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Support for Sediment Bioaccumulation Evaluation: Toxicity Reference Values for San Francisco Bay

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EXECUTIVE SUMMARY

This special study of the Regional Monitoring Program for Water Quality in San Francisco Bay was conducted to support the Dredged Material Management Office (DMMO) process of evaluating results from bioaccumulation testing performed for routine dredging projects. The goal was to use the current DMMO methodology for selecting Toxicity Reference Values (TRVs) from the US Army Corps of Engineers Environmental Residue-Effects Database (ERED), in order to develop a standard list of TRVs for San Francisco Bay. TRVs are used as a conservative screening tool to efficiently evaluate whether observed invertebrate test organism body burdens could indicate adverse ecological effects on benthic organisms *in situ*. Currently, there are no published standard TRVs for the Bay, and TRV selection is presently performed on a case-by-case basis during the evaluation of bioaccumulation testing results submitted by individual dredgers. A standard list would promote consistent application of the methodology and improve the efficiency of dredging project evaluations.

Each study identified for TRV selection from ERED is summarized in this report, and a detailed explanation is provided of how the TRV was derived. Other studies that were evaluated but found to not meet the TRV selection criteria are very briefly summarized with an explanation of why the study was removed from TRV selection. ERED is actively managed and fiscally supported by the US Army Corps of Engineers, and is therefore regularly updated. This study was based on the version of ERED as received from Justin Wilkins (Assistant Program Manager, Dredging Operations Technical Support, US Army Engineer Research and Development Center) on March, 2018.

One of the main challenges with selecting a TRV using the current DMMO methodology was finding well-designed and well-implemented studies with clear results that could be unambiguously used as a basis for TRV recommendations for San Francisco Bay. This report identifies TRVs for total PCBs and total DDTs. TRVs were not identified for the compound classes total chlordane, dieldrin, dioxins and furans, and total PAHs because there were no appropriate studies identified that met all of the current selection criteria. These six contaminant classes were prioritized for TRV selection because bioaccumulation testing triggers have been established for them. It is recommended that the TRVs presented be used cautiously and with an understanding that results are presented with low confidence because of the limited number of data points.

An important finding of this effort is that the current DMMO approach for selecting appropriate (robust, conservative) TRVs from ERED needs to be expanded to increase confidence in TRV selections, particularly for compound classes where there were no or very few appropriate studies identified using the current methodology. Recommendations include expanding the criteria for qualified studies for TRV selection, and expanding the review to include studies in peer-reviewed literature outside ERED.

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1. INTRODUCTION

Every year, millions of cubic yards of sediment are dredged in and around San Francisco Bay to maintain safe navigation. The Dredged Material Management Office (DMMO) is an interagency group responsible for evaluating routine dredging projects, and is comprised of the U.S. Army Corps of Engineers (USACE), U.S. Environmental Protection Agency Region 9 (USEPA), San Francisco Bay Conservation and Development Commission, and San Francisco Bay Regional Water Quality Control Board.

Routine dredging projects are systematically reviewed to evaluate whether exposure to disposed sediment, or to the post-dredging surface sediment, has the potential to cause unacceptable adverse environmental impacts, including via bioaccumulation and food web transfer. If bioaccumulative contaminants are detected at elevated levels in dredged sediment, the contaminants are evaluated using a conservative screening-level hazard assessment approach (discussed below) that considers contaminant concentrations in the sediments and in the tissues of laboratory-exposed marine invertebrates from bioaccumulation studies. Those project-specific results are then used to estimate (model) potential trophic transfer to fish, and when necessary, to wildlife and humans.

The DMMO has established dredged sediment chemistry thresholds for six different contaminant classes for determining whether sediment contaminant levels are elevated to the extent that bioaccumulation testing will be required for the dredged material to be disposed in an unconfined open water disposal site in the Bay. These contaminant classes are polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dichlorodiphenyltrichloroethane and metabolites (DDTs), chlordanes, dieldrin, dioxins/furans, and mercury[1]. Bioaccumulation testing thresholds for total PCBs and total PAHs are based on ambient sediment concentrations from the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP). The current bioaccumulation testing thresholds are summarized in Table 1.

If bioaccumulation testing thresholds are exceeded, then bioaccumulation analysis with benthic organisms is required to determine the bioavailability of the contaminant and the potential for negative impacts to benthic invertebrates if dredged sediment is disposed at in-Bay sites (or the San Francisco Deep Ocean Disposal Site, SF-DODS). Bioaccumulation testing evaluations are typically conducted with the polychaete *Nereis virens*, and the bivalve *Macoma nasuta* in 28-day exposures as a general indication of bioavailability from the sediment into the food web.

[1] The DMMO no longer requires bioaccumulation testing for mercury above the previously established bioaccumulation testing threshold of 0.33 mg/kg dw, based on a programmatic agreement to modify the testing requirement. This decision was based on a review of bioaccumulation testing results from maintenance dredging projects in the San Francisco Bay conducted between 2001 – 2012. The review of sediment and tissue data (n = 50 sediment samples with mercury concentrations between 0.33 and 0.5 mg/kg dw) found little bioavailability of mercury from the sediments tested, and little or no increase in mercury bioavailability with increasing sediment concentration. In addition, because sediment exceeding 0.5 ppm is prohibited from in-Bay disposal by current TMDL requirements, DMMO no longer requires bioaccumulation testing for mercury. DMMO and SFEI are considering a similar evaluation of the PCB bioaccumulation trigger in the future.

Table 1. Dredged material testing thresholds effective in 2016-2019 (https://www.sfei.org/projects/dmmo-ambient-sediment-conditions)

Bioaccumulation Trigger	18	N/A	4,500	50	37	1.9	10
TMDL Limit	29.5	0.47	--	--	--	--	--
Basis	a	a	a	b	b	c	d

[a]Threshold based on San Francisco Bay ambient sediment concentrations determined via the RMP and are recalculated and updated when new data are available.
[b]Published bioaccumulation trigger for Puget Sound marine sediments.
[c]Published marine Screening Level value from the Pacific Northwest Sediment Evaluation Framework.
[d]Toxic Equivalents (TEQs) based on WHO 1998 Toxic Equivalency Factors (TEFs). Value is consistent with the published Puget Sound limit for unconfined aquatic disposal, and is ½ the established limit for placement at the Hamilton Wetlands Restoration Project site.

