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A Probabilistic Ecological Risk Assessment of Tributyltin in the Chesapeake Bay Watershed

Chesapeake Bay Program

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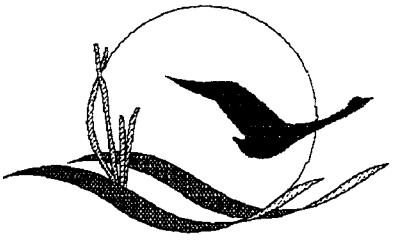

Chesapeake Bay Program
410 Severn Avenue, Suite 109
Annapolis, Maryland 21403
1-800-YOUR-BAY

http://www.chesapeakebay.net/bayprogram

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Final Report

A Probabilistic Ecological Risk Assessment of Tributyltin in the Chesapeake Bay Watershed

Lenwood W. Hall, Jr.
Mark C. Scott
William D. Killen

University of Maryland
Agricultural Experiment Station
Wye Research and Education Center
P. O. Box 169
Queenstown, Maryland 21658

ABSTRACT

The goal of this study was to conduct a probabilistic ecological risk assessment for tributyltin (TBT) in estuarine areas of the Chesapeake Bay watershed by using the following distinct phases: problem formulation, analysis and risk characterization. This probabilistic ecological risk assessment characterized risk by comparing the probability distributions of environmental saltwater exposure concentrations with the probability distributions of species response data determined from laboratory studies. The overlap of these distributions was a measure of risk to aquatic life. Comparative risk from TBT exposure was determined for various basins (tributaries) in the Chesapeake Bay watershed.

Tributyltin saltwater exposure data from the Chesapeake Bay watershed were available from over 3,600 water column samples from 41 stations in nine basins from 1985 through 1996. Most of the stations were located in the Virginia waters of Chesapeake Bay, primarily the James, Elizabeth and York Rivers. In Maryland waters of the Bay, various marina, harbor and river systems were also sampled. As expected, the highest environmental concentrations of tributyltin (based on 90th percentiles) were reported in and near marina areas. The sources of TBT causing these high concentrations were primarily boat hulls and painting/hull cleaning operations. Lower concentrations of TBT were reported in open water areas ,such as the Potomac River, Choptank River and C and D Canal, where the density of boats was minimal. Temporal data from a ten year data base (1986-1996) from two areas in Virginia showed that TBT water column concentrations have declined since 1987 legislation prohibited the use of TBT paints on recreational boats (<25m).

Acute saltwater and freshwater TBT toxicity data were available for 43 and 23 species, respectively. Acute effects for saltwater species were reported for concentrations exceeding 420

ng/L; the lowest acute value for a freshwater species was 1,110 ng/L. The acute 10th percentiles for all saltwater and freshwater species were 320 and 103 ng/L, respectively. The order of sensitivity from most to least sensitive for saltwater trophic groups and corresponding acute 10th percentiles were as follows: zooplankton (5 ng/L), phytoplankton (124 ng/L), benthos (312 ng/L) and fish (1,009 ng/L). For freshwater species, the order of sensitivity from most to least sensitive trophic groups and corresponding acute 10th percentiles were: benthos (44 ng/L), zooplankton (400 ng/L), and fish (849 ng/L). Chronic data for both saltwater and freshwater species were limited to a few species in each water type. Based on these limited data, the saltwater and freshwater chronic 10th percentiles were 5 and 102 ng/L, respectively. Limited mesocosm and microcosm studies in saltwater suggested that TBT concentrations less than 50 ng/L did not impact the structure and function of biological communities.

The saltwater acute (320 ng/L) and chronic (5 ng/L) 10th percentiles were used to determine potential ecological risk because all exposure data were from saltwater areas of the Chesapeake Bay watershed. Highest ecological risk was reported for marina areas in Maryland waters of Chesapeake Bay and for areas in Virginia such as the Elizabeth River, Hampton Creek and Sarah Creek. Low ecological risk was reported for areas such as the Potomac River, Choptank River, C and D Canal and Norfolk Harbor. Regulation of TBT on recreational watercraft in 1987 has successfully reduced water column concentrations of this organometallic compound. However, various studies have shown that TBT may remain in the sediment for years and continue to be source for water column exposures.

ACKNOWLEDGMENTS

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INTRODUCTION

Improvement and maintenance of water quality were identified as the most critical elements for the restoration and protection of the Chesapeake Bay in the 1987 Chesapeake Bay Agreement (Chesapeake Executive Council, 1988). Another goal of this Agreement was the development and adoption of a Chesapeake Bay Basinwide Toxics Reduction Strategy in order to achieve a reduction of toxic substances consistent with the Water Quality Act of 1987. The Chesapeake Bay Basinwide Toxics Reduction Strategy contained various commitments in areas such as research, monitoring and toxic substance management that were directed to overall reduction of toxic chemicals in the Chesapeake Bay watershed (Chesapeake Bay Executive Council, 1988). One commitment specified for the creation of a Toxics of Concern List (TOC) for the Chesapeake Bay. This TOC list was designed to prioritize over 1000 chemicals that may be impacting aquatic life or human health in Chesapeake Bay by using a risk based ranking system and direct future research efforts and management.

The first TOC list was completed in 1990 and was revised in 1996 (U. S. EPA, 1991; U. S. EPA, 1996). The revised list as currently proposed is currently under review. The proposed revised TOC list was developed using a chemical ranking system that incorporates sources, fate, exposure and effects of chemicals on living resources and human health in Chesapeake Bay (Battelle, 1989). The TOC list contains both a list of primary toxics of concern as well as a secondary list (chemicals of potential concern). For both the 1990 and 1996 TOC lists, tributyltin (TBT) was identified as a primary toxic of concern. Tributyltin enters the aquatic environment primarily as an antifouling paint additive used on boat hulls although loading from drydocks during painting and hull cleaning

operations can also occur. Antifouling paints containing TBT prevent the growth of fouling organisms such as tube worms and barnacles on boat hulls. Tributyltin is one of the most effective biocides ever used in antifouling paints but unfortunately, toxic qualities of TBT that make it effective in controlling fouling organisms (target species) also poses a risk to non-target species in the aquatic environment. Imposex (development of male characteristics in female snails) in female dog welks at low ng/L concentrations and shell thickening and reduced productivity of oysters at 100 to 500 ng/L concentrations have raised concern because these concentrations have been reported in the aquatic environment of the Chesapeake Bay watershed (Huggett et al., 1996).

Although TBT has been identified as a toxic of concern in the Chesapeake Bay watershed, a quantitative probabilistic ecological risk assessment has not been conducted for this organometallic compound. The objective of this study was to apply EPA's Ecological Risk Assessment paradigm for assessing ecological risk of TBT in the Chesapeake Bay watershed. Procedures described in the following documents were used for this assessment: Report of the *Aquatic Risk Assessment and Mitigation Dialogue Group* (SETAC, 1994), the *EPA Framework for Ecological Risk Assessment* (U. S. EPA, 1992) and a recent paper entitled "*An ecological risk assessment of atrazine in North American surface waters*" (Solomon et al., 1996). This probabilistic risk assessment characterizes risk by comparing probability distributions of environmental saltwater exposure concentrations with the probability distributions of species response data (determined from laboratory studies). The overlap of these distributions is a measure of potential risk to aquatic life in Chesapeake Bay. This approach has a number of advantages over a quotient method (comparing the most sensitive species with the highest environmental concentrations) because it allows, if not exact quantification, a least a strong sense for the magnitude and likelihood of potential ecosystem effects of TBT in Chesapeake

Bay. An implied assumption of this approach is that protecting a large percentage of species will also preserve ecosystem structure and function. Various studies in basic ecology (Tillman, 1996; Tillman et al., 1996) and of ecological effects of pesticides conducted in aquatic mesocosms (Solomon et al., 1996) support the concept that in ecological risk assessment, some effects can be allowed at the population level provided that these do not impair ecosystem structure and function and keystone species are not impacted. The final result of the risk characterization is expressed as the probability that exposure concentrations of TBT (within a defined spatial and temporal range) will exceed concentrations deemed protective of aquatic life in the Chesapeake Bay watershed.

1.1 Problem Formulation

This ecological risk assessment has the following distinct phases: Problem Formulation, Analysis and Risk Characterization (Figure 1). The problem formulation phase involves the identification of major issues to be considered in the risk assessment. The analysis phase reviews existing data on exposure (environmental monitoring of saltwater TBT concentrations) and ecological effects (primarily laboratory toxicity studies). The risk characterization phase involves estimation of the probability of adverse effects on aquatic populations and communities in potentially impacted areas of the Chesapeake Bay watershed.

The problem formulation phase of this risk assessment identified the following major issues to be addressed: stressor characteristics, ecosystems at risk, ecological effects, endpoints, stressors impacting aquatic communities, and a conceptual model for risk assessment.

1.1.1 Stressor Characteristics

The chemical and physical properties of TBT are described in detail in the Exposure section

of this report. In the problem formulation phase of this risk assessment, the solubility, degradation persistence in water and sediment, metabolism and bioconcentration potential of TBT were considered important.

Solubility of TBT in the water column is influenced by such factors as the oxidation-reduction potential, pH, temperature, ionic strength and concentration and composition of dissolved organic matter (Clark et al., 1988). Maguire et al. (1983) has reported that TBT solubility ranges from 750 to 31,000 ug/L at pH of 2.6 to 8.1. Microbial degradation of TBT to the less toxic di- and monobutyltin compounds has been reported as the most important process limiting pesistence of TBT in the environment (U. S. Navy, 1997). Degradation half lives ranging from 4 to 19 days in seawater have been reported while sediment half lives on the order of months to years have been observed (U. S. Navy, 1997, De Mora et al., 1989). Significant TBT metabolism potential exists in fish and crustaceans with minimal metabolic potential in mollusks. Mollusks also exhibit the highest bioaccumulation factors and highest tissue burdens while fish and crustaceans generally accumulate lower burdens of TBT.

1.1.2 Ecosystems at Risk

The aquatic ecosystem addressed in this risk assessment was the estuarine portion of the Chesapeake Bay watershed. Most of the exposure data for TBT were reported for the Virginia waters of Chesapeake Bay, primarily the James, Elizabeth and York Rivers. Various marina, harbor and river systems were also sampled in the Maryland waters of Chesapeake Bay. Exposure data were available for over 3,600 samples collected at 41 stations between 1985 to 1996.

1.1.3 Ecological Effects

A comprehensive review and synthesis of the TBT aquatic toxicity literature was conducted

by using literature searches (AQUIRE etc.), various regulatory review documents such as the U. S. EPA water quality criteria report (U. S. EPA, 1997) and other TBT review documents (e. g. Hall and Pinkney; 1985, Champ and Seligman, 1996 and U. S. Navy 1997, among others). The ecological effects data used in this risk assessment were derived from 43 saltwater species tested in acute studies and 4 species tested in chronic toxicity tests (where chronic values were reported). Only saltwater toxicity data were used for assessing risk because exposure data were only available from saltwater areas in the Chesapeake Bay watershed. The acute saltwater 10th percentile (protection of 90% of the species) was 320 ng/L for all species. The 10th percentile by trophic group from most sensitive to least sensitive was: zooplankton (5 ng/L), phytoplankton (124 ng/L), benthos (312 ng/L), and fish (1,009 ng/L). A 10th percentile of 5 ng/L was determined from the limited saltwater chronic data (same value reported for zooplankton tested in acute tests). Limited microcosm and mesocosm studies showed that TBT concentrations less than 50 ug/L generally did not impact the structure and function of biological communities.

1.1.4 Endpoints

The selection of appropriate endpoints is a basic element of the risk assessment process. In ecological risk assessment, it is recognized that individual organisms are part of the food wed and are therefore somewhat expendable as they are either consumed or being consumed. Therefore, the focus of ecological risk assessment is the protection of population, community or ecosystem function, rather than individuals. This acknowledges the fact that a population is less sensitive than its most sensitive member and likewise that communities and ecoystems are less sensitive that their most sensitive populations. A consensus of recent ecological risk assessments has lead to an important conclusion- some effects at the organism and population level can be allowed if these effects are restricted in

space and time and keystone species are not impacted (Solomon et al., 1996; Giddings et al., 1997).

The *Framework for Ecological Risk Assessment* has defined two types of endpoints: assessment endpoints and measurement endpoints (U. S. EPA, 1992). Assessment endpoints are the actual environmental values that are to be protected (e.g. fish or shellfish populations). Measurement endpoints are the measured responses to a stressor that can be correlated with or used to protect assessment endpoints (Suter, 1990). With each higher level of testing, measurement endpoints differ while assessment endpoints remain the same.

The assessment endpoints for this risk assessment are the long term viability of aquatic communities in the Chesapeake Bay (fish, invertebrates etc.). Specifically, the protection of at least 90% of the species 90% of the time (10th percentile from species susceptibility distributions) from acute TBT expsoures is the defined assessment endpoint. Measurement endpoints include all acute TBT toxicity data (survival, growth and reproduction) generated from saltwater laboratory toxicity studies.

1.1.5 Cumulative Stressors Potentially Impacting Aquatic Communities

When assessing the potential impact of TBT on aquatic communities in the Chesapeake Bay watershed, it is important to remember that both biotic (food quality and quantity, disease) and abiotic factors (water quality, other contaminants, physical habitat alteration) influence the status of biological communities. As discussed above, individuals within the various biological communities are more sensitive to contaminant stress than the community as a whole. Therefore, individual losses due to a stressor such as TBT may or may not impact the viability (persistence, abundance, distribution) of the population depending on all the factors influencing the population.

1.1.6 Conceptual Model

Problem formulation is completed with the development of a conceptual model where a preliminary analysis of the ecosystem at risk, stressor characteristics and ecological effects are used to define the possible exposure and effects scenarios. The goal is to develop a working hypothesis to determine how the stressor might affect exposed ecosystems. The conceptual model is based on information about the ecosystem at risk and the relationship between the measurement and assessment endpoints. Professional judgement is used in the selection of risk hypotheses. The conceptual model describes the approach that will be used for the analysis phase and the types of data and analytical tools that will be needed. Specific data gaps and areas of uncertainty will be described later in this report.

The hypothesis considered in this risk assessment was:

- TBT may cause permanent reductions at the population and community level for fish, benthos, zooplankton or phytoplankton in the Chesapeake Bay watershed and these reductions may adversely impact community structure and function.

SECTION 2
EXPOSURE CHARACTERIZATION

2.1 Introduction

The potential for exposure of aquatic organisms to TBT is an important component of a probabilistic ecological risk assessment. Exposure data are used in conjunction with effects data (see next section) to conduct a risk characterization. The exposure analysis for TBT considers use rates, sources, loadings, chemical properties and spatial/temporal scale of measured concentrations (data sources, sampling regimes, analytical methods and data analysis).

2.2 Tributyltin Loading in the Chesapeake Bay Watershed

The major source of TBT to Chesapeake Bay is from the use of antifouling paint on watercraft hulls. Loading of TBT into the aquatic environment from either industrial or sewage treatment plant effluents was reported to be minimal (Huggett et al., 1996). Based on this information, it is not surprising that the highest concentrations of TBT have been measured in areas with the greatest number of watercraft. Highest concentrations were generally found in marinas that had a high density of boats painted with TBT and a low flushing rate. Two types of watercraft are generally considered when determining loading of TBT- recreational and commercial. Estimates conducted for the State of Virginia reported that ~ 70% of the TBT entering Virginia waters came from recreational watercraft while ~ 27% was from large commercial vessels such as freighters and tankers (Huggett et al., 1996). The remaining 3% came from miscellaneous sources such as the military.

The logical focus for controlling TBT input to the Chesaepeake Bay's aquatic environment

was to restrict use on recreational watercraft. With this consideration in mind, both Virginia and Maryland passed legislation to restrict use of TBT on vessels <25m in length in 1987. Longer vessels and aluminum craft hulls were exempted but could only use paints that release TBT at a rate of <5 ug cm^{-2} d^{-1}. A number of other states followed the actions of Virginia and Maryland and federal legislation was established in 1988.

2.3 Chemical Properties of Tributyltin

Tributyltin compounds used in antifouling paints consist of a tin atom covalently bonded to three butyl moieties and an associated anion such as chloride or oxide or copolymers such as methacrylate/methyl methacrylate. Copolymer paints allow manufacturers to formulate paints that have better controlled leach rates in seawater (e. g. tributyltin methacrylate). Due to the hydrophobic nature of the TBT antifouling coating, seawater interacts with the copolymer at the surface which initiates a hydrolysis reaction that cleaves TBT from the copolymer backbone and releases it into the water.

