Recommendations for Screening Values for Tributyltin in Sediments at Superfund Sites in Puget Sound, Washington

EPA REGION X

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RECOMMENDATIONS FOR SCREENING VALUES FOR TRIBUTYLTIN IN SEDIMENTS AT SUPERFUND SITES IN PUGET SOUND, WASHINGTON

Prepared for

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Region X Superfund Program
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October 1996

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ARCS QUALITY ASSURANCE CONCURRENCE

Recommendations for Screening Values for Tributyltin in Sediments at Superfund Sites in Puget Sound, Washington

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SECTION 1

INTRODUCTION

An interagency work group comprised of the U.S. Environmental Protection Agency Region X (EPA), Washington State Departments of Ecology (Ecology) and Natural Resources (DNR), U.S. Army Corps of Engineers (Corps), National Oceanic and Atmospheric Administration (NOAA), EVS Environment (EVS), and Roy F. Weston, Inc. (WESTON®) was formed to identify and evaluate various approaches to derive a marine sediment effects-based screening value or cleanup level for tributyltin (TBT) in the absence of a federal or a state regulatory standard. This effort was initiated to assist EPA in selecting sediment screening values and recommending a cleanup approach for TBT-contaminated sediments at Superfund sites in Puget Sound; however, the results can be used for other Puget Sound sediment management programs.

TBT is a man-made organotin compound with many commercial, industrial, and agricultural applications. As a pesticide, it has been widely used in marine paints as an effective means of preventing or retarding the growth of fouling organisms such as barnacles and mussels on the hulls of boats or ships. It is this application that is thought to represent the main contribution of TBT to the marine and estuarine environments in Puget Sound.

The detrimental environmental impacts associated with TBT have given this organotin the distinction of being reported as "the most toxic substance ever deliberately introduced into natural waters" (Stewart and Thompson, 1994). During the Superfund remedial investigation of sediment in the vicinity of Harbor Island, a highly industrialized area in Seattle, Washington, TBT was discovered to have extremely widespread distribution in sediment at concentrations higher than that previously reported for harbors and waterways throughout the United States (WESTON, 1994). Subsequently, EPA Superfund pre-remedial design sampling in the Hylebos, Thea Foss and Wheeler-Osgood waterways in Commencement Bay (Tacoma, Washington) found elevated concentrations of TBT in both intertidal and subtidal marine sediments.

This report represents the current recommendations from EPA Region X regarding the evaluation and cleanup of TBT in Puget Sound sediments. A prior version of this TBT Recommendations Report was made available for external peer review and public comment from April 30, 1996 to June 10, 1996. In addition, EPA sponsored an informational meeting to accept verbal comments on this report on May 20, 1996. Significant verbal comments, including EPA responses, were previously summarized and distributed by EPA on May 28, 1996. All written comments and additional verbal comments are summarized with corresponding responses, as appropriate, in Appendix G. This version of the TBT Recommendations Report has been modified in response to those comments.

1.1 CHARACTERISTICS AND USE

Organotins are polar ionic compounds containing one or more tin-to-carbon covalent bonds, comprising four chemical classes distinguished by the number of alkyl, aryl, or other ring organic groups associated with the tin (Sn) atom, namely mono, di-, tri- and tetra-substituted organotin compounds (Wong et al., 1994). Organotins are the most widely used of the man-made organometallic compounds, with diverse applications (Fent, 1996). The first commercially registered organotin compound was marketed in 1936 for use as a stabilizer for synthetic polymers. The biocidal properties of trialkylated organotins were first recognized in the 1950s, resulting in a considerable increase in the variety of applications, products, and manufacture of organotin compounds. Production of organotins increased from 5,000 tons (t) in 1955 to at least 35,000 t in 1985, which represented approximately 7 percent of the total annual world consumption of tin (Fent, 1996). About 23 percent of the total worldwide organotin production is used as agrochemicals and as general biocides in a broad spectrum of applications. Tri-substituted organotins (such as tributyltins) are most commonly used as pesticides (slimicides, fungicides, bacterialcides, algicides) in commercial and agricultural applications. Tributyltin compounds are also used as biocides for use in cooling towers, pulp and paper mills, and textile mills (Davidson et al., 1995). Specifically, pesticides registered as active ingredients for use as biocides in cooling towers contain TBT compounds. Other products containing tributyltin as an active ingredient include wood preservatives, disinfectant and antimicrobial cleaners, toilet bowl cleaners, and antibacterial carpet and upholstery shampoos (Davidson et al., 1995). Growing consumption of TBT lies in its use as a preservative for timber and wood, textiles, paper, and leather (Fent, 1996).

About 70 percent of the annual world production of organotins is for nonbiocidal uses. Substituted mono- and di-butyl tins (MBT and DBT, respectively) are used primarily for thermal and UV stabilization of rigid and semi-rigid PVC products. These organotins are also used as catalysts in the manufacture of polyurethane foam and silicone elastomers (Fent, 1996; Wong et al., 1994). Mono-substituted organotins are also used in glass coatings.

Organic derivatives of tin were discovered to be far more toxic than inorganic tin. The toxicity of organotins increases with progressive introduction of organic groups at the tin atom (Fent, 1996). Thus, tributyltins represent the most toxic group of the organotins. TBT-containing paints were recognized as 10 to 100 times more effective than copper-containing paints (Wade et al., 1988). Consequently, TBT has been included in antifouling paints since the 1960s and gained widespread application on pleasure boats, large ships and docks in the 1970s and 1980s (Fent, 1996). It was reported in 1988 that 140,000 kilograms (kg) of TBT-containing antifouling paints was used each year in the United States on commercial and recreational boats and ships to retard the growth of fouling organisms such as barnacles, mussels, and tube worms (Wade et al., 1988). Studies have determined that a fouling film (e.g., newly settled barnacles) of only 0.1 mm on a supertanker hull can increase annual fuel costs by approximately $1 million because of increased drag on the hull (Wade et al., 1988);

therefore, the application of such a highly effective antifouling paint represents considerable economic benefits to the shipping industry and the Navy.

In the 1970s, antifouling paints were found to cause detrimental environmental impacts (Fent, 1996). Before restrictions on TBT use were imposed by a number of countries in the 1980s (1988 in the United States), recreational and smaller commercial fleets may have represented one of the most widespread TBT sources to estuarine environments because these vessels spend most of their time in port and their antifouling paints are formulated to give high static release rates (Wade et al., 1988). TBT leaching from paint into the water appears to be the foremost major pathway of entry of TBT into the aquatic environment (Fent, 1996). Releases of fugitive paint and paint chips from vessel repair and dry-dock facilities have also been suggested as a major source of TBT to the aquatic environment (Uhler et al., 1993).

MBT and DBT are released into the environment through different sources. Most of the time, their occurrence is related to degradation pathways of TBT (i.e., TBT undergoes sequential debutylation and breaks down into DBT, which then degrades to MBT). However, there is increasing evidence that MBT and DBT may be introduced directly into the environment via discharge pipes or sewage treatment discharges (Quevauviller et al., 1991). It is thought that the butyltins leach to the water in the pipes and are later discharged to the environment.

Since the 1980s, widespread and significant TBT pollution of marine and freshwater ecosystems has been reported. Elevated TBT levels in marine systems are associated with pleasure and commercial boat activities, marinas, harbors, and vessel repair facilities and dry docks. Studies indicate that the leaching of TBT from marine paints results in higher concentrations in static environments, such as harbors, estuaries, marinas and bays, than in open waters (May et al., 1993). Elevated TBT concentrations have been found in water, sediment, and tissue of aquatic organisms in areas associated with boating and shipping activities. Typically, TBT concentrations were reported in the range of 0.10 to 1.0 micrograms (µg) TBT/Liter (L) in bays and estuaries in the 1980s (WHO, 1990). Because of its lipophilic nature, TBT concentrates in the sea surface microlayer at levels several times greater than the water column (Hall et al., 1986). Concentrations of TBT reported in open surface water areas were commonly lower and ranged from 0.001 to 0.05 µg/L (Fent, 1996). A recent survey (1994-1995) conducted by a consortium of TBT manufacturers under Order to the EPA reported water column concentrations in Puget Sound that ranged from below detection limits to 0.041 µg TBT/L (Parametrix, 1995). The highest concentrations in surface water were associated with marinas; water concentrations measuring 1 meter (m) off the sea bottom were highest in commercial harbors. Surface sediment concentrations from this same study ranged from below detection limits in background areas to 5,651 µg TBT/kg in sediment from shipyards and dry docks. Indigenous bivalve tissue concentrations in Puget Sound averaged 0.434 milligram (mg) TBT/kg (range = 0.024 to 2.78 mg TBT/kg), with the highest TBT concentrations measured in mussels collected from marinas. The NOAA National Status and Trends Program has monitored concentrations of contaminants in mussels and oysters throughout the United States. The results of their 1989-1990 survey (Uhler et al.,

1993) showed that tissue concentrations in bivalve molluscs from the West Coast ranged from 0.01 to 5.28 mg TBT/kg (dry weight) (mean = 0.34 mg TBT/kg) with the highest concentrations associated with bivalves collected near marinas with year-round use and commercial shipping harbors.

Although TBT tends to be elevated in harbors and near shipyards and marinas, the spatial distribution of butyltins in sediments has frequently been reported to be very uneven or "patchy" within these areas (Valkirs et al., 1991; Evans et al., 1995; Krone et al., 1996). Concentrations in sediments have been reported to vary by three orders of magnitude over distances of only a few hundred meters (Krone et al., 1989). This patchiness may be due in part to physical and sedimentary processes (e.g., currents, tides, river discharges) that affect particle distribution in marine and estuarine sediments, along with more intermittent disturbances caused by shipping activities (e.g., anchor drag, prop wash, boat washing, channel maintenance).

The use of TBT-containing antifouling paints is now controlled or banned in many countries, resulting in a reported decrease of TBT contamination in many coastal and harbor waters. In 1988, the United States Congress passed the Organotin Antifouling Paint Control Act (OAPCA) to limit the use of TBT. OAPCA specifically prohibited the application of these paints to non-aluminum vessels under 25 m in length, and required paints to leach TBT at a rate no greater than 4 milligrams per square centimeter per day ($mg/cm^2/day$) for larger vessels. Numerous countries around the world have adopted and implemented similar TBT restrictions. Consequently, annual trends monitored since legislative restrictions have demonstrated that TBT surface water contamination in harbors has significantly declined as a result of the antifouling paint regulation (Valkirs et al., 1991; Dowson et al., 1993b; Fent, 1996; Menconi, 1994; Unger et al., 1995; Waite et al., 1991). Nevertheless, TBT in antifouling paints remains a significant ongoing source of TBT contamination, to the aquatic environment due to its continued use in certain areas where regulations are being disregarded (Huet et al., 1996; Sarradin et al., 1991) and use on large vessels and application in countries without regulations (Fent, 1996). Urban effluent has also been identified as a potential source of TBT entering the estuarine and marine environment. In California (Davidson et al., 1995), the predominant source of TBT in urban effluent was found to be discharge from cooling water systems.

Studies beginning in the early 1990s that documented decreases in water concentrations of TBT following the implementation of TBT use restrictions around the world, also reported that TBT sediment concentrations in these same areas displayed only modest declines. These studies have also shown that the concentrations of butyltin compounds in sediments can be one to three orders of magnitude greater than in the water column (May et al., 1993; Langston and Pope, 1995). When released to the water column, dissolved TBT typically forms TBTCl or TBTOH because of the abundance of these anions in seawater and the inherent stability of these resulting neutral compounds at seawater pH. These forms of TBT can exhibit properties of both an organic and inorganic compound, depending on

environmental conditions. The organic butyl groups in TBT are attracted and sorb to organic material suspended in the water column. As TBTCl or TBTOH, the compound is polar, maintaining positive and negative charges at certain sites on the molecule. Also, a fraction of TBT remains in ionic form in seawater. These polar or charged forms of TBT are attracted to and bind with negatively charged surfaces of suspended mineral particles. Both of these processes foster rapid adsorption to particles. As these suspended particles settle to the bottom, TBT is incorporated into the sediment (May et al., 1993). Because of the paucity of suspended particles in the water column TBT may also directly adsorb to sediment which has both mineral nd organic components. Up to 95 percent of the TBT can be adsorbed to particles (with greater adsorption with increasing salinity), which serves to remove TBT from the water column (Davidson, et al. 1995). For TBT remaining in a dissolved form in the water column, microbial- and photo-degradation of TBT into the less toxic DBT and MBT compounds is known to occur more or less rapidly (Maguire et al., 1983). DBT and MBT further degrade to inorganic tin (Dowson et al., 1993a). This degradation further serves to reduce water column TBT concentrations.

Loss of TBT from the sediment is a function of desorption from the sediment to a water phase, uptake by sediment-dwelling biota, and physical (volatilization), chemical (photodegradation), and biological degradation. All these dynamic processes affect the ultimate fate of TBT in the environment. Volatilization of TBT tends to be negligible in sediment (Maguire, 1987) and photolysis of TBT tends to be a minor factor in sediment because of the insulating properties of the overlying water column. Desorption rates tend to be slow because of the strong affinity of TBT for sediment particles. Given the slow rates of chemical and physical degradation, biological uptake and biodegradation have the greatest influence on limiting the persistence of TBT in sediment (Maguire, 1987).

Although TBT strongly adsorbs to particles, sediments may not represent the ultimate fate of TBT in the environment. Investigators have suggested that adsorption is reversible (Unger et al., 1988; May et al., 1993), which would cause contaminated sediments to act as a continuing source to the overlying water column and aquatic biota. Uptake by filter-feeding aquatic biota (see Section 1.2) following regulation of TBT suggests that TBT continues to be present in the environment in a biologically available form (i.e., dissolved).