When bioaccumulation testing is required by DMMO, test organism tissue concentrations are typically evaluated as follows:

1. *Steady-State Correction*. Tissue concentrations are first steady-state corrected if applicable. Standard 28-day bioaccumulation tests are not sufficient to achieve stable tissue concentrations for some specific test organisms and compounds. Adjustments for bioaccumulation test results are applied based on published uptake and elimination tests (Kennedy et al., 2010).
2. *Initial Screening.* Corrected tissue concentrations are compared to USFDA action levels and to relevant reference sediment bioaccumulation results if available. If tissues are above USFDA action levels, the sediment "fails" (under Federal regulations) and no further analysis is needed. If below USFDA action levels or if there is no USFDA action level for the contaminant of concern, the tissues are compared to reference sediment bioaccumulation results if available. If below tissue concentrations from reference sediment exposures, the sediment passes and no further analysis is needed.
3. *Second Stage Screening: comparison to TRVs.* When corrected tissue concentrations are above reference site tissue concentrations but below USFDA action levels, a second stage screening assessment is conducted which includes comparison with TMDL thresholds, and other relevant indicators of adverse effects to environmental or human health. For environmental indicators, DMMO compares test organism tissue concentrations to relevant toxicity reference values (TRVs) based on measured effects, which are typically selected from USACE Environmental Residue-Effects Database (ERED) (https://ered.el.erdc.dren.mil/). DMMO's current guidance on the selection of appropriate TRV values for dredging projects is described in the Methods Section of this report.
4. *Trophic Transfer Modeling.* If tissue concentrations are less than agreed upon TRVs, no further evaluation is required for most analytes. However, if a tissue concentration is greater than its corresponding TRV, modeling is generally performed to conservatively estimate potential food web concentrations. Currently, the DMMO evaluates biomagnification in the food chain of these contaminant classes using USACE's

Bioaccumulation Risk Assessment Modeling System (BRAMS), which contains two separate tools: the Trophic Trace model (TT) and the Bioaccumulation Evaluation Screening Tool (BEST). For organic compounds, the sediment-based food-web TT model predicts fish concentrations using either user-specified sediment concentrations or tissue concentrations from bioaccumulation tests. For sediment dredging evaluations, the food web is typically modeled with the TT tool by specifying parameters for modeled fish, e.g., lipid content and weight, and their benthic food supply. Modeled biomagnification in fish could be compared to relevant fish toxicity thresholds, or to ambient fish tissue values if available.

5. *Comparison to Ambient Fish Tissue.* San Francisco Bay area dredging evaluations typically model biomagnification in shiner surfperch and white croaker and compare predicted fish concentrations with reported ambient fish tissue concentrations (Sun et al., 2017). If predicted fish tissue concentrations do not exceed ambient San Francisco Bay fish tissue concentrations, no further analysis is needed. Predicted PCB fish tissue results are also compared to SF Bay PCB TMDL fish tissue target levels (SFRWQCB, 2008) If exceedance of ambient fish tissue concentrations is predicted, additional analysis (beyond this screening approach) is indicated.[2]

Selection of appropriate TRVs is therefore a critical step in the evaluation of dredging projects. TRVs are used as a conservative screening tool to efficiently evaluate whether observed invertebrate test organism body burdens could indicate adverse ecological effects on benthic organisms in situ. Applicable studies for TRV selection are not limited to the test organism species because the TRV values are meant to conservatively screen potential adverse effects on a wide variety of benthic organisms. Currently, there are no published standard TRVs for the Bay, and TRV selection is presently performed on a case-by-case basis during the evaluation of bioaccumulation testing results submitted by individual dredgers. Different projects have used varying approaches and criteria in identifying proposed TRVs. In addition, it was discovered that some of the specific studies published in ERED, which had been the basis of some TRVs, were incorrectly described in ERED. This has led to inconsistencies and inefficiencies in the DMMO agency's evaluation of dredging project results. Therefore, DMMO asked for assistance from SFEI in developing a standard list of appropriate candidate TRVs from ERED, based on a consistent methodology coupled with an assessment of the reliability of the individual studies that appeared to set each candidate TRV.

2. METHODS

The DMMO has informally communicated guidance on how to select appropriate TRVs based on the lowest relevant tissue-residue effects values from USACE's ERED database. The DMMO guidance is based on USACE guidance with some modifications as described in this section. **The purpose of this report is to apply current DMMO guidelines for identifying the most "relevant" TRVs, and after evaluating published toxicity studies that meet the selection criteria, provide a recommended list of TRVs based on studies most relevant to Bay sediment. This report also discusses data gaps associated with the current guidance,**

[2] Additional steps may include, for example, detailed site-specific (rather than screening-level) risk assessment, management actions such as disposal of the dredged material at a confined site, or not dredging the area.

and makes recommendations for updating the guidance to improve confidence in the TRVs identified.

Appropriate studies for TRV development are those where “toxic effects identified are most clearly linked to factors suspected to greatly influence population sustainability” (USACHPPM, 2000). The general preferred characteristics outlined by the DMMO for the identification of candidate TRVs from ERED are in order of priority:

1. a marine or estuarine organism;
2. invertebrate;
3. whole-organism endpoints with adverse effects on the survival, growth, or reproduction;
4. sediment or sediment + water exposure or dietary exposure;
5. identify the lowest effect concentration (LOEC) (rather than No Observable Effects Level); and
6. if there are no LOECs available, then use the appropriate uncertainty factor (USACHPPM 2000) to calculate the TRV from available toxicity endpoints.

DMMO has typically guided dredgers to use ERED for the selection of TRVs because the database is expected to provide reasonable screening level results, as well as being actively managed and fiscally supported by the U.S. Army Corps of Engineers. Therefore, this study focuses on applying DMMO’s TRV selection criteria on studies listed in ERED. In this report, studies that provide only a No Observable Adverse Effect Concentration (NOAEC) were not used, consistent with DMMO guidance. After studies were filtered from ERED that satisfy the DMMO selection criteria above, then studies with the lowest tissue concentration resulting in an applicable whole-body endpoint were reviewed to confirm that the study design and results are relevant for Bay area sediment.