The most important process limiting the persistence of TBT in the aquatic environment is microbial degradation to the less toxic dibutyltin (DBT) and monobutyltin (MBT) compounds. Degradation half-lives in various seawater experiments were reported to vary from 4 to 19 days (U. S. Navy, 1997). Lee et al. (1989) also reported that phytoplankton were active in degrading TBT to the less toxic DBT and MBT; both 2 and 6 day half-lives were reported. Photolysis and chemical degradation were reported to be insignificant in the degradation of TBT in seawater (U. S. Navy, 1997). Degradation of TBT in sediments is much slower than in the water. Various studies have reported half-life values in sediments to range from months to years in anaerobic sediments (Stang and Seligman, 1986; De Mora et al. 1989; Dawson et al. 1993). These data suggest that that

sediments may remain a source for TBT after limiting water column concentrations through regulation.

Due to the hydrophobic nature of TBT it partitions rapidly to particulate material in the water column and bottom sediments. Partitioning rates are dependent on TBT concentration, suspended sediment, load, pH, salinity and organic carbon (U. S. Navy, 1997). Langston and Pope (1995) have reported a partitioning coefficent of 25,000 L/kg at a water column concentration of 10 ng/L (a realistic environmental concentration). Various investigators have reported that partitioning coefficients can vary between 340 to 39,000 (Valkirs et al. 1986,1987; Harris et al. 1996).

Laughlin (1996) has reported that TBT is accumulated by nearly all taxa that have been evaluated. Mollusks were reported to have the highest bioaccumulation factors and highest tissue burdens. Fish and crustaceans generally accumulate lower burdens of TBT because they possess the active cytochrome P-450 enzyme system that oxides TBT to less toxic components (Lee, 1996). Bioaccumulation factors (BCFs) range from about 200 in some fish tissues to 100,000 in American oysters and mussels (U. S. Navy, 1997). Salazar et al. (1987) reported that bioconcentration factors showed an inverse relationship to concentrations in the field, with lower exposures leading to higher bioconcentration factors in bivalves.

Although the potential for sediment-bound TBT to cause risk to sediment dwelling aquatic biota exists, the focus of this risk assessment was an evaluation of risk to aquatic biota from exposures to surface water concentrations. Probabilistic risk assessment techniques for assessing risk of aquatic species to sediment exposures is still developmental and contains a higher degree of uncertainty than water column exposures. By using surface water concentrations in this risk assessment, the results can be more closely related to regulatory issues such as the proposed U. S.

Environmental Protection Agency's chronic marine water quality criteria of 10 ng/L TBT (U. S. EPA, 1997).

2.4 Measured Concentrations of Tributyltin in the Chesapeake Bay Watershed

2.4.1 Data Sources and Sampling Regimes

Tributyltin exposure data (seawater measurements) were available from three primary data sources from 1985 to 1996 for over 3,600 samples at 41 stations (Figure 2, Tables 1 and 2). Approximately 92% of the measurements were from Virginia waters of Chesapeake Bay. The remaining samples were measured from marinas, harbors and river systems in Maryland waters of the Chesapeake Bay. The data sources are briefly described below:

Hall et al Data (Hall et al., 1987, 1988, 1989, and 1992)

These data were collected from 1985 to 1989. During the 1985-86 effort, samples were collected monthly from July through June at eight stations located in four small and large marinas, a large harbor, two major river systems and a heavily used shipping channel (Hall et al., 1987). For the other three studies, samples were collected bi-weekly from June-September of 1986, 1988 and 1989 at six stations in or near marinas in Back Creek (Annapolis, MD) and one location in the Severn River near the confluence of Back Creek and the Severn River (Hall et al., 1988, 1989, and 1992).

Navy Data (Valkirs et al., 1995)

Samples were collected during the summer of 1986 and/or quarterly from 1988 to 1992 at 12 stations in the Elizabeth River, 10 stations in Norfolk Harbor and one station in Hampton River (see Figure 2 and Table 2).

VIMS Data (Unger, personal communication)

These data were collected monthly at five stations in Hampton River and four stations in Sarah Creek (York River basin) from 1986 through 1996 (See Figure 2 and Table 2).

2.4.2 Methods of Tributyltin Analysis

A summary of preparation procedures and analytical methods for the various TBT monitoring studies is presented in Table 3. Detection limits were generally less than 5 ng/L for all studies (except the Hall et al. 1987 - Hall et al 1985 data). In all cases, the water samples (grab samples) collected for analysis were unfiltered and iced for preservation. The analytical method used for all studies except the Navy monitoring was Gas Chromatograph - Flame Photometric Detector (GC-FPD) (Unger et al., 1986). In all cases, TBT was speciated from the degradation products MBT and DBT.

2.4.3 Methods of Data Analysis

Approaches for handling values below the detection limits include assigning these values as zero, one-half the detection limit or the detection limit (MacBean and Rovers, 1984; Giddings et al., 1997). For this risk assessment, TBT values below the detection limit were assumed to be log-normally distributed. The distribution of exposure data was calculated based on the measured values and the concentrations of the non-detects were assumed to be distributed along a lower extension of this distribution. For example, if 80 out of 100 were reported as non-detects, the 20 measured values were assigned ranks from 81 to 100 and the frequency distribution was calculated from these 20 values. For the very few cases where more than one value was available at the same time and station, the highest value was used in the frequency distribution.

For data sets arranged by basin or station with four or more values above the detection limit, log-normal distributions of exposure concentration were determined as follows. The observations in each data set were ranked by concentration and for each observation the percentile ranking was

calculated as n/(N+1) where n is the rank sum of the observation and N is the total number of observations including the non-detects. Percentile rankings were converted to probabilities and a linear regression was performed using the logarithm of concentration as the independent variable and normalized rank percentile as the dependent variable. Although non-detected observations were not included in the regression analysis, they were included in the calculation of the observation ranks. The 90th percentile concentrations (exceedence of a given value only 10% of the time) were calculated for sampling stations (or basins) based on the calculated log-normal concentration distributions.

2.5 Measured Concentrations by Basin

A summary of maximum concentrations and 90th percentiles of individual stations and pooled stations by basin or drainage is presented in Table 2. Maximum TBT concentrations by basin ranged from below detection limit in the Choptank River and C and D Canal to 1801 ng/L in the Back Creek marina area in Maryland. The 90th percentile values by basin for locations with at least 4 detected concentrations, ranged from 4.1 ng/L in Norfolk Harbor to 387 ng/L in Pier 1 Marina in Maryland. As expected, the highest 90th percentiles (138 to 387 ng/L) were reported in marina areas with high densities of boats using TBT paints; much lower values were reported in open water areas such as the Potomac and Choptank Rivers.

2.6 Temporal Trends

Tributyltin saltwater monitoring data were available from 1986 to 1996 in Sarah Creek and Hampton Creek in Virginia to assess temporal trends in TBT (M. A Unger, personal communication).

These data showed a clear trend of decreasing concentrations in the water column after the 1987 legislation (effective in 1988) restricted the use of TBT on recreational watercraft in Chesapeake Bay watershed (Figure 3 and 4). For Sarah Creek, 90th percentile values dropped from approximately 40 ng/L in 1987 to approximately 9 ng/L in 1996 (Figure 3). The reduction of 90th percentiles values in Hampton Creek was from 160 ng/L in 1987 to approximately 15 ng/L in 1996 (Figure 4).

2.7 Summary of Exposure Data

Highest environmental concentrations of TBT (based on 90th percentiles) in the Chesapeake Bay watershed were reported in and near marina areas. Sources of TBT responsible for these high exposures were boat hulls and/or painting and hull cleaning operations. As expected, lower concentrations of TBT were reported in open water areas such as rivers where the density of boats was minimal. Temporal trends analysed from a 10 year data base (1986 to 1996) in two areas in Virginia showed that TBT water column concentrations have declined after 1987 legislation prohibited the use of TBT paints on recreational watercraft (<25m). Due to the long half-life of TBT concentrations in sediment and the equilibrium shift occurring with lower water column concentration, sediments will continue to be a source for TBT.

SECTION 3
ECOLOGICAL EFFECTS

3.1 Modes of Toxicity

Both aquatic plants and animals have enzyme systems that can metabolize TBT to less toxic derivatives. Plants such as eel grass, diatoms and dinoflagellates have been shown to metabolize TBT (Lee, 1996). Diatoms produce a series of hydroxylated derivatives and it is likely that the algal dioxygenase system is involved. For animal species, crustaceans, annelids and fish have enzyme systems that rapidly metabolize TBT. The hydroxylation of TBT that occurs in aquatic vertebrates and invertebrates is controlled by the microsomal cytochrome P-450 systems present in the hepatic, intestinal and kidney tissues of these organisms. These hydroxylated derivatives are conjugated to sulfate or carbohydrate by phase two enzyme systems, which facilitates the elimination of TBT (Lee, 1996). Mollusks have low cytochrome P-450 content and mixed function oxygenase activity and therefore exhibit TBT accumulation with slow depuration rates. Various TBT effects in mollusks include shell thickening, reduced growth rates and imposex (Champ and Seligman, 1996).

3.2 Methods of Toxicity Data Analysis

The primary toxicity benchmark used for this risk assessment was the 10th percentile of species sensitivity (protection of 90% of the species) from acute and chronic exposures. The implied assumption when using this benchmark is that protecting a large percentage of the species assemblage will preserve ecosystem structure and function. This level of species protection is not universally accepted, especially if the unprotected 10% are keystone species and have commercial or recreational significance. However, protection of 90% of the species 90% of the time (10th percentile) has been

recommended by the Society of Environmental Toxicology and Chemistry (SETAC, 1994) and others (Solomon et al., 1996; Giddings et al. 1997). Recent mesocosm studies have reported that this level of protection is conservative (Solomon et al.,1996; Giddings, 1992).

Tributyltin toxicity data were analyzed as a distribution on the assumption that the data represented the universe of species. An approximation was made since it is not possible to test all species in the universe. This approximation assumes that the number of species tested (N) is one less than the number in the universe. To obtain graphical distributions for smaller data sets that are symmetrical (normal distributions) percentages were calculated from the formula (100 x n/(N + 1)) where n is the rank number of the datum point and N is the total number of data points in the data set (Parkhurst et al., 1994). This formula compensates for the size of the data sets as small (uncertain) data sets will give a flatter distribution with more chance of overlap than larger (more certain) data sets. In cases where there were multiple data points for a given species, the lowest value was used in the regression analysis of the distribution. When data were available for multiple life stages of a species the lowest values were generally reported for early life stages. Using the lowest value therefore provides a conservative approach for protecting the most sensitive life stage of a species. Data were plotted using Sigma Plot (Jandel Corporation, 1992) .

3.3 Effects of Tributyltin from Laboratory Toxicity Tests

Acute and chronic TBT toxicity data used in this risk assessment were obtained from the AQUIRE database through 1995, U. S. EPA water quality criteria documents (U. S. EPA, 1997), literature review documents (Hall and Pinkney, 1985; Hall and Bushong, 1996; Champ and Seligman, 1996) and manual searches of grey literature from academia, industry and government sources.

Only data that met the various criteria established by the U. S. EPA for use in water quality criteria development were used in the analysis (acceptable control survival, complete description of test methods etc.). Tributyltin acute and chronic toxicity data by water type (saltwater and freshwater) are discussed below. However, only the saltwater acute and chronic data were used for risk characterization since all exposure data were from Chesapeake Bay saltwater environments .

3.3.1 Acute Toxicity of Tributyltin

Acute saltwater TBT toxicity data were available for 43 species, including five algal species, five zooplankton species, 24 benthic species and nine fish species (Table 4, Figure 5) The range of acute toxicity values was 420 ng/L for the mysid, *Acanthomysis sculpta* to 330,000 ng/L for an algal species. The acute 10th percentile for all saltwater species was 320 ng/L (Table 5). A breakdown of 10th percentiles by trophic group from most to least sensitive was as follows: zooplankton (5 ng/L), phytoplankton (124 ng/L), benthos (312 ng/L) and fish (1,009 ng/L) (Table 5).

Acute freshwater toxicity data were available for 23 species (Table 6, Figure 6). The data base included three zooplankton species, five fish species and 11 benthic species. The range of acute toxicity for freshwater species was 1,110 ng/L for the hydra, *Hydra littoralis* to greater than 114,000,000 ng/L for the adult clam, *Ellipito complanata*. The high value for the clam likely resulted from shell closure during the acute exposure. The acute 10th percentile of all freshwater species was 103 ng/L (Table 5). The 10th percentiles by trophic group from most to least sensitive were as follows: benthos (44 ng/L), zooplankton (400 ng/L) and fish (849 ng/L).

3.3.2 Chronic Toxicity of Tributyltin

Chronic saltwater TBT toxicity data, where chronic values were reported, were limited to four invertebrate species (Table 7, Figure 7). These chronic values ranged from 14 to 131 ng/L. The 10th

percentile for these four saltwater species was 5 ng/L (Table 5).

The freshwater chronic TBT toxicity data, where chronic values or no observed effect level (NOEL) were reported, were also limited to only three species (Table 8, Figure 8). These chronic values ranged from 137 to 253 ng/L for the cladoceran and fish species. The chronic 10th percentile for the freshwater species was 102 ng/L (Table 5).

3.4 Mesocosm/Microcosm Studies

Saltwater mesocosm and microcosm studies with TBT were limited (Henderson, 1985, 1986, 1988). A three month mesocosm study by Henderson (1985, 1986) with TBT concentrations ranging from 500 to 1,800 ng/L showed the following: (1) annelid worms, crustaceans and fish were insensitive to the exposures; (2) larval stages of various animals species such as corals, anemones, echinoderms and mollusks were most sensitive. In later three month microcosm studies with TBT concentrations ranging from 40 to 2,500 ng/L, Henderson (1988) reported the following: (1) significant declines in pre-established fouling communities occurred at 500 ng/L and higher; (2) significant reductions in number of species and species diversity of larval forms and reductions in the condition index of the American oyster occurred at 100 ng/L and (3) oyster condition index, species diversity and mortality did not occur at concentrations of 40 ng/L. The conclusion from these studies is that TBT concentrations in the environment should be less than 50 ng/L to avoid effects on aquatic communities.

Two microcosm studies with durations of 24 to 55 days were conducted in freshwater (Delupis and Miniero, 1989; Miniero and Delupis, 1991). In both studies effects were immediate at 80,000 ng/L dose as *Daphnia magna* disappeared, ostracods increased and algal species increased

immediately and then gradually dissappeared. The lowest concentration (4,700 ng/L) to even suggest an effect in these studies caused a temporary reduction in metobolism (oxyen consumption). This suggested effect concentration of 4,700 ng/L is much higher that concentrations typically measured in the environment.

3.5 Summary of Effects Data

Acute effects with saltwater species were generally reported at concentrations greater than or equal to 420 ng/L. The 10th percentile for all species derived from the acute TBT saltwater toxicity data base was 320 ng/L. The order of sensitivity from most to least sensitive trophic group and corresponding 10th percentiles were as follows: zooplankton (5 ng/L), phytoplankton (124 ng/L), benthos (312 ng/L) and fish (1,009 ng/L). For freshwater acute TBT studies, effects were reported at concentrations at or above 1,110 ng/L. The acute freshwater 10th percentile for all species was 103 ng/L. The 10th percentiles by trophic group from most to least sensitive were as follows: benthos (44 ng/L), zooplankton (400 ng/L) and fish (849 ng/L).

Chronic data from both saltwater and freshwater studies were limited to a few species. The saltwater and freshwater chronic 10th percentiles for all species were 5 and 102 ng/L, respectively. Limited mesocosm/microcosm studies in saltwater demonstrated that TBT concentrations less than 50 ng/L generally did not impact the structure and of biological communities. Freshwater microcosm studies suggested that concentrations as high as 4,700 ng/L only caused temporary reductions in biological community metabolism.

SECTION 4
RISK CHARACTERIZATION

4.1 Characterizating Risks

The report of the *Aquatic Risk Assessment Dialogue Group* (SETAC, 1994) recommends using tiers when assessing the risk of pesticides in the aquatic environment. The first tier is a simple and commonly used risk quotient. Risk quotients are simple ratios of exposure and effects concentrations where the susceptibility of the most sensitive species is compared with the highest environmental exposures. If the exposure concentration equals or exceeds the effects concentration an ecological risk is suspected. The quotient method is a valuable first tier assessment that allows a determination of a worst case effects and exposure scenario for a particular contaminant. However, some of the major limitations of the quotient method for ecological risk assessment are that it fails to consider variability of exposures among individuals in a population, ranges of sensitivity among species in the aquatic ecosystem and the ecological function of these individual species. The quotient method also assumes that that there is a 100% probability of co-occurrence of the stressor and the most sensitive organism and that the most sensitive organism is a keystone organism in the environment. The probabilistic approach addresses these various concerns as it expresses the results of an exposure or effects characterization as a distribution of values rather than a single point estimate. Quantitative expressions of risks to aquatic communities are therefore determined by using all relevant single species toxicity data in conjunction with exposure distributions. A detailed presentation of the principles used in a probabilistic ecological risk assessment are presented by Solomon et al. (1996) and Hall et al. (in press).

