INTRODUCTION

Tributyltin (TBT) is a special chemical of concern under the PSDDA program and is classified as a deleterious substance under the SMS rule. Testing for this chemical in areas where it is likely to be found (e.g., marinas, ship repair facilities, shipping lanes) may be required under both programs. In 1988, the PSDDA agencies conducted a study on the presence of TBT in marinas in Puget Sound, and funded a risk assessment of TBT (Cardwell, 1989). In 1988, the PSDDA agencies developed a screening level (SL) and bioaccumulation trigger (BT) for use in the PSDDA program, based on the best available knowledge of this chemical and its properties.

In the past year, additional information has come to light on TBT, its distribution in Puget Sound, and its effects on the environment that support a change in the way the agencies approach evaluation of TBT in sediments. Most recently, an interagency work group was convened by EPA to develop a site-specific screening value for the Commencement Bay Nearshore/Tideflats and Harbor Island Superfund sites (see EPA, 1996). This paper discusses some of the issues raised by this new information and modifications to the PSDDA and SMS programs to address these issues.

PROBLEM IDENTIFICATION

Worldwide information documenting TBT's adverse impact on the aquatic environment is extensive. In addition to direct mortality, adverse impacts on a wide variety of aquatic organisms include reduced larval growth, sexual abnormalities, reproductive failure, gross morphological abnormalities, immune system dysfunction, nervous system disorders, and skin and eye disorders. TBT has a strong inhibitory effect on the cytochrome P450 system, reducing the ability of the organism to metabolize and detoxify environmental pollutants, and on ATP synthesis, reducing the ability of the organism to produce energy. These effects are generalized enough to occur in many organisms.
(including invertebrates, fish and mammals). Available evidence indicates that serious chronic effects resulting in population declines occur at water concentrations in the parts per trillion (ng/L) to parts per billion (ug/L) range, depending on the species (Fent, 1996; EPA, 1991).

The available literature indicates that the toxicity and bioaccumulation of TBT are affected by a variety of factors, including organic carbon in sediment and water, pH, salinity, clay fraction, and the presence of inorganic constituents such as iron oxides. TBT partitioning is further complicated by the fact that it occurs in several forms, including TBT+, TBTCI, and TBTOH and may interconvert among these forms with fluctuations in salinity and pH (Fent, 1996; EPA, 1991). Finally, TBT has been released into the environment in a variety of forms, including leaching directly from vessel hull paints (the most toxic and bioavailable form) and in the form of paint wastes from sandblasting (which may be less bioavailable but may represent a long-term source of the contaminant).

Sediment sampling in Puget Sound and elsewhere indicates that sediments in areas with vessel activity (e.g., marinas, harbors, boatyards, shipyards) are a significant reservoir of TBT (Parametrix, 1995). Worldwide, TBT-contaminated sediments adversely impact benthic organisms and contribute to water column concentrations that continue to be toxic to aquatic life (Fent, 1996). Very high, widespread TBT sediment concentrations have been found in the waterways of Commencement Bay, Elliott Bay (Harbor Island), and the Salmon Bay/Ship Canal area. Additional ongoing sources include domestic vessels that are still allowed to use TBT paints and shipping traffic from countries without TBT regulations.

Efforts to interpret environmental data in Puget Sound have been frustrated by the complexity of TBT partitioning in the environment and uncertainty over appropriate effects levels, testing strategies, and interpretive criteria. Recent data provided by NOAA suggest that the bioassay tests routinely used in the PSDDA and SMS program may not be of long enough duration to accurately reflect in situ effects due to TBT, and that other approaches may be more appropriate to the types of toxicity exhibited by this chemical (Meador et al., 1996 in press).