For a few contaminant classes addressed in this effort, there were no studies in ERED that satisfied all the desired criteria. Selection criteria used to filter results for each compound class are described in detail in the Results section. After applicable results were filtered in ERED, the original references that reported the lowest applicable residue effects were obtained and reviewed carefully. A summary of studies reviewed through this process is presented in the Results section.

In cases where a LOEC was not available in ERED, uncertainty factors listed in Table 2 were used to calculate a LOEC from the available data. In cases where a single chronic effect concentration was reported, but a LOEC value was not calculated because a dose-response curve was not measured in the study, we used an uncertainty factor of 10 to estimate the LOEC from that single concentration. This is the same uncertainty factor recommended for extrapolating a chronic response from an acute response (Table 2), and is consistent with guidance preference that factors used in extrapolation be limited to an order of magnitude (USACHPPM, 2000).

Table 2. Uncertainty factors to convert toxicity endpoints to LOEC-based TRVs in cases of limited data availability.

Type of Toxicity data	Uncertainty Factor to estimate LOEC-based TRVs	Reference
Chronic LOEC	1	USACHPPM 2000
Subchronic LOEC[a]	4	USACHPPM 2000
Acute LOEC	10	USACHPPM 2000
LC50[b]	20	USACHPPM 2000

[a]LOEC = lowest observable effects concentration measured in tissue
[b]LC50 = Tissue concentration required to kill 50% of the population in a given time period

This approach to TRV selection focuses only on the potential ecological impacts to benthic invertebrates exposed to contaminants in sediment. It does not directly consider harm to higher trophic organisms through bioaccumulation or human exposure. Another limitation of the current evaluation protocol is that only the parent compounds are analyzed - toxicity may be underestimated if the parent compounds are partially metabolized, degraded, or transformed.

3. RESULTS AND DISCUSSION

This report provides an evaluation of residue-effects studies in ERED for potential TRV selection for the compound classes total polychlorinated biphenyls (PCBs), total DDTs, total chlordanes, dieldrin, dioxins and furans, and total PAHs. These compound classes were prioritized for TRV evaluations because bioaccumulation testing triggers have been established (Table 1). The review was conducted by obtaining the journal articles that established each candidate TRV. All studies reviewed, including those that were not used for TRV selection, are summarized.

3.1 Total PCBs

The primary concern with total PCB contamination in Bay sediment is bioaccumulation in the food chain, starting with benthic organisms that live in the sediment and that transfer residues to fish and humans. The TMDL Implementation Plan for the Bay specifies a maximum in-Bay dredged material disposal limit for total PCBs; but below this limit, dredgers are required to perform bioaccumulation testing if total PCB concentrations in dredging project sediment exceed the current Bay ambient total PCB concentration (current TMDL limits and bioaccumulation triggers shown in Table 1).

ERED entries were filtered for studies meeting the TRV selection criteria. Because the PCB congener distribution in Bay sediment is skewed towards heavier PCB congeners (i.e., congeners that are abundant in Aroclors 1254, and to a lesser extent Aroclor 1260), studies with less-chlorinated mixtures (e.g., Aroclor 1016) were excluded. Studies meeting TRV selection criteria are summarized in Table 3, while studies excluded from consideration are summarized in Table 4.

Den Besten et al. (1989) described a developmental toxicity study, where fertilized embryos were observed for normal development. The effect assessment was based on observations of “normal” embryo development. Starfish, *Asteria rubens*, were fed mussels containing 600 µg/kg ww total PCB (Clophen A50, which is similar to Aroclor 1254 (Schulz et al., 1989) and after 5 months of exposure, the gonads of male and female animals contained 730 and 1,620 µg/kg ww total PCBs[3], respectively.

No difference was observed from the spermatozoa from the PCB-exposed male sea stars. However, a smaller percentage of oocytes from PCB-exposed female sea stars developed normally to the blastula, gastrula, and bipinnaria stage compared to unexposed sea stars, and the difference was statistically significant. This was a chronic exposure study, but the measured tissue concentration is not a LOEC because a full dose/response curve was not measured. Therefore, although this was a chronic test, it did not generate a LOEC, and an uncertainty factor of 10 was applied to the measured effects concentration of 1,620 µg/kg ww measured in the female gonads to calculate the LOEC-based TRV in Table 3. The total PCB concentrations measured in the female gonads are expected to be higher than whole body tissue concentrations due to higher lipid content in the gonads.

Veldhuizen-Tsoerkan et al. (1991) fed mussels, *Mytilus edulis*, with food contaminated with total PCBs (Clophen A50 or Aroclor 1254), and survival under anoxic conditions was measured. PCB-exposed organisms showed reduced survival rates under anoxic conditions when exposed to PCBs for 6 months. This was measured based on time period in anoxia before survival was reduced to 50%, and was measured as 9.7 days for control mussels, and 8.6 days for PCB-exposed mussels. The PCB tissue concentration was 7,000 µg/kg ww after 6 months of exposure. This study also did not measure a full dose-response curve to calculate a LOEC. Therefore, an uncertainty factor of 10 was used to estimate a LOEC-based TRV from a single observed effects concentration in Table 3.

[3] This study (den Besten et al., 1989) has previously been cited as a reference for a TRV value for total PCBs (e.g. Data Report Assessment of Z-Layer Sediments Collected from the Port of Richmond’s Terminals 7&8: Potential for Bioaccumulation/Biomagnification, October, 2016). Previous versions of ERED had incorrectly cited an effects concentration of 146 ppb. This was because the 730 µg/kg total PCB concentration measured in male sea star gonads, was previously incorrectly recorded as the dry weight PCB concentration, and a 146 µg/kg ww was calculated by assuming a dry weight: wet weight ratio of 1:5. Additionally, this is the wrong tissue concentration to use because no effects were observed from the spermatozoa from the PCB-exposed male sea stars. The updated version of ERED, no longer shows the 146 ppb value.

Table 3. Selected TRV references for total PCB.