The following section will summarize the results of the risk characterization phase of this

probabilistic ecological risk assessment of TBT in the Chesapeake Bay watershed. The toxicity benchmarks used for the risk characterization will be both the saltwater acute and chronic 10th percentiles for all species since all exposure data were reported in saltwater environments. Both the acute 10th percentile for all species (320 ng/L) and the chronic 10th percentile for all species (5 ng/L) are similar to the proposed U. S. EPA acute (370 ng/L) and chronic (10 ng/L) TBT criteria (U. S. EPA, 1997). It is also important to note that the chronic 10th percentile of 5 ng/L also equals the acute 10th percentile of the most sensitive trophic group (zooplankton) resulting from acute laboratory toxcity tests. Therefore, the most sensitive trophic group (zooplankton) will be protected in this risk characterization.

4.2 Risk Characterization of Tributyltin in the Chesapeake Bay Watershed

Potential ecological risk from TBT exposure was characterized by using both acute and chronic saltwater effects data (10th percentiles for all species) since all exposure data were collected in saltwater areas of the Chesapeake Bay. Using the acute 10th percentile as a toxicity benchmark generally results in low risk for all areas sampled (Table 9). The greatest risk (12% exceedence) at Back Creek marina in the Severn River would still be considered in the low risk range. The use of the chronic benchmark of 5 ng/L results in some significant ecological risk in all marinas and Baltimore harbor (> 97% exceedence), Hampton River (73% exceedence), Sarah Creek (52% exceedence) and the Elizabeth River (33% exceedence). These data suggest that TBT may be posing a risk to aquatic biota in specific areas of Chesapeake Bay associated with boating activity. The low ecological risk reported in the Potomac River, Choptank River, C and D Canal and Norfolk Harbor using the chronic 10th percentile indicates that potential ecologial risk is not present throughout the

entire Chesapeake Bay.

4.3. Uncertainty in Ecological Risk Assessment

Uncertainty plays a particularly important role in ecological risk assessment as it impacts problem formulation, analysis of exposure and effects data and risk characterization. Uncertainty in ecological risk assessment has three basic sources: (1) lack of knowledge in areas that should be known; (2) systematic errors resulting from human or analytical error and (3) non-systematic errors resulting from the random nature of the ecosystem (e.g. Chesapeake Bay watershed). The following sections will address specific uncertainty from the above three sources as associated with exposure data, effects data and risk characterization.

4.3.1 Uncertainty Associated with Exposure Characterization

The tributyltin exposure data used for this risk assessment were obtained from three different data sources from 1985 to 1996 as described in Section 2. The spatial scale of these data (41 stations in 10 basins, primarily in Virginia) was somewhat limited considering that there are at least 50 major rivers that discharge into the Chesapeake Bay and numerous marinas where exposures are unknown. Extensive exposure data from basins in Maryland waters of Chesapeake Bay were particularly limited on a temporal scale. Uncertainty also existed because the exposure data used in this risk assessment were not collected from random sampling designs compatible with unbiased statistical analysis of frequency distributions. In fact, these data were biased toward high values because many of the stations were located in areas where concentrations were expected to be high (near marinas and harbors) and samples were collected during the high use season (summer) for antifouling coatings such as TBT.

Analytical techniques differed among three the laboratories - a GC-FPD method was used by Hall et al and VIMS while the Navy used an AAS technique. Detection limits among the laboratories were less than 5 ng/L for all measurements except the Hall et al 1985 data ($\leq$ 20 ng/L). Sample preparation techniques were consistent among all the laboratories; therefore, this area of uncertainty was somewhat reduced.

4.3.2 Uncertainty Associated with Ecological Effects Data

Due to the relatively small number of species that can be routinely cultured and tested in laboratory toxicity studies, there is uncertainty when extrapolating these toxicity data to responses of natural taxa found in the Chesapeake Bay watershed. In the case of TBT in the Chesapeake Bay watershed, saltwater acute and chronic toxicity data were available for 43 and 4 species, respectively, for use in the calculation of the 10th percentile. Although the acute data provide a reasonable representation of species in the Bay environment, the chronic data were limited and should be expanded to reduce uncertainty in this risk assessment.

Variability in the results of toxicity tests for a given species tested in different experiments or by different authors is a potential source of random and systematic errors. In this assessment, the most conservative (lowest) effect value was used when multiple data points were available for a given species. The range of toxicity data among trophic groups differed for the acute saltwater toxicity data as the 10th percentiles ranged from 5 ng/L for zooplankton to 1,005 ng/L for fish. Using the distribution of susceptibility accounts for this range of data points. Distributions will be flatter, with greater chance of overlap with exposure distributions, when the range is large.

Acute and chronic saltwater TBT toxicity data were used in the risk characterization as previously discussed. The use of acute (and chronic) data for predicting ecosystem effects is often

questioned and assumed to be an area of significant uncertainty. However, Slooff et al. (1986) in their review of single species and ecosystem toxicity for various chemical compounds , have reported that there is no solid evidence that predictions of ecosystem level effects from acute tests are unreliable. The result of Slooff et al. (1986) coupled with the use of a distribution of acute toxicity data reduces some of the uncertainty associated with using acute data.

4.3.3 Uncertainty Associated with Risk Characterization

Many of the uncertainties associated with the variability in the exposure and effects characterizations discussed above are incorporated in the probabilistic approach used in this risk assessment (SETAC, 1994). Quantitative estimation of risks are analyzed as a distribution of exposure and effects data.

Ecological uncertainty includes the effects of confounding stressors such as other contaminants and the ecological redundancy of the functions of affected species. In the Chesapeake Bay watershed, numerous contaminants other than TBT may be present simultaneously in the same aquatic habitats near marinas and harbors; therefore, "joint toxicity" may occur. The concurrent presence of various contaminants along with TBT makes it difficult to determine the risk of TBT in isolation.

Ecological redundancy is known to occur in aquatic systems. Field studies have shown that resistant taxa tend to replace more sensitive species under stressful environmental conditions (Solomon et al., 1996; Giddings et al., 1992) The resistant species may replace the sensitive species if it is functionally equivalent in the aquatic ecosystem and the impact on overall ecosystem function is reduced by these species shifts. For this risk assessment, information on the ecological interactions among species would help to reduce this area of uncertainty.

SECTION 5
CONCLUSIONS AND RESEARCH NEEDS

Potential ecological risk from TBT exposure was reported for various areas in Chesapeake Bay that are in close proximity to boating or shipping activity. Highest risk was reported for marinas in Maryland but significant potential ecological risk was also reported for areas in Virginia such as the Elizabeth River, Hampton Creek, and Sarah Creek. Low ecological risk was reported for areas such as the Potomac River, Choptank River, C and D Canal and Norfolk Harbor. Temporal exposure data has demonstrated that TBT concentrations in the water column have declined since 1987 regulation of this compound on recreational watercraft in Chesapeake Bay. Although these declining water column concentrations are beneficial in reducing risks to aquatic biota, various studies have showed that the TBT in the sediment may last for years and continue to remain a source for TBT exposure in the water column. The use of TBT by commercial watercraft (>25m) and associated painting and hull cleaning activities also continues to contribute to TBT loading in Chesapeake Bay.

The following research is recommended to supplement existing data for assessing the ecological risks of TBT in the Chesapeake Bay watershed:

(1) Post-regulation exposure assessments for TBT in water and sediment for Sarah Creek and Hampton Creek in Virginia should be continued as a long term monitoring effort since a 10 year data base has already been established in these areas. These data will allow an analysis of TBT trends. Similar type post-regulation monitoring activities should also be conducted in the Severn River/Back Creek areas of Maryland where exposure data have also been collected.

(2) Chronic TBT toxicity experiments are recommended for various keystone Chesapeake Bay species (sensitive bivalve species) to determine the lowest observed effect concentrations (LOEC) for these valuable species. In the current chronic saltwater toxicity data base, chronic values were only available for four species.

(3) Biological communities such as fish and benthos (community metric approaches) should be evaluated in areas where potential ecological risk of TBT is reported to be the greatest (near marinas and harbors). Imposex in gastropods should also be assessed in these areas. These data would provide a validation step for this ecological risk assessment.

SECTION 6
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TABLES

Table 1. Summary of three data sources used for this risk assessment.

Reference	Data ID	Total # samples	Sample Period	Detection Limit (ng/L)
Hall et al., 1987	Hall Data 85	96	monthly July 1985-June 1986	20
Hall et al., 1988	Hall Data 86	63	June-September 1986	5
Hall et al., 1989	Hall Data 88	63	June-September 1988	2
Hall et al., 1992	Hall Data 89	63	June-September 1989	2
Valkirs et al., 1995	Navy	1,027	summer 1986; quarterly 1988-1992	0.2
M.A. Unger, pers. comm.	VIMS	2,307	monthly 1986-1996	1

Table 2. Summary of TBT exposure data for all basins and stations. Maximum concentrations and 90th percentile values (minimum of four detected concentrations) are presented by station and basin.

Drainage Data ID	Station	# Samples	# Detections	TBT Concentration (ng/L) Maximum	90th percentile
James Basin, Elizabeth River					
NAVY	Elizabeth River Station 15	7	4	8.9	11.1
NAVY	Elizabeth River Station 17A	10	5	10.7	10.2
NAVY	Elizabeth River Station 19	82	80	41	19.7
NAVY	Elizabeth River Station 21	10	8	13.4	28.4
NAVY	Elizabeth River Station 32	85	84	29.4	18.6
NAVY	Elizabeth River Station 13A	7	6	9.8	12.8
NAVY	Elizabeth River Station 11	84	79	45.4	16.0
NAVY	Elizabeth River Station 10	82	78	14.3	10.0
NAVY	Lafayette River Station 37	6	0	BLD	-
NAVY	Naval Station 9	79	72	8.9	6.4
NAVY	Naval Station 4	80	74	9.8	5.7
NAVY	Naval Station 3	79	72	7.9	5.5
Elizabeth River	all stations combined	611	562	45.4	14.2
James Basin, James mainstem/Norfolk Harbor					
NAVY	Hampton Roads Station 29	79	71	9.8	4.9
NAVY	Hampton Roads Station 35	4	0	BLD	-
NAVY	Hampton Roads Station 23	5	0	BLD	-
NAVY	Hampton Roads Station 3A	74	70	10.7	3.3
NAVY	Hampton Roads Station 34	3	0	BLD	-
NAVY	Hampton Roads Station 1	79	70	6.1	4.5
NAVY	Hampton Roads Station 25	78	69	5.1	5.4
NAVY	Hampton Roads Station 25A	14	13	5.3	4.5
NAVY	Hampton Roads Station 25B	14	13	3.2	3.0
NAVY	Hampton Roads Station 36	4	0	BLD	-
Norfolk Harbor	all stations combined	354	306	10.7	4.1
James Basin, Hampton River					
VIMS	OPC	258	252	42	7.2
VIMS	HRM2	258	257	1,300	337
NAVY	Station 33	86	84	38	10
VIMS	HRM1	257	257	180	41
VIMS	HYC	256	256	340	54
VIMS	CD	257	257	95	26
Hampton River	all stations combined	1372	1363	1,300	77
York Basin, Sarah Creek					
VIMS	A	256	251	120	27
VIMS	B	255	255	72	31
VIMS	C	256	253	23	14
VIMS	D	254	122	16	3.6
Sarah Creek	all stations combined	1021	881	120	23
Potomac					
Hall Data	Potomac River	12	2	24	-
Choptank					
Hall Data	Choptank River	12	0	BLD	-
West	Hartge Marina	12	10	186	138

Drainage Data ID	Station	# Samples	# Detections	TBT Concentration (ng/L) Maximum	90th percentile
Severn	six Back Creek stations	174	174	1,801	351
	Severn River	27	27	89	53
Mid-Bay	Pier 1 Marina	12	10	307	387
Chester	Piney Narrows Marina	12	11	338	354
Patapsco	Baltimore Harbor	12	8	112	129
C&D Canal	C&D Canal	12	0	BLD	-

Table 3. Summary of TBT sample preparation procedures and analytical methods for the various monitoring studies.

Database ID	Detection Limits ng/L	Filtered/ Unfiltered	Preservation	Sample Type	Analytical Method
Hall Data 85	20	unfiltered	iced	grab	GC -FPD
Hall Data 86	5	unfiltered	iced	grab	GC -FPD
Hall Data 88	2	unfiltered	iced	grab	GC -FPD
Hall Data 89	2	unfiltered	iced	grab	GC -FPD
Navy	0.2	unfiltered	iced	grab	AAS
VIMS	1	unfiltered	iced	grab	GC-FPD

Table 4. Saltwater acute TBT toxicity data measured as TBT (ng/L). Concentrations marked by an asterisk* were converted from reported compounds to TBT. The abbreviations used are: N= nominal, M= measured, S= static, R= renewal, FT= flowthrough, LC= life cycle, ELS= early life stage and NR= not reported.

Species	Method & Exposure type	LC50 (ng/L)	Reference
Mysid *Acanthomysis sculpta*	M, R	96 hr LC50 420 ng/L	Davidson et al. 1986a,b
Sand Dollar *Dendraster excentricus*	NR	1.3 hr EC50 465 ng/L	Brix et al. 1994
Copepod *Eurytemora affinis*	M, FT	72 hr LC50 500 ng/L	Bushong et al., 1988
Copepod *Acartia tonsa*	M, R	144 hr LC50 535 ng/L*	U'ren, 1983
Copepod *Eurytemora* sp.	M, S	24 hr LC50 681 ng/L*	Naval Oceans Systems Center, 1981
Eastern Oyster *Crassostrea virginica*	M, R	48 hr LC50 710 ng/L	Roberts, 1987
Mussel *Mytilus galloprovincialis*	N, S	96 hr LC50 831 ng/L*	Robert and His, 1981
Mysid *Metamysidopsis elongata*	N, S	7 d LC50 973 ng/L	Salazar and Salazar, 1989
Copepod *Acartia* sp.	M, S	24 hr LC50 973 ng/L*	Naval Oceans Systems Center, 1981
Alga *Thalassiosira pseudonana*	N, S	72 hr EC50 1002 ng/L*	Walsh et al., 1985

Hardshell clam *Mercenaria mercenaria*	M,S	48 hr LC50 1007 ng/L*	Roberts, 1987
Mysid *Mysidopsis bahia*	M, FT	96 hr LC50 1100 ng/L	Goodman et al., 1988
Amphipod *Gammarus* sp.	M, FT	96 hr LC50 1300 ng/L	Bushong et al, 1988
Chinook Salmon *Oncorhynchus tshawytscha*	M, S	96 hr LC50 1460 ng/L	Short and Thrower., 1986
Amphipod *Eohaustorius washingtonianus*	M, R	10 d LC50 1500 ng/L	Meador et al., 1993
Amphipod *Eohaustorius estuarius*	M, R	96 hr LC50 1500 ng/L	Meador, 1993
Pacific Oyster *Crassostrea gigas*	NR, R	48 hr LC50 1557 ng/L	Thain, 1983
Sheepshead Minnow *Cyprinodon variegatus*	N, S	6 d LC50 1654 ng/L*	Cramm, 1979
Shrimp *Crangon crangon*	NR, R	96 LC50 1946 ng/L*	Thain, 1983
Sole *Solea solea*	NR, R	96 hr LC50 1946 ng/L*	Thain, 1983
Polychaete *Arenicola cristata*	N, S	96 hr LC50 2000 ng/L	Walsh et al., 1986
Alga *Prorocentrum mariae-bebouriae*	N, S	120 hr EC50 2148 ng/L*	Ho, 1984

Mussel *Mytilus edulis*	N, R	48 hr LC50 2238 ng/L	Thain, 1983
Inland Silverside *Menidia beryllina*	M, FT	96 hr LC50 3000 ng/L	Bushong et al., 1988
Barnacle *Balanus amphitrite*	M, S	24 hr LC50 3893 ng/L*	Naval Oceans Systems Center, 1981
Grass Shrimp *Palaemonetes pugio*	N, R	96 hr LC50 4070 ng/L	Khan et al., 1993
Atlantic Menhaden *Brevoortia tyrannus*	M, FT	96 hr LC50 4500 ng/L	Bushong et al., 1988
Flatfish *Citharichthys stigmaeus*	M, S	96 hr LC50 4866 ng/L*	Salazar and Salazar., 1989
Phytoplankton assemblage from York River	N, S	2 hr EC50 5008 ng/L*	Ho, 1984
Polychaete *Neanthes arenaceodentata*	N, S	96 hr LC50 6812 ng/L	Salazar and Salazar, 1989
Pink Shrimp *Penaeus duoarum*	N, S	96 hr LC50 7396 ng/L*	M & T Chemicals Co., 1981
Alga *Isochrysis galbana*	N, S	120 hr EC50 8537 ng/L*	Ho, 1984
Atlantic Silverside *Menidia menidia*	M, FT	96 hr LC50 8900 ng/L	Bushong et al., 1988
Crab *Carcinus maenas*	NR, R	96 hr LC50 9732 ng/L	Thain, 1983

Amphioxus *Branchiostoma caribaeum*	N, FT	96 hr LC50 <10000 ng/L	Clark et al., 1987
Amphipod *Rhepoxynius abronius*	M, R	10 d LC50 11000 ng/L	Meador et al., 1993
Amphipod *Orchestia traskiana*	M, R	9 d LC50 >14600 ng/L	Laughlin et al., 1982
Poacher *Agonus catophractus*	NR, R	96 hr LC50 15571 ng/L*	Thain, 1983
Mummichog *Fundulus heteroclitus*	M, FT	96 hr LC50 17200 ng/L	Pinkney et al., 1989
Clam *Protothaca staminea*	M, S	10 d LC50 97320 ng/L*	Salazar and Salazar, 1989
European Oyster *Ostrea edulis*	NR, R	96 hr LC50 198922 ng/L*	Thain, 1983
Rotifer *Brachionus plicatilis*	N, S	24 hr LC50 300000 ng/L	Snell et al., 1991b
Alga *Minutocellus polymorphus*	NR	48 hr EC50 330000 ng/L	Walsh et al., 1988

Table 5. The 10th percentile intercepts for freshwater and saltwater tributyltin toxicity data by test duration and trophic group. These values represent protection of 90% of the test species.

