phased approach involves temporally sequenced analysis of sampled sediment over multiple weeks within approved sediment holding times. This requires archiving sediment samples by freezing at $-18 \pm 2^{\circ}\text{C}$, which extends the standard holding time for most chemicals of concern.

The DMMP User Manual (DMMP, 2018) allows a 28-day holding time for total mercury stored at $\leq 6^{\circ}\text{C}$ based on U.S. EPA's method 7471B (Mercury in Solid or SemiSolid Waste) which specifies that some forms of mercury (e.g., elemental) are volatile and unstable and should be analyzed as quickly as possible. However, the DMMP User Manual does not provide an extended holding time for total mercury in frozen sediments. SCUM (Ecology, 2019; Chapter 4) follows the Puget Sound Estuary Protocols (PSEP, 1997; Table 2) which allows a 28-day holding time for total mercury stored at 4°C or -18°C , with the recognition that some studies have demonstrated that freezing sediment samples may extend the holding time for mercury up to 6 months.

In general, mercury in sediments is bound to sulfur functional groups associated with organic matter making it very stable so it can be stored frozen for up to one-year without appreciable loss. However, this may not be the case for highly contaminated sediment (e.g., industrial or mining sites) which may have higher fractions of elemental mercury.

Keeping within the 28-day holding time for total mercury can be difficult unless costly expedited analysis is done. This is because laboratory results can take as long as 28 days to receive and agencies also need time for decision-making to pursue further analysis. Given this, it isn't practical to conduct phased testing within the 28-day holding time for sites with elevated total mercury.

Proposed Clarification

DMMP and TCP propose adding an extended 1-year holding time for total mercury in sediment stored at $-18 \pm 2^{\circ}\text{C}$. The holding time for unfrozen sediment stored at $4 \pm 2^{\circ}\text{C}$ will remain 28 days. An extended

holding time will not be allowed in sediment sampled from sites with known or potential elemental mercury releases.

Rationale

Sediments associated with most projects in the Puget Sound region are likely to have stable forms of mercury (i.e. sulfur-bound compounds, etc.) that would not degrade in frozen storage. Allowing an extended holding time would be beneficial for DMMP and TCP projects to facilitate phased analysis and effective decision making.

The practice of freezing sediment to extend the holding time of total metals, including mercury, is allowed in other state and federal programs as provided in Table 1 below. While this list is not exhaustive, we believe that it is a fair representation of programs across the United States.

Table 1. List of state and federal programs that allow extended holding times for total mercury in sediment and/or solids.

Reference	Program	Media	Reference section cited	Temperature	Holding time
1	California SWAMP QAPP ¹	Sediment	Appendix F (Table 2)	<-20°C	1 year, 14 days within thawing
2	California, CalFed Mercury project	Solids	Appendix D, SOP -CALFED.D09, Page 109	<-10°C	1 year
3	Massachusetts, Compendium of Analytical Methods	Solids	Page 19, footnote 3	-10°C (within 24 hrs of collection)	1 year
4	Southeast Regional Implementation Manual (SERIM)	Sediment & Tissue	Page 259	Not provided	6 months (mercury grouped with all metals)
5	Southern California Bight 2018 Regional Monitoring Program	Sediment	Field Operations Appendices, Page 59	Frozen	6 months
6	USEPA Appendix D Method 1631	Sediment	Appendix D, Section A8.3.3	<-15°C ²	1 year
7	USGS Method for Preparation for the Analysis of Solids and Suspended Solids for Total Mercury	Solids	Page 9	<-15°C	Extended holding time allowed but no specified holding time ³

Notes:

¹ Also used by San Francisco Estuary Institute (SFEI) and Bay Area Delta Regional Monitoring Program.

² Guidance specifies that samples should be weighed and aliquoted prior to being frozen because of potential clumping, but labs routinely re-homogenize aliquots in jars prior to subsampling to break up any clumps.

³ USGS guidance states that a certified reference material from National Institute of Standards and Technology (NIST) is stable for 9 years.

References

1. California's Surface Water Ambient Monitoring Program (SWAMP) QAPP. Inorganic Analytes in Freshwater Sediment and Marine Sediment. Prepared by the SWAMP Quality Assurance Team. September 1, 2008. (Appendix F, Table 2).
Main document:
https://www.waterboards.ca.gov/water_issues/programs/swamp/docs/qapp/qaprp082209.pdf
Appendix F:
[https://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/inorganic %20analytes freshwater sediment and marine sediment.pdf](https://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/inorganic%20analytes%20freshwater%20sediment%20and%20marine%20sediment.pdf)
2. CalFed Mercury Project QAPP, Appendix D: Analytical SOP's and Supporting Documents, SOP-CALFED.D09. Prepared by Frontier Geosciences. March 2000. (Appendix D, Page 109).
Main document:
<https://loer.tamug.edu/calfed/QA%20Documents/CALFED%20QAPP%20frontspiece.pdf>
Appendix D: <https://loer.tamug.edu/calfed/QA%20Documents/CALFED%20Appdx%20D.pdf>
3. Massachusetts Compendium of Analytical Methods (MassCAM), Quality Control Requirements and Performance Standards for the Analysis of Mercury by Cold Vapor Atomic Absorption (CVAA) Spectrometry in Support of Response Actions under the Massachusetts Contingency Plan. Prepared by Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup. July 1, 2010. (Page 19, Footnote 3).
<https://www.mass.gov/guides/compendium-of-analytical-methods-cam#-metals-methods->
4. Southeast Regional Implementation Manual (SERIM), Requirements and Procedures for Evaluation of the Ocean Disposal of Dredged Material in Southeastern U.S. Atlantic and Gulf Coast Waters. Prepared by USACE and U.S. EPA. August 2008. (Page 259).
https://www.epa.gov/sites/production/files/2016-05/documents/r4_serim_final_august_2008.pdf
5. Southern California Bight 2018 Regional Marine Monitoring Program, Sediment Quality Assessment Field Operations Manual Appendices. Prepared by Bight '18 Field Sampling and Logistics Committee. July 2018. (Field Operations Appendices, Page 59).
Main document:
<https://www.sccwrp.org/about/research-areas/regional-monitoring/southern-california-bight-regional-monitoring-program/bight-program-documents/bight-18/>
Field Operations Appendices:
https://ftp.sccwrp.org/pub/download/BIGHT18/Bight18SedQualityFieldManual_Appendices.pdf
6. USEPA, 2001. Appendix D to Method 1631, Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation, EPA-821-R-01-013. Prepared by U.S. EPA. January 2001.
<https://nepis.epa.gov/Exe/ZyPDF.cgi/40001F6A.PDF?Dockkey=40001F6A.PDF>

7. USGS, 2004. Method for Preparation for the Analysis of Solids and Suspended Solids for Total Mercury, Chapter 8 of Book 5, Laboratory Analysis, Section A, Water Analysis. USGS, US Department of the Interior. 2004. <https://pubs.usgs.gov/tm/2005/tm5A8/pdf/TM5A-8.pdf>

Additional Citations

1. DMMP, 2018. *Dredged Material Evaluation and Disposal Procedures (User Manual)*. Dredged Material Management Program, updated December 2018.
2. Ecology, 2019. Sediment Cleanup User's Manual, Publication No. 12-09-057. Washington Department of Ecology, Toxics Cleanup Program. December 2019.
3. PSEP, 1997. Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound. Puget Sound Estuary Protocols, Table 2. Prepared for U.S. EPA Region 10 and Puget Sound Water Quality Action Team. April 1997.