Contaminant	Test Organism - Exposure	Reported "Effects" Conc. (µg/kg ww)	Calculated LOEC-TRV (µg/kg ww)	Observed Toxicity	Reference
Clophen A50[a]	Starfish - dietary exposure	1,620	162 (UF[b] 10)	Abnormal embryo development. Single chronic exposure concentration.	den Besten et al., 1989
Clophen A50[a]	Mussels - dietary exposure	7,000	700 (UF[b] 10)	Reduced survival under anoxic conditions. Single chronic exposure concentration.	Veldhuizen-Tsoerkan et al., 1991

[a]Clophen A50 is similar to Aroclor 1254, which is more representative of the PCB congener profile found in the Bay compared to other Aroclor mixtures, such as Aroclor 1016.
[b]UF = Uncertainty Factor used to calculate LOEC-based TRV value.

Table 4. Additional ERED references reviewed for total PCB, but removed from TRV selection.

ERED Reference	**Reason for Removing from TRV Evaluation**
Chu et al., 2003	PCB concentrations were reported for specific organs, not whole-body. Concentrations measured in oyster adductor muscle, gills, mantle, digestive gland, and gonads ranged between 500-3500 µg/kg dw. Results are difficult to interpret because PCBs were also measured in the control similar to low dose PCB-exposed oysters.
Dillon, 1984	Recently removed from ERED because it is a review study. Dillon 1984 conducted a comprehensive literature review to evaluate sublethal effects from bioaccumulation of contaminated sediments and corresponding body burdens of aquatic animals (at which there would be a meaningful ecological effect). 2181 papers were reviewed, but only 131 papers (6%) had useful tissue concentrations. The average reported effect concentration was 45,000 µg/kg based on 15 studies using various organisms including fish.
Duke et al., 1970	This study was de-prioritized for TRV selection because the exposure route was water only. Pinfish, shrimp, and oysters were exposed to water spiked with Aroclor 1254 for 96-hour acute toxicity bioassays, and for 30-day chronic assays. Pink shrimp were the most sensitive organisms tested. After 48-hour exposure, pink shrimp had tissue residue concentration of 3,900 µg/kg, and experienced 100% mortality.
Hansen et al., 1974	This study used Aroclor 1016 for exposure, which is not representative of PCBs in the Bay.
Lowe, 1972	This study found oysters were more tolerant to PCBs than marine crustaceans and fish. Morphology changes were observed from PCB exposure, but whole-body effects were not observed.
Nimmo et al., 1974	This study exposed grass shrimp to PCB-contaminated sediment for 3 months, and measured bioaccumulation in tissue. This study did not detect significant mortality from sediment exposure, and did not measure other toxic endpoints.
Sanders and Chandler, 1972	This study did not measure toxicity endpoints. The purpose of study was to measure accumulation and biomagnification of Aroclor 1254.
Zeng et al., 2003	Toxic effects observed in this study were attributed to PAH in sediment, not PCB exposure.

3.2 Total DDT

DDT was historically widely used as an organochloride pesticide. The primary concern with total DDT is toxicity to benthic organisms and risks to humans and piscivorous wildlife due to bioaccumulation in the food chain. Total DDT in ambient Bay sediment is composed mostly of 4,4'-DDE and 4,4'-DDD, and significantly smaller amounts 4,4'-DDT, 2,4'-DDD, 2,4'-DDE, and 2,4'-DDT. After filtering ERED entries for DDT and DDT metabolites (DDE, DDD, and DDMU), only the two studies shown in Table 5 met TRV selection criteria. Studies reviewed and removed from TRV selection are summarized in Table 6, including a study (Derr and Zabik 1972) previously cited as a TRV[4].

In Lotufo et al. (2001), the estuarine amphipod, *Leptocheirus plumulosus*, was exposed to sediment spiked with radiolabeled DDT in 10-day and 28-day toxicity tests. Sediment was prepared by spiking clean sediment with radiolabeled 4,4'-DDT, and homogenizing for 14 days. DDT in the sediment had degraded to mostly DDD at the end of the 28-day experimental period. DDD was also the predominant DDT metabolite in the amphipod tissue after 28 days. This study did not calculated an LOEC value from toxicity studies, but did derive an LC50 value from survival tests. The LC50 for the 28-day experiment was calculated to be 7.6 nmol/g ww. This is equivalent to a tissue concentration of 2,690 µg/kg ww, using the molecular weight of DDT (7.6 nmol/g ww * 354 ng/nmol = 2,690 µg/kg ww). The LOEC-TRV in Table 5 was calculated using an uncertainty factor of 20 to convert the LC50 value to a LOEC-based TRV.[5] Even though ERED classified this study as an exposure to 4,4'-DDT, the study measured exposure to total DDT, including the DDT metabolites.

An additional study was added to ERED after discussion with the ERED manager in October of 2018, and was reviewed for this study. Since ERED is continuously being updated and reviewed, these recent discussions with the ERED manager were meant to ensure that selected TRV values were as up to date as possible. Lotufo et al. (2000) fed DDT-spiked sediment and DDT-spiked supplemental food to the marine polychaete, *Neanthes arenaceodentata*, and observed the influence of DDT-exposure source, worm density, and sex on the bioaccumulation and toxicity of isotopically labeled DDT. The study found a relationship between biomass growth and DDT body residue in worms exposed to DDT-spiked sediment, where the 28-day biomass in worms decreased with increasing DDT body residue. The study found biomass was reduced in worms corresponding to a tissue residue of 69,480 µg/kg. Based on the linear relationship, a tissue residue concentration of 73,500 µg/kg ww would be associated with a 50% reduction in growth. An LOEC value was not derived from this relationship, and therefore an uncertainty factor of 10 was used to estimate a LOEC-based TRV from this observed effects concentration in Table 5.

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[4] E.g. Characterization of the Sediment from the Plains All American Terminal Berth: Results of Sediment Sampling and Analysis. Revised December 2016.

[5] However, this study did not measure statistically significant toxicity affects at body burdens well above the calculated LOEC-TRV shown in Table 5. DMMO should determine and whether and how to apply uncertainty factors in such a situation.

Table 5. Selected TRV references for DDT.