The rates of TBT degradation in water and sediment differ greatly. After release in water, TBT degradation rates (measured as half-lives) reportedly range from days (Seligman et al., 1990; Stewart and de Mora, 1990) to months (Quevauviller and Donard, 1990) depending on temperature and other natural factors. In sediment, biological degradation tends to be the main process by which TBT is changed into less toxic forms (Maguire et al., 1986). It is generally acknowledged that adsorption of organic pollutants such as TBT onto sediment can inhibit biodegradation (Dowson, et al., 1993b); thus, it is not surprising that estimates of TBT degradation in sediments average 2 to 3 years (Waldock et al., 1990; Evans and Huggett, 1991; Sarradin et al., 1995), causing sediments to remain contaminated for longer periods of time (Fent, 1996). Site-specific TBT degradation rates depend on the nature of the sediment

and the form of TBT present, and values reported in the literature include: 1.85 years (de Mora et al., 1989), 1.9 to 2.3 years (Sarradin et al., 1995), 0.9 to 5.2 years (Dowson et al., 1993a), 2 years (Waldock et al., 1990), and 4 months (Maguire and Tkacz, 1985). The persistence of TBT in some sediment may be greater than these experimental (field and laboratory) estimates of half-lives because natural sediments may be anaerobic, which tends to slow the microbial degradation processes. As an example, TBT was found in 10-year old sediments in New Zealand (de Mora et al., 1989). Similarly, Astruc et al. (1989) reported that TBT was the major organo-tin species in sediments deposited between 8 and 15 years prior to their study.

Predictions of TBT distributions in the environment (i.e., whether or not TBT occurs in a dissolved or sediment-sorbed phase) can be estimated based on its chemical partitioning behavior. Distribution (or partitioning) coefficients (K_d; expressed in units of L/kg) measure the relative affinity of a chemical for the particulate phase, and are calculated based on the ratio of the chemical concentrations in water relative to the concentrations in the sediment, assuming equilibrium conditions between water and sediment. A larger distribution coefficient indicates a greater affinity for sediment. K_d values for TBT reported in the literature vary widely and range from about 300 to 64,000 L/kg with the majority falling between 1,000 and 3,000 (Fent, 1996). K_ds were calculated from recent data generated by the Port of Seattle (Johns, 1996a) in the Duwamish Waterway (an estuarine environment) and ranged from 650 and 5,500 with an average of 1,900 L/kg. The majority of these values fell with the average range of K_ds reported in the literature and indicate that, while variable within a site, TBT has an overall greater affinity for adsorption to particles rather than occurring in a dissolved form in this estuarine environment.

Chemical partitioning behavior is controlled by a number of factors that differ for organic and inorganic compounds. However, TBT compounds exhibit chemical properties that are characteristics of both. In seawater, TBT typically acts as a neutral compound and the organic butyl groups are the active binding sites on the molecule. These groups preferentially sorb to other organic molecules and their behavior can be predicted (in large measure) by the amount of organic carbon available in the environment (including colloidal and dissolved organic carbon).

TBT compounds in seawater can also exhibit polar or ionic characteristics. The binding behavior of polar or ionic compounds is heavily influenced by the mineral makeup of the sediment, pH, salinity and redox potential of the environment (Fent, 1996; Langston and Pope, 1995; Unger et al., 1988; Kram et al., 1989). In marine environments, salinity and pH tend to be more constant and have less of an affect on the observed variability in partitioning than the other factors. The ionic portion of the compound competes with the organic butyl groups for binding with the sediment. In these cases, environmental parameters will modify which characteristic binding behavior is favored.

For TBT in estuarine sediments, research conducted by Langston and Pope (1995) suggests that organic matter (measured as organic carbon and carbonate together) and fine silts have a strong influence on TBT partitioning. In their work, higher K_ds occurred in sediment with higher organic matter. Further, a highly significant correlation between ^{14}C-TBT and organic matter was measured. Significant correlations between fine silts and K_d (r=0.63) were also measured. However, Langston and Pope subsequently concluded that organic matter was the most important sediment attribute that affected TBT partitioning. In this same study, there was no significant correlation between K_d and the clay fraction, suggesting that grain size *per se* does not strongly affect adsorption.

Parametrix, as part of their National TBT Long-Term Monitoring Program, examined the correlation between TBT concentrations in sediment and grain size (as silt and clay, separately) and sediment TBT concentrations and total organic carbon (TOC), and found significant but weak (r=0.52, 0.49, and 0.62, respectively) correlations (Parametrix, 1995). It should be noted that the correlations calculated as part of this work are impacted by the presence of paint chips in the sediment at many of the sites. This tends to weaken the relationship among variables of interest. Recent data generated by the Port of Seattle also suggest a lack of correlation between bulk sediment TBT concentrations and grain size (Johns, 1996a). However, in this data set, no correlation was observed between TOC and TBT concentrations.

As part of the review of this recommendations document, Aura Nova Consultants (Boatman, 1996a) conducted an evaluation of the correlation between K_d and TOC and percent fines (silt plus clay fraction). This evaluation was based on data reported by Unger et al. (1988) and Dowson et al. (1993b). Resulting correlations suggested that percent fines explained the variability of K_d to a greater degree than TOC (r=0.85 and 0.40, respectively). This same result was achieved when Aura Nova reanalyzed Langston and Pope's 1995 data based on percent fines alone (Boatman, 1996b). However, these results are based on only a few data points and cannot be considered definitive.

Finally, the strong role of organic carbon in TBT adsorption is implied in a recent study of container adsorption of TBT compounds; greater adsorption to container walls was related to greater organic character of the test cell material (Carter et al., 1989). This indicates that adsorption involves the organic butyl groups of the TBT compound, rather than the inorganic polar component of the molecule. The highly elevated concentrations of TBT in the seasurface microlayer (which are lipid-rich) also suggests that organic sorption is a strong component of TBT partitioning. As discussed above, the organic butyl groups are potentially always available for binding with other organic molecules. The ionic activity will tend to be highly variable based on environmental conditions.

Based on the information presented above, both organic carbon and mineral characteristics of the sediment influence TBT partitioning. The quantitative relationship between these two factors combined and K_d has not been defined and represents a data gap in our ability to

predict the fate of TBT in the aquatic environment. Of note, in the environment TOC and grain size (as a surrogate for mineral makeup) tend to be highly correlated (r>90) with each other. It may not be possible to distinguish the contribution of TOC and finer sediment in the partitioning behavior or TBT. However, it is clear that a linear relationship does exist between organic carbon and K_d, given that other environmental factors remain constant and carbon is present in sufficient quantities on the mineral surface to compete with ionic binding.

1.2 TOXICITY OF TBT

The ecotoxicological hazards of organotin compounds were first recognized after deleterious effects were observed in the late 1970s on oyster populations in Arcachon Bay, France. From 1977 to 1983, the shells of Pacific oysters (*Crassostrea gigas*) were observed to exhibit morphological abnormalities and the spatfall declined dramatically, resulting in estimated economic losses of approximately $150 million (Fent, 1996). Subsequent studies soon recognized adverse responses in other TBT-exposed aquatic organisms. In 1981, the imposition of male sex organs (termed "imposex" or "pseudohermaphroditism") on female mud snails (*Nassarius obsoletus*) was linked to TBT contamination, with severe reduction or loss of snail populations in the vicinity of harbors and marinas (Fent, 1996).

Later investigations found TBT in water to be acutely toxic above 0.5 µg TBT/L to many aquatic organisms, with chronic effects occurring below 0.01 µg TBT/L for many sensitive organism life stages (e.g., molluscan larvae) (Cardwell and Meador, 1989). The draft proposed water quality criterion for TBT calculated by EPA to protect marine organisms from chronic effects is 0.010 µg TBT/L (four-day average once every three years) and 0.360 µg TBT/L for acute effects (one-hour average once every three years) (EPA, 1991).

Less information is available regarding toxic effects associated with exposure to TBT in sediments. No observed effects concentrations (NOECs) for the acute toxicity of TBT in sediments are estimated to be at least 1,000 times higher than comparable NOECs for water (Cardwell and Meador, 1989). Previous investigations found that sediments containing 300 to >600 µg/kg of TBT were not toxic to the copepod *Acartia tonsa*, the mysid *Acanthomysis sculpta*, and a flatfish *Citharichthys stigmaeus* (cited in Cardwell and Meador, 1989). Further, acute toxicity NOECs for exposure to grass shrimp (*Palaemonetes pugio*) and the hemichordate *Branchiostoma* were between 1,000 and 10,000 µg/kg. Assuming a sediment-water partitioning coefficient (K_d) for TBT of 3,000 and a water quality criterion of 0.531 µg/L for acute toxicity, and 0.047 µg/L for chronic toxicity, Cardwell and Meador (1989) calculated that sediment containing less than 1,593 µg TBT/kg should not be acutely toxic to marine invertebrate species, while sediments possessing less than 141 µg TBT/kg should not be chronically toxic to most marine invertebrate species.

Uptake of TBT from sediment to tissue appears to be fairly complex. The lipophilic properties of TBT allow accumulation via solubilization in lipids, and the ionic properties of

TBT allow TBT to bind to macromolecules. These characteristics, combined with the limited ability of certain organisms (such as oysters and mussels) to metabolize TBT, result in the bioaccumulation of TBT by these organisms (Espourteille et al., 1993). Recent work by Ecology to develop bioaccumulation factors for various polar organic compounds (PTI, 1995) suggests that uptake from sediment to tissue is not a straight linear function but may be better approximated by a power function. Meador et al. (1996) reported that the processes of uptake and elimination varied widely among species, thus explaining, in part, the broad range of sediment concentrations associated with deleterious effects among even closely related genera. Factors controlling the bioavailability of TBT (chemical form, pH, organic content of sediment) in sediment further serve to moderate uptake.

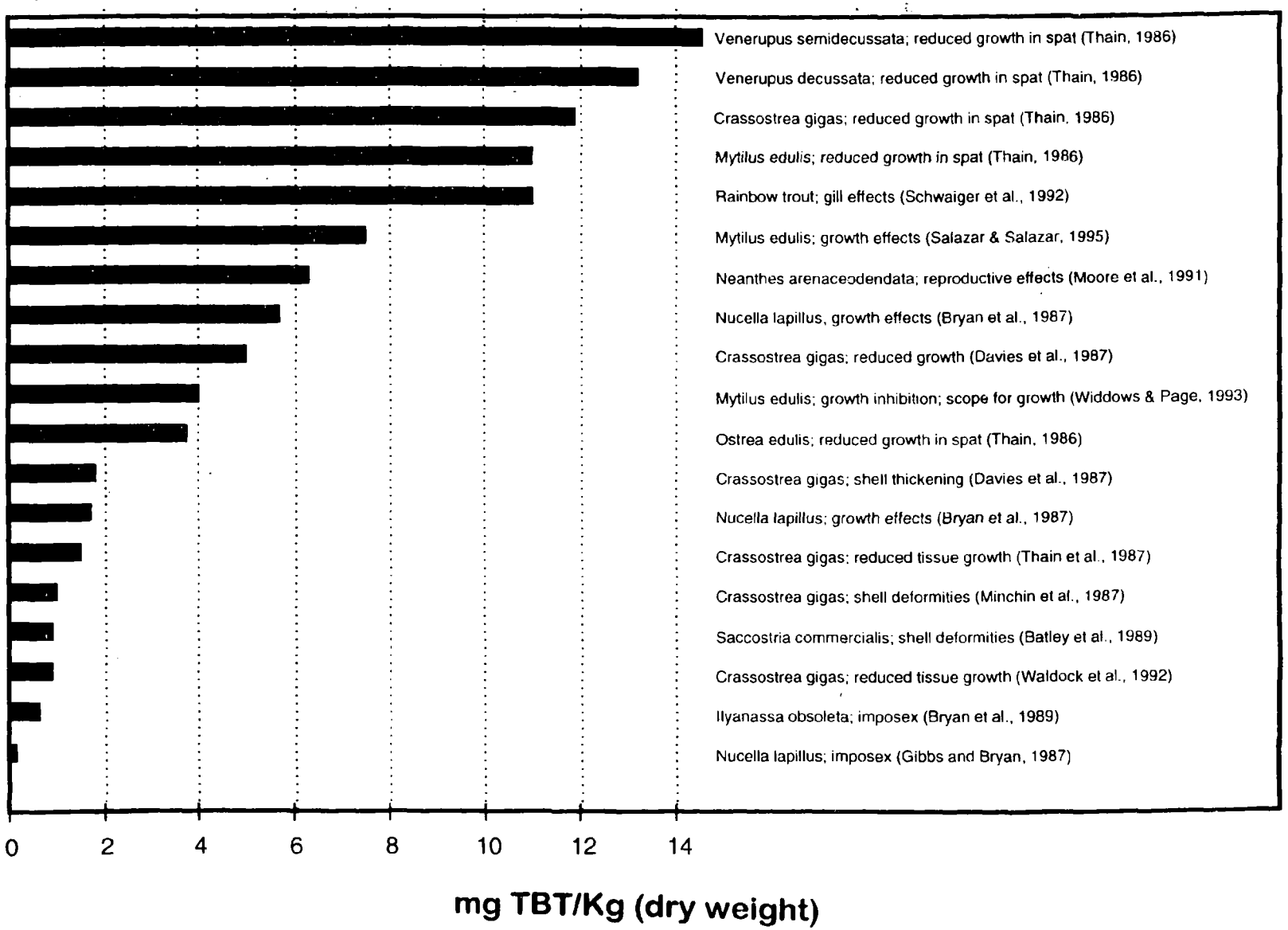
Deleterious effects associated with measured body burdens have been summarized in Figure 1 from Beaverson et al. (1996). Imposex, shell deformities, and reduced growth in the most sensitive molluscs (*Ilyanassa obsoleta, Nucella lapillus, Crassostrea gigas*) occur at extremely low body burdens (<2 mg TBT/kg; dry weight). Additional deleterious effects on growth and reproduction in other species and phyla were associated with tissue concentrations ranging from 4.0 to 15.0 mg TBT/kg. Meador et al. (1996) reported the average lethal dose for 50 percent of the population (LD_{50}) for two species of amphipod and one species of polychaete ranged from 34 to 89 mg TBT/kg (dry weight), with the most sensitive organism being *Eohaustorius washingtonianus* at 34 to 49 mg TBT/kg. The overall average LD_{50} among both invertebrate species and fishes was about 50 mg TBT/kg. Although some reviewers have expressed a concern about use of body burdens to define an effects threshold, the data discussed above establish that exposure to TBT is occurring and is associated with both sublethal and lethal effects.

These data suggest that humans may be exposed via ingestion of TBT-contaminated fish and shellfish. Acceptable daily intakes (ADIs) may be fairly high based on the proposed ADI (see Section 3.3 for additional details) considered by the Japanese Ministry of Health and Welfare (Wada and Manabe, 1986 as excerpted from Fent, 1996). However, detailed risk evaluations are needed before impacts to human health can be accurately assessed.

