

TRIBUTYLTIN (TBT) MEASUREMENT BASIS

Prepared by Kelsey van der Elst (U.S. Army Corps of Engineers) and Erika Hoffman (U.S. Environmental Protection Agency) for the DMMP agencies.

Introduction

Tributyltin (TBT) is a special chemical of concern under the Dredged Material Management Program (DMMP). For characterizations in marine waters, TBT analysis is only required in areas where it is likely to be found, such as marinas, ship repair facilities, and in areas where TBT has previously been detected. In 1996 the DMMP agencies reviewed available literature and concluded that the most environmentally relevant method for analyzing TBT was with porewater analysis (EPA, 1996; Michelsen, 1996). Following the 1996 SMARM the DMMP agencies adopted porewater TBT analysis as the standard for the program.

Questions and difficulties with the analysis of TBT in porewater led to an interim technical clarification paper on the proper extraction and analysis techniques for TBT (DMMP, 1998). In the following year, the DMMP agencies contracted with Striplin Environmental Associates and Avocet Consulting to conduct surveys of the various laboratories, consultants, and regulated parties to better understand their concerns and recommendations about porewater TBT extraction/analysis methods and the bioavailability of TBT. The results of these surveys were presented and discussed at the 1999 SMARM (DMMP, 1999).

Responses to the survey on TBT porewater protocols indicated that laboratories were successfully following the DMMP's interim guidelines although there were specific differences in their methods which may affect TBT extraction and measurement (e.g., aerobic versus anaerobic extraction conditions; filtration of porewater; GC/MS versus Flame Photometric detection methods). When questioned whether to focus on porewater versus bulk sediment TBT, respondents recommended that the fraction which best correlates with bioaccumulation/toxicity results should be selected and that site-specific factors (TBT source and form) would dictate whether to measure TBT in bulk sediments or in porewater. Respondents also thought that sample holding, processing and porewater extraction methods introduce the most variability in the results, and that TBT in freshwater may be more susceptible to state and oxidation changes than in marine sediments. Suggestions were made for additional investigation, including evaluation of holding times, refinement of porewater extraction techniques, and conducting additional bioavailability studies. Funding constraints have limited the DMMP agencies' ability to invest in further research. Instead, the agencies have sought to refine the methodology by applying lessons learned from individual dredging projects.

In the 15 years since the last TBT clarification, porewater analysis has presented logistical challenges and the resulting data have not shown a consistent positive correlation with TBT bioavailability. This has caused the DMMP agencies to re-evaluate porewater analysis as the basis for sediment characterization of TBT.

Problem identification

Experience with a variety of projects underscores many of the difficulties with porewater TBT analysis:

- Collection of sufficient porewater is commonly a challenge, especially for samples with high sand content and in highly consolidated sediments such as deep Z-samples.
- The holding time for sediment samples prior to the extraction of porewater is 7 days, making analysis of porewater impractical for a tiered Z-sampling approach. For example, if TBT is found to be elevated in the dredge prism, the corresponding Z-sample analysis will, by necessity, be of bulk TBT since the holding time for porewater extraction will have expired by the time the Z-samples are analyzed. Since porewater TBT in the dredged material cannot be compared with bulk TBT in the Z-samples, an additional bulk analysis of the dredged material may be needed in order to make an antidegradation determination.
- Consistent porewater/tissue relationships for TBT have not been observed within or between studies from various urban embayments of Puget Sound. Eight regional studies have evaluated TBT in both porewater and tissues from standard laboratory bioaccumulation tests of sediments from West Waterway (EVS Solutions, 1999), East Waterway (DMMP, 1997, 1999 and 2003; WindWard, 2003), Olympia Harbor (DMMP, 2000), Hylebos Waterway (DMMP, 2000), and Anacortes (DMMP, 2001). The two largest studies (East Waterway T-18 and West Waterway Superfund) observed little to no relationship between porewater and tissue concentrations. Likewise, porewater/tissue correlations between studies are inconsistent with a given porewater TBT concentration being associated with significant bioaccumulation at one location and negligible accumulation at another.
- The inconsistency of porewater/tissue relationships may be a reflection of the differences in the porewater extraction efficiency of various laboratories' methods (e.g., centrifugation vs filtration, centrifugation speeds) or the loss of TBT on laboratory glassware used in sample processing and porewater extraction. The relative influence of method-related loss versus environmental heterogeneity on quantification of porewater TBT has proven to be difficult to quantify and control.
- Projects in freshwater may need to analyze for both porewater and bulk TBT. The freshwater TBT sediment standards adopted by Ecology in 2013 are expressed as bulk butyltins, while the DMMP marine guidelines are based on porewater analysis. Thus, for projects located in freshwater areas proposing disposal at a DMMP disposal site in marine waters (such as projects in Lake Union and Lake Washington), analysis of bulk butyltins for antidegradation evaluation and porewater TBT to determine suitability for open-water disposal are both required.