Compound	**Test Organism - exposure route**	**Reported "Effects" Conc. (µg/kg ww)**	**LOEC-TRV (µg/kg ww)**	**Toxicity**	**Reference**
Total DDT	Amphipod - sediment	2,690	134 (UF[b] = 20)	LC50a	Lotufo et al., 2001
Total DDT	Polychaete – sediment	69,480	6,948 (UF[b] = 10)	Growth	Lotufo et al., 2000

[a]LC50 = Tissue concentration at which 50% mortality was observed during 28-day experiment.
[b]UF = Uncertainty factor used to calculate LOEC-based TRV value.

Table 6. Additional ERED references reviewed for DDT, but removed from TRV selection.

ERED Reference	**Reason for Removing from TRV Evaluation**
Leffler 1975	This study evaluated increase in metabolic rates, which is difficult to assess as a whole-body effect. Dillon (1984) advised that metabolism data are variable, making data challenging to use for regulatory purposes; Dillon further advised to use metabolism when measured in conjunction with another measurement, such as growth.
Neufeld and Pritchard1979	This study measured effects on osmoregulation, which is not a whole-body effect.
Mulsow and Landrum1995	This study measured effects on feeding rate, which is not a whole-body effect.
Derr and Zabik 1972	This study measured accumulation, not toxicity endpoints. This reference has been removed from updated version of ERED.
Bengtsson et al. 2004	This study measured reduced grazing rates due to exposure, which is not a whole-body affect.

3.3 Total Chlordanes

Chlordane was historically used as an organochlorine pesticide. The RMP defines total chlordane to be the sum of cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonchlor, oxychordane. The primary concern with chlordane is toxicity to benthic organisms and risks to humans and piscivorous wildlife due to bioaccumulation in the food chain. Due to relatively high method detection limits, which are typically in the low µg/kg dw range (ppb), chlordane is infrequently detected in sediment chemistry tests. When chlordane is detected near the bioaccumulation trigger, typically other compounds are also triggered for bioaccumulation testing according to the DMMO.

There were no studies in ERED that met all of the TRV selection criteria. There was only one study that met all the other selection criteria except that the exposure was via water only, instead of via sediment or diet. DMMO should consider whether and how to update the TRV selection guidelines to address such a situation. As an example of what a TRV for chlordanes would be if the criteria were to allow water-only exposures to be included, this manuscript was still reviewed (Table 7).

Parrish et al. (1976) exposed a suite of marine organisms to water spiked with technical grade chlordane in acute 96-hour toxicity tests. Test organisms included eastern oysters (*Crassostrea virginica*), pink shrimp (*Penaeus duorarum*), grass shrimp (*Palaemontes pugio*), sheepshead minnows (*Cyprinodon variegatus*), and pinfish (*Lagodon rhomboides*). The most sensitive organism was pink shrimp, which experienced 55% mortality corresponding to an average whole-body residue concentration of 1,700 µg/kg ww. Whole body-residue concentrations were measured in live animals remaining at the end of the exposure. For pink shrimp, a whole-body residue concentration of 710 µg/kg ww corresponded with 10% mortality**.** The tissue residue concentration of 1,700 µg/kg ww which resulted in an observed LC55 was multiplied by an uncertainty factor of 20 to calculate the potential LOEC-TRV in Table 7.

Table 7. Potential TRV reference for chlordane.

Compound	**Test organism**	**Reported "Effects" Conc. (µg/kg ww)**	**LOEC TRV (µg/kg ww)**	**Toxicity**	**Reference**
Technical grade chlordane	Pink shrimp - water exposure	1,700	85 (UF[c] 20)	LC55[b]	Parrish et al., 1976

[a]LC82 = Tissue concentration at which 82% mortality was observed during 96-hour exposure.
[b]LC55 = Tissue concentration at which 55% mortality was observed during 96-hour exposure.
[c]UF = Uncertainty factor used to calculate the LOEC-based TRV value.

3.4 Dieldrin

Dieldrin is another organochlorine pesticide (a cyclodiene) that is acutely toxic to certain non-target estuarine animals and a concern for humans and piscivorous wildlife due to bioaccumulation in the food chain. Ambient concentrations of cyclodienes in the Bay are composed mostly of dieldrin, with significantly smaller amounts of aldrin and endrin (Yee and Trowbridge, 2016). Detection limits for dieldrin are typically relatively high in the low ppb range, and bioaccumulation testing triggers are rarely exceeded according to the DMMO.

Similar to the challenge with chlordane, we found very limited ERED entries for dieldrin that met all of the TRV selection criteria. There were six studies for dieldrin with ERED entries for marine invertebrates. Three of these studies were removed from TRV selection, because only NOEC values were reported, and a fourth study was removed because the measured effect was on behavior. Of the remaining two studies, the chemical exposure route was aqueous. After initial review, the study Estenik et al. (1979) was also removed from consideration because the test was conducted with freshwater.

As with chlordane above, DMMO should consider whether and how to update the TRV selection guidelines to address such a situation. As an example of what a TRV for dieldrin would be if the criteria were to allow water-only exposures to be included, the remaining manuscript was still reviewed (Table 8).

Parrish et al. (1974) exposed a suite of organisms (American oysters, pink shrimp, grass shrimp, sheepshead minnows) to unfiltered seawater spiked with technical grade dieldrin in 96-hour acute toxicity tests. Organisms were exposed to different concentrations, and concentrations in the animals were measured in the surviving organisms. Pink shrimp was the most sensitive species. A dose-response was observed, and observed mortality increased with increasing water concentration and increasing measured whole-body residue. An effect of 55% mortality was observed in pink shrimp corresponding to a whole body residue of 250 µg/kg ww at a water concentration of 1 µg/L. Mortality in 25% of test organisms was observed with a whole-body residue of 80 µg/kg ww at a water concentration of 0.32 µg/L. The LC55 value was used as a basis for TRV calculation, and an uncertainty factor of 20 was applied to calculate the LOEL-based TRV value in Table 8. Grass shrimp were less sensitive, with a mortality rate of 30% at a water concentration of 10 µg/L and a corresponding whole-body residue of 3,300 µg/kg ww.

Table 8. Selected TRV references for dieldrin.

Compound	**Test Organism**	**Reported "Effects" Conc. (µg/kg ww)**	**LOEC TRV (µg/kg ww)**	**Toxicity**	**Reference**
Dieldrin	Pink shrimp	250	12.5 (UF[b] 20)	LC55[a]	Parrish et al., 1974

[a]LC55 = Tissue concentration at which 82% mortality was observed during 96-hour exposure.
[b]UF = Uncertainty factor used to calculate LOEC-based TRV value.

