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Determination of a tissue and sediment threshold for tributyltin to protect prey species of juvenile salmonids listed under the US Endangered Species Act

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ABSTRACT

1. The purpose of this report is to determine the concentrations of tributyltin in sediments that would be protective against adverse effects on prey species of salmonids listed under the US Endangered Species Act.
2. Two approaches for determining adverse sediment concentrations due to tributyltin (TBT) contamination are presented here. The first is the equilibrium partitioning (EqP) approach, which relies on a sediment-water partition coefficient and toxicological data for water exposures. The EqP approach utilizes the large water quality database that has been generated over the last two decades for TBT and provides strong evidence for adverse effects at low exposure concentrations.
3. The second approach involves determination of a TBT tissue residue that is considered harmful for most species, which is then used to predict the sediment concentration that would likely produce this adverse tissue concentration.
4. Both approaches are presented here because they generally support each other but based on the information presented below, and the inherent difficulty in measuring porewater concentrations, the tissue residue approach is the recommended method for determining adverse sediment concentrations.
5. Using this analysis, the protective sediment concentration for TBT proposed here is 6000 ng g^{-1} organic carbon. Direct effects are not expected on salmonids at this sediment concentration because of their relatively short residence time in the estuary, general lack of interaction with sediment, and relatively high metabolic capacity. This concentration may ensure adequate abundance of salmonid prey species; however, it may not be low enough for the protection of sensitive benthic species.
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KEY WORDS: tributyltin; endangered species; salmon; prey; sediment; toxicity threshold

INTRODUCTION AND BACKGROUND

The National Marine Fisheries Service has authority under the US Endangered Species Act (ESA) to protect listed salmonid species and their prey from any adverse actions that may jeopardize the

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population's ability to recover and increase to sustainable levels. Species such as the chinook salmon (*Oncorhynchus tshawytscha*) can spend several weeks feeding on the normally abundant invertebrate populations in the estuarine environment during their physiological adjustment from freshwater to marine water (Thorpe, 1994). Some of these listed salmonid species in the Northwest United States travel through urban areas in their migration and they depend on these areas for an abundant supply of prey. The concern is that contaminants are bioaccumulated by salmon and their prey to levels that may directly or indirectly alter the ability of individual salmon to grow and mature normally. The intent of this paper is to provide a framework for determining the tissue and sediment concentrations of tributyltin (TBT) that will protect invertebrate species from severe adverse sublethal effects and decreased abundance. A reduction in invertebrate populations in the estuary would indirectly affect listed salmonid species by providing less food needed for growth. Salmon generally grow rapidly in the estuary, which is presumably due to abundant invertebrate food sources (Higgs *et al.*, 1995; Weatherley and Gill, 1995). Juvenile salmon in estuaries of the Pacific northwest commonly feed on amphipods, mysids, copepods, cladocerans, decapod larvae, fish, and insects (Higgs *et al.*, 1995). Many of these prey are epibenthic and are among the more sensitive taxa to tributyltin exposure (Cardwell and Meador, 1989).

This analysis focused on salmonid prey species, specifically benthic invertebrates. Salmonids migrating through the estuary are expected to respond to higher TBT sediment concentrations than those for invertebrates, primarily due to their reduced exposure to sediment, relatively short residence time, relatively high metabolism, and the general lack of biomagnification from one trophic level to the next. However, it should be noted that fish species can also exhibit adverse effects at low exposure concentrations. Fish larvae are very sensitive to TBT and often exhibit effects in the $0.5\,\mathrm{ng\,ml^{-1}}$ range (Fent, 1996). One recent study found that a flounder (*Platichthys flesus*) exposed to low concentrations of TBT in sediment ($150\,\mathrm{ng\,g^{-1}}$) exhibited significantly lower blood osmolality than control fish (Hartl *et al.*, 2000). This reduction was likely caused by a reduced ability to osmoregulate as a consequence of TBT's well-known action on ATPase (Aldridge, 1976; Fent, 1996). Because very little research has been conducted on the response of juvenile fish to TBT exposure, the above assumptions regarding their sensitivity may be altered in light of new information.