Proposed Clarification

In order to simplify the analysis of TBT and align DMMP requirements with freshwater sediment standards, the DMMP agencies will require only bulk TBT analysis for sediments being proposed for open-water disposal. Bulk TBT data will be evaluated using the existing bioaccumulation trigger of 73 µg/kg. Porewater TBT analysis will be considered at the request of the applicant or for special evaluations (Tier IV) when additional information on the bioavailability of TBT is needed. In those cases where porewater testing is conducted, data will be compared to the existing bioaccumulation trigger of 0.15 µg/L.

References

DMMP, 2003. Determination on the Suitability of Dredged Material Tested Under the East Waterway Terminal Stage 1A Characterization (2003-2-00074), Evaluated Under Section 404 of the Clean Water Act (CWA) for Open-Water Disposal at the Elliott Bay Disposal Site. Prepared by USACE for the DMMP Agencies. February 11, 2003.

DMMP, 2001. Determination of the Suitability of Dredged Material Tested Under DMMP Evaluation Procedures for the Port of Anacortes Cap Sante Marina Dredging Project (2001-2-00399) with Proposed Disposal at the Rosario Strait Open Water Disposal Site. Prepared by USACE for the DMMP Agencies. April 11, 2001.

DMMP, 2000a. Determination of the Suitability of the Dredged Material Tested Under DMMP Evaluation Procedures for the Olympia Harbor Navigation Project for Disposal at the Anderson/Ketron Open Water Disposal Site. Prepared by USACE for the DMMP Agencies. May 17, 2000.

DMMP, 2000b. Determination on the Suitability of Dredged Material Evaluated for Weyerhaeuser Company Section 404 of the Clean Water Act (CWA) for Open-Water Disposal at the Commencement Bay Disposal Site. Prepared by USACE for the DMMP Agencies. November 27, 2000.

DMMP, 1999a. Sediment Management Annual Review Meeting Summary. May 5, 1999.

DMMP, 1999b. Determination on the Suitability of Dredged Material Tested Under the East Waterway Stage II Project and U.S. Coast Guard Slip 36, Evaluated Under Section 404 of the Clean Water Act (CWA) for Open-Water Disposal at the Elliott Bay Disposal Site. Prepared by USACE for the the DMMP Agencies. November 2, 1999 with Erratum on August 8, 2007.

DMMP, 1998. Tributyltin Analysis: Clarification of interstitial water extraction and analysis methods – interim. Prepared for the DMMP agencies by Erika Hoffman. December 22, 1998.

DMMP, 1997. Determination of the Suitability of Dredged Material Tested Under PSSDA Evaluation Procedures for the Port of Seattle Terminal 18 Dredging Project (95-02133) for Disposal at the Elliott Bay Open-Water Site. Prepared by USACE for the DMMP Agencies. March 17, 1997.

EPA, 1996. Recommendations for Screening Values for Tributyltin in Sediments at Superfund Sites in Puget Sound, WA. Prepared for EPA Region 10, Superfund by Roy F. Weston, Seattle, WA.

EVS Solutions, 1999. Tributyltin in Marine Sediments and the Bioaccumulation of Tributyltin: Combined Data Report. Prepared for the Port of Seattle, Lockheed Martin Corp. and Todd Shipyards Corp. Project No. 8/203-16.3, May 1999.

Michelsen, T., T.C. Shaw, and S. Stirling, 1996. Testing, reporting and evaluation of tributyltin data in PSDDA and SMS programs. Final PSDDA Issue Paper/SMS Technical Information Memorandum, October 1996.

Windward Environmental, 2003. Bioaccumulation Data Summary Report for the East Waterway Operable Unit, Harbor Island Superfund Site. Prepared for the U.S. EPA Region 10. December 2003.