3.5 Dioxins and Furans

The main concern with dioxins is bioaccumulation in the food chain and risks to wildlife and humans from eating fish. Invertebrates tend to be less sensitive to dioxins, compared to fish and fish-eating birds and mammals (Loonen et al., 1996). Dioxin concentrations are often summarized in toxic equivalents (TEQs), summing the contribution from dioxin congeners to overall toxic potency. In calculating the dioxin TEQs, the measured concentration of the chemical is multiplied by a toxic equivalency factor (TEF), or relative toxicity of a dioxin-like compound compared to the most toxic dioxin compound, 2,3,7,8-tetrachlorodiobenzo-p-dioxin. Other contaminants, such as PCBs, also have dioxin-like potency, and can be included in calculated TEQs using established TEFs. In the Bay, PCB TEQs generally exceed TEQs from only dioxins and furans (Davis et al., 2014). Proposed in-Bay sediment dredging projects include testing for dioxins and furans (referred to collectively as dioxins below), in areas where it is expected to be present at elevated levels or where information about its potential presence. Bioaccumulation testing is required by DMMO when dioxin TEQs exceed 10 parts per trillion.

Most of the tissue residue data for dioxins in ERED are for freshwater fish. There were only seven studies relating to invertebrates, and all the studies were for freshwater. Since the TRV selection process was designed for protection of marine invertebrates, there were insufficient data to select a TRV that met the specified selection criteria. DMMO should consider whether and how to update its TRV selection guidelines to address such a situation. Studies reviewed are summarized in Table 9.

Table 9. ERED references reviewed for dioxins, but removed from TRV selection.

ERED Reference	**Reason for Removing from TRV Evaluation**
Ashley 1996	Freshwater crayfish, *Pacifastacus leniusculus*, were dosed with TCDD by cephalothoracic injection. A concentration of 30 µg/kg caused 50% mortality, and results were reproducible in three separate experiments. A 3 µg/kg dose led to 25% mortality.
Branson et al.1985	After rainbow trout were initially exposed to 107 ng/L of 2,3,7,8-TCDD water, fish accumulated 2.58 ng/g. They were allowed to depurate for 139 days, and tissue concentrations reduced to 0.65 µg/kg. Growth rates were significantly reduced. Tissue concentrations were not at steady state.
Cook et al.1993	This was an Interim Report on assessment of 2,3,7,8-TCDD risk to aquatic life, including a review of studies on TCDD exposure. Toxicity to invertebrates was low - experiments with high body burdens measured no toxic effects (Table 4-1 shows concentrations of >500,000-2,000,000 pg/g with no toxic effect recorded). For fish a body burden of 80 pg/g in fish was evaluated to be a high risk to sensitive organisms, associated with a lowest exposure concentration that will likely cause severe effects (an EC50 or LC50). This concentration was based studies by Walker (1991,

	1992, 1993). Egg concentrations between 40-100 were associated with a 23% - 100% mortality in sac fry of lake trout. Exposure was conducted either by water, egg injection, or diet (maternal fish fed TCDD contaminated food).
Mehrle et al.1988	Chronic toxicity of rainbow trout was evaluated by continuously exposing them to various concentrations of TCDD (0-789 pg/L) and TCDF (0-8.78 ng/L). Effects were observed even at the lowest tested concentration. Tissue residue concentrations after 28 days of exposure at the lowest 2,3,7,8 TCDD exposure level was 0.98 µg/kg ww. At this concentration, mortality observed after 28 days was 6%, but after another 28 days of exposure, mortality was 45%. After 28 days of exposure at 0.41 ng/L of 2,3,7,8-TCDF, whole body residue concentration was 2.48 µg/kg ww. This concentration resulted in reduced feeding rate.

3.6 Total PAHs

Polycyclic aromatic hydrocarbons (PAHs) are derived from incomplete combustion of organic materials. and tend to accumulate in marine sediment. This is of particular concern in a highly urbanized area like San Francisco Bay where there are PAH inputs from multiple sources. PAH bioaccumulation in invertebrate prey can be toxic to Bay wildlife.

Similar to the selection process for other compound classes, we searched for studies that exposed marine invertebrates to total PAHs in order to capture the cumulative exposure to PAHs in Bay sediment. However, there were no studies for total PAHs in ERED that met all of the TRV selection criteria. TRVs have previously been identified[6] from ERED for the individual PAH analytes acenaphthene (Donkin et al., 1989), benzo(a)pyrene (Eertman et al., 1995), fluoranthene (Weinstein and Sanger, 2003; Lotufo, 1998), phenanthrene (Donkin et al., 1989; Emery and Dillon, 1996), and pyrene (Donkin et al., 1989). After review of these previously cited references, only the two studies for fluoranthene met DMMO TRV selection criteria, and are therefore summarized in Table 10. All other studies did not meet TRV selection criteria and are summarized in Table 11. In this review, we did not search for additional studies that would meet TRV selection criteria for individual PAH values because we were looking for whether appropriate TRV values existed for total PAHs.

Lotufo (1998) exposed two species of meiobenthic crustaceans to sediment spiked with different doses of radiolabeled fluoranthene in 10-day sediment bioassays. The copepods were *Schizopera knabeni* and *Coulana* sp. At sublethal concentrations, *S. knabeni* was the more sensitive species, and the LOEC where the number of offspring was affected was 0.6 mol/g ww,

[6] E.g. see Sediment Analysis and Characterization Report for the Port of San Francisco Mission Bay Ferry Landing and Water Taxi Landing Projects. December 2017. (available at http://www.dmmosfbay.org/site/alias__8904/170000/default.aspx)

and the LOEC where feeding rate was affected was 0.3 µmol/g ww. The LOEC where the number of offspring was affected is an effect on reproduction, and the calculated effect concentration is 121,000 µg/kg ww (0.6 µmol/g ww * 202 µg/µmol = 121,000 µg/kg ww). Since the exposure was for a short 10-day period, this is treated as an acute LOEC value, and an uncertainty factor of 10 was used to convert this acute LOEC value to a chronic LOEC value of 12,100 µg/kg ww in Table 10. The reported NOEC tissue value for effect on offspring is reported as 0.2 µg/g ww or 40,400 µg/kg ww of fluoranthene. At lethal concentrations, *Coulana* sp. was the more sensitive species, and with an LC50 value of 1.2 µmol/g ww or 242 µg/kg ww (1.2 µmol/g ww * 202 µg/µmol = 242,400 µg/kg ww). The LC50 was divided by an uncertainty factor of 20 to convert the LC50 value to a chronic LOEC.