1.3 DOCUMENT ORGANIZATION

The results of the interagency work group efforts are reported in this document. Section 2 presents the approaches that were evaluated, followed by the results in Section 3. Section 4 presents a discussion, followed by recommendations regarding calculation and selection of screening values for use in sediment management decisions in Section 5.

Figure 1. Summary of measured effects and associated tissue TBT concentrations.



SECTION 2

APPROACH

A number of approaches for deriving a marine/estuarine sediment effects-based cleanup or screening value for TBT were investigated, including the following:

- Summarization of concentrations of TBT in Puget Sound sediments along with corresponding biological effects.
- Identification of concentrations of TBT in water and sediment causing deleterious effects to marine aquatic organisms, based on an extensive literature search.
- Identification of regulatory values promulgated for TBT in the U.S. and other countries.
- Identification of sediment cleanup values for TBT that have been developed for other EPA Superfund sites.
- Calculation of an apparent effects threshold (AET) value following the approach developed by PTI (1988) using Puget Sound chemical and biological effects data.
- Calculation of effects ranges following Long and Morgan's (1990) approach using Puget Sound data.
- Estimation of partitioning between sediment and mussel tissue using local and regional data, with a concomitant comparison to body burdens associated with deleterious effects, for the purpose of back-calculating a sediment cleanup or screening value.
- Back-calculation of a sediment cleanup or screening value based on an organic carbon partitioning coefficient between sediment and water derived experimentally by the NOAA National Marine Fisheries Service (NMFS) researchers.

Each of the above approaches is further detailed in the following subsections. Results obtained for each approach are presented in Section 3 (Results) and further discussed in Section 4 (Discussion).

2.1 LITERATURE SEARCH AND REVIEW

An initial search of the AQUIRE database was used to identify information regarding the toxicity of TBT in sediment. Although several hundred citations were identified, the majority of the literature reported toxicity associated with TBT in water. These data are discussed further in Section 3. Several critical review documents including Fent (1996), Meador et al. (1996), EPA (1991), WHO (1990), Cardwell and Meador (1989), Seligman et al. (1989), Waldock et al. (1987), Maguire (1987), and Hall and Pinkney (1985) were identified for use by the work group and were included in the review. As part of revisions to the EPA Recommendations Report, additional data compiled by Parametrix (Parametrix, in prep) as part of a TBT risk assessment are also included in the compilation of effects data in water.

2.2 IDENTIFICATION OF REGULATORY STANDARDS, CRITERIA AND GUIDELINES

As part of the literature search, any information relating to regulatory standards or criteria for TBT was compiled. A summary of these standards and guidelines is presented in Section 3.2.

As part of this effort, EPA Region X also reviewed the Superfund Record of Decision (ROD) database to determine if cleanup levels for TBT in sediment had been selected for Superfund sites in the U.S.

2.3 CALCULATION OF AN AET VALUE

An Apparent Effects Threshold (AET) is defined as the sediment concentration of a given chemical above which statistically significant ($P \leq 0.05$) deleterious biological effects relative to reference sediment are always expected to occur (PTI, 1988; EPA, 1992). If any chemical exceeds its AET for a particular response, an adverse effect is expected for that response. AET values are empirically derived from paired field data for sediment chemistry and a range of biological effects indicators (EPA, 1992). AETs form the basis of the Washington State Sediment Management Standards, the Puget Sound Dredged Disposal Analysis (PSDDA) screening levels, and the Sediment Quality Objectives (SQOs) defined in the Commencement Bay Nearshore/Tideflats ROD for a number of commonly detected contaminants.

Calculation of an AET value includes the following:

1. Collection of synoptic chemical and biological effects data.

2. Identification of biologically "impacted" and "nonimpacted" stations relative to reference.

3. Identification of the highest detected chemical concentration associated with a biologically nonimpacted station.

4. Reliability testing (i.e., for sensitivity, efficiency, and overall reliability).

WESTON attempted to calculate an AET value for TBT using chemical and biological data collected in Puget Sound, Washington. Specifically, synoptic sediment TBT and biological data were available for three local Superfund sites: 29 potentially affected stations plus 2 reference stations for the Hylebos Waterway (SEA, 1996; EVS, 1995) and 27 potentially impacted stations along with 4 reference stations for the Thea Foss/Wheeler-Osgood waterways (Hart-Crowser, 1996) in Commencement Bay; and 35 site stations and 3 reference stations for the Harbor Island (EVS, 1996) site in Elliott Bay. Use of these data meet EPA's (1992) and the State's recommendation of a minimum of 50 data points for calculating a reliable AET.

For the Hylebos Waterway data set, the sediment chemistry and biological data (benthic infauna, amphipod mortality, polychaete growth) are synoptic. However, the original echinoderm effective mortality data were rejected, and thus new sediment samples were collected from the same station locations at a later date for re-analysis. These "nonsynoptic" echinoderm data were included in the AET data set in an attempt to make the resulting AET calculation more robust. Nonsynoptic sediment chemical and biological data were also available for 8 stations at the Puget Sound Naval Shipyard (URS, 1993; Clapp, 1995) Superfund site in Sinclair Inlet. Although these data were not synoptically collected, they were also included for use in the calculations. It should be noted that inclusion of these nonsynoptic data does not strictly comply with the state's QA review process used in AET calculations.

The sediment chemical, conventional, and biological data for each of these studies are provided in Appendix A.1 (Tables A-1 through A-4). Figures showing station locations are provided in Appendix A.2.

All biological data were subjected to a quality assurance review following Washington State Sediment Management Standards (SMS; Ecology, 1991, 1995), Puget Sound Estuary Program (PSEP; 1989 with 1995 updates), and Puget Sound Dredged Disposal Analysis (PSDDA; EPA and COE, 1994 with 1995 ARM revision) program guidelines prior to use. All data were acceptable for use. Based on a review of the data, no anomalous values were identified for the "no hit" samples. Results are summarized in Appendix A.1 (Tables A-5 and A-6). Chemical data were validated as part of the original state or federal program they were collected for and were thus accepted as reported.

Biologically impacted stations were determined based on the criteria listed below. Additional details regarding analytical procedures for data evaluation are provided in Appendix B.

- Amphipod (*Rhepoxynius abronius* or *Ampelisca abdita*) bioassay—Test sediment mortality > 25 percent and significantly different from reference sediment per ANOVA ($P \leq 0.05$) or t-test (P-level adjusted based on the number of comparisons) results.

- Larval (*Dendraster excentricus* or *Mytilus spp.*) bioassay—Test sediment effective mortality (combined mortality and abnormality) > 15 percent above reference sediment effective mortality and significantly different from reference sediment per ANOVA ($P \leq 0.05$) or t-test (P-level adjusted based on the number of comparisons) results.

- Juvenile polychaete (*Neanthes arenaceodentata*) bioassay—Test sediment growth rate < 70 percent of reference sediment growth rate and significantly different from reference sediment per ANOVA ($P \leq 0.05$) or t-test (P-level adjusted based on the number of comparisons) results.

- Benthic invertebrate community structure—Test sediment major taxa group (crustacean, mollusc, polychaete) abundance < 50 percent of reference sediment abundance and significantly different from reference sediment per ANOVA ($P \leq 0.05$) or t-test (P-level adjusted based on the number of comparisons) results.

In this report, the use of an ANOVA with *a posteriori* pair-wise testing or a t-test with a P-level adjusted for the number of comparisons deviates from the process used by Washington State in AET calculations. However, the AET approach does not intrinsically require a specific method of statistical analysis for determination of significance of biological effects relative to reference conditions (EPA, 1992). It is likely that use of a simple pair-wise test (two-sample ANOVA or t-test), as implemented by the state, would identify more significant differences than the statistical methods implemented herein, and in the absence of confounding factors, may potentially increase the sensitivity and the overall reliability of the calculated AET. WESTON also applied the threshold or numeric criteria for adverse biological effects from the SMS to the determination of which samples were hits; this process may also tend to identify fewer "hits" than if the decision were based solely on significant differences. This issue is further discussed in Section 3.3.

Within the individual data sets, stations were ranked according to TBT concentration (from highest to lowest dry-weight concentration and from highest to lowest TOC-normalized) and the highest TBT concentration at which no biological impacts occurred was identified for each type of biological test for use as a potential AET value. In addition, all data sets were combined and the above steps repeated. Sensitivity (i.e., are *all* biologically impacted sediments identified by the predictions of the chemical sediment criteria?), efficiency (i.e., are *only* biologically impacted sediments identified by the predictions of the chemical sediment criteria?), and overall reliability (i.e., are stations correctly predicted as impacted or non-impacted?) were also calculated and expressed as a percent for each preliminary AET value,

using the formulae defined in PTI (1988) and as presented below. Results of the AET calculations are presented in Section 3.3.

Sensitivity = C/B * 100

Efficiency = C/A * 100

Overall Reliability = ((C + D)/N) * 100

where,

A = number of stations predicted to be impacted
B = number of stations known to be impacted
C = number of stations correctly predicted to be impacted
D = number of stations correctly predicted to be unimpacted
N = total number of stations evaluated.

2.4 CALCULATION OF EFFECTS RANGES

Low and median effects ranges (ER-Ls and ER-Ms) were developed by NOAA as guidelines (rather than regulatory criteria) for assessing the potential for adverse biological effects of sediment-sorbed contaminants at sites sampled as part of the National Status and Trends (NS&T) Program (Long and Morgan, 1990). These values were derived for several inorganic and organic constituents using a preponderance of evidence approach, which included assembling and reviewing available reports in which effects-based screening levels were determined or could be derived and determining apparent ranges in individual chemical concentrations for which effects were considered likely to occur. Approaches that are represented in NOAA's compilation of the effects-based values generally included sediment-equilibrium partitioning (EP), spiked-sediment bioassays, screening level concentrations, bioeffects/contaminant co-occurrence analyses, and the AET approach. Of key importance in Long and Morgan's approach, chemical and biological data that did not show concordance or effects-gradients (i.e., increasing chemical concentrations resulting in increased observed or predicted adverse biological effects) were excluded from further review. Screened data were then assembled and ranked. ER-L values were established as those concentrations equivalent to the lower 10th percentile of the data set; ER-M values were established as those concentrations equivalent to the 50th percentile of the screened data.

In addition to ER-Ls and ER-Ms, other sediment effects concentrations (SEC) have been developed to identify concentrations of contaminants above which toxicity is frequently observed. In recent work, Ingersoll et al. (1995; in preparation) attempted to calculate sediment effect concentrations (i.e., ER-L, ER-M, Threshold Effect Level, Probable Effect Level, and No Effect Concentration) for butyltins using the amphipod *Hyalella azteca* and the midge *Chironomus riparius*.

2.5 SEDIMENT-TISSUE PARTITIONING

Sediment-tissue partitioning was investigated as a potential approach to deriving a sediment effects-based cleanup or screening value for TBT. It was hypothesized that if a threshold for deleterious tissue concentrations could be identified and correlated with TBT concentrations in sediment, then a cleanup or screening value could be back-calculated for sediment.

Sources of matched sediment and tissue TBT data included the national TBT monitoring project being conducted by TBT manufacturers under an Order from EPA (Parametrix, 1995), a companion study being conducted by the Navy in selected harbors (NOSC, unpublished), and data collected as part of the Harbor Island Superfund site Remedial Investigation (RI) (Salazar et al., 1994).

Using the Navy's San Diego Bay and Pearl Harbor data sets (NOSC, unpublished), correlation analyses were first conducted to examine the relationship between TBT concentrations in sediment and bivalve tissue. Correlation results for these same endpoints, as described in the data report for the national TBT monitoring project, were also reviewed. It was hypothesized that the presence of significant and strong correlations would suggest that the uptake of TBT in tissue was a function of the concentration of TBT in the sediment, and would support the back-calculation of a sediment cleanup or screening value based on concentrations observed in tissues that were reported to cause deleterious effects. However, based on the inconclusive results obtained for the correlations (see Section 3.4), these tissue and sediment data were evaluated to determine if a preponderance of evidence approach could be developed such that certain sediment concentrations resulted in significant accumulations of TBT in tissue that were associated with biological effects. The approach involved identifying a lowest-observed-effects level for TBT in tissue and characterizing the sediment TBT concentrations associated with tissue above and below this level. The data collected as part of the Harbor Island Superfund RI were used to establish the lowest tissue concentration associated with reduced growth. This tissue level was then compared to the concentrations of TBT measured in bivalves collected as part of the Navy's investigations of San Diego Bay to identify corresponding sediment concentrations at which potentially minimal impacts might be expected.

2.6 SEDIMENT-WATER PARTITIONING

The bioavailability of organotins, and thus the toxicity, depends on the chemical speciation in water. Chemical speciation, in turn, determines whether or not TBT will adsorb to particles or dissolve in water (where it is more likely to be taken up by organisms). Several environmental factors are known to alter the bioavailability of chemicals, primarily by controlling speciation and complexation (Fent, 1996). When dissolved in water, TBT may react with common anions present in water, depending primarily on the pH of the water and to some extent salinity and temperature. If the resulting organotins are uncharged or are in a

neutral form (TBT is generally present in a neutral form at the pH characteristic of seawater), then they can easily transfer across biological membranes, which then results in bioaccumulation and toxicity.

TBT tends to have low solubility in water, while being moderately soluble in lipids (a major component of organic material). Thus, TBT readily adsorbs to organic particles and passes through biological membranes. Octanol-water partitioning coefficients (K_{ow}) have been used to predict the behavior of TBT in partitioning from water to environmental and physiological organic matter. K_{ow}s are also strongly affected by pH and salinity, as evidenced by the wide range of K_{ow}s reported for TBT (200 to 7,000) under a variety of experimental conditions (Laughlin et al., 1986). However, the bioaccumulation potential predicted by K_{ow}s tends to be much lower than that actually measured, suggesting that K_{ow}s may not accurately predict the behavior of TBT in the environment.