TECHNICAL BACKGROUND AND DISCUSSION

Analytical Methods

Analytical methods and detection limits for TBT are provided in the 1996 PSEP Organics Protocol, Appendix A (PSWQA, 1996). The recommended method involves reaction with sodium borohydride, methylene chloride extraction and analysis by GC/MS (Matthias et al., 1986). However, this method is somewhat experimental and is not available at most commercial laboratories. Alternative methods involve methylene chloride extraction, followed by Grignard derivatization and analyzed by GC/MS (Krone et al., 1989) or GC/FPD (Unger et al., 1986).
Reported Conventions

TBT data have historically been reported in a number of different ways. For example, in the literature TBT may be reported as Sn, TBT, TBTCI, or TBTO. For the same environmental concentration, these reporting conventions result in different numerical values because each of these forms has a different molecular weight. This has resulted in some confusion interpreting the data and in setting standards.

It is important that all data be reported in comparable units, and that any standards or guidance levels also be in those same units. The PSDDA program has used Sn in the past and the existing SL and BT are based in units of Sn. However, much of the analytical and research community recommends reporting TBT as the TBT ion (TBT+).

A simple conversion based on the ratio of molecular weights can be used to convert older data into these units for comparison with newer data:

<table>
<thead>
<tr>
<th>To convert TBT reported as:</th>
<th>To:</th>
<th>Multiply By:</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg Sn/kg</td>
<td>mg TBT/kg</td>
<td>2.44</td>
</tr>
<tr>
<td>mg TBTCI/kg</td>
<td>mg TBT/kg</td>
<td>0.89</td>
</tr>
<tr>
<td>mg TBTO/kg</td>
<td>mg TBT/kg</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The existing PSDDA SL for sediments (30 ug Sn/kg) corresponds to 73 ug TBT/kg.

TBT and Apparent Effects Threshold Values

The interagency work group followed the traditional approach in establishing regulatory thresholds for Puget Sound sediments by attempting to establish apparent effects threshold (AET) values for TBT. This effort was unsuccessful because of the widely varying responses in the bioassay and benthic data reviewed over a wide range of TBT concentrations (EPA, 1996). In some cases, despite extremely high TBT concentrations in sediments, no acute toxicity was exhibited by the standard suite of bioassay organisms. Current research shows that TBT partitioning is highly complex, and the relationship between concentrations and observed effects data is much stronger for interstitial water and tissue concentrations. Therefore, the work group discontinued efforts to develop AET values and instead focused its attention on using effects data associated with interstitial water and tissue concentrations as regulatory endpoints. However, Ecology will evaluate any additional synoptic data that are collected to further explore whether a reliable AET value can be calculated.

Interstitial Water Concentrations

As part of the TBT work group's efforts, an extensive literature review and compilation of effects levels in marine waters was developed for use in setting a site-specific screening value for the Commencement Bay Nearshore/Tideflats Superfund site
EPA, 1996). The reader is referred to this report, which received substantial public and technical review, for a detailed presentation of effects levels in water. TBT water concentrations that result in acute and chronic adverse effects to a wide range of marine species have been reported in the literature (Fent, 1996; EPA, 1991; EPA, 1996). Chronic effects to aquatic organisms have been reported at concentrations ranging from 0.002 - 74 ug TBT/L, with the majority of species responding below 0.5 ug TBT/L. Acute effects have been reported at concentrations ranging from 0.3 - 200 ug TBT/L.

The consensus of the TBT work group was that an interstitial water concentration of 0.05 ug TBT/L corresponds to a no adverse effects level that would protect most (approximately 95%) of the Puget Sound species that have been tested. This level is conceptually equivalent to the SQS under the Sediment Management Standards, and is consistent with the EPA approach to developing water quality and sediment criteria. For comparison, the EPA proposed draft marine chronic water quality criterion has been set at 0.01 ug TBT/L (EPA, 1991).