Because there is a general lack of sediment quality criteria or guidelines for tributyltin, there is a need to characterize this compound's potential to cause ecologically significant effects to organisms living in proximity to contaminated sediment. The following sections examine the basic properties, environmental partitioning behaviour, and toxicity for tributyltin. By understanding these properties and chemical behaviour, predictions can be made regarding the expected amount that is bioaccumulated and the resulting toxicity. Two approaches for generating sediment quality guidelines (SQG) are presented. One uses equilibrium partitioning to predict sediment concentrations based on sediment–water partitioning and the other uses the critical body residue approach which relates adverse tissue concentrations to sediment concentrations via bioaccumulation factors. Background information is provided on both approaches below. Following that is a section that utilizes these methods to predict adverse sediment concentrations.

Properties

TBT is an organometallic compound that exhibits the properties of both a metal and an organic compound. This compound is ionizable and it exhibits a pK_a acidity constant of 6.25, meaning that at this pH, half of the molecules occur in the cationic form (TBT^+). When added to water, TBT complexes with several anions, including hydroxide, sulfate, and chloride. In seawater, it has been demonstrated that TBT occurs mainly as the hydroxide complex (Arnold *et al.*, 1997). TBT also exhibits a strong propensity to associate with non-polar substances, such as lipid and organic carbon. Determination of its octanol-water partition coefficient ($25\,000 = 4.4$ in $\log_{10}$ units) at pH 8 confirms its tendency to associate with hydrophobic phases (Meador, 2000).

Tributyltin was used extensively as an antifoulant compound on submerged surfaces of ships to retard the growth of fouling organisms before its use was restricted. In 1988, the United States Congress passed the Organotin Antifouling Paint Control Act (OAPCA) (US Congress, 1988) to limit the use of TBT. This compound was banned on vessels <25 m in length, but allowed on larger vessels. Due to the restrictions, water concentrations of TBT dropped dramatically; however, sediment concentrations have shown only modest declines (Valkirs *et al.*, 1991). Recent surveys, some several years after restrictions were enacted, show TBT concentrations in sediment over time are relatively constant (Krone *et al.*, 1996; Fent, 1996; Maguire, 2000).

Equilibrium Partitioning

Equilibrium partitioning (EqP) was developed to explain and predict the partitioning behaviour between sediment, water, and tissue for neutral hydrophobic organic compounds (HOCs), such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) (McFarland, 1984; Di Toro *et al.*, 1991). The basic premise for EqP is that when sediment and water are in equilibrium, the organism receives an equivalent exposure from each phase allowing predictions of the accumulated dose using either phase. The organismal lipid, total organic carbon (TOC) in sediment, and water can be considered as three phases that exhibit predictable concentrations at equilibrium due to equal chemical activity or fugacity. Because of this assumption, the route of exposure (e.g. water ventilation or prey/sediment ingestion) is immaterial because at equilibrium the concentration in each phase is a function of the thermodynamic properties, not the kinetics of accumulation. EqP has generally been successful in predicting sediment–water partitioning and bioaccumulation for the non-metabolized, neutral HOC compounds, but has not been explored for ionizable organic compounds or organometallics, such as TBT.

Sediment–water partitioning

The K_{oc} is the sediment–water partition coefficient that has been normalized to the organic carbon content of sediment. This normalization greatly reduces the variability in the sediment–water partition coefficients observed among different sediment types. K_{oc} values are chemical specific and are related to the compound's affinity for organic carbon. The equation is

$$K_{oc} = \frac{[\text{sediment}]/f_{oc}}{[\text{water}]} \tag{1}$$

where [sediment] is the sediment concentration in dry weight, [water] is the observed water concentration, and f_{oc} is the fraction of organic carbon (g g^{-1} dry wt). [sediment] and [water] are in the same units (e.g. ppb, ppm, or M).

Several studies show the $\log_{10} K_{oc}$ value for TBT to be in the range of 4.2–5.0 (Maguire and Tkacz, 1985; Unger *et al.*, 1988; Tas, 1993; Meador *et al.*, 1997; Poerschmann *et al.*, 1997; Day *et al.*, 1998). Regression analysis of the sediment-water partition data provided by these studies determined the $\log_{10} K_{oc}$ to be 4.5 ($=32\,000$) and supports the hypothesis that organic carbon in sediment controls the amount of TBT in water (Meador, 2000).