Research conducted by Meador et al. (1996) indicates that the bioaccumulation and toxicity of TBT is strongly influenced by the amount of organic carbon in sediment. The main mechanism is based on the partitioning of TBT from sediment to interstitial water, although bulk sediment properties (mineral makeup) may also influence partitioning. Meador's conclusion is consistent with numerous studies, such as Swartz et al. (1990) and Parkerton et al. (1993) that show that the biological effects of contaminants in sediments are more closely related to contaminants bound to organic carbon (i.e., sediment concentrations normalized to sediment organic carbon) or to interstitial (pore) water than to their bulk sediment concentrations. Interstitial water, which plays an important role in chemical bioavailability, is formed due to the entrainment of water during the sedimentation process and is essentially isolated from the water column (Batley and Giles, 1980, as cited in Knezovich et al., 1987).

A sediment-water partitioning coefficient based on the amount of organic carbon in the sediment (K_{oc}) was measured as part of Meador's research. The measured K_{oc} value was then used to calculate a marine sediment concentration that would be predictive of concentrations associated with adverse effects. Concentrations known to cause adverse effects in water formed the basis for this calculation using the following mathematical relationship:

$$[Sed_{oc}] = [Water] * K_{oc}$$

where,

Sed_{oc} = organic-carbon normalized sediment concentration (µg/kg)
Water = effects concentration in water (µg/L)
K_{oc} = organic carbon based partitioning coefficient (L/kg)

This equation, which assumes that a chemical is in equilibrium between sediment interstitial water and particulate organic carbon phases, shows the relationship between the particulate and dissolved phases of the chemical. Essentially, this equation provides a ratio of the

concentration of TBT "held" by the sediment fractions to the concentration of TBT "remaining" in the interstitial water.

Using water quality effects data for TBT as reported in the literature, WESTON was able to use the above formula to calculate a range of organic carbon-normalized sediment concentrations that could potentially be used in sediment management decisions, depending upon the degree of protectiveness of aquatic life desired by different sediment management programs (see Section 3.5). This water quality criteria-based approach is compatible with EPA's methodology for establishing water quality criteria (Stephan et al. 1985) and sediment criteria (Parkerton et al., 1993; EPA 1994a,b).

SECTION 3

RESULTS

The following sections present the results of the interagency TBT work group efforts to develop a cleanup or screening value for TBT in marine sediment that would be applicable for Puget Sound sediment management programs.

3.1 LITERATURE SEARCH AND REVIEW

A bibliography of the articles compiled as part of the literature search is presented in Appendix C. The majority of the literature available presents toxicity of TBT compounds for water. Effects of TBT in water are included as part of the discussion in Section 3.6.1. Few investigations reported toxicity values associated with sediment; those reported are presented in Table 1. The reported toxicity values for TBT in sediment varied widely among species because of marked differences in the biological uptake and elimination of TBT and length of exposure of the organism. Effects concentrations ranged from 18,743 to 3,500,000 µg TBT/kg organic carbon (OC). As shown in this table, *Eohaustorius washingtonianus* exhibited the greatest sensitivity to TBT in sediment, while *Rhepoxynius abronius* was the least sensitive in terms of a mortality endpoint (i.e., significant mortality was only observed at the highest concentration in the range).

Table 1—Summary of Effects of TBT in Sediment

Organism	Endpoint	Effects Concentration µg TBT/kg OC
Rhepoxynius abronius (amphipod)	Acute (10-day) mortality[a]	3,500,000
Eohaustorius washingtonianus (amphipod)	Acute (10-day) mortality[a]	170,000
E. washingtonianus (amphipod)	Acute (41-day) mortality[a]	78,000
Armandia brevis (worm)	Acute (10-day) mortality[a]	930,000
Scrobicularia plana (clam)	36-day growth[b]	18,743

[a] From Meador et al., 1996.
[b] Ruiz, et al., 1994.

3.1.1 TBT Conversion Factors

While conducting the literature search, compilation and reporting of the findings was often hindered by documentation (or lack thereof) of the reporting basis for TBT compounds. TBT is commonly analyzed as bis(tributyltin) oxide, tributyltin acetate, tributyltin chloride, or tin

and may or may not be stated as such in a journal article. Because the molecular weights vary substantially among the various compounds, it is important to standardize the reported basis. In the PSDDA program, TBT is reported as tin. However, the tri-substituted portion of the various compounds represents the toxic portion; therefore, WESTON ultimately converted all data to tributyltin (the ion). Table 2 presents the unit conversion factors for various forms of TBT.

For future sampling programs, it is recommended that TBT sediment data be reported as TBT (the ion) and on both a dry-weight and carbon-normalized basis. Tissue should be reported on a dry-weight and lipid-normalized basis.

Table 2—Unit Conversion Factors for Tributyltin

Multiply:	by	To Obtain:
TBT	0.41	Sn
TBT	1.12	TBT Cl
TBT Cl	0.36	Sn
TBT Cl	0.89	TBT
TBTO	0.97	TBT
Sn	2.74	TBT Cl
Sn	2.44	TBT

Molecular weight of tin (Sn) = 118.7.
Molecular weight of TBT (TBT) ion = 289.7.
Molecular weight of TBT chloride (TBT Cl) = 325.2.
Molecular weight of bis(tributyltin) oxide (TBTO) = 595.4

3.2 REGULATORY STANDARDS, CRITERIA, AND GUIDELINES

TBT is not included in the Washington State Sediment Management Standards (SMS) nor was it addressed in the development of the Apparent Effects Threshold (AET) values that formed the basis of the sediment quality objectives (SQOs) set forth in the Record of Decision (ROD) for the Commencement Bay Nearshore/Tideflats (CBN/T) Superfund site. However, the Puget Sound Dredged Disposal Analysis (PSDDA) program has developed a preliminary screening level (SL). The SL serves only to trigger additional biological effects testing where TBT is present in sediments to be dredged and potentially disposed of in open water disposal sites; the SL does not define a cleanup level. The SL was derived using a risk-based approach that accounts for environmental partitioning and is set at 30 micrograms (µg) of tin per kilogram (Sn/kg) on a dry weight (DW) basis, which is equivalent to

approximately 73 µg TBT (as the ion)/kg (DW). Additional details regarding the derivation of the SL are presented in Appendix D.

Investigation of regulatory criteria or standards for TBT resulted in identification of several national advisories or regulatory criteria for TBT in water and sediment. Regulatory standards or criteria have been implemented for TBT in marine waters by a number of governmental agencies throughout the world, including the United States, the Netherlands and Great Britain, and are summarized in Table 3.

Guidelines for TBT in sediment are generally nonexistent in other countries, with the exception of the Netherlands, which has published a guideline of 1.5 µg TBT/kg (Watson et al., 1993). This value has been normalized for a TOC sediment content of 10 percent.

As part of this effort, EPA also scanned the Superfund ROD database. No TBT sediment cleanup values were documented in any of the RODs queried. It was also noted that TBT sediment data have not been reported for any other Superfund marine sediment site.

Limited information is available on human health criteria or standards for TBT in fish and shellfish tissue. The Food and Drug Administration (FDA) sets action levels for unavoidable chemical contaminants that persist in the environment when they pose threats to the safety of food to consumers in interstate commerce. In the case of fish, most action levels are for banned pesticides. A FDA action level has not been established for TBT in fish and shellfish for human food.

Human health Acceptable Daily Intake (ADI) values of 1.6 µg bis(tributyltin)oxide (TBTO)/kg-day of body weight (Japanese Ministry of Health and Welfare)(Wada and Manabe, 1986) and 3.2 µg TBTO/kg-day of body weight (Schweinfurth et al., 1987) have been proposed. An ADI value of 1.6 µg TBTO/kg-day of body weight means a person weighing 70 kg can ingest up to 112 µg TBT daily, without incurring unacceptable health effects. These two proposed ADI values are much higher than the Reference Dose (RfD) value of 3×10^{-5} mg TBTO/kg-day of body weight that is currently found in EPA's Integrated Risk Information System (IRIS). An RfD value of 3×10^{-5} mg TBTO/kg-day of body weight means a person weighing 70 kg can ingest up to 2.1 µg TBT daily, without adverse effects.

EPA recently provided guidance for health officials responsible for issuing fish and shellfish consumption advisories. This guidance included information on a monitoring strategy and a risk-based procedure for calculating human health screening values for contaminants, including TBT, in edible fish and shellfish tissue (EPA, 1995). Based on use of a 6.5 g/day consumption rate over a 70-yr lifetime, a 70-kg adult body weight, a RfD of 3×10^{-5} mg/kg-day for TBTO (HQ=1), and an assumption of no loss of contaminants during preparation or cooking, a human health screening value of 300 ppb TBT in edible tissue was calculated.

Table 3—Guidelines for TBT in Marine Waters[1]

Government	Standard Criterion/Guideline	Conditions/Endpoint
ASEAN[3]	10 ng/L	24-hr average
California	5 ng/L	30-day average; protection of estuarine and marine organisms
California	1.4 ng/L	30-day average; protection of oceanic species
Guam	10 ng/L[4]	Chronic
Hawaii	10 ng/L	24-hr average
Maryland	1 ng/L[4]	Chronic
North Carolina	2 ng/L	Conditions not specified
Northern Marianas Islands	10 ng/L[4]	Chronic
Quebec	266 ng/L	Acute
Quebec	10 ng/L	Chronic
Texas	240 ng/L	24-hr average (acute)
Texas	43 ng/L	7-day average (chronic)
The Netherlands	10 ng/L	Conditions not specified;applicable to any TBT compound
United Kingdom	1 ng/L	For protection of saltwater fishes
United Kingdom	1 ng/L	For protection of other aquatic life
United States	360 ng/L[2] (total)	Acute effects criterion; 1-hr (draft proposed)
United States	10 ng/L[2] (total)	Chronic effects criterion; 4-day (draft proposed); the draft calculated final chronic value of 0.0485 µg/L was lowered to 0.01 µg/L to protect growth of commercially important molluscs and survival of the ecologically important copepod *Acartia tonsa*
Virginia	1 ng/L	Not to exceed criterion; Virginia currently considering defining value as a chronic criterion

[1] Excerpted from: Watson, D., D. Setiapermana, and G. Vigers (Editors), 1993. To convert from ng/L (ppt) to µg/L (ppb), multiply by 100.

[2] Excerpted from EPA, 1991. EPA Region 10 reviewed the most recent draft water quality criteria document for TBT (dated 1993), and the saltwater section, including data and criteria, has not been modified from the 1991 version.

[3] Association of Southeast Asian Nations.

[4] Excerpted from: Commonwealth of Virginia, 1996.

The report strongly recommends the evaluation and use of other screening values for site-specific exposure scenarios by adjusting values for consumption rate, body weight, exposure period, and contaminant loss. The monitoring strategy is designed to sample more intensively those waterbodies where exceedances of screening values have been found in order to assess the magnitude and the geographic extent of the contamination.

Elevated tributyltin concentrations in clams, crabs, and fish in certain areas of the Coos Bay estuary in Oregon led the state and local environmental and health officials in 1995 to issue an advisory against public harvesting and consumption of shellfish for certain areas. This advisory was supported by a risk-based analysis, and used a human health screening value of 112 ppb TBT in shellfish tissue.

3.3 AET CALCULATIONS

Results of the preliminary AET calculations for the various biological endpoints investigated are presented in Tables 4 and 5. As indicated by these results, a maximum no-effect concentration (either dry-weight or TOC-normalized) could often not be established using the Puget Sound data sets because, in several cases, the highest sediment TBT concentration associated with no biological effects was also the highest concentration measured among all of the stations sampled. Where AET values for TBT could be derived using individual biological data sets, sensitivities were typically low (5 to 42 percent) and generally decreased when all data sets were combined. However, low sensitivities for an individual chemical group are fairly typical. As reported in the 1988 AET document (PTI, 1988), the highest sensitivity of a chemical group was for PAHs at about 25 percent for amphipod bioassays and 32 percent for infaunal abundance. Other chemical groups only contributed a small increment to the overall sensitivity. Also, it is recognized that sensitivity analyses are generally performed for all chemicals in the State's SEDQUAL database. However, these calculations could not be performed here and thus are only used as a general indicator of performance.

Only the endpoints based on benthic infaunal abundance from Thea Foss/Wheeler-Osgood waterways and polychaete growth measured as part of the supplemental remedial investigation at Harbor Island yielded sensitivities greater than 75 percent, but the dry-weight AET values derived (100 and 7,591 µg TBT/kg) for these endpoints were nearly 2 orders of magnitude different. In addition, the dry-weight AET value derived for polychaete growth was based on a data set in which only one impacted station (out of a possible 35) was observed, and when the sediment data were normalized to TOC content, a confirmed AET value could not be calculated.

The dry-weight AET value derived for benthic infaunal abundance using the Thea Foss/Wheeler-Osgood waterways data appeared more promising. However, a substantial difference was observed between this value (100 µg TBT/kg) and the dry-weight AET value calculated for the same endpoint using data collected from the Hylebos Waterway data

Table 4—AET Calculation for Dry-Weight TBT (Ion; µg/kg) Concentrations in Puget Sound Sediment

TBT (Ion; µg/kg Dry-Weight)	LABORATORY BIOASSAYS					BENTHIC INFAUNA
	10-Day Amphipod *(Rhepoxynius abronius)* (Mean % Mortality)	10-Day Amphipod *(Ampelisca abdita)* (Mean % Mortality)	48-Hour Echinoderm Larval *(Dendraster excentricus)* (Mean % Effective Mortality)	60-Hour Bivalve Larval *(Mytilus galloprovincialis)* (Mean % Effective Mortality)	20-Day Juvenile Polychaete *(Neanthes arenaceodentata)* (Mean Growth Rate; mg/org/day)	SMS Major Taxa Groups (Mean Abund; # Ind./0.1 m2)
HYLEBOS WATERWAY						
Max. No-effects Conc.	>581	NT	561	NT	>581	561
Sensitivity (%)	0		20		0	5
Efficiency (%)	0		100		0*	100
Overall Reliability (%)	96		86		100*	31
THEA FOSS WATERWAY						
Max. No-effects Conc.	>90	271	>551	NT	>551	99
Sensitivity (%)	0	42	0		0	76
Efficiency (%)	0*	100	0		0*	100
Overall Reliability (%)	100*	53	96		100*	81
HARBOR ISLAND						
Max. No-effects Conc.	>13556	NT	NT	>5556	7591	NT
Sensitivity (%)	0			0	100	
Efficiency (%)	0			--	100	
Overall Reliability (%)	97			79	100	
SINCLAIR INLET (PSNS)						
Max. No-effects Conc.	NT	NT	NT	NT	NT	>88
Sensitivity (%)						0
Efficiency (%)						0
Overall Reliability (%)						75
COMBINED DATA SETS						
Max. No-effects Conc.	>13556	271	561	>5556	7591	561
Sensitivity (%)	0	42	17	0	100	3
Efficiency (%)	0	100	100	--	100	100
Overall Reliability (%)	97	53	89	79	100	34

NT = Not tested.