Water type	Test type	Trophic Group	n	10th Percentile (ng/L)
Freshwater	acute	All species	23	103
		zooplankton	3	400
		benthos	11	44
		fish	5	849
Freshwater	chronic	All species	3	102
Saltwater	acute	All species	43	320
		phytoplankton/algae	5	124
		zooplankton	5	5
		benthos	24	312
		fish	9	1,009
Saltwater	chronic	All species	4	5

Table 6. Freshwater acute TBT toxicity data measured as TBT (ng/L). Concentrations marked by an asterisk* were converted from reported compounds to TBT. The abbreviations used are: N= nominal, M= measured, S= static, R= renewal, FT= flowthrough, LC= life cycle, ELS= early life stage and NR= not reported.

Species	Method & Exposure type	LC50 (ng/L)	Reference
Hydra *Hydra littoralis*	M, S	96 hr LC50 1110 ng/L	TAI Environmental Sciences, Inc. 1989a
Hydra *Hydra oligactis*	M, S	96 hr LC50 1140 ng/L	TAI Environmental Sciences, Inc. 1989a
Three spine Stickleback *Gasterosteus aculeatus*	N, R	96 hr LC50 1265 ng/L*	Mathisssen-Spiekman et al., 1989
Water Flea *Daphnia magna*	N, S	48 hr LC50 1580 ng/L	Leblanc, 1976
European Frog *Rana temporaria*	N, S	96 hr LC50 1606 ng/L*	Hooftman et al., 1989
Hydra *Chlorohydra viridissmia*	M, S	96 hr LC50 1800 ng/L	TAI Environmental Sciences, Inc. 1989b`
Rainbow Trout *Salmo gairdneri*	NR	48 hr LC50 1890 ng/L	Alabaster, 1969
Fathead Minnow *Pimephales promelas*	M, FT	96 hr LC50 2600 ng/L	Brooke et al., 1986a,b
Lake Ontario Algae (natural community)	N, S	4 hr IC50 2920 ng/L*	Wong et al., 1982
Midge *Chironomus riparius*	N, S	96 hr LC50 3270 ng/L*	Hooftman et al., 1989

Amphipod *Gammarus pseudolimnaeus*	M, FT	96 hr LC50 3700 ng/L	Brooke et al., 1986b
Annelid *Lumbriculus variegatus*	M, FT	96 hr EC50 5400 ng/L	Brooke et al., 1986b
Channel Catfish *Ictalurus punctatus*	M, FT	96 hr LC50 5500 ng/L	Brooke et al., 1986b
Bluegill *Lepomis macrochirus*	N, S	96 hr LC50 7200 ng/L	Buccafusco, 1976a
Snail *Biomphalaria glabrata*	N, S	24 hr LC50 7531 ng/L*	Smith et al., 1979
Mosquito *Culex* sp.	M, S	96 hr EC50 10200 ng/L	Brooke et al., 1986b
Snail *Biomphalaria sudanica*	N, S	24 hr LC50 11633 ng/L*	Webbe and Sturrock, 1964
Snail *Bulinus nasutus*	N, S	24 hr LC50 12464 ng/L*	Webbe and Sturrock, 1964
Cyanobacterium *Anabaena flosaquae*	N, S	4 hr IC50 12652 ng/L*	Wong et al., 1982
Alga *Scenedesmus quadricauda*	N, S	4 hr IC50 15571 ng/L*	Wong et al., 1982
Mosquito *Aedes aegypti*	N. S	24 hr LC50 16544 ng/L*	Das et al., 1984
Rotifer *Brachionus calyciflorus*	N, S	24 hr LC50 19000 ng/L	Snell et al., 1991a

Ostracod *Cypridopsis hartwigi*	N, S	96 hr LC50 116784 ng/L*	Floch et al., 1964
Asiatic Clam *Corbicula fluminera*	N, NR	24 hr LC50 2043720 ng/L*	Foster, 1981
Freshwater Clam *Elliptio complanata*	N, S	96 hr LC50 114837600 ng/L *	Buccafusco, 1976b

Table 7. Saltwater chronic TBT toxicity data measured as TBT (ng/L). Concentrations marked by an asterisk* were converted from reported compounds to TBT. The abbreviations used are: N= nominal, M= measured, S= static, R= renewal, FT= flowthrough, LC= life cycle, ELS= early life stage and NR= not reported.

Species	Method & Exposure	Chronic value (ng/L)	Reference
Copepod *Acartia tonsa*	M, FT	144 hr 14 ng/L*	Bushong et al., 1990
Mussel *Mytilus edulis*	M, R	33 days 17 ng/L	Lapota et al. 1993
Copepod *Eurytemora affinis*	NR, LC	13 day <88 ng/L	Hall et al. 1988
Mysid *Acanthomysis sculpta*	NR, LC	63 day 130.8 ng/L	Davidson et al, 1986a,b

Table 8. Freshwater chronic TBT toxicity data measured as TBT (ng/L). Concentrations marked by an asterisk* were converted from reported compounds to TBT. The abbreviations used are: N= nominal, M= measured, S= static, R= renewal, FT= flowthrough, LC= life cycle, ELS= early life stage and NR= not reported.

Species	Method & Exposure type	Chronic value (ng/L)	Reference
Cladoceran *Daphnia magna*	LC	21 day 137 ng/L*	Brooke et al. 1986a,b
Rainbow Trout *Salmo gairdneri*	N, FT	110 d NOEL 178 ng/L*	Seinen et al., 1981
Fathead Minnow *Pimephales promelas*	ELS	33 day 253 ng/L*	Brooke et al. 1986a,b

Table 9. The percent probability of exceeding the TBT acute and chronic saltwater 10th percentiles for all species.

Drainage	Station	acute saltwater tests - all species (320 ng/L)	chronic saltwater tests (5 ng/L)
James Basin, Elizabeth River			
	Elizabeth River Station 15	<0.01	30
	Elizabeth River Station 17A	<0.01	74
	Elizabeth River Station 19	<0.01	61
	Elizabeth River Station 21	0.12	49
	Elizabeth River Station 32	<0.01	70
	Elizabeth River Station 13A	<0.01	60
	Elizabeth River Station 11	<0.01	50
	Elizabeth River Station 10	<0.01	35
	Lafayette River Station 37	-	-
	Naval Station 9	<0.01	15
	Naval Station 4	<0.01	13
	Naval Station 3	<0.01	12
Elizabeth River	all stations combined	<0.01	33
James Basin, James mainstem/Norfolk Harbor			
	Hampton Roads Station 29	<0.01	10
	Hampton Roads Station 35	-	-
	Hampton Roads Station 23	-	-
	Hampton Roads Station 3A	<0.01	3
	Hampton Roads Station 34	-	-
	Hampton Roads Station 1	<0.01	8
	Hampton Roads Station 25	<0.01	11
	Hampton Roads Station 25A	<0.01	8
	Hampton Roads Station 25B	<0.01	3
	Hampton Roads Station 36	-	-
Norfolk Harbor	all stations combined	<0.01	7
James Basin, Hampton River			
	OPC	<0.01	26
	HRM2	12.0	99
	Station 33	<0.01	26
	HRM1	0.02	83
	HYC	0.13	85
	CD	<0.01	80
Hampton River	all stations combined	1.12	73
York Basin, Sarah Creek			
	A	<0.01	69
	B	<0.01	88
	C	<0.01	59
	D	<0.01	5.9
Sarah Creek	all stations combined	0.08	52
Potomac	Potomac River	-	-
Choptank River	Choptank River	-	-
West	Hartge Marina	0.99	97

Drainage	Station	acute saltwater tests - all species (320 ng/L)	chronic saltwater tests (5 ng/L)
Severn	six Back Creek stations	12.0	>99
	Severn River	0.01	97
Mid-Bay	Pier 1 Marina	10.0	97
Chester	Piney Narrows Marina	8.40	99
Patapsco	Baltimore Harbor	0.12	>99
C&D Canal	C&D Canal	-	-

FIGURES

Figure 1. Ecological risk assessment approach

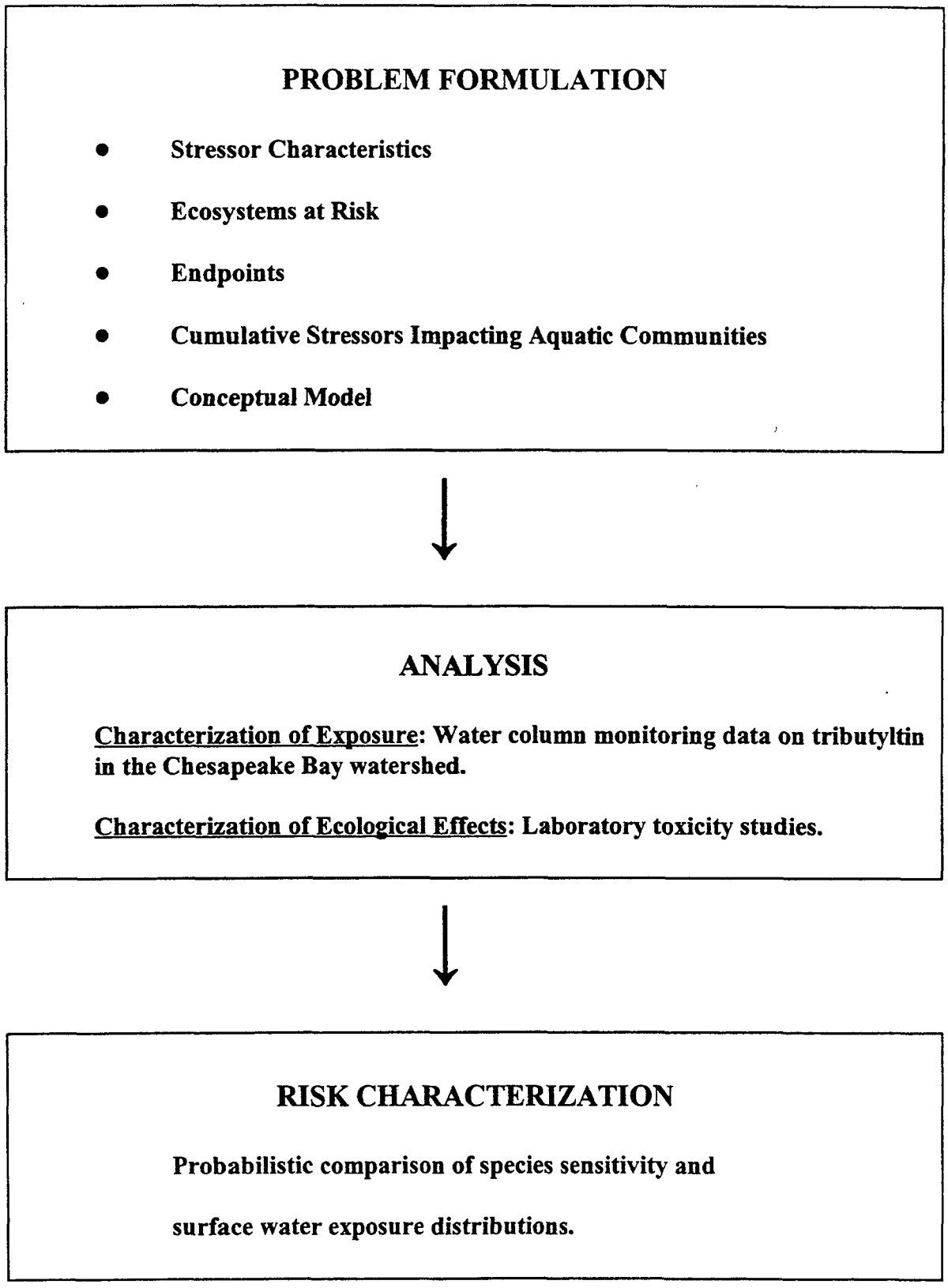


Figure 2. Location of 41 stations where TBT was measured from 1985 to 1996. See key to map where stations are described.

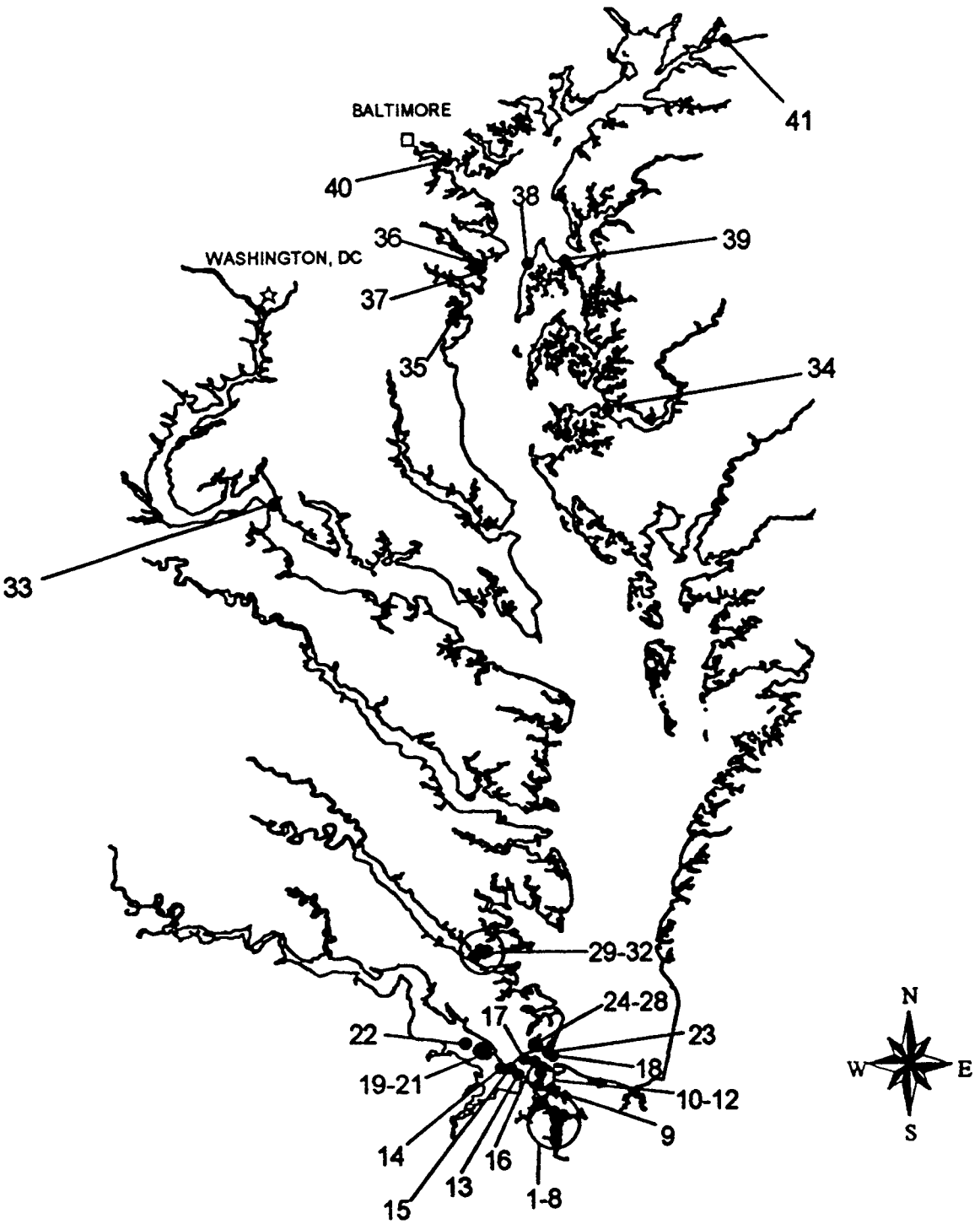


Figure 2. continued.