It has been shown for many neutral hydrophobic compounds that the octanol–water partition coefficient (K_{ow}) is a good predictor of the K_{oc}. Several authors have developed equations that predict K_{oc} values from the K_{ow} for various hydrophobic compounds (see Meador, 2000). These studies show the K_{oc} for HOCs to range from $0.4K_{ow}$ to $1.0K_{ow}$. The $\log_{10} K_{ow}$ for TBT of 4.4 and the mean $\log_{10} K_{oc}$ of 4.5 are very close and support the utility of these equations as predictors of sediment–water partitioning. Because TBT in marine systems occurs predominantly as the hydroxide, the partitioning behavior of TBT may be similar to that observed for neutral hydrophobic compounds and predictions generated by EqP may be valid.

Tissue-sediment partitioning

Bioaccumulation factors for HOCs are generally expressed as the tissue to sediment concentration ratio (BAF; equation (2)) or the biota-sediment accumulation factor (BSAF; equation (3)). The BSAF is the lipid and organic carbon normalized bioaccumulation factor:

$$\mathrm{BAF} = \frac{[\text{tissue}]}{[\text{sediment}]} \tag{2}$$

$$\mathrm{BSAF} = \left(\frac{[\text{tissue}]}{f_{\mathrm{lip}}}\right) \Big/ \left(\frac{[\text{sediment}]}{f_{\mathrm{lip}}}\right) \tag{3}$$

where [tissue] and [sediment] are in dry weight (ppb or ppm), f_{oc} is the dry-weight fraction organic carbon in sediment ($\mathrm{g\,g^{-1}}$), and f_{lip} is the dry-weight fraction of lipid in tissue ($\mathrm{g\,g^{-1}}$). The convention is to express all BSAF components as dry weights (Lee *et al.*, 1993); however, as long as the terms are consistent within the numerator or denominator, the same result is obtained because these are ratios (e.g. [tissue] wet weight divided by f_{lip} wet weight equals the same value when both terms are expressed as dry weights). In this paper, all tissue and sediment concentrations are in terms of dry weight, unless noted. Several factors, such as variable uptake and elimination rates, reduced bioavailability, and insufficient time for sediment–water partitioning or tissue steady state can affect bioaccumulation and ultimately the BSAF. Based on EqP theory, the theoretical maximum BSAF is unity (Di Toro *et al.*, 1991) and the empirical maximum values generally range from 2 to 4 (USEPA/USACE, 1991; Boese *et al.*, 1995) for neutral HOCs that are not metabolized. Because of the amounts of chemical expected in lipid and organic carbon, it is generally believed that HOCs will produce predictable levels of bioaccumulation.

Tributyltin does not bioaccumulate in organisms according to the EqP approach, which predicts one BSAF value for all species that do not metabolize the compound of interest. A review of the available data (Meador, 2000) indicates that species-specific toxicokinetics can predict the bioaccumulation of TBT, not thermodynamic partitioning between tissue and environmental concentrations (e.g. water or sediment). For many species, the bioconcentration factor (BCF) or biota-sediment BSAF is far above that predicted based on the expected thermodynamic maximum, which is determined by the lipid content in tissue and partitioning properties of the compound (K_{ow}). Therefore, because lipid does not appear to control TBT bioaccumulation, it is not needed for making predictions. However, because the organic-carbon normalized sediment concentration ($\mathrm{sed_{oc}}$) is related to the amount of TBT available for bioaccumulation (Meador, 2000) and the BSAF equation is convenient for expressing species-specific bioaccumulation, the equation can be used in conjunction with an average lipid content for each species. Alternatively, a bioaccumulation factor with only the sediment component normalized to organic carbon ($\mathrm{BAF_{oc}}$) may be used to describe TBT bioaccumulation and would be more appropriate for those species where lipid content is highly variable:

$$\mathrm{BAF_{oc}} = \frac{[\text{tissue}]}{[\text{sediment}]/f_{oc}} \tag{4}$$

It should be noted that this equation will produce smaller values than those obtained with the BAF or BSAF equation. The following equation can be used for converting the BSAF to the equivalent $\mathrm{BAF_{oc}}$:

$$\mathrm{BAF_{oc}} = \mathrm{BSAF} \times f_{\mathrm{lip}} \tag{5}$$

Several studies have reported BAF values for invertebrates exposed to field-contaminated sediments. These studies report BAFs from 3 to 100 (Langston *et al*., 1987; Bryan *et al*., 1989; King *et al*., 1989; Bryan and Gibbs, 1991; Langston and Burt, 1991; Kure and Depledge, 1994; Stäb *et al*., 1996). The mean BAFs in Langston *et al*. (1987) varied from 3 for *Nereis diversicolor* to 78 for *Mya arenaria*. Because of the low lipid content (0.7–1% wet wt) reported for these species, their BSAFs could be relatively high. For example, if the sediment TOC content was 2.0%, the dry-weight BSAF for *M. arenaria* would be approximately 40, which is approximately 40 times higher than that predicted by the EqP approach.