SMS = Sediment Management Standards.

* No impacted stations within data set, number of stations correctly predicted to be impacted set at zero.

Table 5—AET Calculation for Organic Carbon Normalized (lon; µg/kg OC) Concentrations in Puget Sound Sediment

TBT (lon; µg/kg OC)	LABORATORY BIOASSAYS					BENTHIC INFAUNA
	10-Day Amphipod *(Rhepoxynius abronius)* (Mean % Mortality)	10-Day Amphipod *(Ampelisca abdita)* (Mean % Mortality)	48-Hour Echinoderm Larval *(Dendraster excentricus)* (Mean % Effective Mortality)	60-Hour Bivalve Larval *(Mytilus galloprovincialis)* (Mean % Effective Mortality)	20-Day Juvenile Polychaete *(Neanthes arenaceodentata)* (Mean Growth Rate; mg/org/day)	SMS Major Taxa Groups (Mean Abund; # Ind./0.1 m2)
HYLEBOS WATERWAY						
Max. No-effects Conc.	>29229	NT	>29229	NT	>29229	>29229
Sensitivity (%)	0		0		0	0
Efficiency (%)	0		0		0*	0
Overall Reliability (%)	96		82		100*	28
THEA FOSS WATERWAY						
Max. No-effects Conc.	>3929	7974	>11984	NT	>11984	3428
Sensitivity (%)	0	17	0		0	76
Efficiency (%)	0*	100	0		0*	100
Overall Reliability (%)	100*	41	93		100*	81
HARBOR ISLAND						
Max. No-effects Conc.	>759111	NT	NT	>759111	>759111	NT
Sensitivity (%)	0			0	0	
Efficiency (%)	0			--	0	
Overall Reliability (%)	97			77	97	
SINCLAIR INLET (PSNS)						
Max. No-effects Conc.	NT	NT	NT	NT	NT	>2584
Sensitivity (%)						0
Efficiency (%)						0
Overall Reliability (%)						75
COMBINED DATA SETS						
Max. No-effects Conc.	>759111	7974	>29229	>759111	>759111	>29229
Sensitivity (%)	0	17	0	0	0	0
Efficiency (%)	0	100	0	--	0	0
Overall Reliability (%)	97	41	89	77	99	27

NT = Not tested.

SMS = Sediment Management Standards.

* No impacted stations within data set; number of stations correctly predicted to be impacted set at zero.

(561 µg TBT/kg), which exhibited a sensitivity of only 5 percent (note: no benthic infauna data were collected at Harbor Island). Given the disparity between these results and that the subtidal surface sediments collected from these two sites were characterized by a similar range of TBT concentrations (20 to 581 µg TBT/kg), it appears that other chemicals may be contributing to the observed effects and thus data were not useful in calculating a sediment effects-based cleanup value for TBT.

In this report, the overall reliability for this single chemical ranged from 34 to 100 percent. However, the higher reliability was associated with endpoints that showed little to no effects (e.g., amphipod mortality and juvenile polychaete growth) over the range of TBT concentrations measured in sediment. For those endpoints demonstrating deleterious effects at higher concentrations, the resulting AET tended not to be predictive.

A comparison was made of these results with those that would have been generated by use of simple t-tests ($P \leq 0.05$) and only synoptic data (i.e., per Ecology's approach for deriving AET values). Although specific results are not reported here, the outcome was essentially the same. No effects and effects were interspersed over the range of bulk sediment TBT concentrations reported. In several cases, a maximum no-effects concentration could be identified but was only followed by a single adverse effect or "hit," making the calculated AET value uncertain. This pattern of interspersed effects and no-effects data is also evident in the sediment effects data compiled by MacDonald Environmental Sciences, Ltd., for the Florida Department of Environmental Protection (MacDonald, 1994). For those data, all but the most extreme bulk sediment TBT concentration (100 mg/kg TBT in sediment) generally showed both adverse effects ("hits") and no adverse effects ("no hits") at similar sediment TBT concentrations.

WESTON's results, which did not support a clear identification of an AET value for TBT, were similar to a recent effort by Ecology to calculate an AET based on amphipod mortality (Gries, 1996) from data currently in the SEDQUAL database (22 samples from pre-1989 surveys). Ecology determined that a valid and reasonable AET for TBT could not be recommended for use in regulatory programs at this time. Ecology noted, however, that additional synoptic data collected in the future may be useful in calculating a usable AET value for TBT.

3.4 EFFECTS RANGES

WESTON did not derive an effects range (ER-L or ER-M) for TBT for two primary reasons. First, as described above, the approach to developing such values relies primarily on the existence and availability of sediment effects-based concentrations and numerous data sets containing synoptic chemical and biological data. Results of WESTON's literature search and review revealed few investigations in which synoptic data were available, and sediment effects-based screening levels were non-existent. Second, review of the Puget Sound data sets

used to calculate an AET value for TBT (see Section 2.3), as well as the values calculated, indicated an overall lack of concordance among sediment TBT concentrations and observed biological effects (see Section 3.3). In accordance with Long and Morgan's approach, these data would not be acceptable for inclusion in the preponderance of evidence approach to developing screening guidelines. These limitations effectively precluded the calculation of an ER-L or ER-M for TBT. In addition, MacDonald (1994) reported effects ranges for tributyltin data compiled as part of a biological effects database for sediment that was used to support the derivation of sediment quality guidelines for marine and estuarine ecosystems. In this effort, effects concentrations co-occurred with no reported effects throughout the entire range of concentrations evaluated. Although Ingersoll et al. (1995) attempted to calculate a sediment effects concentration (SEC) for butyltins using the amphipod *Hyalella azteca* and the midge *Chironomus riparius*, he was unable to calculate an effects level because the ranges of detected sediment concentrations were too narrow or there were too few measured concentrations in the database.

3.5 SEDIMENT-TISSUE PARTITIONING

The relationship between sediment and tissue concentrations of TBT was examined using a correlation analysis to determine if a sediment cleanup concentration could be back-calculated from a bivalve body burden representative of minimal deleterious effects. Results of the correlation analyses among TBT concentrations suggested an association exists among the two endpoints, but that other environmental (e.g., organic carbon in sediment, TBT form) or physiological (e.g., metabolism, elimination) factors are influencing the bioavailability of TBT in sediment and subsequent accumulation of TBT in tissue.

Two of the three data sets with paired sediment and bivalve tissue TBT data [San Diego Bay data set (NOSC, unpublished) and a Puget Sound data set collected as part of the national monitoring program (Parametrix, 1995)] exhibited significant ($P \leq 0.05$) but not strong correlations [correlation coefficients (r)<0.70] among concentrations of TBT in sediment and tissues. Correlation coefficients for these data sets were 0.46 and 0.59, respectively. Coefficients greater than 0.7 would be considered indicative of a strong linear relationship among the assessment endpoints (see Appendix B). However, as noted by Salazar (1996), the lack of correlation between TBT in water, sediment, and tissue as measured by NOSC (unpublished) and Parametrix (1995) may be due to the fact that samples were not collected from the same location, and thus were not truly paired (an assumption used in the correlation analysis). The presence of such a relationship (indicating predictability from one variable to the other) would have supported the back-calculation of a sediment cleanup value based on tissue (rather than effects) concentrations.

Given the presence of a substantial but not strong correlation, it was hypothesized that the statistical relationships could possibly be clarified by normalizing the sediment TBT concentrations to organic carbon content, as this variable likely influences the partitioning

(and subsequent bioavailability) of TBT (see Sections 2.7 and 3.4). However, TOC data were not available for the San Diego sediment sampling stations, and the Puget Sound sediment data collected as part of the national monitoring program were never normalized to TOC content for use in correlation analyses due to "inconsistent correlations" between TOC and TBT concentrations in sediment (Parametrix, 1995). However, further review of the correlation results obtained for TOC and TBT in sediment using the Puget Sound data collected by Parametrix suggested that a relatively strong relationship was present between these two endpoints ($r = 0.62$ at $P \leq 0.01$). In addition, the correlation was based on a data set combining sediment collected from shipyards, drydocks, commercial harbors, marinas, and "ecologically significant" (i.e., relatively noncontaminated) areas. The form of TBT in some of these areas (i.e., the presence of paint chips versus natural sediments) likely affected the observed relationship; exclusion of data associated with sand blast grit may have increased the correlation between TOC and TBT, but these data were unavailable in electronic format for testing of this hypothesis. Finally, evaluating the bioavailability of sediment-sorbed TBT through a sediment-tissue partitioning approach is probably better studied using a deposit-feeding clam (e.g., *Macoma*) rather than a water-column suspension feeder (e.g., *Mytilus*).

To further evaluate the potential relationship between sediment TOC and TBT concentrations, and the subsequent influence on the use of a sediment-tissue partitioning approach, WESTON evaluated the relationship between these endpoints using the Puget Sound Superfund data sets (i.e., the Harbor Island, Hylebos Waterway, and Thea Foss Waterway data sets). When all three data sets were combined, no significant ($P \leq 0.05$) correlation among sediment TBT concentrations and TOC content was obtained. Because of the potential differences in TBT form (e.g., presence of paint chips) and TOC content (e.g., presence of organically enriched sediments) among the three data sets evaluated, additional correlations were conducted in which each data set was examined individually. Only the data collected from the Hylebos Waterway exhibited a significant ($P \leq 0.05$) result with a substantial (but not strong) association ($r = 0.52$). It is likely that the presence of sand blast grit/paint chips in the Harbor Island data set and the presence of organically enriched sediments of anthropogenic origin (average TOC = 3.9 percent) in the Thea Foss Waterway data set contributed to the lack of any significant correlations among those data.

In an attempt to establish a link between TBT in tissue and potential biological effects, the bioaccumulation and growth data collected as part of the Harbor Island RI (Salazar et al., 1994) were used to establish a range of tissue concentrations associated with significantly ($P \leq 0.05$) reduced growth in juvenile mussels (*Mytilus edulis*). In this study, juvenile and adult mussels were deployed at 12 locations in the lower Duwamish River, including one site at the southern tip of Kellogg Island. Mussels were also deployed at one reference station in Carr Inlet [see excerpted figure from Salazar et al. (1994) in Appendix A.2]. Mussels were stationed about one meter off of the bottom, which was thought to be representative of mussels feeding on resuspended sediment. Tissue concentrations for selected contaminants [metals, total polychlorinated biphenyls (PCBs), total polycyclic aromatic hydrocarbons

(PAHs), and TBT] in composited samples, and weights and lengths of individual mussels were measured following 82 days of exposure.

Because paired sediment and tissue data were not available, exposure concentrations were developed by averaging the TBT concentrations from the nearest (up to 150 meters) sediment stations sampled as part of the RI. Average sediment concentrations at the mussel stations were estimated to be from 84 to 583 µg TBT/kg around Harbor Island and 29 µg TBT/kg at Carr Inlet, using this method. Tissue concentrations ranged from 9 to 42 µg TBT/kg at the same Harbor Island locations and was 15 µg TBT/kg in tissues collected from Carr Inlet. Juvenile mussels deployed at all 12 sites around Harbor Island, including Kellogg Island, exhibited significantly reduced growth relative to Carr Inlet; however, a range in reductions was observed [see excerpted tables from Salazar et al. (1994) in Appendix A.2].

Based upon the above analysis, it was recognized that the Harbor Island data could not be used to select a "no-effects" level; however, the use of the lowest tissue concentration associated with reduced growth (17 µg TBT/kg) was considered a body burden associated with a lower level of effects. This tissue concentration was then compared to mussel (*M. edulis*) tissue data from San Diego Bay to identify tissue and associated sediment concentrations at which potentially no or minimal impacts might be expected. Review of the data indicated that the range of tissue concentrations measured in San Diego Bay (28 to 1,513 µg TBT/kg) exceeded the lowest tissue concentration associated with reduced growth for Harbor Island; therefore, a sediment-based cleanup value could not be derived (see Appendix A.1, Table A-7).

3.6 SEDIMENT-WATER PARTITIONING

Research conducted by Meador et al. (1996) examined the bioavailability and thus the toxicity of TBT for three different invertebrate species (*Rhepoxynius abronius*, *Eohaustorius washingtonianus*, and *Armandia brevis*) by varying the organic carbon content and TBT concentrations in sediment for a series of bioassays of varying duration. TBT concentrations were measured in bulk sediment, interstitial water, and tissues at the termination of each test. Partitioning coefficients were calculated based on the TBT concentrations in sediment and interstitial water and the fraction of organic carbon present. Lethal concentrations and lethal doses causing mortality in 50 percent of the population (LC_{50} and LD_{50}, respectively), were calculated using a generalized linear model (Kerr and Meador, in press).

The results of this research indicate that the bioaccumulation and toxicity of TBT is strongly influenced by the amount of organic carbon in sediment (the more TOC, the less bioavailable TBT is). The main mechanism is based on the partitioning of TBT from sediment to interstitial water. Bulk sediment properties (such as the binding capacity of the clay minerals) may also strongly influence partitioning, but can be accounted for by the actual measurement of partitioning between matrices. An average sediment-water partitioning coefficient based on

carbon-normalized sediment (K_{oc}) was measured as 25,100 L/kg as part of Meador et al. (1996). The K_{oc} values ranged from 23,400 to 104,700 L/kg for TOC values ranging from 0.1 to 1.0 percent. This work, as with all equilibrium partitioning approaches, assumes that the chemical being evaluated is at (or near) equilibrium with respect to solids/water partitioning. Meador et al. reported that the average value was similar to that measured by Unger et al. (1988). This statement has been challenged by reviewers of the TBT Recommendations Report, while citing Unger's wide range of K_{oc}s and his statement that TOC is not a good predictor of TBT partitioning. However, Meador's conclusion was based on exclusion of Unger's freshwater sites and an anomalously low TOC value. Based on that evaluation, the average of the remaining K_{oc} values is similar to the average K_{oc} value reported by Meador et al.