A higher adverse effects level was also evaluated by the TBT work group; however, less consensus was achieved on an upper or maximum allowable regulatory level. As one possibility, the work group discussed a value of 0.7 ug TBT/L. This concentration is lower than most of the acute effects levels reported in the literature. However, significant chronic effects are likely at this concentration, particularly to bivalve species present in Puget Sound. On the basis of the work group discussion and an associated report (EPA, 1996), an interstitial water concentration of 0.7 ug TBT/L was selected by EPA as the basis for a site-specific sediment trigger level for cleanup in the Hylebos Waterway (Commencement Bay Nearshore/Tideflats Superfund site). This value is not currently proposed as an upper regulatory level for either the PSDDA or SMS programs. For comparison, the EPA proposed draft marine acute water quality criterion has been set at 0.36 ug TBT/L (EPA, 1991).

**Tissue Concentrations**

In contrast to toxicity levels based on TBT water concentrations, which range over several orders of magnitude for various species, recent studies on tissue concentrations in Puget Sound organisms indicate that a much narrower range of tissue concentrations is associated with adverse effects to these organisms (see citations below). Different species have widely varying uptake, metabolic, and elimination rates for TBT, in part explaining the widely varying sediment and water concentrations that yield similar tissue concentrations and associated effects.

This finding provides an opportunity to develop tissue TBT concentrations that are directly correlated with observed effects in a wide range of ecologically relevant species. Meador et al. (1993; 1996 in press) have reported acute toxicity (LD50s) for Rheopoxynius abronius, Eohaustorius washingtonianus and Armandia brevis at concentrations ranging from 34 - 89 mg TBT/kg body weight (dry weight). Tissue concentrations within or above this range would represent a severe adverse effect and sediments associated with
these levels would exceed the level at which cleanup would be required, and would also be inappropriate for open-water disposal.

However, PSDDA and SMS require consideration of both acute and chronic effects. Chronic effects levels for species of concern in Puget Sound can be found in the literature (Salazar and Salazar, 1992, 1995; Moore et al, 1991; Davies et al., 1987, 1988; Page and Widdows, 1991; Widdows and Page, 1993; Thain et al., 1987; Waldock et al., 1992; Waldock and Thain, 1983; Meador et al., in press; Minchin et al., 1987; Alzieu and Heral; these values typically fall within a range of 2-12 mg TBT/kg body weight (dry weight), with a median value of about 4.

Direct measurements of TBT in tissues of biota collected from the site and in situ bioaccumulation studies are considered promising methods for assessing TBT toxicity, and may be recommended by the agencies to support sediment management decisions. The ranges discussed above provide a starting point for interpretation of bioaccumulation data from dredging projects or cleanup sites.

**PSDDA Screening Level for TBT**

A review of the existing SL was conducted to evaluate its relationship to known effects levels in water. Butyltins were added to the list of chemicals-of-concern for limited areas in the PSDDA Management Plan Report - Phase II (PSDDA, 1989). At the time of the listing, an interim SL for TBT was established at 30 ug/kg (as Sn). This SL was established using the available information on TBT contamination in Puget Sound and an equilibrium partitioning model that estimated interstitial water concentrations of TBT based on TBT sediment concentrations. In addition, the professional judgment of dredged material decision-makers in other regions of the country was sought in selecting the interim SL.

The interstitial water TBT concentration corresponding to the SL can be calculated using an equilibrium partitioning approach and a representative partitioning coefficient of 25,000 (sd = 5,500) derived from Meador et al. (1996 in press). Assuming a sediment organic carbon content of 2%, the SL of 30 ug/kg TBT (as Sn) corresponds to an interstitial water concentration of 0.06 ug/L TBT (as Sn) or 0.15 ug/L TBT (as TBT). Because there are many uncertainties associated with the original PSDDA SL and with the partitioning approach described above, this proposed interstitial water level was further evaluated based on a comparison to acute and chronic adverse effects levels compiled by EPA (1996).