Very few studies report BSAF values. A field study of TBT concentrations in a freshwater lake reported BSAFs for several invertebrate species in the range of 3–10 and even higher for some fish (Stäb *et al*., 1996). Meador *et al*. (1997) determined BSAF values for three marine invertebrates ranging from 0.4 to 4.6 in laboratory exposures, which were expected to be even higher when steady state between tissue and sediment occurred and metabolism was considered. For these species the BAF_{oc} values ranged from 0.02 for a tolerant species to 0.5 for the one that was relatively sensitive to TBT exposure. Relatively high bioaccumulation values for TBT are generally characteristic of species with a high rate of uptake or a low rate of metabolic conversion and elimination.

Based on this information, it was concluded that TBT bioaccumulation factors for benthic organisms are generally high compared to those for other compounds. When bioaccumulation was expressed as a BSAF, values reported by various authors were somewhat variable and often much higher than that predicted by equilibrium partitioning theory. The mean (S.D.) BSAF for 11 invertebrate species was 9.5 (11.8) (Langston *et al*., 1987; Stäb *et al*., 1996; Meador *et al*., 1997). (The BAFs in Langston *et al*., 1987 were converted to BSAFs by assuming a sediment TOC of 2% dry wt). The 50th and 75th percentiles for these 11 BSAFs were 4.2 and 11.2, respectively.

TBT toxicity in aquatic organisms

Exposure-based toxicity

Several studies demonstrate that TBT is very toxic to marine invertebrates (Maguire, 1987; Cardwell and Meador, 1989; Heard *et al*., 1989; Fent, 1996; Maguire, 2000) and because of its persistence in sediment, there is still a concern about its impact on organisms. It is known that marine species exhibit a range in responses when exposed to TBT in water (Cardwell and Meador, 1989; Meador, 1997; Fent, 1996); however, their response to sediment-associated TBT has not been fully studied. Mortality responses for TBT in water exposures have been reported from approximately 0.5 ng ml^{-1} to over 200 ng ml^{-1}, a range of about 400 fold (Cardwell and Meador, 1989). Most of this variability is due to differences in the uptake and elimination kinetics between species; however, some of these values underestimate the toxic response because of insufficient time for exposure. For example it takes approximately 75 days for tissue concentrations to reach steady state in *Eohaustorius washingtonianus*, an amphipod with a slow rate of elimination (Meador, 1997). Consequently, many of the reported values underestimate the true response because of presteady-state conditions (Meador, 2000).

Sublethal responses to water exposure are also highly variable ranging from the low (0.01 ng ml^{-1}) to high (0.5 ng ml^{-1}) parts per trillion (Cardwell and Meador, 1989; Fent, 1996). The most common sublethal endpoints measured are growth inhibition, shell chambering in oysters, histological and behavioural abnormalities, and imposex in prosobranch gastropods. In terms of exposure concentrations and sublethal effects, it is clear that molluscs are the most sensitive taxon to TBT, primarily due to their weak ability to metabolize this compound and their high rate of uptake. It should be noted that many of the sublethal responses reported for TBT exposure would eventually lead to death of the organism in the environment.

In terms of sediment concentrations, the few available studies indicate that sediment concentrations in the 100–1000 ng g^{-1}range can have severe effects. For example Fent and Hunn (1995) noted that clams had disappeared in areas where sediment TBT exceeded 800 ng g^{-1}dry wt and Meador and Rice (2001) found

moderate to severe reductions in growth for the polychaete *Armandia brevis* for sediment concentrations in this range (100–1000 ng g^{-1} dry wt). Langston and Burt (1991) and Bryan and Langston (1992) also suggested that some populations of bivalves (*Macoma balthica* and *Scrobicularia plana*) have disappeared in locations with TBT sediment concentrations over 700 ng g^{-1}dry wt.