EPA reviewed the literature to determine whether multiple K_{oc} values, rather than a single value, could be used in this approach. EPA found that there are currently too few data to support the use of multiple K_{oc} values. Uncertainties associated with use of a single K_{oc} value are described in Section 4.

3.6.1 Calculation of a Sediment Screening Value for TBT

The measured K_{oc} value of 25,100 L/kg (Meador et al., 1996) was used to calculate a marine sediment concentration that would be predictive of TBT concentrations associated with minor adverse effects. Concentrations known to cause adverse effects in water formed the starting point for this calculation.

The data reported in the literature for concentrations of TBT (ion) in water that cause deleterious effects to marine and estuarine organisms is large (see Fent, 1996; EPA, 1991; WHO, 1990). The range of reported values for acute toxicity is provided in Table 6, while chronic effects concentrations are presented in Table 7. A listing of effects data by species is provided in Appendix H. Reported data are based on total, not dissolved, concentrations of TBT. Concentrations causing effects with known implications to organism, population or community health range from 0.002 µg TBT/L to 204 µg TBT/L. The majority of the chronic effects usually occur at well below 1 µg TBT/L, while many acute effects to common marine organisms occur between 1 and 5 µg TBT/L.

Using these data and the sediment-water partitioning approach, EPA calculated a range of sediment screening values for use in sediment management decisions at Superfund sites (Table 8). [For reasons discussed in Section 4, EPA is not referring to these "screening values" as "cleanup levels.] EPA and the interagency work group selected 0.05 µg TBT/L as the basis for calculating a sediment concentration that was considered protective of most marine organisms and lifestages from most acute and chronic effects (Table 9). This value results in a lower sediment screening value of 1,255 µg TBT/kg OC. EPA further selected 0.7 µg TBT/L as the basis for calculating a sediment screening value for Superfund sites that was considered protective of many organisms from most acute and some chronic

Table 6—TBT Acute Toxicity Data by Effects Concentration

TBT µg/L	Acute Effects Species	Endpoint	Citation
0.285	Crassostrea gigas (Pacific oyster)	48-hr LC50	Battelle 1989
0.292	Mysid shrimp juveniles	96-hr LC50	Valkirs et al. 1987 (#350 in Fent 1996)
0.310	Crassostrea virginica juvenile (Atlantic oyster)	96-hr EC50 (shell growth)	U.S. EPA 1991
0.389	Acartia tonsa	6-day LC50	U'Ren 1983 (#342 in Fent 1996)
0.389	Marine diatoms	72-hr EC50	Walsh et al. 1985 (#340 in Fent 1996)
0.420	Acanthomysis sculpta juvenile (mysid)	96-hr LC50	U.S. EPA 1991
0.465	Dendraster sp. sperm cell (sand dollar)	1.3-hrs EC50 (Sperm cell fertilization)	Parametrix 1995
0.500	Eurytemora affinis subadult (copepod)	72-hr LC50	U.S. EPA 1991
0.500	Isognomon californicum embryo (bivalve)[a]	48-hr EC50 (Embryo development)	Ringwood 1992
0.500	Scorbicularia plana larvae	48-hr EC50	Ruiz et al. 1995
0.530	Eurytemora affinis subadults	72-hr LC50	Bushong et al. 1987 in WHO 1990
0.600	Eurytemora affinis subadult (copepod)	72-hr LC50	U.S. EPA 1991
0.610	Acanthomysis sculpta juvenile (mysid)	LC50	U.S. EPA 1991
0.630	Acartia tonsa	96-hr LC50	U'Ren 1983 in 1991 AWQC Table 1
0.710	Crassostrea virginica embryo (Atlantic oyster)	LC50	U.S. EPA 1991
0.770	Crassostrea virginica embryo (Atlantic oyster)	48-hr Abnormal shell development	U.S. EPA 1991
0.770	Mercenaria mercenaria larvae (hardshell clam)	48-hr Delayed development	U.S. EPA 1991
0.778	Onchorhynchus tshawytscha	96-hr LC50	Short and Thrower 1986 (#168 in Fent 1996)
0.860	Crassostrea gigas embryo (Pacific oyster)	24-hr Abnormal development	U.S. EPA 1991
0.876	Crassostrea virginica embryo (Atlantic oyster)	LC50	U.S. EPA 1991
0.900	Crassostrea gigas embryo (Pacific oyster)	24-hr Abnormal development	U.S. EPA 1991
0.970	Mytilus edulis larvae (blue mussel)	LC50	U.S. EPA 1991
0.973	Metamysidopsis elongata juvenile (mysid)	LC50	U.S. EPA 1991
0.979	Acartia tonsa	49-hr LC50	Bushong et al. 1987 in WHO 1990
0.979	Mercenaria mercenaria embryos	48-hr LC50	Roberts 1987 (#352 in Fent 1996)
0.979	Mysidopsis bahia	96-hr LC50	Goodman et al 1988 in WHO 1990
1.000	Mytilus edulis larvae (blue mussel)	96-hr Reduced survival	U.S. EPA 1991
1.100	Acartia tonsa	48-hr LC50	Bushong et al. 1988 (#343 in Fent 1996)
1.100	Mysidopsis bahia juvenile (mysid)	LC50	U.S. EPA 1991
1.130	Mercenaria mercenaria embryo (hardshell clam)	LC50	U.S. EPA 1991
1.160	Crassostrea virginica embryos	48-hr LC50	Roberts 1987 (#352 in Fent 1996)
1.160	Gammarus sp. young	96-hr LC50	Bushong et al. 1988 in WHO 1990
1.300	Crassostrea virginica embryo (Atlantic oyster)	LC50	U.S. EPA 1991
1.300	Gammarus sp. subadult (amphipod)	LC50	U.S. EPA 1991
1.360	Mytilus sp. (mussel)	LC50	Battelle 1989
1.400	Eurytemora affinis subadult (copepod)	LC50	U.S. EPA 1991
1.460	Crangon crangon larvae	96-hr LC50	Thain 1983 in WHO 1990
1.460	Oncorhynchus tshawytscha juvenile (Chinook salmon)	LC50	U.S. EPA 1991
1.470	Mercenaria mercenaria larvae	48-hr LC50	Roberts 1987 in WHO 1990
1.500	Eohaustorius estuarius (amphipod)	10-day LC50	Meador 1993
1.557	Crassostrea gigas larvae (Pacific oyster)	LC50	U.S. EPA 1991

Table 6—TBT Acute Toxicity Data by Effects Concentration

TBT µg/L	Acute Effects Species	Endpoint	Citation
1.600	Eohaustorius washingtonianus	10-day LC50	Meador et al. 1996
1.650	Mercenaria mercenaria larvae (hardshell clam)	LC50	U.S. EPA 1991
1.700	Eohaustorius estuarius (amphipod)	10-day EC50 (mortality + failure to rebury)	Meador et al.1993
1.745	Homarus americanus larvae (American lobster)	LC50	U.S. EPA 1991
1.800	Echinometra mathaei sperm cell (sea urchin)	1-hr EC50 (Sperm cell fertilization)	Ringwood 1992
1.877	Nitocra spinipes adult (copepod)	LC50	U.S. EPA 1991
1.946	Nitocra spinipes adult (copepod)	LC50	U.S. EPA 1991
1.960	Eurytemora affinis subadults	48-hr LC50	Hall et al. 1988 in WHO 1990
2.000	Eohaustorius estuarius	10-day LC50	Meador 1993 (#348 in Fent 1996)
2.000	Mysidopsis bahia juvenile (mysid)	LC50	U.S. EPA 1991
2.200	Eurytemora affinis juvenile (copepod)	LC50	U.S. EPA 1991
2.200	Mysidopsis bahia juvenile (mysid)	LC50	U.S. EPA 1991
2.238	Mytilus edulis larvae (blue mussel)	24-hr No effect on sister chromatid exchange	U.S. EPA 1991
2.315	Cyprinodon variegatus juvenile (sheepshead minnow)	LC50	U.S. EPA 1991
2.500	Eurytemora affinis subadult (copepod)	LC50	U.S. EPA 1991
2.581	Crassostrea gigas larvae (Pacific oyster)	48-hr 100% mortality	U.S. EPA 1991
3.000	Menidia beryllina larvae (Silverside)	96-hr LC50	U.S. EPA 1991
3.450	Onchorynchus mykiss	LC50	U.S. EPA 1991
3.520	Crassostrea virginica larvae	48-hr LC50	Roberts 1987 in WHO 1990
4.000	Isognomon californicum sperm cell (bivalve)[a]	1-hr EC50 (Sperm cell fertilization)	Ringwood 1992
4.070	Palaemonetes pugio larvae (grass shrimp)	96-hr LC50	Khan et al. 1993
4.304	Crassostrea gigas embryo (Pacific oyster)	24-hr Abnormal development, 30-40% mortality	U.S. EPA 1991
4.600	Armandia brevis	10-day LC50	Martin et al. 1989 (#249 in Fent 1996)
4.720	Gammarus sp. adult	96-hr LC50	Bushong et al. 1988 in WHO 1990
5.030	Arenicola cristata larvae (lugworm)	LC50	U.S. EPA 1991
5.200	Brevoortia tyrannus juvenile (Atlantic menhaden)	LC50	U.S. EPA 1991
6.300	Crangon crangon larvae	96-hr LC50	Thain 1983 in WHO 1990
6.812	Neanthes arenaceodentata juvenile (worm)	LC50	U.S. EPA 1991
8.900	Menidia menidia (Silverside)	LC50	U.S. EPA 1991
9.732	Carcinus maenas larvae (shore crab)	LC50	U.S. EPA 1991
10.000	Branchiostoma caribaeum (Amphioxis)	LC50	U.S. EPA 1991
12.310	Cyprinodon variegatus juvenile (sheepshead minnow)	LC50	U.S. EPA 1991
14.200	Rhepoxynius abronius (amphipod)	10-day EC50 (mortality + failure to rebury)	Meador et al.1993
14.600	Orchestia traskiana adult (amphipod)	LC50	U.S. EPA 1991
17.200	Fundulus heteroclitus juvenile (mummichog)	LC50	U.S. EPA 1991
18.500	Citharichthys sp. (speckled sanddab)	96-hr LC50	U.S. EPA 1991
19.400	Paleomonetes pugio subadult	96-hr LC50	Walsh 1986 in WHO 1990
22.300	Mytilus edulis larvae	48-hr LC50	Thain 1983 in WHO 1990
22.800	Rhepoxynius abronius (amphipod)	10-day LC50	Meador et al.1993
23.400	Fundulus heteroclitus adult (mummichog)	LC50	U.S. EPA 1991
23.800	Fundulus heteroclitus subadult (mummichog)	LC50	U.S. EPA 1991

Table 6—TBT Acute Toxicity Data by Effects Concentration

TBT µg/L	Acute Effects Species	Endpoint	Citation
25.900	Cyprinodon variegatus subadult (sheepshead minnow)	LC50	U.S. EPA 1991
28.000	Rhepoxynius abronius	10-day LC50	Meador et al. 1996
29.800	Rhepoxynius abronius (amphipod)	10-day LC50	Meador et al.1993
30.000	Palaemonetes pugio (grass shrimp)	20-min No avoidance	U.S. EPA 1991
31.000	Palaemonetes sp. subadult (grass shrimp)	LC50	U.S. EPA 1991
34.900	Rhithropanopeus harrisi larvae (mud crab)	LC50	U.S. EPA 1991
36.900	Mytilus edulis adults	96-hr LC50	Thain 1983 in WHO 1990
51.000	Rhepoxynius abronius (amphipod)	4-day LC50	Meador 1993
72.740	Nucella lapillus juvenile (snail)	96-hr LC50	Harding et al. 1995
83.280	Hemigrapsus nudus larvae (shore crab)	LC50	U.S. EPA 1991
138.000	Rhepoxynius abronius (amphipod)	4-day LC50	Meador 1993
173.000	Rhepoxynius abronius (amphipod)	4-day LC50	Meador 1993
204.000	Ostrea edulis adults	96-hr LC50	Thain 1993 in WHO 1990
57.52	95th percentile		
9.87	75th percentile		
1.95	Median		
0.98	25th percentile		
0.69	15th percentile (14.6)		
0.41	5th percentile		