Weinstein and Sanger (2003) exposed two oligochaete species, *Monopylephorus rubroniveus* and the polychaete *Streblospio benedictii*, to sediment spiked with different doses of fluoranthene. Organisms were exposed under normoxic and moderately hypoxic conditions. *M. rubroniveus* did not experience mortality. *S. benedicti* was the more sensitive species with estimated tissue LC50 values of 365,700 µg/kg dw under normoxic conditions (>80% dissolved oxygen saturation), and 420,100 µg/kg dw under moderately hypoxic conditions. The reported wet weight: dry weight ratio is 3.2 (365,700/3.2 = 114,000 µg/kg ww). The LC50 tissue wet weight concentration was further divided by an uncertainty factor of 20 to calculate an LOEC-TRV in Table 10.

Table 10. Previously cited TRV references for fluoranthene that met TRV selection criteria.

Compound	**Test Organism**	**Reported "Effects" Conc. (µg/kg ww)**	**LOEC TRV (µg/kg ww)**	**Toxicity**	**Reference**
Fluoranthene	Polychaete - sediment	114,000	5,700 (UF 20)	LC50	Weinstein and Sanger, 2003
Fluoranthene	Copepods - sediment	240,000	12,120 (UF 20)	LC50	Lotufo, 1998
Fluoranthene	Copepods - sediment	121,000	12,100 (UF 10)	LOEC - number of offspring	Lotufo, 1998

Table 11. PAH references reviewed that did not meet TRV selection criteria.

ERED Reference	**Reason for Removing from TRV Evaluation**
Anderson 1981.	Bacteria were injected into mollusk hemolymph, and the mollusk ability to clear bacteria was measured. At a benzo(a)pyrene tissue concentration of 2.21 µg/kg ww, there was statistically significant reduction in bacteria dose cleared compared to the control. The endpoint does not fit DMMO selection criteria.
Bechman et al. 2010	Adult shrimp and their embryos were exposed to North Sea oil dispersed in water for 3 months. Survival and development of larvae were observed. Removed from TRV selection because unclear whether observed effects were due to PAH accumulation or oil exposure.
Donkin et al. 1989.	Measured tissue burdens that reduced the feeding rate of the mussel, *Mytilus edulis*. This study was removed from TRV selection because a change in behavior was observed, and not a change in growth rate. The tissue concentration at which the feeding rate was reduced by 50% (TEC_{50}) was 626,600 µg/kg for fluoranthene; 29,400 µg/kg for acenaphthene; 30,700 µg/kg for phenanthrene; >189,000 µg/kg for pyrene.
Eertman et al. 1995	*Mytilus edulis* were exposed to seawater spiked with fluoranthene (1 µg/L) and benzo(a)pyrene (6 µg/L). Increased tolerance to air exposure was observed at lower concentrations, and decreased tolerance to air exposure was observed at higher concentration. This study was removed from TRV selection because exposure was through seawater, not sediment. In previous versions of ERED, this reference was also incorrectly recorded as an effect on reproduction. This same study also reported a reduction in clearance rate after exposure to a suspension of sediment contaminated with PAHs and heavy metals. However, from the reported results, it is not possible to attribute the reduction in clearance rate to bioaccumulation of a particular analyte.
Emery and Dillon 1996	Worms exposed to phenanthrene dissolved in water showed reduction in fecundity. However, this study was removed from TRV selection because worms were exposed through water, not sediment. Also, the results are difficult to interpret because while the phenanthrene exposure reduced fecundity (eggs/brood) compared to the carrier control, the fecundity was higher than the seawater control. Moreover, the fecundity was higher in both the carrier control and phenanthrene exposure, compared to the seawater

	control. The measured phenanthrene concentration in tissue was 780 µg/g ww.
Geffard et al. 2003	Mature oysters were exposed to PAH-contaminated sediment elutriate. The sediment contained a total PAH concentration of 31,665 µg/kg dw, and the sediment also contained cadmium, copper, and zinc. This study was not selected for TRV selection because organisms were exposed to sediment elutriate instead of sediment. Additionally, the observed effect was based on subjective observations of "normal" and "abnormal" larvae development, rather than quantitative measures of survival or reproduction. The total PAH concentration in the PAH-exposed larvae tissue was 280 µg/kg dw. Assuming a dry weight percentage of 20%, the calculated wet weight concentration is 60 µg/kg.
Perez-Cadahia 2004	DNA damage was measured in mussels were exposed to oil collected from an oil spill. Study not included in TRV selection because whole-body effects were not observed.
Selck 2003.	Worms were exposed to water only, or porewater and sediment treatments with fluoranthene. While growth was marginally affected, the results are difficult to interpret because fluoranthene marginally affected growth in worms exposed only to water, but not to worms exposed to porewater and sediment.

4. Summary of Data Gaps

In this study, we found the main challenge with selecting a TRV using the described methodology was finding ideal, well-designed, and well-implemented studies with clear results that could be unambiguously used as a basis for TRV recommendations for San Francisco Bay. There were cases where even though the study appeared to meet the selection criteria for inclusion in the ERED database, careful review of the manuscript revealed design flaws that made the results less appropriate for TRV selection. A related challenge was the lack of studies in ERED that are applicable for San Francisco Bay contaminant classes. Most studies listed in ERED are based on exposure to a single analyte, while DMMO sediment testing thresholds are established for contaminant classes that include several related analytes and metabolites.

Another issue is that the current DMMO methodology for selecting TRVs from ERED was developed to identify impacts to benthic invertebrates and may not be protective of benthic-dwelling fish. Additional effort would be needed to develop an approach that would also be protective of benthic fish.