TBT toxicity based on tissue residues

Several studies have found that when toxicity is expressed as a tissue residue, the variability between species, time periods, and exposure conditions is greatly reduced (McCarty, 1991; van Wezel and Opperhuizen, 1995; Meador, 2000). Analysis of tissue residues (concentrations) in terms of the toxic response has been called the critical body residue (CBR) approach (McCarty, 1991). The observed data indicate that for some toxicants there is a narrow range in tissue concentrations across species that is associated with a given mode of action and biological response. Sublethal effects, such as growth or reproductive impairment can occur at tissue concentrations that are from 10 to 100 times lower than those for lethality, with a typical acute to chronic ratio of 10 (McCarty and Mackay, 1993). While there is some variability in the tissue residue effect number for a given mode of action, a large percentage of this can be due to variable lipid content found in organisms (van Wezel *et al.*, 1995).

Acute TBT toxicity is likely caused by uncoupling of oxidative phosphorylation. Several studies have examined the lethal response for TBT and report that mortality occurs at a relatively consistent whole-body tissue residue of 30–115 μg g^{-1}dry wt (Meador, 2000). Based on these studies, the mean and standard deviation LR50 for 11 species (including fish) exposed to TBT was determined to be approximately 48 (5) μg g^{-1}dry wt. (= 166 nmol g^{-1}) (Meador, 2000). The LR50 is a statistic that defines the lethal residue (tissue concentration) associated with the response affecting 50% of the population. This statistic is distinguished from the LD50, which is the dose causing a 50% response (Meador, 1997). For some toxicants the dose administered to an organism can be very different than the actual tissue concentration associated with the effect because of metabolic elimination. Defining the toxic response in terms of the associated tissue concentration (*vis-à-vis* dose administered) has great utility when assessing contaminant-related effects in organisms from the field.

Growth inhibition and imposex in molluscs comprise most of the sublethal data reported for TBT exposure. There are many other biological responses reported in the literature (e.g. behavioural alterations, immunotoxicity, and developmental abnormalities), which have not been extensively studied. These organismal responses to TBT are a manifestation of one or several modes of action and they are generally associated with tissue concentrations that occur at 10–100 times lower than those reported for the lethal response, which is in agreement with the data of McCarty and Mackay (1993). An analysis of the available data found that growth impairment occurred at a relatively consistent whole-body tissue concentration of approximately 3 μg g^{-1}dry wt (= 10.4 nmol g^{-1}). These values were the lowest tissue concentration where a statistically significant growth impairment was demonstrated and are termed lowest observed effect residue (LOER) (Table 1). Results for impaired growth as a function of tissue concentrations were obtained for seven species, all of which produced very similar results. Two species (*Crassostrea gigas* and *Mytilus edulis*) were examined in multiple studies producing consistent results. While only some of these species in Table 1 may be considered as prey for salmonids, the consistency in the growth impairment response among diverse species indicates that this magnitude of response may be observed in many types of species, including several species that would be consumed by salmonids.

Reproductive impairment was also examined for a few species (mainly stenoglossan snails exhibiting the imposex condition) and it was concluded that the threshold tissue concentration for severe adverse effects (sterilization) occurred at approximately 0.3 μg g^{-1}dry weight (1 nmol g^{-1}), with complete sterilization at 1–3 μg g^{-1} dry wt (3.5–10.3 nmol g^{-1}) (Table 2). Because there are so few data, it is not known if reproductive effects will occur in other non-gastropod species at these tissue concentrations. It is possible

Table 1. Critical body residue data for growth response due to tributyltin exposure[a]

	Source	Species	Common name	Type	Tissue TBT ($\mu g\,g^{-1}$dry wt)	Response
1.	Seinen *et al.* (1981)	*Oncorhynchus mykiss*	Trout	Lab	2.1	Red. growth[b]
2.	Batley *et al.* (1989)	*Saccostrea commercialis*	Oyster	Field	1.1	Shell curl[b,c]
3.	Batley *et al.* (1989)	*Crassostrea gigas*	Oyster	Field	2.1	Shell curl[b,c]
4.	Meador and Rice (2001)	*Armandia brevis*	Polychaete	Lab	2.4	Red. growth
5.	Moore *et al.* (1991)	*Neanthes arenaceodentata*	Polychaete	Lab	6.3	Red. growth
6.	Davies *et al.* (1988)	*Crassostrea gigas*	Oyster	Field	3.3	Red. condition index and growth
7.	Widdows *et al.* (1990)	*Arca zebra*	Mussel	Field	0.8–1.1	SFG[d]
8.	Salazar and Salazar (1998)	*Mytilus edulis*	Mussel	Field	4.0	Red. growth
9.	Widdows and Page (1993)	*Mytilus edulis*	Mussel	Field	5.4	Red. condition index
10.	De Vries *et al.* (1991)	*Oncorhynchus mykiss*	Trout	Lab	2.0	Red. growth
11.	Guolan and Yong (1995)	*Mytilus edulis*	Mussel	Lab	3.0	Red. growth and shell length