This concentration is below approximately 2/3 of the chronic effects levels reported in the literature, and is below the entire range of acute effects levels reported in the literature. PSDDA disposal sites have been carefully sited to avoid sensitive habitat areas (such as shellfish growing areas) and most are sited in deep water. For these reasons, many of the chronic impacts to bivalves and other species that would be predicted at lower concentrations are not expected to occur at the disposal sites. This interstitial water level is therefore expected to be protective of acute and most chronic effects, without
being overconservative. Thus, an interstitial water concentration of 0.15 ug/L TBT is appropriate for use as an SL for the PSDDA open-water disposal sites.

**Bioassay Testing**

Exceedances of the SL for TBT currently trigger the requirement to conduct bioassay testing. The PSDDA bioassays include a 10-day amphipod mortality test, a sediment larval bioassay and the 20-day *Neanthes* biomass test. Bioassay testing under SMS includes these same bioassays, although Microtox or benthic analysis can be substituted for the biomass test. However, recent project data and evidence from the scientific literature indicate that most or all of the bioassay tests typically used under SMS and PSDDA may not be appropriate for evaluation of TBT toxicity, particularly with the short testing durations routinely used (Meador *et al*., in press; Moore *et al*., 1991; Langston and Burt, 1991; Fent, 1996). Most of the bioassay organisms currently used have been demonstrated to show serious acute and chronic toxicity associated with TBT in sediments, but at much longer exposure periods than employed in the standard PSEP bioassay protocols (EPA, 1996; Salazar and Salazar, 1991, 1996).

Results from recent projects (e.g., Puget Sound Naval Shipyards, Commencement Bay, Coos Bay, Harbor Island) would seem to bear out this prediction. Several sites have shown adverse benthic effects in areas with high TBT sediment concentrations, even when acute and/or chronic bioassays did not show adverse effects. In addition, bioaccumulation of TBT and associated adverse effects have been demonstrated at a number of these sites when short-term laboratory bioassays did not show a response. This may be because the longer-term bioaccumulation studies and *in situ* benthic assemblages better reflect the chronic endpoints with which TBT is associated and include long enough exposure durations for TBT in sediments and water to come into equilibrium with the organisms.

**PSDDA Bioaccumulation Testing for TBT**

The TBT bioaccumulation trigger was established at 219 ug/kg (as Sn), based on a multiple of the SL (PSDDA, 1989). Bioaccumulation testing is required when this threshold is exceeded. However, using the method described above for the SL, the existing BT corresponds to an interstitial water concentration of 1.07 ug/L (as TBT). This concentration is well above a level considered protective by the PSDDA agencies and the EPA Superfund work group. Based on the evidence provided above, significant bioaccumulation and adverse effects may occur at much lower concentrations. The interstitial water SL (0.15 ug/L TBT) corresponds to a level above which adverse reproductive and population-level effects due to bioaccumulation of TBT have been observed, and will also be used as the BT.

**PROPOSED ACTIONS/MODIFICATIONS**

**Testing Locations**
The SMS program and PSDDA agencies have required testing for TBT in marinas, boat maintenance areas, and other locations where TBT is likely to be present. Sediment testing in Commencement Bay (Thea Foss and Hylebos Waterways), in the Duwamish River, and in Salmon Bay and Lake Union Ship Canal have shown TBT to be present throughout the waterways and at levels substantially above the existing sediment SL. These studies show that TBT is more widely distributed, and at higher levels, than previously thought. For this reason, the SMS and PSDDA agencies will require testing for TBT in areas where past data have demonstrated its presence (particularly urban bays), and at other appropriate project locations where it would be likely to be present, such as marinas shipyards, boatyards, and in the vicinity of large CSOs or treatment plant outfalls. Persons who have evidence that TBT is not present at their project location can ask to have this requirement waived.

**TBT Testing Strategy for PSDDA Projects**

*The available evidence indicates that neither sediment chemistry screening levels nor the existing PSEP bioassay protocols may be as useful in predicting actual environmental effects as measurement of TBT concentrations in interstitial water and tissues.* Therefore, the current tiered testing protocol utilizing bulk sediment chemistry and short-term bioassays is not considered appropriate for evaluating the potential adverse effects of TBT. Because of the complexity of TBT speciation in the aquatic environment (including ionic forms) and because other factors may strongly affect its bioavailability, an alternative testing strategy is proposed.