Table 7—TBT Chronic Toxicity Data by Effects Concentration

TBT µg/L	Non-Mortality Chronic Effects Species	Endpoint	Citation
0.002	Nucella spp. (dog whelk snail)	Sterilization	Bryan et al. 1986 and Gibbs et al.1988 (#21 and #24 in Fent 1996)
0.010	Acartia tonsa (copepod)	5-day reduced egg production	U.S. EPA 1991
>0.010	Mercenaria mercenaria (hardshell clam)	14-day reduced growth	U.S. EPA 1991
0.016	Nucella lapillus (snail)	MATC (egg capsule production)(17 months)	Harding et al. 1995
0.017	Mytilus edulis larvae (mussel)	25-day growth	Lapota et al. 1993 (#355 in Fent 1996)
0.019	Ostrea edulis (European flat oyster)	20-day significant reduction in growth	U.S. EPA 1991
0.020	Crassostrea gigas (oyster)	48-day reduced growth	U.S. EPA 1991
0.020	Ostrea edulis (European flat oyster)	Decreased weight (20 days, lowest conc. tested)	Thain and Waldock 1985
0.020	Ostrea sp. spat (flat oyster)	Reduced growth	Thain and Waldock 1983
0.023	Crassostrea gigas (oyster)	Reduced number of normal larvae (21 days)	U.S. EPA 1991
0.050	Crassostrea gigas (oyster)	14-day reduced O2 consumption and feeding rates	U.S. EPA 1991
0.070	Mytilus edulis (mussel)	Reduced growth (196 days)	U.S. EPA 1991
0.090	Menidia beryllina larvae (Silverside)	28-day growth	Hall et al. 1988 (#378 in Fent 1996)
0.093	Menidia beryllina (Silverside)	28-day reduced growth	U.S. EPA 1991
0.097	Marine diatoms	Growth	Beaumont and Newman 1986 (#341 in Fent 1996)
0.097	Mytilus edulis (mussel)	51% mortality, reduced growth (15 days)	U.S. EPA 1991
0.100	Crassostrea virginica (oyster)	Decrease in condition index (57 days)	U.S. EPA 1991
0.100	Neanthes arenaceodentata (worm)	10-week growth (TBT introduced in food slurry)	Moore et al.1991
0.100	Ophioderma brevispina (brittle star)	Retarded arm generation (28 days)	U.S. EPA 1991
0.130	Algae	Reduction in photosynthesis	Extrapolated from Cardwell and Meador 1989 Figure 2
0.131	Acanthomysis sculpta (mysid)	MATC (Reproduction)	U.S. EPA 1991
0.142	Crassostrea gigas spat (oyster)	Reduced growth (56 day)	Waldock and Thain 1993 (in 1991 AWQC Table 6)
0.157	Mytilus edulis (mussel)	Reduced condition (56 days)	U.S. EPA 1991
0.180	Onchorynchus mykiss embryo, larvae (salmonid)	110-day reduced growth	U.S. EPA 1991
0.200	Crassostrea gigas (oyster)	30% mortality, abnormal development (113 days)	U.S. EPA 1991
0.200	Mytilus edulis juvenile (mussel)	7 to 14-day reduced growth (field study)	U.S. EPA 1991
0.239	Ostrea edulis (European flat oyster)	Decreased growth (45 days)	U.S. EPA 1991
0.240	Crassostrea gigas (oyster)	45-day 40% mortality, reduced growth	U.S. EPA 1991
0.240	Mytilus edulis (mussel)	Significant reduction in growth (45 days)	U.S. EPA 1991
0.240	Ostrea edulis (European flat oyster)	Complete inhibition of larval production (75 days)	U.S. EPA 1991
0.240	Ostrea edulis (European flat oyster)	Retardation of sex change (75 days)	U.S. EPA 1991
0.250	Crassostrea gigas, Mytilus edulis, Venerupis decussata	Growth	Thain 1986 (#17 in Fent 1996)
0.292	Gammarus oceanus (amphipod)	8-week reduced survival and growth	U.S. EPA 1991
0.310	Mytilus edulis (mussel)	66-day significant reduction in shell growth	U.S. EPA 1991
0.389	Mytilus edulis (mussel)	7-day significant reduction in growth	U.S. EPA 1991
0.500	Menidia beryllina larvae (Silverside)	28-day growth	Hall et al. 1988 (#378 in Fent 1996)
0.500	Uca pugilator (fiddler crab)	Retarded limb regeneration and molting (<24 days)	U.S. EPA 1991
0.500	Uca pugilator (fiddler crab)	Reduced burrowing (21 days)	U.S. EPA 1991
0.500	Uca pugilator (fiddler crab)	Limb malformation (7 days)	U.S. EPA 1991
0.584	Onchorynchus mykiss adult (salmonid)	Immune function depression	Schwaiger et al. 1992 (#377 in Fent 1996)
0.600	Fucus sp. (brown algae)	Community primary productivity	U.S. EPA 1991

Table 7—TBT Chronic Toxicity Data by Effects Concentration

TBT µg/L	Non-Mortality Chronic Effects Species	Endpoint	Citation
0.600	Mercenaria mercenaria (hardshell clam)	35% mortality, reduced growth (8 days)	U.S. EPA 1991
0.730	Crassostrea gigas embryos/spat (oyster)	Body weight	Valkirs et al. 1987 (#350 in Fent 1996)
0.730	Crassostrea virginica (oyster)	Decrease in body weight (67 days)	U.S. EPA 1991
0.890	Onchorynchus mykiss embryo, larvae (salmonid)	110-day reduced growth and mortality	U.S. EPA 1991
2.600	Ostrea edulis (European flat oyster)	Prevention of gonadal development (75 days)	U.S. EPA 1991
14.200	Rhithropanopeus harrisii larvae (crab)	11-day reduced growth	Laughlin et al. 1983
14.600	Rhithropanopeus harrisii (mud crab)	Reduced development and growth (15 days)	U.S. EPA 1991
18.950	Rhithropanopeus harrisii (mud crab)	Reduced development and growth (15 days)	U.S. EPA 1991
30.000	Fundulus heteroclitus (mummichog)	Teratotogy (10 days)	U.S. EPA 1991
74.000	Leuresthes tenuis (California grunion)	50% reduction in hatching success (10 days)	U.S. EPA 1991
165.006	SUM		
16.99	95th percentile		
0.70	82nd percentile		
0.54	75th percentile		
0.22	Median		
0.09	25th percentile		
0.05	18th percentile		
0.02	5th percentile		

MATC = Geometric mean of the acute LOEL and LOEC

effects (Table 9). (The use of this higher screening value at Superfund sites was generally supported by the interagency work group, except that NOAA only concurred with the use of the lower screening value.) Based on reported scientific research data (see Tables 6 and 7), this higher value would protect a large number of adult organisms from diverse phyla (mollusks, crustaceans, polychaetes and fishes) as well as several sensitive lifestages (larval or juvenile forms) of important aquatic resources including oysters, mussels and salmonids. This higher value would not be considered protective of effects on certain life stages of more sensitive organisms (e.g., oyster spat, mussel larvae), including organisms considered salmonid prey species (e.g., mysid shrimp). This water concentration results in a sediment screening value of 17,570 µg TBT/kg OC. It is understood that at Superfund sites, EPA will select a site-specific cleanup level that is protective of human health and the environment based on an analysis of EPA's nine evaluation criteria set forth in the National Contingency Plan (NCP)(40 CFR 300.43).

At this time, EPA has only selected a site-specific cleanup level for the Hylebos Waterway (EPA, 1996a, b). EPA determined that the cleanup level for TBT in the Hylebos Waterway will be a sediment concentration of 17,570 µg TBT/kg OC, or an interstitial water concentration of 0.7 µg TBT/L. Given the low number of stations exceeding the TBT cleanup level, and the co-occurrence of TBT "hits" with other elevated contaminants, it is unlikely that TBT will alter cleanup decisions. However, in those few cases where TBT concentrations in bulk sediment were near the cleanup level, the Hylebos Cleanup Committee (HCC) has elected to conducted interstitial water sampling to confirm the predicted exceedance. Neither sediment nor interstitial water TBT screening values have been selected for other Superfund sites. For general information, existing sediment data for the Thea Foss/Wheeler-Osgood waterways (see Table A-2) show that 4 of 27 stations are below the lower sediment screening value of 1,255 µg TBT/kg OC, and all stations are below the higher sediment screening value of 17,000 µg TBT/kg OC (maximum concentration of 11,000 µg TBT/kg OC). For Harbor Island (see Table A-3), existing sediment data show that all stations are higher than the lower screening value, and 31 of 35 stations are higher than the higher screening value. Final screening levels for these projects have not been selected yet.

The interagency work group recognized the uncertainties in the approach described above and has identified additional work that is needed to refine the screening for use in Puget Sound sediment management programs. This additional work is described in Sections 4 and 5 of this report.

Table 8—Range of Potential TBT Sediment Screening Values Based on Effects Concentrations in Water

Water Concentration Associated with Impacts (µg TBT/L)	Estimated Protective Sediment Concentration (µg TBT/kg OC)	Endpoint Addressed by Sediment Concentration
0.01	251	EPA draft proposed chronic water quality criterion
0.05	***1,255***	***18th percentile for chronic effects, Lower Screening Value***
0.09	2,259	25th percentile for chronic effects
0.22	5,522	Median value for chronic effects
0.36	9,036	EPA draft proposed acute water quality criterion
0.41	10,291	5th percentile for acute effects
0.54	13,544	75th percentile for chronic effects
0.70	***17,570***	***82nd percentile for chronic effects, 15th percentile for acute effects, Higher Screening Value***
0.98	24,598	25th percentile for acute effects
1.95	48,945	Median value for acute effects
9.87	247,737	75th percentile for acute effects

Table 9—TBT Screening Values Selected for Sediments at Superfund Sites in Puget Sound

Screening Value	Interstitial Water Concentration[a] (µg TBT/L)	Sediment Concentration[b] (µg TBT/kg OC)
Lower Screening Value	0.05	1,255
Higher Screening Value	0.70	17,570

[a] Interstitial water is porewater extracted from whole sediments.

[b] Assuming 2 percent TOC, the lower screening value is approximately equivalent to 25.1 µg TBT/kg (dry weight) and the higher screening value is equivalent to 351 µg TBT/kg (dry weight). However, this document recommends use of the TOC-normalized value (see Section 3.6 for further information). Bulk sediment analyses quantify both the TBT concentrations in the porewater and the sediments.

SECTION 4

DISCUSSION

Efforts to correlate TBT concentrations in sediment to significant deleterious biological effects were generally not successful and precluded the ability to calculate a cleanup level using methods applied to other chemicals of concern in Puget Sound programs, including calculation of an AET value. Specifically, although data from more than 50 stations were available to calculate an AET value and these data represented a range of sediment TBT concentrations, a relationship between biological response and bulk sediment TBT concentrations was not observed. In brief, the lack of strong correlations between sediment concentrations and observed effects is likely related to several factors:

- Bulk sediment concentrations may be a poor predictor of the bioavailable fraction of a contaminant because of the complex partitioning behavior of TBT. Under equilibrium conditions, the most important pathway for contaminant uptake by a sediment-dwelling organism is likely to be through interstitial water (i.e., pore water extracted from bulk sediments). Although sediment ingestion can also be a route of exposure, it is expected to be less important at the community level.

- TBT is introduced into the environment in a variety of phases and formulations including dissolved "leachate" from boat hulls painted with TBT (some of which adsorbs to sediment) and solid wastes such as paint chips and paint dust in sand-blast grit. These different forms appear to have widely different bioavailabilities, based on bioaccumulation studies.

- Environmental factors such as salinity, pH, organic carbon, and sorption capacity of the sediment strongly influence the form and fate of TBT in aquatic environments and thus its bioavailability.

- Several of the bioassay species (*Rhepoxynius abronius, Neanthes arenaceodentata*) commonly used in effects tests appear to be insensitive to TBT. This is due, in part, to their greater capacity (compared to other, more sensitive species) to eliminate TBT through metabolic processes. Furthermore, the duration of tests (10-day exposure for amphipods and 48- to 96-hour exposure for molluscan larvae or echinoderm embryos) used in various Puget Sound sediment management programs may provide inadequate exposure for more sensitive species (i.e., species exhibiting greater effects with less exposure).

The observed lack of relationship between sediment TBT concentrations and biological responses (i.e., increasing chemical concentrations do not appear to be associated with increasing biological effects) does not meet one of the general assumptions for generating

AET values. This lack of correlation between bulk sediment concentrations of TBT and adverse biological effects has been reported by other investigators. In the National Monitoring Program, Parametrix (1995) indicated that significant correlations between bulk sediment concentrations and toxicity have not been identified. For these reasons, EPA believes that further work to derive an AET or other sediment effects concentration for TBT may not be successful. EPA further believes that interstitial water measurements of TBT and biological testing more accurately assess the bioavailability of TBT.

The sediment-water partitioning approach applied to the calculation of sediment screening levels for TBT deserves a discussion of some of the caveats that may affect its application at sites where TBT is a contaminant of concern. First, use of a partitioning approach assumes that the main route of exposure for organisms is via TBT dissolved in water, rather than ingestion as the primary pathway. While ingestion may be an important route for some infaunal organisms, many of the species tested have greater exposure via water. In addition, a criterion based on the chemical concentration in water will generally protect for dietary exposure if the water (in this case, interstitial water) and bulk sediment concentration are in equilibrium (Di Toro et al., 1991).

The partitioning approach further assumes a large database is available for development of water quality criteria. While this is true for TBT effects in water, the data that provide the basis for selecting a TBT screening value are from many different studies of varying age and quality. An attempt was made to address data quality by primarily using those data that were deemed of acceptable quality in the EPA 1991 water quality criteria document for TBT. Also, the use of water column species as a surrogate for benthic organisms has some uncertainty associated with it. However, Hansen (1996) and Di Toro et al. (1991) have demonstrated that benthic organisms are equivalent in sensitivity to toxicants as water column organisms. Finally, the water quality effects data summarized in Tables 6 and 7 include species that are not resident to Puget Sound, and data are not available for some sensitive life stages of organisms. To address this issue, in part, all endpoints that were based on mortality alone were excluded from the compilation of chronic effects levels in Table 7.

Also, as implied by its name, the equilibrium partitioning approach assumes that the chemical being evaluated is at (or near) equilibrium with respect to solids/water partitioning. This assumption may not be met in physically disturbed sediments or sediments that aren't continually saturated by water (e.g., intertidal sediments). Other environmental factors also affect equilibrium. TBT is a speciating compound, and the different forms it takes in seawater are determined by interactions of a number of variables, which, in turn, have a large influence on TBT bioavailability. As an example, changes in pH have a marked effect on TBT speciation and can result in forms being charged or not. As a general rule, charged organic molecules do not dissolve into natural organic material (e.g., lipids), whereas neutral forms do. The equilibrium of TBT speciation products is reported to be very sensitive to displacement by small changes in salinity within the environmental range (Laughlin et al., 1986). If there is much variation in salinity among porewaters it seems likely this will affect

bioavailability by altering the relative proportions of bioavailable species of TBT. In addition, salinity affects the partitioning of TBT, which further complicates assessing potential bioavailability.

The research conducted by Meador et al. (1996) was based on laboratory studies, with all the inherent problems regarding extrapolation to the natural environment that laboratory studies face. In addition, the range of TOC used in the experimental design (less than 1 percent TOC) only encompassed the lower range of TOC found in Puget Sound. Although the effects of higher TOC (> 1 percent) on partitioning of TBT could be extrapolated from this experimental range (and should be similar), the actual outcome is unknown at this time.

There are uncertainties associated with the use of a single K_{oc} value in the sediment-water partitioning approach to estimate interstitial water TBT concentrations. Statistical analyses of existing data sets suggest that there is not a strong correlation between sediment TBT concentrations and TOC, and the laboratory-derived K_{oc} value selected in this report has not been field validated. Options for addressing this concern are described in Section 5.