[a] All values are lowest observed effect residues (LOER) associated with a statistically significant reduction in growth. Wet weight tissue values from literature times 5 to obtain dry weight values. 'Type' is the location of exposure (laboratory or field collected). SFG is Scope for Growth. Red. is reduction. The mean and standard deviation of all values is 3.2 (1.6) $\mu g\,g^{-1}$dry wt ($=11\,nmol\,g^{-1}$).
[b] Tissue TBT concentration based on the CBR equation (McCarty and Makay 1993), which was modified for the sublethal response (LOER = BCF × LOEC); see Meador (2000) for additional details. All other values based on direct relationship between tissue concentration and effect.
[c] Excluded from mean because other toxicants shown to be correlated with reduced growth.
[d] Authors state that shell curl is a severe shell deformity that is associated with reduced tissue growth.

that reproductive impairment in gastropod snails (imposex) occurs by a very different mechanism as that for other species. Consequently, any CBR analysis should be cognizant of the mode of action responsible for the biological response of interest because the tissue residues associated with the effect may be different and unique to the specific action.

Table 2. Critical body residue data for imposex due to tributyltin exposure[a]

	Source	Species	Type	Tissue TBT $\mu g\,g^{-1}$dry wt	Response
1.	Shim *et al.* (2000)	*Thais clavigera*	Field	0.20	80% RPL
2.	Horiguchi *et al.* (1994)	*Thais clavigera*	Field	0.25	50% RPS
3.	Horiguchi *et al.* (1994)	*Thais bronni*	Field	0.25	50% RPS
4.	Stroben *et al.* (1992)	*Nucella lapillus*	Lab	0.49	Stage 3 VDS
5.	Gibbs *et al.* (1988)	*Nucella lapillus*	Lab	0.59	50% RPS
6.	Oehlmann *et al.* (1998)	*Nucella lapillus*	Field	0.25	Stage 3 VDS
7.	Bryan *et al.* (1989)	*Ilyanassa obsoleta*	Field	0.10	50% freq of imposex
8.	Bauer *et al.* (1997)	*Littorina littorea*	Field	0.44	ISI = 1
9.	Stroben *et al.* (1992)	*Hinia reticulata*	Lab	2.7	Stage 3 VDS

[a] All TBT values are dry weight TBT ion. Wet weight tissue values from literature times 5 to obtain dry weight values. 'Type' is the location of exposure (laboratory or field collected). The indices of imposex are (1). relative penis length (RPL) = the mean female penis length/male penis length × 100, (2). Relative penis size (RPS) which is the same as the RPL except that each component is cubed, (3). The vas deferens sequence (VDS), which is given in stages of development (0 – 6), and (4). ISI = intersex index. An RPS of 50% is equivalent to an RPL of 80%. The values presented are generally associated with a relatively low percentage of sterility in the population (<20%). Snails exhibit a high percentage of sterility primarily when RPS > 80%, VDS > stage 5, and ISI > 2. Value for study 8 determined by personal communication from author. The mean and standard deviation of all values is 0.32 (0.17) $\mu g\,g^{-1}$ dry weight ($=1.1\,nmol\,g^{-1}$) (excluding no. 9). All species are gastropod snails.

METHODS

Predicting adverse sediment concentrations

Methods for determining sediment quality guidelines should include components of the EqP, toxicokinetic, and critical body residue approaches because of their utility in predicting bioaccumulation and biological effects. The goal is to protect the sensitive species against sublethal effects, such as altered growth or impaired reproduction, which may affect population dynamics and their ability to thrive.

Equilibrium partitioning (EqP) approach

One of the main advantages of EqP is to utilize the very large water-quality database developed over the years and consider biological responses in terms of the concentration of a contaminant found in sediment (Di Toro *et al.*, 1991). Because the toxicity of TBT in sediment is not as well studied as the toxicity caused from exposure to TBT contaminated water, the principles of EqP can be applied to determine equivalent sediment concentrations for regulatory purposes. Water quality data can be converted to sediment concentrations with the following equation:

$$[\text{sediment}] = K_{\text{oc}} \times f_{\text{oc}} \times [\text{water}] \tag{6}$$

where [water] is the concentration selected to protect species against adverse effects (e.g. lowest or no observed effect concentration (LOEC or NOEC) or a water quality criteria), K_{oc} is the organic-carbon normalized sediment-water partition coefficient and f_{oc} is the fraction of organic carbon in sediment (= %TOC/100). Because of the large variability found among species in their response to environmental concentrations of TBT, only sensitive species with high bioconcentration or bioaccumulation factors should be considered when determining the effect concentration.