Station number	Drainage Basin	Dataset	Station	Latitude	Longitude
1	James	NAVY	Elizabeth River station 15	36.7755	76.2953
2	James	NAVY	Elizabeth River station 17A	36.7973	76.2938
3	James	NAVY	Elizabeth River station 19	36.8031	76.2949
4	James	NAVY	Elizabeth River station 21	36.8216	76.2920
5	James	NAVY	Elizabeth River station 32	36.8323	76.2961
6	James	NAVY	Elizabeth River station 13A	36.8398	76.2757
7	James	NAVY	Elizabeth River station 11	36.8472	76.3000
8	James	NAVY	Elizabeth River station 10	36.8700	76.3295
9	James	NAVY	Lafayette River station 37	36.9065	76.3072
10	James	NAVY	Naval Station 9	36.9159	76.3416
11	James	NAVY	Naval Station 4	36.9491	76.3343
12	James	NAVY	Naval Station 3	36.9611	76.3322
13	James	NAVY	Hampton Roads station 29	36.9453	76.3913
14	James	NAVY	Hampton Roads station 35	36.9610	76.4365
15	James	NAVY	Hampton Roads station 23	36.9613	76.4108
16	James	NAVY	Hampton Roads station 3A	36.9781	76.3497
17	James	NAVY	Hampton Roads station 34	36.9849	76.3750
18	James	NAVY	Hampton Roads station 1	36.9928	76.3017
19	James	NAVY	James River station 25	36.9988	76.4744
20	James	NAVY	James River station 25A	37.0051	76.4925
21	James	NAVY	James River station 25B	37.0142	76.4785
22	James	NAVY	James River station 36	37.0242	76.5252
23	James	VIMS	Hampton River station OPC	37.0005	76.3138
24	James	VIMS	Hampton River station HRM2	37.0163	76.3442
25	James	NAVY	Hampton River station 33	37.0164	76.3411
26	James	VIMS	Hampton River station HRM1	37.0170	76.3417
27	James	VIMS	Hampton River station HYC	37.0205	76.3442
28	James	VIMS	Hampton River station CD	37.0228	76.3438
29	York	VIMS	Sarah Creek station D	37.2458	76.5005
30	York	VIMS	Sarah Creek station A	37.2553	76.4797
31	York	VIMS	Sarah Creek station C	37.2597	76.4675
32	York	VIMS	Sarah Creek station B	37.2628	76.4850
33	Potomac	Hall Data	Potomac River	see map for remaining locations	
34	Choptank	Hall Data	Choptank River		
35	West	Hall Data	Hartge Marina		
36	Severn	Hall Data	Back Creek (6 stations)		
37	Severn	Hall Data	Severn River		
38	Mid-Bay Mainstem	Hall Data	Pier 1 Marina		
39	Chester	Hall Data	Piney Narrows Marina		
40	Patapsco	Hall Data	Baltimore Harbor		
41	C&D Canal	Hall Data	C&D Canal		

Figure 3. Temporal trend of 90th percentile concentrations of TBT for Sarah Creek from 1986-1996.

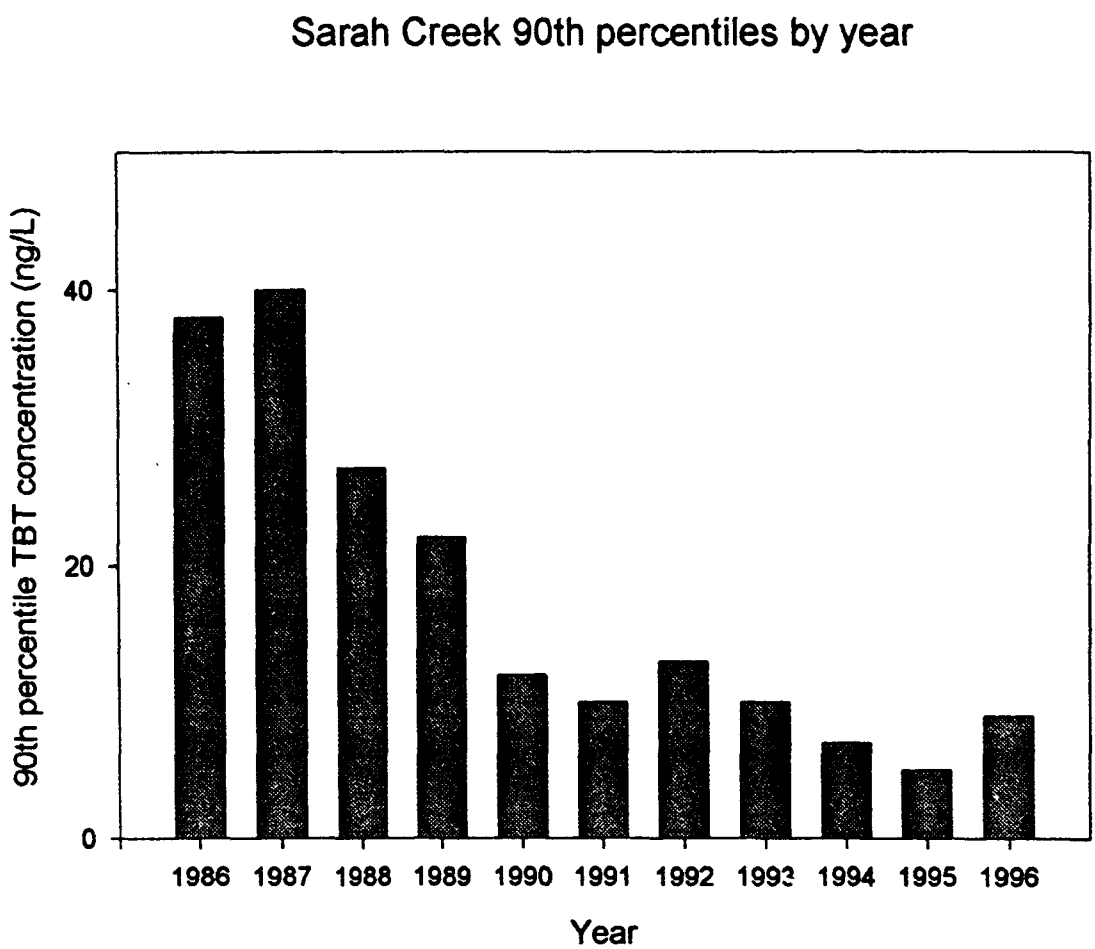


Figure 4. Temporal trend of 90th percentile concentrations of TBT for Hampton Creek from 1986-1996.

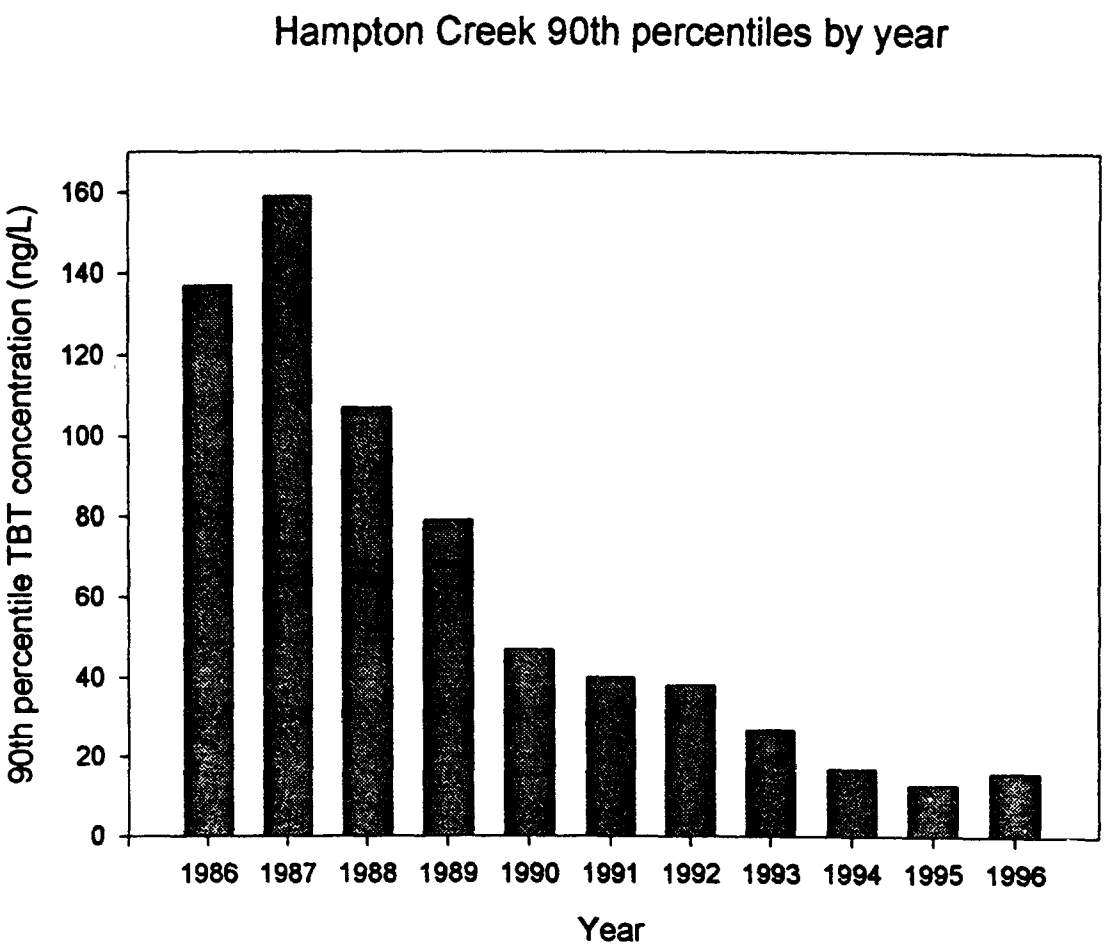


Figure 5. Distribution of TBT acute saltwater toxicity data.

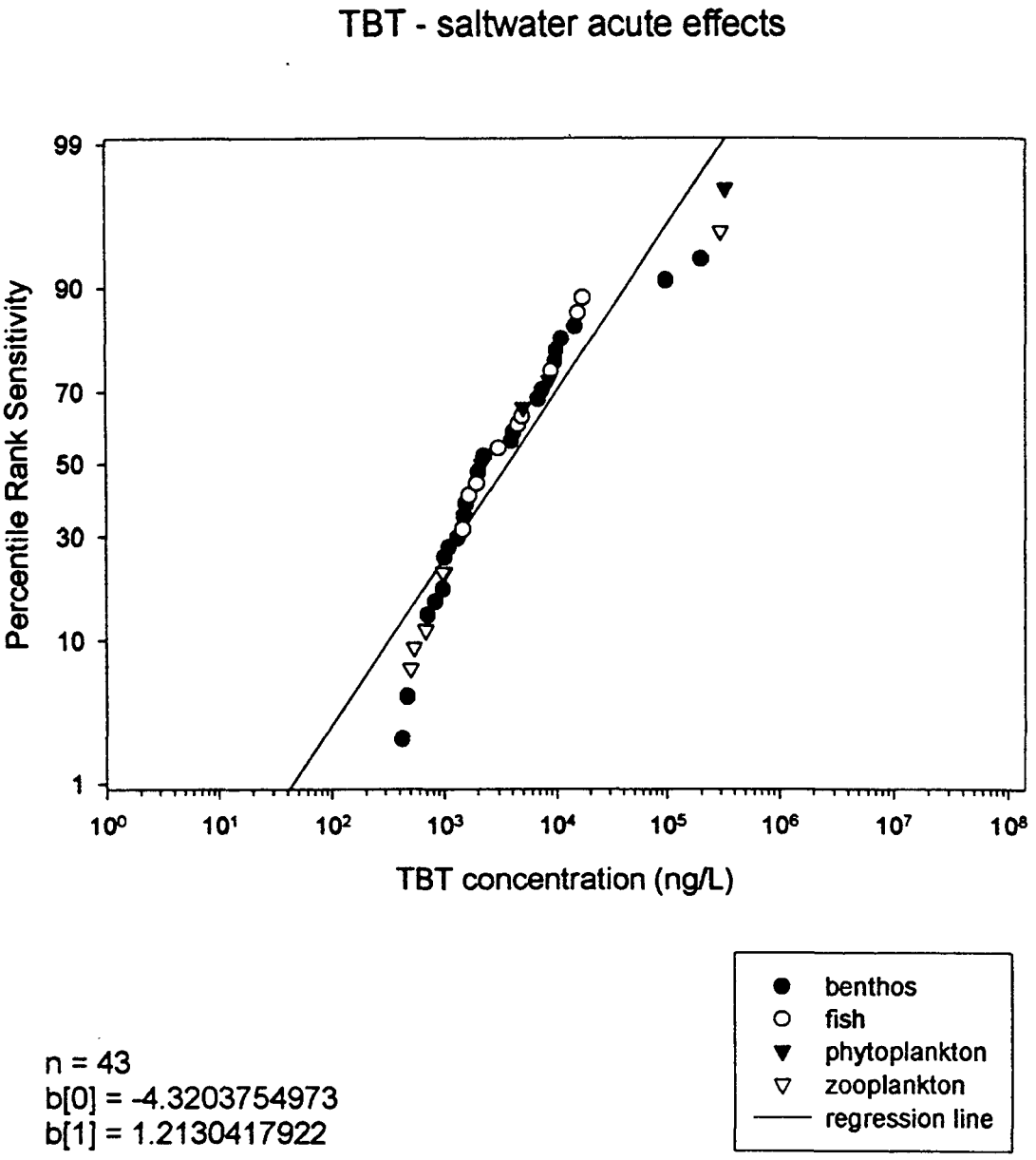


Figure 6. Distribution of TBT acute freshwater toxicity data.