One other issue to be considered is that the form of TBT in sediment (i.e., TBT in paint chips or paint dust versus TBT adsorbed to sediment) is likely to affect the dissolution of TBT from solids to water, and thus affects the bioavailability of TBT. TBT bound in paint chips may be less bioavailable than TBT bound to sediment particles because this compound must first diffuse from within the paint chip before desorbing to water, whereas TBT-sorbed to a sediment particle is readily exposed to water. Average TBT concentrations collected in sediment from shipyards and harbors as part of the National TBT Study (Parametrix, 1995) was reported to be higher than TBT concentrations in sediments from marinas, yet mussel tissue concentrations were higher in marinas compared to shipyards, thus suggesting differential bioavailability based on TBT form. These data also suggest that TBT in paint chips continues to function as originally designed and contributes to either interstitial or overlying water column TBT contamination by leaching. However, there are no studies that definitively show that TBT-containing paint chips deposited in sediments continue to leach TBT to either interstitial water or the overlying water column. It is interesting to note that as part of the National TBT Study (Parametrix, 1995), paint chips were never "visually observed" in any sediment samples (except possibly one case), and results of laboratory studies (as well as an inventory of numerous laboratories across the country) indicated that it was not possible to analytically determine whether TBT-containing paint chips are present in sediments. Furthermore, EVS (Johns, 1996b) indicated that as part of their Harbor Island Supplemental RI work, they were also unable to identify the presence of paint chips in sediments. Analyses of these same sediments with different solvents (e.g., methylene chloride, hexane, and seawater) resulted in a wide a wide range in TBT concentrations extracted from sediments, suggesting that paint chips may be present when higher concentrations were detected using stronger solvents. Dowson et al. (1992) reported that wet sieving of high TBT-contaminated sediments has revealed visible paint flakes in the past.

Disturbance of the sea bed by either physical or biological activity may serve to re-expose paint chips or paint dust and increase TBT releases. In a recent study, Page et al. (1996) reported results from elutriate tests that were performed to estimate the extent to which resuspension of TBT-contaminated sediments at two shipyard sites would introduce TBT into the water column. Page et al. reported that only 0.14 percent of the potentially available TBT in the sediments was released to the water, and suggested that this indicated that the sediments likely contained fine particles of antifouling paint residue. Where TBT is present as TBT-containing paint residue, Page et al. suggests that the release of TBT to the water column would not be governed by water solubility, but by the leaching rate of TBT from the paint matrix.

The approach presented in this report supports a range of TBT cleanup levels for sediment, and does not specifically address waste materials (e.g., sand-blast grit mixed with TBT-containing paint chips). A project-specific evaluation of sediment-to-water partitioning should be considered where paint chips or TBT-contaminated sand-blast grit are found[1].

For the aforementioned reasons, EPA has determined that at this time a marine sediment cleanup level for TBT cannot be defined. Instead, EPA believes that a range of sediment screening values for TBT can be established using the sediment-water partitioning approach, and a range of interstitial water screening values for TBT can be established using published chronic and acute water quality effects data. The range of screening values allows for the site-specific selection of a screening value (for either sediment or interstitial water, or both) based on the protectiveness that is considered appropriate for the given sediment management decision. Recommendations for biological effects and bioaccumulation testing (which might be performed if an interstitial water screening value is exceeded) and for defining cleanup actions where TBT is a contaminant of concern in sediments are further described in Section 5. As previously stated, EPA will select site-specific cleanup levels for TBT based on the criteria set forth in the NCP (40 CFR 300.43).

Finally, for your information, it is noted that the PSDDA program and Ecology Sediment Management program are using information prepared as part of this work group to propose modifications to the PSDDA and SMS programs. These proposals were presented as part of the Annual Review Meeting on 8 May 1996 (Michelsen et al., 1996), and the agencies are currently preparing a response to public comments received on those proposals. Currently, PSDDA and SMS programs believe that the existing PSDDA screening level (SL) of 30 µg TBT/kg (as tin) is protective of acute and chronic effects without being overly conservative. Using the sediment-water partitioning approach and the Meador et al. (1996) K_{oc} of 25,000 L/kg, and assuming 2 percent TOC, the PSDDA SL of 30 µg Sn/kg (73 ug TBT/kg)

[1] It is recognized that grit and paint chips may be cleaned up based on a policy decision not to allow waste materials in aquatic environments, because they represent a continuing, long-term source to the marine environment and are an inappropriate substrate for healthy benthic communities.

corresponds to an interstitial water concentration of 0.15 µg/L TBT (Michelsen et al., 1996). Also, the use of the existing PSDDA bioaccumulation trigger of 219 µg TBT/kg (as tin) is likely to be revised downward. In a recent Port of Seattle sediment characterization project for PSDDA, bulk sediment TBT were initially analyzed and interstitial water TBT concentrations were then calculated using the sediment-water partitioning approach. For the 15 samples that exceeded the proposed SL of 0.15 µg/L TBT, archived sediment was used to collect interstitial water for TBT analysis (Johns, 1996a). When measured directly, all interstitial water TBT concentrations were lower than was predicted by the sediment-water partitioning calculation. However, with the exception of several outliers, the relationship between predicted versus actual interstitial water concentrations appeared to be consistent. The measured interstitial water TBT concentrations in 2 of 15 samples exceeded the proposed SL of 0.15 µg/L TBT. There are uncertainties associated with this data interpretation, including issues regarding the use of archived sediments and the analytical method; therefore, these results are not considered a definitive test of the predictiveness of the recommended screening levels. However, based on this preliminary case, the proposed screening levels for bulk sediment appear to be sufficiently protective of organisms exposed to interstitial water.

Regarding human health issues, the Agency for Toxic Substances and Disease Registry (ATSDR, 1996) believes that the screening values and recommendations in this report are sufficient to protect public health. While recognizing that there are uncertainties about the consequences of chronic human exposure to low levels of organotin compounds, the scientific literature on TBT reviewed by ATSDR supports the concept that marine life are a more sensitive environmental endpoint than humans for the Commencement Bay Nearshore/Tideflats and Harbor Island Superfund sites.

SECTION 5

RECOMMENDATIONS

The following approach is recommended for defining cleanup actions where TBT is a contaminant of concern in sediment based on detected concentrations in the bulk sediment. This approach assumes that bulk sediment data have already been collected and analyzed for TBT (see recommendations below if TBT sediment data have not yet been collected). These recommendations attempt to address some of the uncertainties in application of a sediment screening value, as discussed in the prior section.

- Screen existing bulk surface sediment chemistry data using a site-specific value selected from within the range of the proposed TBT sediment screening values. (Bulk sediment concentrations refer to the concentration of TBT adsorbed to sediment particles and also incorporate TBT concentrations in interstitial water). If the site-specific sediment screening value is exceeded, it is recommended that the following step be implemented (if sediment TBT data have not already been collected, it is recommended that instead of collecting sediment data the following step be implemented):

- Collect sediment at those stations or areas that exceeded the site-specific TBT sediment screening value, and measure interstitial water (IW) concentrations of TBT. (Interstitial water is pore water extracted from bulk sediments). If the concentrations of TBT in IW exceed the level selected by the agency (between 0.05 µg TBT/L and 0.7 µg TBT/L), the project proponent or the agency may choose to include the areas defined by a TBT exceedance in existing cleanup areas, or conduct the following step:

- Conduct toxicity testing (e.g., bioassays), and/or bioaccumulation testing in conjunction with a sublethal effects endpoint, to confirm the ecological significance of the interstitial water TBT concentrations.

In reviewing these recommendations, it is important to recognize that EPA developed sediment TBT screening values because an extensive bulk sediment TBT data set had already been collected at three Superfund sites. In order to move forward with remedial design and remedial action at these Superfund sites, and recognizing that there were no state or federal sediment criteria for TBT, it was necessary for EPA to develop sediment screening values for evaluating these TBT sediment data.

To clarify how the sediment TBT screening values will be used at each of the three Superfund sites referenced in this report, EPA will compare the existing bulk sediment TBT data to a site-specific TBT screening value, which will be selected by the EPA site manager

and will range from the lower (1,255 µg TBT/kg OC) to the higher (17,570 µg TBT/kg OC) sediment screening value. At Superfund sites, EPA will select a site-specific screening value that is protective of human health and the environment based on an analysis of EPA's nine evaluation criteria set forth in the NCP (40 CFR 300.43).

No further action will be required for TBT-contaminated sediments that are below the site-specific screening value (i.e., these sediments are "screened out" and do not need to be cleaned up or further evaluated). For those TBT-contaminated sediments that are above the site-specific sediment screening value, EPA will recommend that additional testing be performed (i.e., these sediments are "screened in" for further analysis). In general, this additional testing will include interstitial water analyses for TBT, and as appropriate, may include biological testing (e.g., bioassays, bioaccumulation). As required under Superfund, if sensitive habitats or resources are present (or near) a contaminated sediment area, additional consideration of the protection of those resources will be given. This tiered approach is consistent with EPA's overall contaminated sediment strategy, which uses sediment chemical concentrations as a first step, and uses subsequent biological testing for confirming sediment risks. However, this general approach may be modified, as appropriate, for each Superfund site. For example, if sediments exceeding the TBT screening value co-occur with sediments that have already been earmarked for cleanup, additional testing may not be necessary because a sediment cleanup decision has been made based on other sediment contaminants.

Because of the uncertainties associated with development and application of sediment screening values based on sediment-water partitioning (see Section 4 of the report), and because research results strongly suggest that bioavailable TBT (when water and sediments are in equilibrium) is primarily associated with interstitial water (not the sediments), it is strongly recommended that sediment cleanup decisions at sites be based on TBT concentrations in interstitial water (and results of any subsequent biological effects testing) rather than relying on the bulk sediment screening effort. Evaluating bulk sediment using the recommended screening values may be a highly conservative approach, as indicated by the Port of Seattle results (Johns, 1996a). Direct measurement of interstitial water should more accurately reflect TBT concentrations of concern to biota; biological testing would assist in confirming the ecological impacts associated with the interstitial water concentration.

To support sediment characterizations based on measurements of TBT in interstitial water and results of biological effects testing specific to TBT, additional work will be required by Puget Sound sediment management programs and regulatory agencies. Specifically, the following protocols and guidance need to be developed:

- Protocol for collection and handling of intertidal sediment, to address the uncertainty regarding whether or not intertidal sediments and interstitial water are in equilibrium. An approach was proposed for use in the Hylebos Waterway that could form the basis of the protocol and initial agency review. Briefly, the intertidal sample

collection protocol included an extended holding time (5 days) prior to interstitial water extraction to allow sediments and interstitial water to reach equilibrium.

- Protocol for field collection and analysis of TBT in interstitial water to address concerns including centrifugation (extraction via centrifugation will disrupt equilibrium and result in values that may not be representative of actual exposure concentrations in the field), filtering (should filtration be done; is a 0.45µm filter adequate; is <0.45µm filter too "state of the art"; how important are the colloidal particles?), and to develop a protocol that is reasonable and implementable by a diverse group of sampling personnel and laboratories.

- Protocol for biological effects tests that address the mechanisms of TBT toxicity. It is recommended that interstitial water bioassays using bivalve larvae or echinoderm sperm be evaluated. Both of these bioassay protocols are well documented and can address some of the issues with respect to the primary exposure pathway of TBT (considered to be water), the length of exposure necessary to achieve steady-state (it is likely that an interstitial water bioassay would be minimally effected by repartitioning processes, if ambient salinities, pH, and temperature are maintained), and the ease of sample collection (interstitial water bioassays require minimal sample volumes). Other recommendations include re-evaluating the current bulk sediment test species and test durations for their potential adaptation for use in measuring TBT effects.

- Protocol for *in situ* or laboratory bioaccumulation testing. Any bioaccumulation test protocols should consider concurrent measurement of a sublethal effects endpoint, such as growth or reproductive impairment, so that the significance of TBT concentrations in the organism's tissue can be assessed. Further, all tests must reflect exposure via bedded sediment (i.e., tests based on water column exposures are considered unacceptable). In addition, species selected for testing must not readily eliminate TBT (e.g., fish tend to break down TBT within several weeks, and thus may not be good candidate test species). Some investigators (Salazar, 1996) recommend 60-day laboratory exposures with *Macoma nasuta* to assess the potential for bioaccumulation (using tissue and shell growth as effects endpoints) from TBT-contaminated sediments, and recommend use of bioaccumulation in field-collected samples (either natural populations or caged experiments) to establish relationships between tissue residues and effects levels in laboratory experiments and natural populations. This information could also be used to develop site-specific biota-sediment accumulation factors.

The development of protocols or guidance for biological effects testing of TBT must be coordinated with ongoing regulatory efforts, including recommendations set forth under the PSDDA and SMS programs.

It is important to note that the interagency work group supported EPA's recommendation that any future sediment sampling efforts that are designed to evaluate TBT contamination should require collection and analysis of interstitial water for TBT, rather than the collection and analysis of bulk sediments for TBT. However, it is recognized that under certain conditions (e.g., for research purposes or for purposes of collecting information to support an AET calculation), it might be useful to collect synoptic data sets (sediment chemistry, bioassays, benthic infauna) that include bulk sediment TBT data. If a sediment characterization effort only requires bulk sediment data analyses (and not biological testing), then only interstitial water TBT analyses (and not bulk TBT sediment analyses) should be used for decision-making.

If it is desired by agencies or project proponents to continue using the equilibrium approach to predict interstitial water concentrations from bulk sediment TBT concentrations, additional recommendations are provided in order to improve the predictiveness of any resulting sediment screening level:

- As interstitial TBT data are collected at the existing Superfund sites referenced in this report, the degree of conservatism afforded by the recommended screening levels should be examined.

- Based on the uncertainties associated with using a single K_{oc} value in the sediment-water partitioning approach to estimate interstitial water TBT concentrations, consideration could be given to obtaining actual K_{oc} measurements for specific sites being investigated. This would involve collection of interstitial water, bulk sediment, and organic carbon data in representative areas of the site.

- Because of the complexity in TBT partitioning, consider collection of sediment grainsize data along with TOC to assist in refining the assumptions regarding partitioning of TBT in sediments.

- Partitioning coefficients could be measured over a range of sediment conditions in Puget Sound to develop linear isotherms rather than using single-point partitioning coefficients to predict interstitial water, because of the complex relationships among mineral surfaces, organic material, and TBT adsorption/desorption. This consideration is based in part on comment from Kram et al. (1989) who stated that it is "unwise to overgeneralize about partitioning properties of sediments with respect to butyltin. Physical and chemical properties operating in one region may not be applicable to others." However, this type of study would necessitate the coordination and approval of appropriate study methods, and the collection of extensive synoptic bulk sediment and interstitial water data from areas with different sediment types and organic content (and without paint chips, which would confound results).

- Another approach that may be used is a spiked sediment laboratory study, using site-specific sediment to calculate partitioning coefficients.

SECTION 6

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