Tissue residue approach

An alternative method to the one above utilizing water concentrations for generating sediment quality guidelines would be based on tissue concentrations. Because the organic carbon content of sediment is correlated to the amount of TBT accumulated by a species, the BAF_{oc} or BSAF can be used to relate tissue concentrations to those found in sediment. A tissue residue deemed to be protective for most species (e.g. LOER or NOER; lowest or no observed effects tissue residue), that is determined from well-controlled laboratory studies, would be converted to a sediment concentration by utilizing the BAF_{oc} value for an appropriate and sensitive test species. The following equation can be used to determine the organic-carbon normalized sediment concentration (sed_{oc}) that would be expected to be protective against adverse effects:

$$[\text{sed}_{oc}] = \frac{[\text{tissue}]}{\text{BAF}_{\text{oc}}} \tag{7}$$

where [tissue] is the tissue residue used for protection (e.g. ER_{10}, LOER, or NOER) and sed_{oc} is the organic-carbon normalized sediment concentration. (ER_{10} is the effective residue associated with a sublethal response affecting 10% of the population.)

As stated earlier, the BSAF is a convenient bioaccumulation factor, even though organismal lipid content does not affect TBT bioaccumulation. A BSAF value could be used to determine the [sed_{oc}] because lipid content cancels out and is not needed; however, use of this equation would require a relatively constant lipid content in the species of interest.

$$[\text{sed}_{oc}] = \frac{[\text{tissue}]}{\text{BSAF} \times f_{\text{lip}}} \tag{8}$$

where f_{lip} is the average lipid content for this species.

Due to differences in ability to bioaccumulate TBT from sediment, the sediment quality value would have to be determined with sensitive test species (based on exposure concentration) for protection of most species that would inhabit the impacted site. In other words, only species that exhibit a high steady-state BAF_{oc} should be selected when using equations (7) or (8) to determine the sediment concentration that is to be considered harmful. Assuming steady state for sediment-water-tissue partitioning and a consistent tissue-residue effect concentration, a sensitive species with a higher BAF will respond to a much lower sediment concentration. For example, *Eohaustorius washingtonianus*, which has a high uptake clearance (k_1) and slow rate of elimination (k_2) (Meador *et al.*, 1997) exhibits a high steady-state BSAF of $\approx$ 12 ($BAF_{oc} \approx 0.50$) and is affected by low sediment concentrations of TBT (LC50 $\approx$ 260 ng g^{-1}sediment) (Meador, 2000).

ANALYSIS

EqP approach

The EqP approach was used only to predict water concentrations from the sediment-water partitioning characteristics of TBT and relate those concentrations to controlled laboratory toxicity experiments based on water exposure. As noted earlier, the EqP approach is useful for predicting sediment–water partitioning for TBT and the amount available for uptake, but not the amount bioaccumulated (i.e. the tissue concentration expected at steady state).

A compilation of the available data (51 studies at that time) on TBT determined the median water concentration for chronic toxicity to be 0.22 ng ml^{-1}; the 5th percentile concentration was 0.02 ng ml^{-1} (Weston, 1996). Many of the results for these 51 studies are LOECs based on growth impairment. Using the K_{oc} value of 32 000 determined in Meador (2000), the median water concentration of 0.22 ng ml^{-1} would be expected from a sediment concentration (normalized to organic carbon) of 7040 ng TBT g^{-1}organic carbon. For a TOC of 2%, this would equal a concentration of 141 ng g^{-1} sediment dry weight. Because this value is derived from the median concentration for all sublethal effect studies, some adverse responses would be expected for this level of exposure.

Several areas in Puget Sound, Washington have TBT sediment concentrations that exceed this value. In a recent study of TBT around the Harbor Island Superfund site in Seattle, WA (EVS, 1999), 95% of the sediment samples exceeded the 7040 ng g^{-1} OC value. Also, 60% of the stations sampled produced porewater concentrations above the median water concentration (0.22 ng ml^{-1}) associated with all sublethal effects. These concentrations were measured in an estuary where chinook salmon that are protected under the ESA feed and make the transition from freshwater to marine water. Other studies (Krone *et al.*, 1989, 1996) also indicate that tributyltin concentrations in Puget Sound sediments routinely exceeded 7040 ng g^{-1} OC.