Measurement of TBT in interstitial water provides a more direct measure of potential bioavailability, and hence toxicity, than bulk sediment concentrations. This approach also avoids the difficulties inherent in extrapolating to a sediment cleanup level, particularly where paint wastes or other less bioavailable forms may be present. Therefore, *the agencies propose that interstitial water analysis replace bulk sediment analysis* as the initial step in a tiered assessment of TBT toxicity for PSDDA projects.

TBT should be analyzed using approved methods as described above, and reported as TBT. A standard method for collection of interstitial water has not yet been determined though several techniques are available. Recommendations for a standardized method will be developed over the next year and discussed at the 1997 SMARM.

If the TBT concentration in the interstitial water is above 0.15 ug TBT/L, bioaccumulation testing of project sediments must be conducted using the PSDDA bioaccumulation guidelines in effect at the time of testing. Acute bioassay testing will not be required (other chemicals of concern may trigger acute toxicity testing). If unacceptable tissue concentrations are measured at the end of the bioaccumulation test, the sediment will be found unsuitable for open-water disposal.

**TBT Testing for SMS Cleanup Sites**
Although specific regulatory levels corresponding to the SQS and CSL have not yet been promulgated, a similar conceptual approach will be used for evaluation of TBT toxicity at SMS sites. As is typical of cleanup sites, a preponderance of evidence approach may be used rather than a strict tiered testing approach. However, interstitial water data and bioaccumulation (tissue) data will be given more weight in evaluating potential ecological effects than sediment concentrations or short-term bioassay results. Either laboratory or in situ bioaccumulation tests may be employed.

At many sites, bioassay testing will be conducted to evaluate the ecological effects of other chemicals in sediments. To evaluate ecological effects of TBT at these sites, longer-term bioassay/bioaccumulation studies could be considered as alternative chronic tests to those listed in SMS. Such alternative testing approaches may be particularly appropriate when other chemicals are also present that are slow to reach equilibrium in the laboratory, such as dioxins/furans and pesticides. Biological tests that measure both bioaccumulation and associated effects endpoints are recommended to assess the significance of measured tissue concentrations.

At sites where these alternative approaches are used to assess the effects of TBT, site-specific cleanup standards will need to be set based on the interstitial water and tissue effects ranges described in this paper. Consistent with the narrative standards set forth in WAC 173-204-100(3) and (7), site-specific cleanup standards shall include consideration of acute and chronic effects to aquatic organisms and human health, and shall range between no adverse effects and minor adverse effects levels. With respect to TBT, the presence of natural or cultured bivalve growing or collection areas shall be given special consideration in setting protective cleanup standards, since very low levels of TBT in water and sediments are known to adversely affect reproduction and growth of these culturally and economically important resources.

**Further Development of Bioassay/Bioaccumulation Tests**

Public comments recommended a wide variety of possible bioassay and bioaccumulation test strategies. Recommendations included side-by-side testing of amphipod species to determine relative sensitivity to TBT; use of a 60-day *Neanthes* bioassay with growth and reproduction endpoints; use of a 20-day *Macoma nasuta* test with bioaccumulation, tissue growth, and shell growth as endpoints; field-validation of laboratory bioaccumulation tests; use of longer-term larval tests with sensitive organisms such as oysters, mysids, and the copepod *Acartia tonsa*; and interstitial water bioassays. Although it is not currently within the PSDDA budget to conduct such studies, it may be possible to conduct some studies as part of large cleanup projects or through academic or agency research projects. The PSDDA agencies welcome and will carefully consider any information that is useful in better defining appropriate chronic tests for assessment of TBT and other compounds for which existing short-term bioassays may be inadequate to predict chronic effects.

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