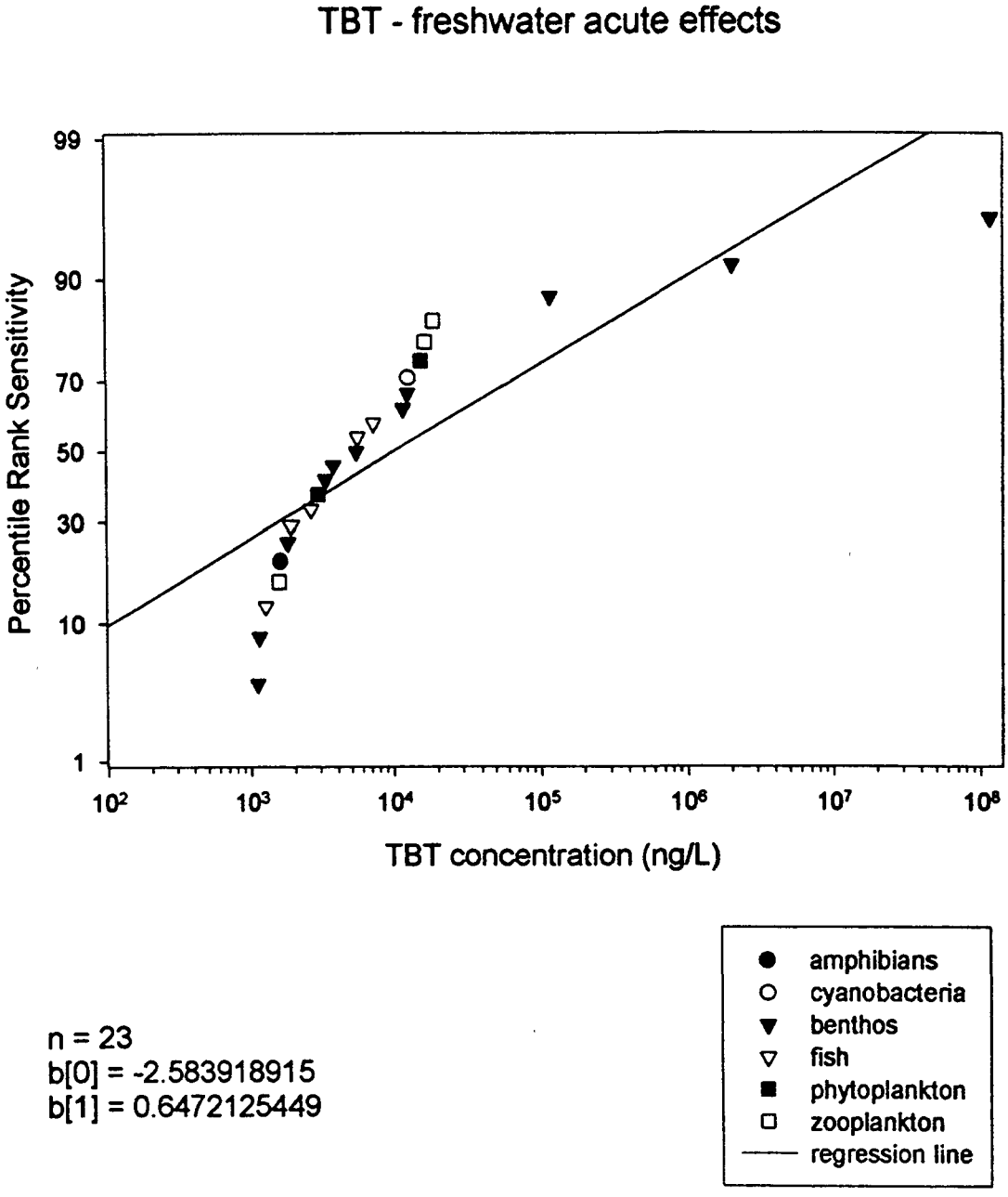


Figure 7. Distribution of TBT chronic saltwater toxicity data.

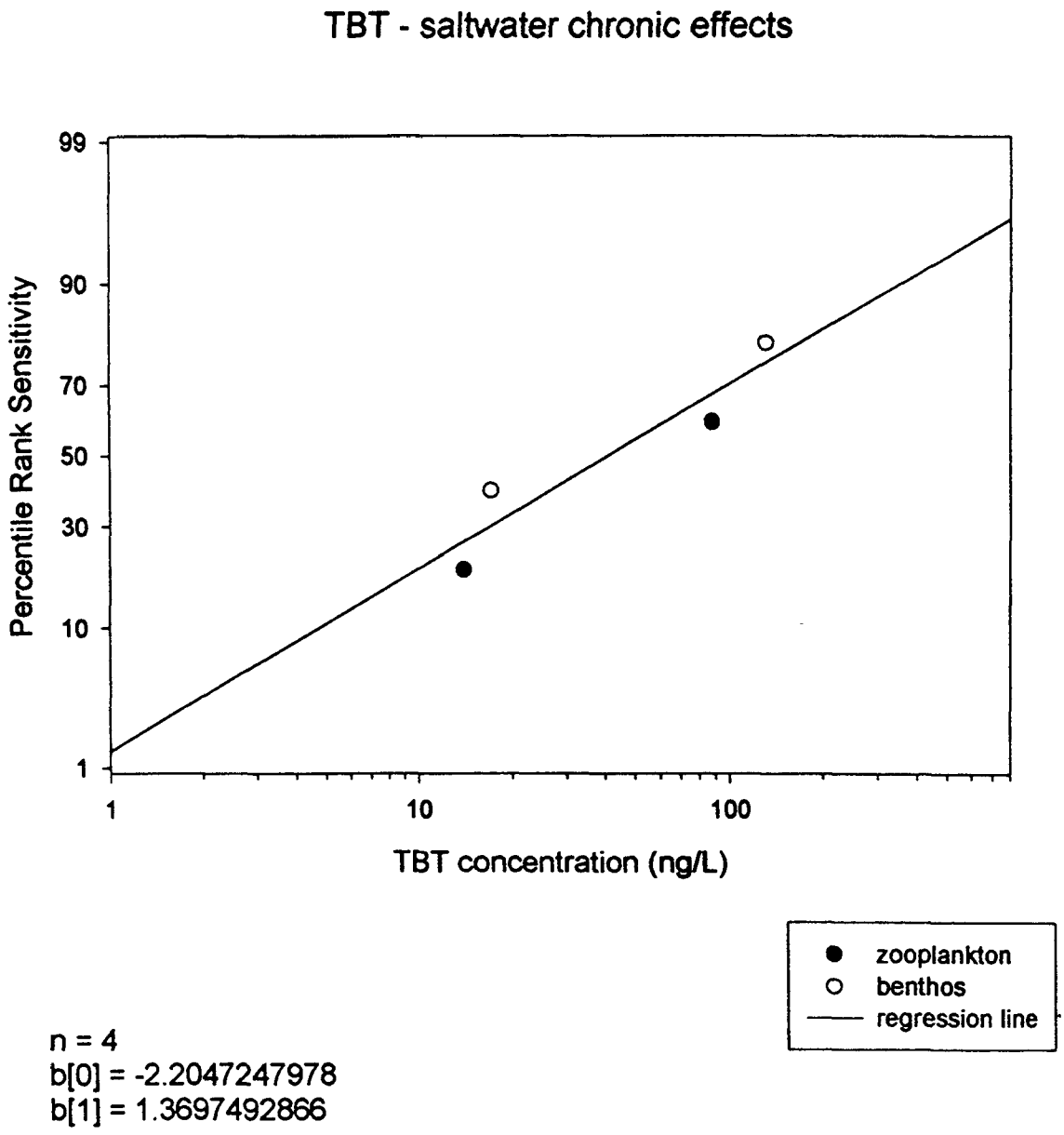
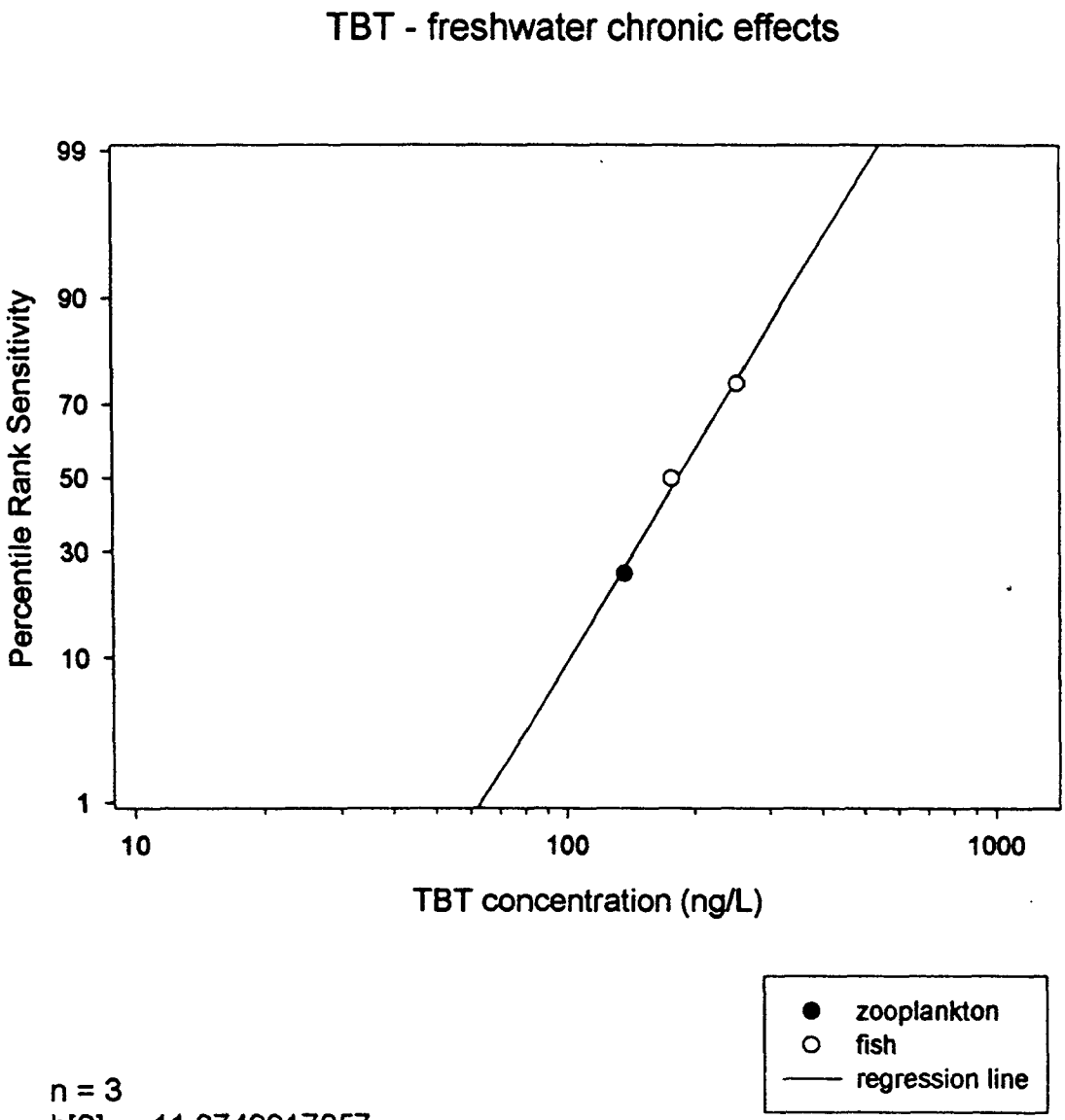
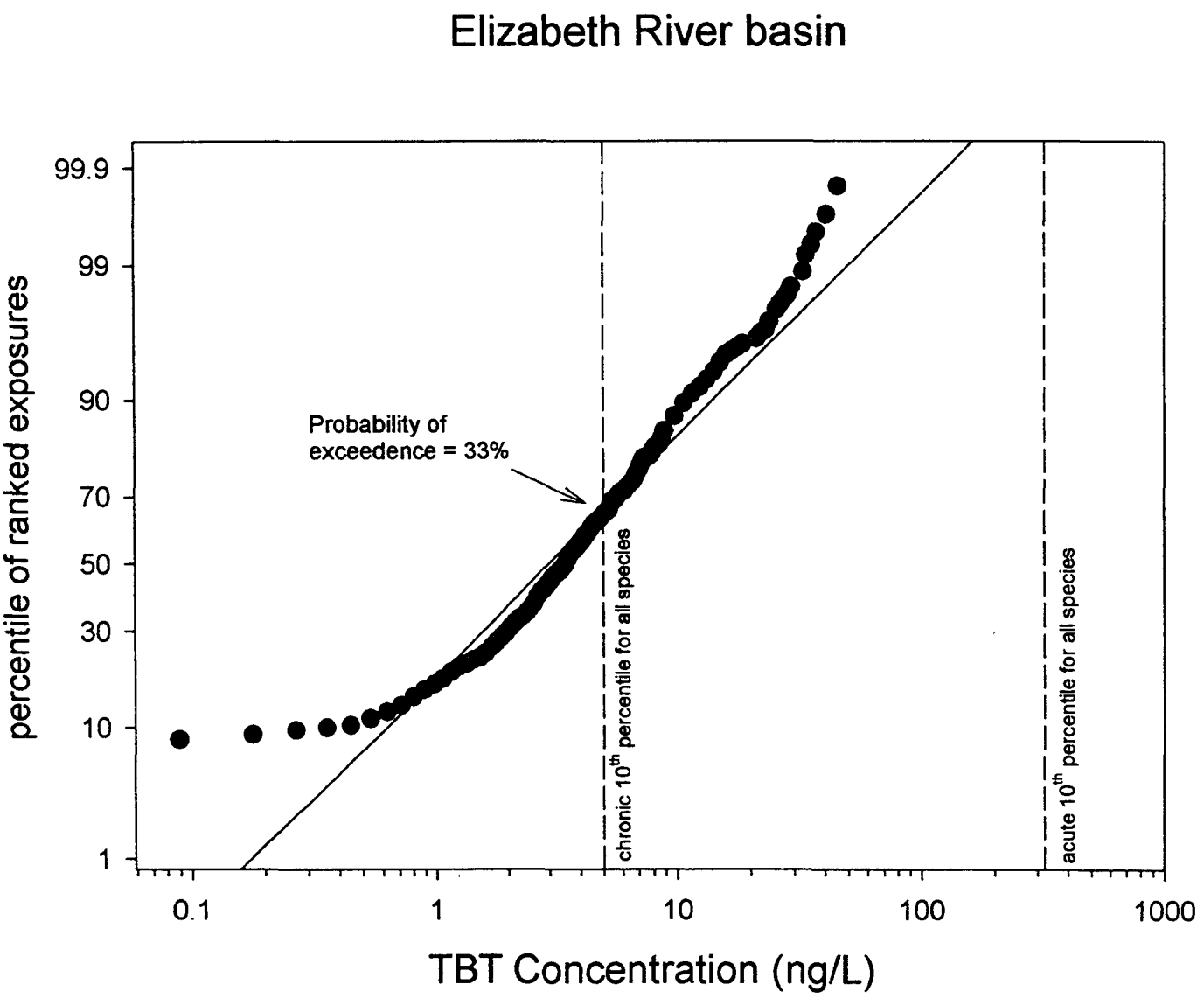


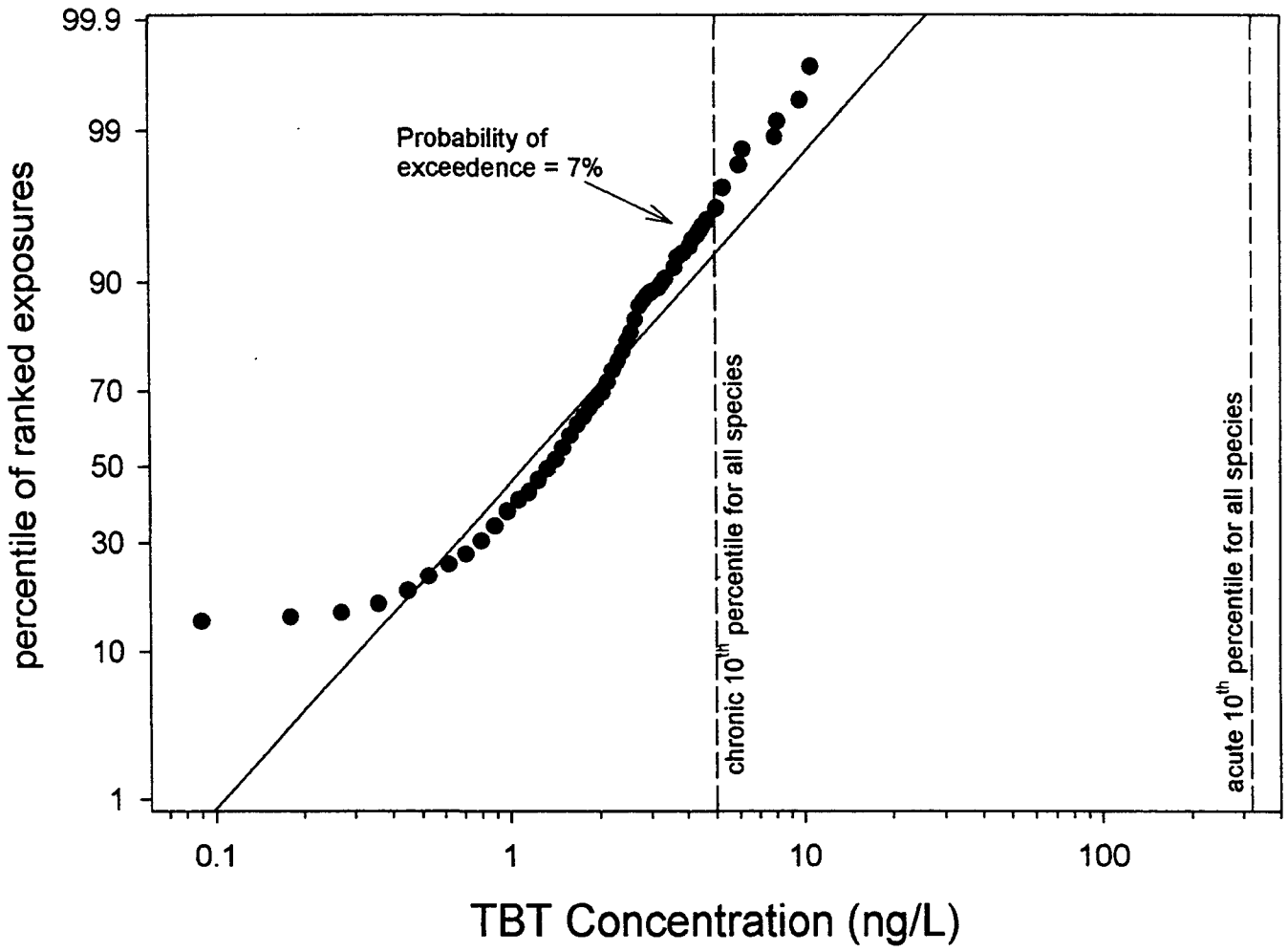
Figure 8. Distribution of TBT chronic freshwater toxicity data.