It should be noted that the proposed US EPA water quality criterion for TBT is 0.01 ng ml^{-1}, which was generated to protect at least 95% of the species from chronic (long term) and sublethal effects. Chambering in oysters and imposex in snails were the primary biological responses that were responsible for this low value. While the purpose of this review is to relate toxicity to a sediment concentration, the water quality criterion could also be applied to an estuary of interest for the protection of sensitive species.

Tissue residue approach

If the tissue residue approach is adopted, a tissue concentration of 3 μg g^{-1}(dry wt) is recommended as the level to protect against severe adverse sublethal effects in salmonid prey. This tissue concentration was recently selected as the 'tissue trigger level' for remediation of sediments at the Harbor Island Superfund site (US EPA, 1999) and it has been correlated with reduced growth in at least seven different species (Table 1). The tissue residue associated with reproductive impairment (Table 2) was not selected because

most of the studies used to derive this value were based on stenoglossan gastropods, which are not usually prey for juvenile salmonids. However, at least one study with a copepod crustacean demonstrated reproductive impairment in the same range of water concentrations as that reported for imposex in snails (Johansen and Mohlenberg, 1987). If adverse reproductive impacts are found in additional salmonid prey species, then an analysis similar to the one presented above deriving a sediment concentration from the threshold tissue concentration for reproductive effects instead of growth impairment would be warranted.

As stated above, many invertebrates exhibit BSAFs for TBT in the range of 2–10 or higher. For example, even a species such as the polychaete *Armandia brevis*, which is not considered highly 'sensitive' to TBT, exhibits a steady-state BSAF of 4.2 ($BAF_{oc} \approx 0.2$) (Meador *et al.*, 1997). For determination of the threshold sediment concentration, a BAF_{oc} of 0.5 was selected as representative for relatively sensitive species. This is comparable to a BSAF of 10 for a sensitive invertebrate with a lipid content of 5% dry wt., which is a reasonable average lipid content for invertebrates (Boese and Lee, 1992). This value is close to the 75th percentile of BSAF values reported in the literature (see the Section Tissue–Sediment Partitioning above). Based on equations (7) or (8), using the appropriate bioaccumulation factor, the resulting sed_{oc} is $6000\,ng\,g^{-1}$ organic carbon. For a sediment with 2% TOC, this would equal $120\,ng\,TBT\,g^{-1}$ sediment dry weight.

CONCLUSIONS

Based on the tissue residue approach (recommended) and the available data, protection against severe adverse sublethal effects for many, but not all salmonid prey species, should be achieved with a TBT sediment concentration of $6000\,ng\,g^{-1}OC$. For a sediment with 2% TOC, this would equal $120\,ng\,g^{-1}$ dry wt. This value is based on a tissue residue approach using a LOER of $3\,\mu g\,g^{-1}$ dry wt and a $BAF_{oc} = 0.5$ ($BSAF \approx 10$). In general, the EqP and tissue residue approaches support one another, indicating adverse effects in benthic species at relatively low exposure concentrations. At this sediment concentration, no adverse effects on migrating salmon are expected; however, if substantial tissue residues are detected (e.g. $> 500\,ng\,g^{-1}$ dry wt) in juvenile salmon, then these recommendations should be reconsidered. The goal here is to protect salmonid prey species against severe effects; however, at this sediment concentration some sublethal effects on benthic invertebrates, especially molluscs, are expected. If the intent was to protect all benthic species against sublethal effects, a sediment value approximately ten times (or more) lower would be more appropriate.

One drawback to this approach of determining a protective sediment concentration for one toxicant is that cumulative or interactive effects are not considered. Because the relationship between biological effects and a particular class of contaminants is generally determined in laboratory tests with single toxicants, there is no assessment of the interactive effects that are expected from other toxicants found in environmental matrices. Consequently, responses to tributyltin may occur at even lower tissue concentrations than those deemed protective because of the additive or synergistic effects produced by other contaminants bioaccumulated at the site. Because of this, the proposed tissue or sediment effect concentration may actually be lower when additional toxicants are considered, which is a factor that must be addressed on a site-specific basis.

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