For compounds with multiple studies relating tissue concentrations to effects in marine invertebrates, DMMO could consider aggregating all relevant results into a single plot relating tissue concentrations with magnitude of effect (e.g. % mortality, % growth rate reduction). This would allow evaluating the lowest published effect concentration in context of other measured data points, and identify any outliers that could be due to errors in measurement or design flaws. This would allow a more robust selection of a TRV by evaluating multiple data points instead of a single data point.

DMMO could also consider expanding its TRV guidance to include review of ERED for marine and estuarine fish studies, and for water-only exposures in instances where there are no studies using sediment or dietary exposures.

Due to the challenges described of finding sufficient relevant studies and data points, this study identifies the best available TRV value using the methodology identified at the beginning of the study, while acknowledging that none of the identified TRVs are developed with a high degree of confidence. Therefore, the TRV selection results presented in Table 12 should be used with caution, understanding the limitations in how the values were derived.

In the case of total PCBs, two studies listed in ERED were the best fits for the TRV selection criteria. However, both studies measured a chronic effect from bioaccumulation of total PCBs at a single concentration, and the studies were not designed to derive a LOEC value. One study (den Besten et al., 1989) observed abnormal starfish embryo development from adult female sea stars. Since this study only reported a single abnormal embryo development concentration, and not the LOEC, a LOEC TRV was calculated using an uncertainty factor of 10. The calculated LOEC-TRV is within a factor of five with the calculated LOEC-TRV from the second study, which found reduced survival under anoxic conditions for mussels that had accumulated total PCBs. The guidance provided by DMMO regarding TRV selection between multiple applicable studies is to choose the lower more conservative tissue residue value. Therefore, the identified TRV through this process is based on the lower of these two values. Since the TRV is based on two studies, both of which did not calculate a LOEC value, the derived TRV is assigned a low confidence level.

A low confidence was also assigned to the total DDT TRV, because it is based on two studies that did not measure an LOEC. The lower of the two effects residue concentration from the two studies is shown in Table 12 as the lowest available TRV based on the standard methodology described at the beginning of the study. This study measured the LC50 dose of DDT and DDT metabolites that had bioaccumulated in amphipods exposed to DDT-spiked sediment. And an uncertainty factor was applied to calculate an LOEC value based on the lethal dose.

No TRV could be selected for total chlordanes and total dieldrin because there were no studies in ERED that met all of DMMOs current selection guidelines. However, Table 12 shows potential TRVs derived from water-only exposures, should DMMO decide to allow inclusion of such studies. Even so, these potential TRVs are given a low degree of confidence because they are each based on a single study that measured an LC50 value.

Similarly, no TRV was selected from ERED for dioxins and furans because there were no studies that met all the selection criteria. There was also no TRV selected for total PAHs, because we did not find a study that met the selection criteria. There were three studies found that met selection criteria for one individual PAH, fluoranthene. The toxicity of fluoranthene is generally lower than other PAHs with higher solubility and lower octanol-water coefficients

(Donkin et al., 1989). However, one consideration is that this method would still not consider toxicity contributions from PAH metabolite.

Table 12: Summary of identified LOEC-TRVs for marine invertebrate toxicity based on this review of ERED references.

Compound	Identified LOEC-TRV (µg/kg ww)	Notes[a]	Confidence Level	Recommendations
Total PCBs	162	Calculated from a chronic developmental study using a UF of 10.	**Low.** Based on two studies: 1) a subjective embryo development study and 2) acute toxicity study.	Expand literature review outside ERED for studies reporting an LOEC for benthic organisms.
Total DDTs	134	Calculated from an LC50 value and UF = 20.	**Low.** Based on two studies: 1) single lethal dose concentration and 2) effect on growth	Expand literature review outside ERED for studies reporting an LOEC for benthic organisms.
Total Chlordane	85[b]	Calculated from an LC50 value and UF = 20.	**Low.** Based on a single study using aqueous exposure.	Expand literature review outside ERED for relevant sediment-exposure studies.
Dieldrin	12.5 [b]	Calculated measured LC55 value for pink shrimp and using an uncertainty factor of 20	**Low.** Uncertainty in value because based on single study using aqueous exposure.	Expand literature review outside ERED for relevant sediment-exposure studies.
Dioxins/ Furans	N/A	No reported studies in ERED for benthic invertebrates	N/A	Model fish tissue concentrations using BRAMS and compare modeled fish tissue concentrations to derived TRV value from ERED based on fish studies.
Total PAHs	N/A	No appropriate	N/A	Expand literature review

		study in ERED		for invertebrates and fish outside ERED. Model fish tissue concentrations using BRAMS.

[a] UF = Uncertainty factor used to calculate LOEC-based TRV value.
[b] Potential TRV based on water-only exposure (does not meet current DMMO selection guidelines)
LCXX = Tissue concentration at which XX% mortality was observed.

5. Recommendations to Address Data Gaps

In order to increase the confidence of TRV selection, and to develop TRVs for additional compounds, we recommend several approaches be considered for future efforts. These include expanding the DMMO methodology for selecting TRVs from ERED (e.g., evaluating studies on fish and evaluating prey invertebrate tissue concentrations[7]; considering water-only exposures when sediment or dietary exposure studies are lacking; evaluating use of Uncertainty Factors in specific cases to estimate LOEC-TRVs); looking outside ERED for additional relevant sediment toxicity studies for evaluation; and considering developing a method to summarize a large number of relevant studies in aggregate. A search for additional relevant toxicity studies would include published, peer-reviewed toxicity studies not included in ERED.

Besides the compound classes reviewed in this study, there are many more bioaccumulative compounds that may be of concern in San Francisco Bay sediment. For example, USEPA Region 10 revised its Bioaccumulative Contaminants of Concern List (Hoffman, 2007). Before embarking on deriving TRVs for additional bioaccumulative compounds of interest, we recommend an evaluation of the TRV selection methodology and improvements to expand the number of applicable studies.

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[7] The ERED database has significantly more data on fish than invertebrates, which indicates the database may provide more data points for fish toxicity endpoints compared to invertebrates. For example, ERED reports that 60% of the records are for fish compared to less than 15% for either category of invertebrate (molluscs, snails) and invertebrate (insects, crustaceans).

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