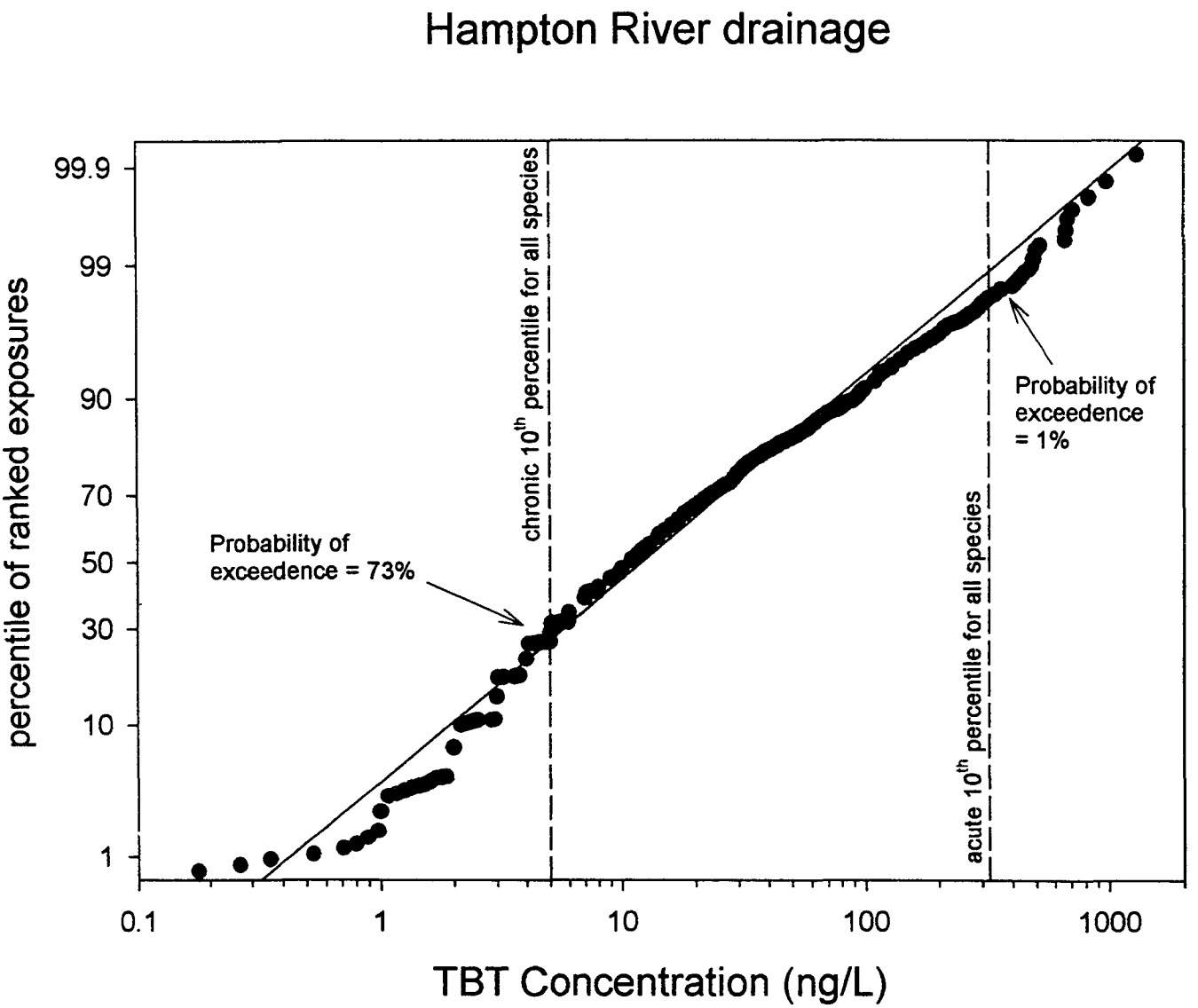


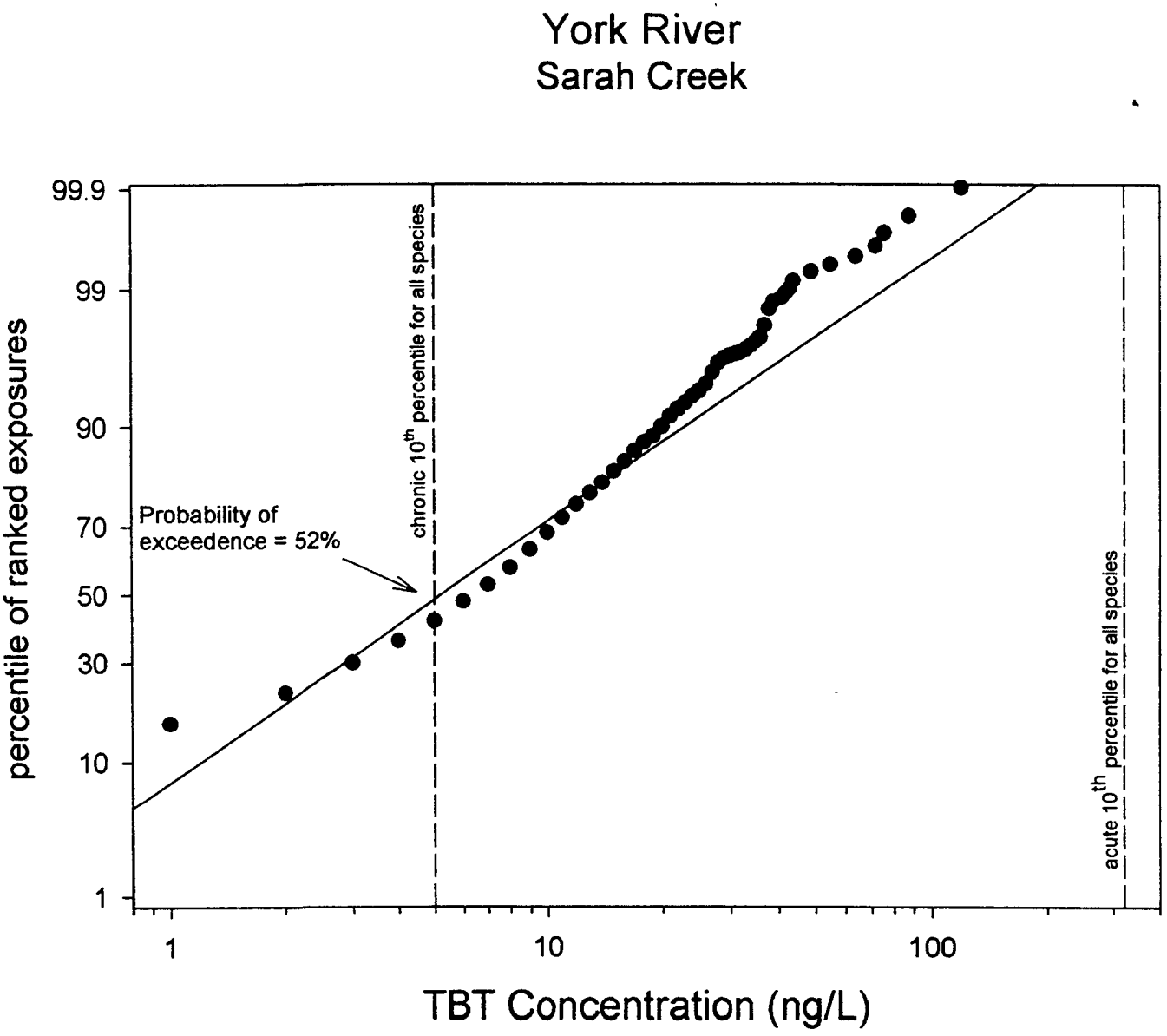
APPENDIX A

Tributyltin risk characterization by basin and station

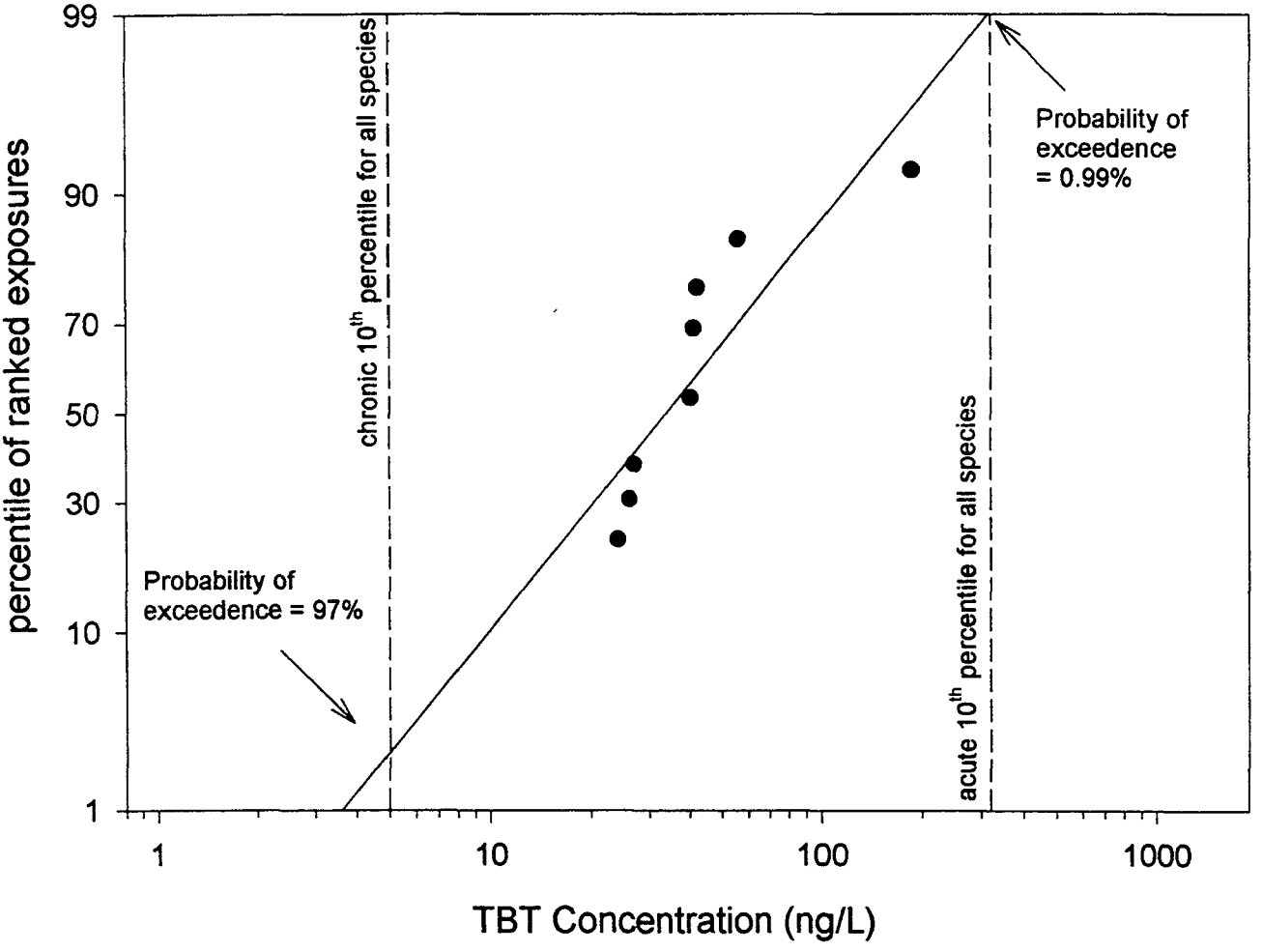

Elizabeth River basin
percentile of ranked exposures
99.9
99
90
70
50
30
10
1
Probability of
exceedence = 33%
chronic 10th percentile for all species
acute 10th percentile for all species
0.1
1
10
100
1000
TBT Concentration (ng/L)

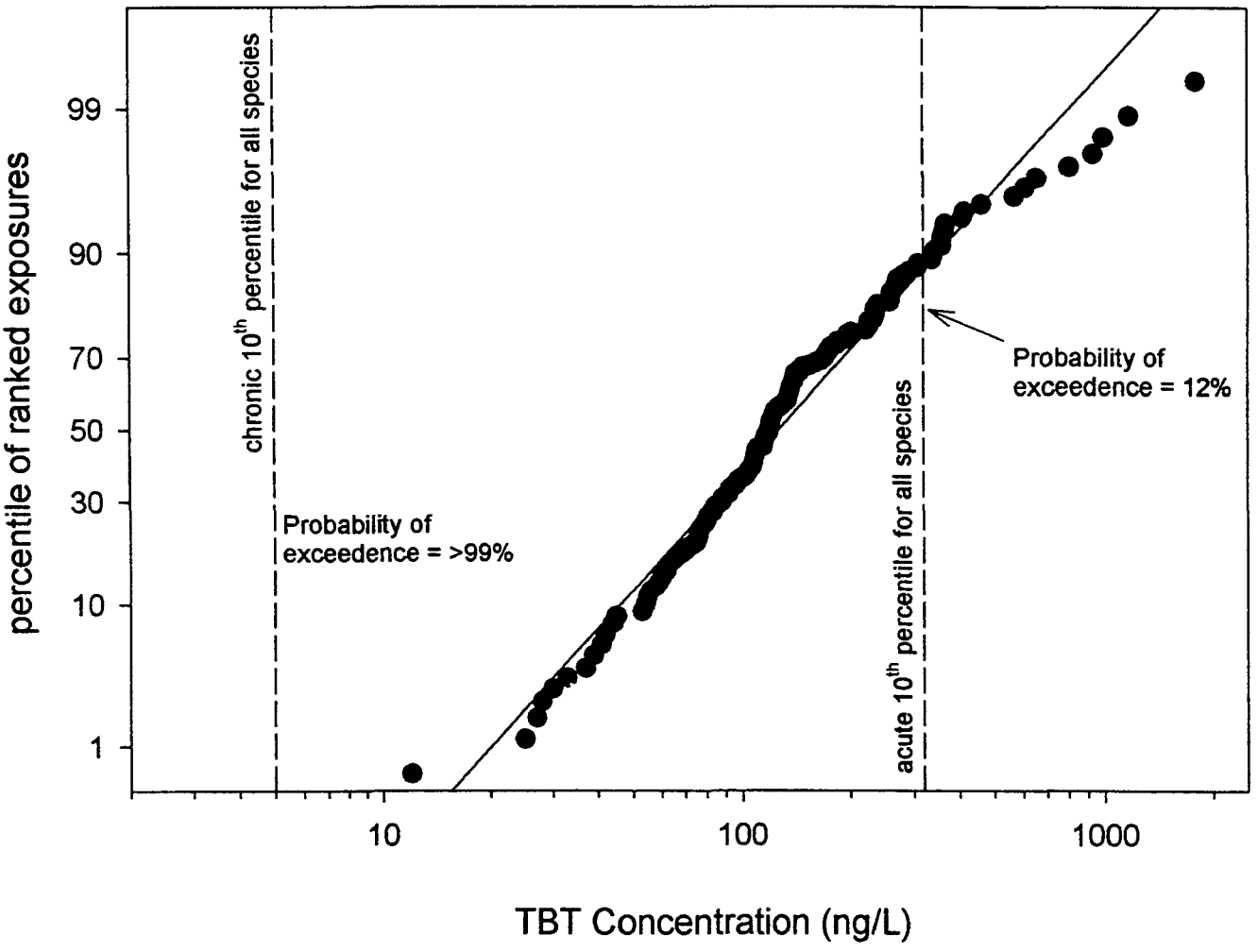

James River
Norfolk Harbor
99.9
99
90
70
50
30
10
1
percentile of ranked exposures
Probability of
exceedence = 7%
chronic 10th percentile for all species
acute 10th percentile for all species
0.1
1
10
100
TBT Concentration (ng/L)

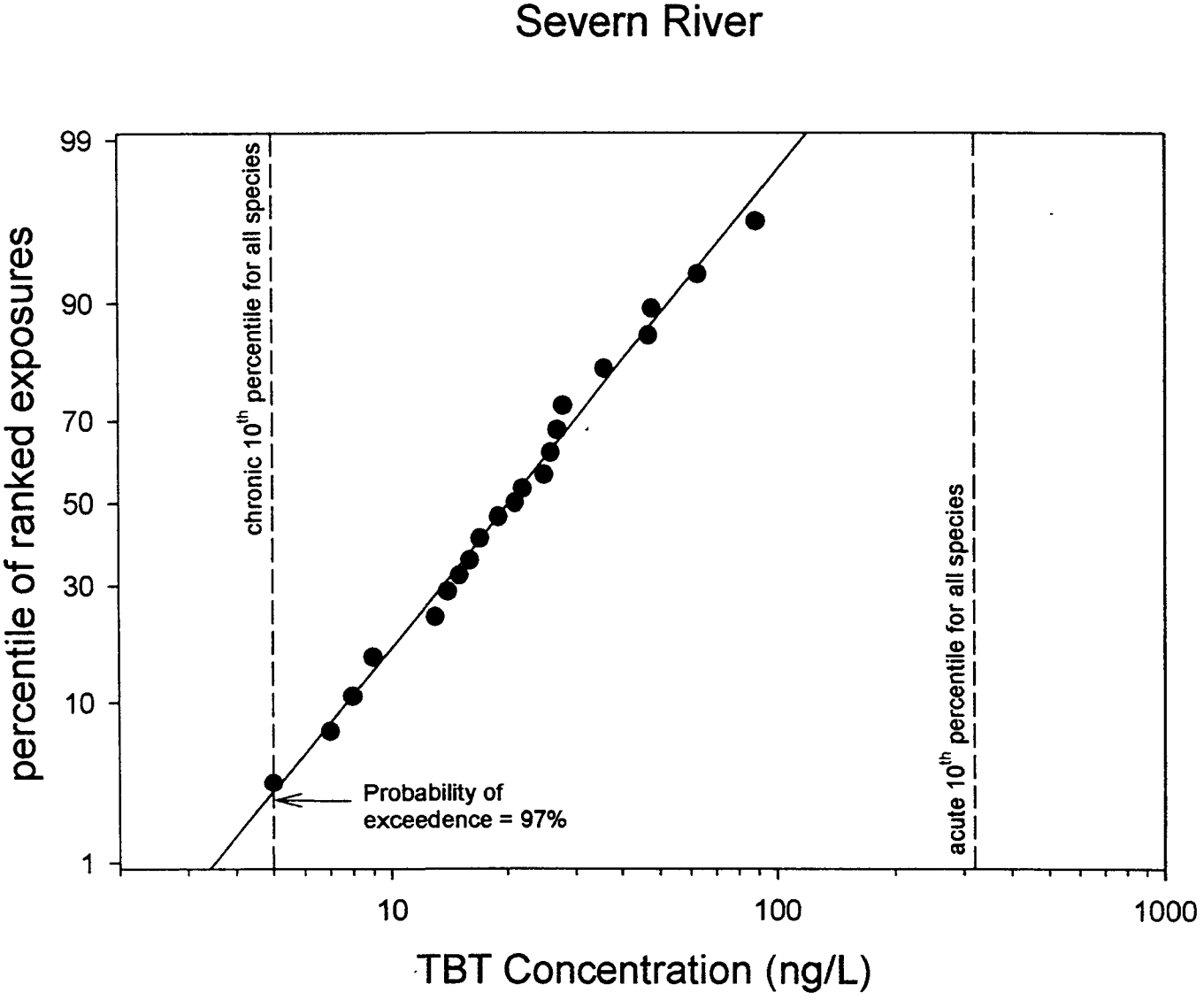

Hampton River drainage
percentile of ranked exposures
99.9
99
90
70
50
30
10
1
0.1
1
10
100
1000
TBT Concentration (ng/L)
chronic 10th percentile for all species
acute 10th percentile for all species
Probability of exceedence = 73%
Probability of exceedence = 1%


York River
Sarah Creek
99.9
99
90
70
50
30
10
1
percentile of ranked exposures
Probability of
exceedence = 52%
chronic 10th percentile for all species
acute 10th percentile for all species
1
10
100
TBT Concentration (ng/L)

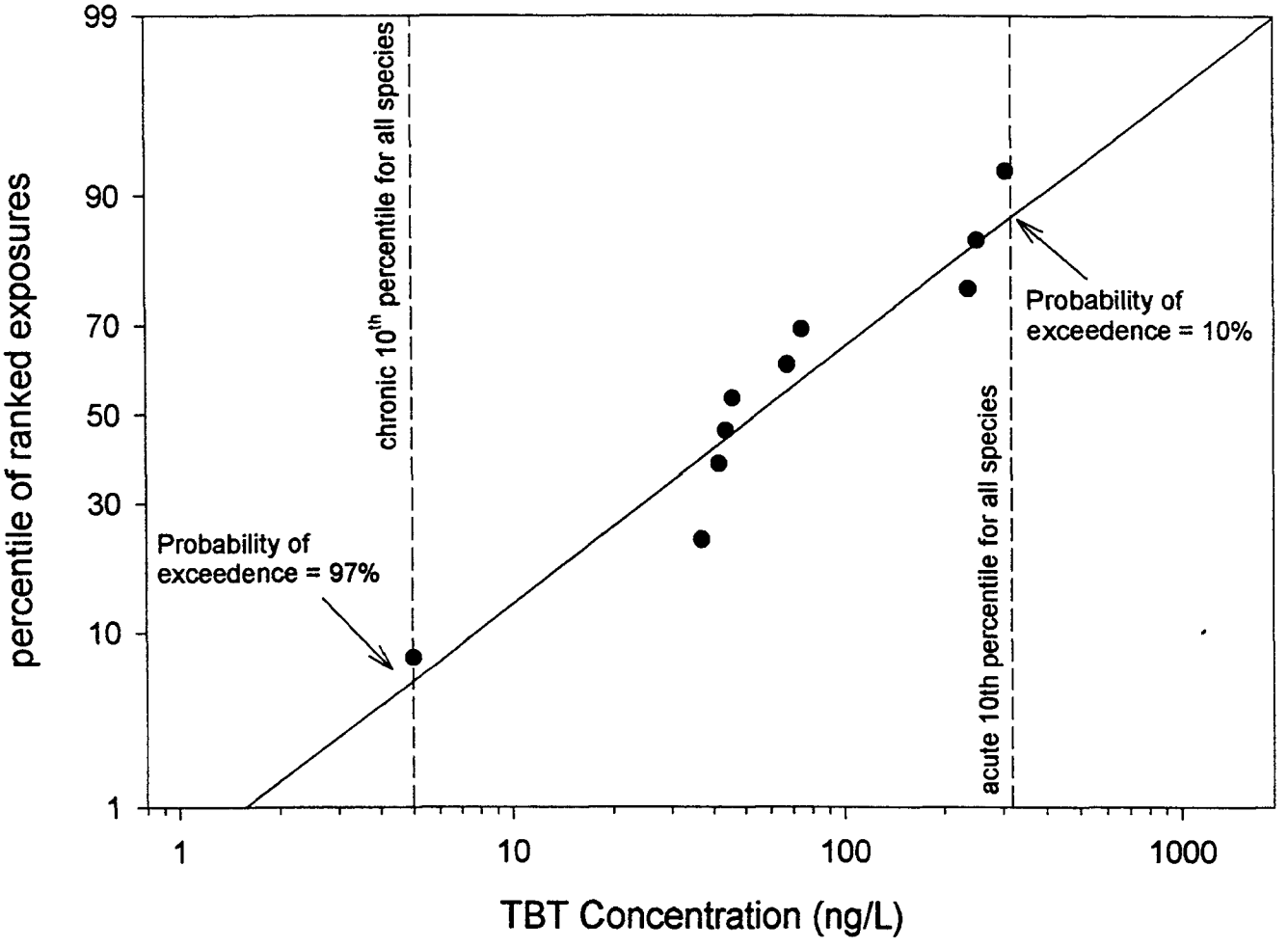
Hartge Marina



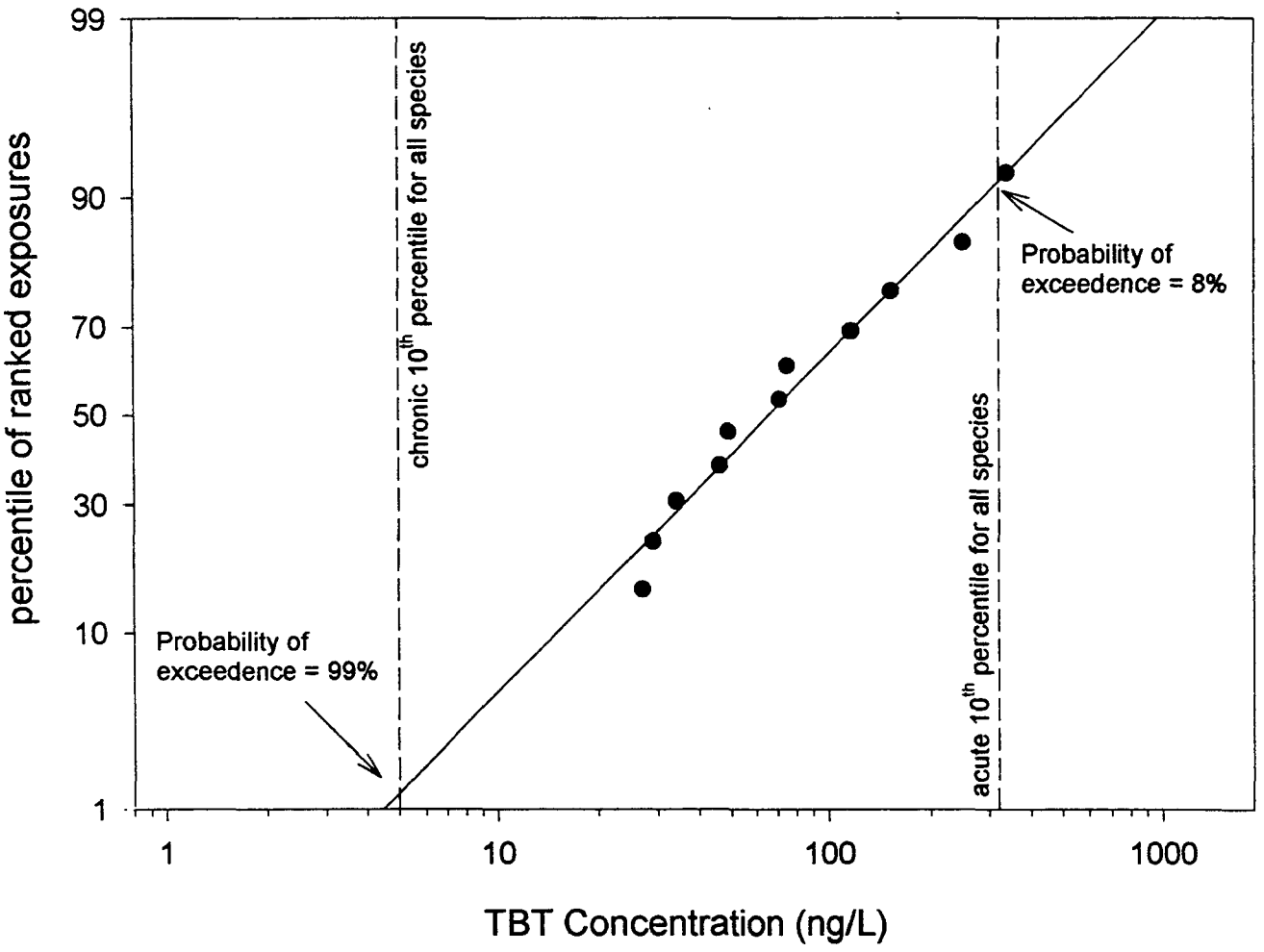

Six Back Creek Stations
percentile of ranked exposures
99
90
70
50
30
10
1
chronic 10th percentile for all species
acute 10th percentile for all species
Probability of exceedence = >99%
Probability of exceedence = 12%
10
100
1000
TBT Concentration (ng/L)

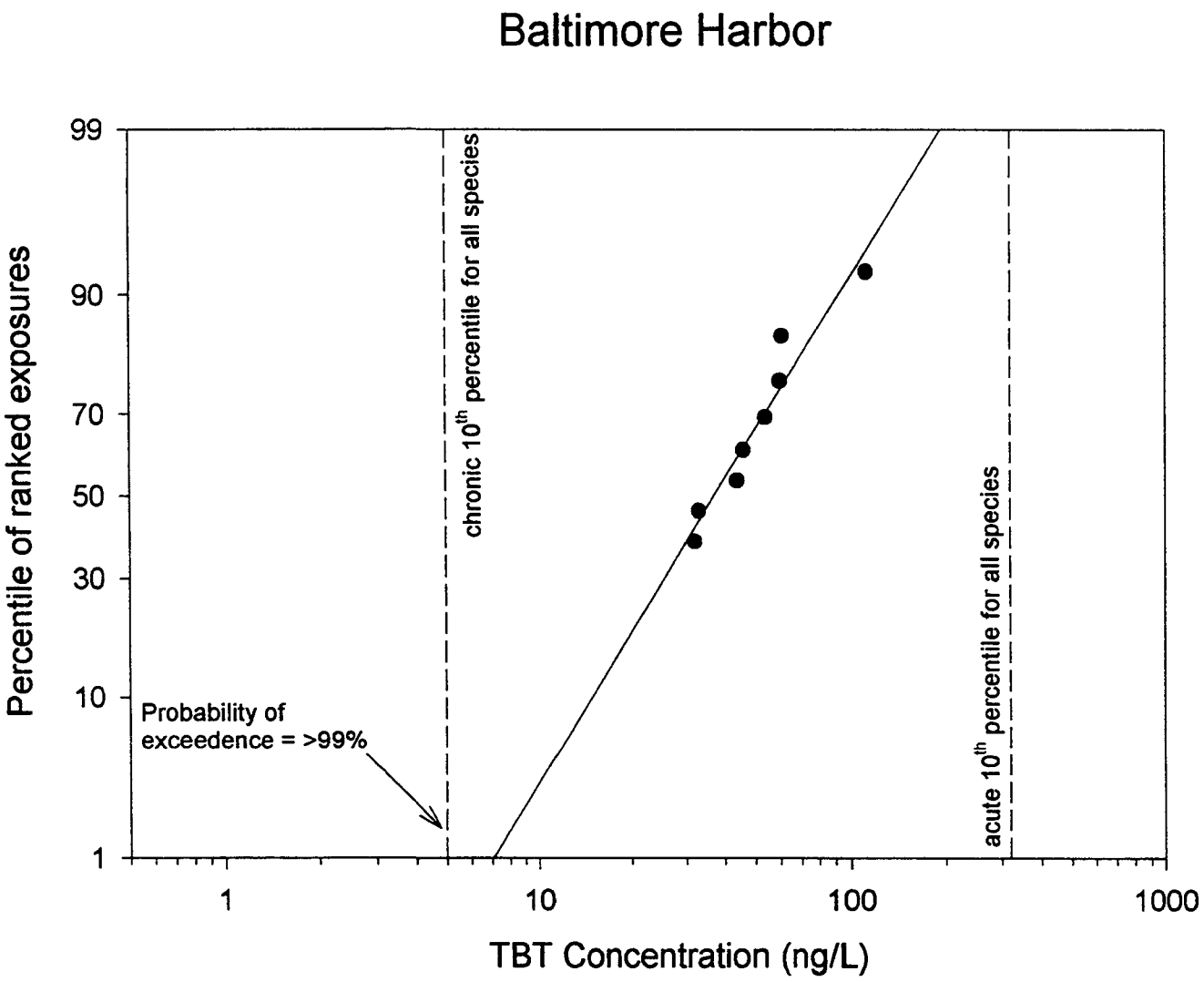

Severn River
percentile of ranked exposures
99
90
70
50
30
10
1
chronic 10th percentile for all species
acute 10th percentile for all species
Probability of
exceedence = 97%
10
100
1000
TBT Concentration (ng/L)

Pier 1 Marina



Piney Narrows Marina




Baltimore Harbor
Percentile of ranked exposures
99
90
70
50
30
10
1
chronic 10th percentile for all species
acute 10th percentile for all species
Probability of exceedence = >99%
1
10
100
1000
TBT Concentration (ng/L)