COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF ENVIRONMENTAL PROTECTION
BUREAU OF CLEAN WATER

RATIONALE FOR THE DEVELOPMENT OF AMBIENT WATER QUALITY CRITERIA FOR PROTECTION OF AQUATIC LIFE USE

Tributyltin

May 2022

Executive Summary

Section 303 of the federal Clean Water Act (CWA) requires states to periodically, but at least once every three years, review and revise as necessary their water quality standards. The federal water quality standards regulation at 40 CFR 131.11(b)(1) requires states to adopt numeric water quality criteria that are based on section 304(a) criteria recommendations developed by the United States Environmental Protection Agency (USEPA), section 304(a) criteria recommendations modified to reflect site-specific conditions, or other scientifically-defensible methods. Additionally, the CWA directs states to adopt criteria for toxic pollutants "the presence of which in the affected waters could reasonably be expected to interfere with a state's designated uses." 33 U.S.C. § 303(c)(2)(B).

USEPA published nationally recommended ambient water quality criteria for tributyltin (TBT) to protect aquatic life in December 2003 (USEPA 2003). This USEPA recommendation was developed through its authority under section 304(a) of the CWA. Under the CWA, states and authorized tribes must adopt water quality criteria into their water quality standards to protect designated uses.

The Pennsylvania Department of Environmental Protection (Department) has reviewed USEPA's 2003 TBT aquatic life criteria recommendations and has determined that they will provide an appropriate level of aquatic life protection to surface waters of this Commonwealth. Therefore, the Department is recommending the Environmental Quality Board (Board) adopt a criteria maximum concentration (CMC) of 0.46 ug/L to protect aquatic life from acute exposures to TBT and a criterion continuous concentration (CCC) of 0.072 ug/L to protect aquatic life from chronic exposures to TBT.

Background

TBT falls within a large class of chemicals described as organotins, which consist of one to four organic substituents plus a tin atom. TBT is formed when three butyl groups are attached to the tin molecule, and the formula is $(C_4H_9)_3Sn^+$. TBT derivatives include dibutyltins and monobutyltins and tins with some methyltins detected when sulfate reducing conditions are present (USEPA 2003).

Organotins, such as TBT, are used extensively in the manufacturing of plastic products and less extensively as biocides and as preservatives for wood, textiles, paper, leather, and electrical equipment. They are used as an anti-yellowing agent in clear plastics and as a catalyst in poly vinyl chloride products. Organotins are used in anti-fouling paints applied to the wet bottom of ship hulls to deter the growth of barnacles and other fouling organisms. The most common organometallics used in these paints are TBT oxide and TBT methacrylate. The largest direct release of TBT into aquatic environments is most likely the result of these anti-fouling paints being used on ships, boats, nets, crab pots, docks and water cooling towers (USEPA 2003).

Currently, there is no available data to characterize TBT in discharges or surface waters of this Commonwealth. The Department reviewed water quality sample data for TBT in the national Water Quality Portal. The Water Quality Portal is a cooperative service provided by the United States Geological Survey (USGS), USEPA, and the National Water Quality Monitoring Council (NWQMC). A search of the database generated zero sample results for TBT in Pennsylvania surface water. A search of National Pollutant Discharge Elimination System (NPDES) permits issued under the Department's Clean Water Program generated zero permits with discharge effluent limitations or monitor and report requirements for TBT. Additional searches of permits and conversations with other Department programs identified no additional permits or discharges of TBT within this Commonwealth, including sites identified under the Hazardous Sites Cleanup Program.

Aquatic Life Toxicity and TBT

The toxicity of organotins is dependent upon the number of organic components that are bonded to the tin atom and the number of carbon atoms in each of the organic components. Toxicity to aquatic organisms generally increases as the number of organic components increases from one to three and decreases with the incorporation of a fourth, making triorganotins more toxic than other forms. Within the triorganotins, toxicity increases as the number of carbon atoms in the organic moiety increases from one to four, then decreases. Thus, the organotin most toxic to aquatic life is TBT (USEPA 2003).

Many acute and chronic toxic effects of TBT have been demonstrated both in the laboratory and the environment. TBT disrupts the normal flow of ions across cell membranes as it promotes chloride exchange across membranes.

Acute toxicity tests generally determine the amount of a substance it takes to kill 50% of the test organisms, but tests may also include determination of the amount of substance it takes to negatively affect or inhibit an organism. These values are often referred to as a lethal concentration (LC50), an effective concentration (EC50), or an inhibitory concentration (IC50). Depending upon the organism, acute toxicity tests are most often conducted over a 48- or 96-hour period. During USEPA's review of TBT, toxicity test data were available for nine freshwater genera including hydras (*Gammarus pseudolimnaeus*), freshwater mussels *(Elliptio complanatus*), annelids (*Lumbriculus variegatus*), mosquito *(Culex* sp.), cladocerans *(Daphnia magna*), and several fish species including Fathead Minnow (*Pimephales promelas*), Rainbow Trout *(Oncorhynchus mykiss*), Juvenile Catfish *(Ictalurus punctatus*), and Bluegill (*Lepomis macrochirus*). Despite the molluscicidal properties of TBT, the freshwater hydras exhibited the most sensitivity to acute exposures. This discovery is likely at least partly explained by the fact that freshwater mussels can temporarily close themselves off from the environment to avoid exposures to surface waters when water quality is poor (USEPA 2003).

Chronic toxicity tests measure longer-term effects associated with exposures to lower concentrations of a pollutant over an extended period of time. Chronic toxicity tests measure lethal and sublethal effects, which include growth, development, behavior, and reproduction. The typical endpoint for chronic exposure is the EC20, which is the concentration that it takes to affect 20% of the test organisms, but endpoints may include a no-observed-effect-concentration (NOEC) or a lowest-observed-effect-concentration (LOEC). TBT has been shown to negatively affect survival, growth and reproduction in *D. magna* and *P. promelas*. It is also an endocrine disrupting chemical and can cause masculinization of certain female gastropods including one known freshwater species. This process, known as imposex, superimposes male sexual characteristics on female gastropods. Imposex has been associated with reduced reproductive potential and altered density and population structure. Plant species sensitivity was highly variable, but several green alga species appeared to be as sensitive as many of the animal species tested (USEPA 2003).

Bioaccumulation has been measured in at least one species of freshwater mussel, zebra mussel (*Dresissena polymorpha),* and four species of freshwater fish. Bioaccumulation factors (BAF), or bioconcentration factors (BCF), were calculated for Rainbow Trout (*Oncorhynchus mykiss*), Common Carp (*Cyprinus carpi*), guppy (*Poecilia reticulatus*), and goldfish (*Carassius auratus*). The BAF/BCFs ranged from 240 L/kg to 17,483 L/kg indicating the TBT's bioaccumulation potential is low to medium (USEPA 2003).

<u>Guidelines for TBT</u>

Current USEPA 304(a) Water Quality Criteria Recommendations for TBT

The current federal recommendations are designed to protect aquatic life in freshwater from the acute and chronic effects of TBT. Table 1 below provides the final calculated values for the magnitude of both the CMC, or acute criterion and the CCC, or chronic criterion. Duration and frequency are also given in Table 1. USEPA typically recommends average durations of one hour for the CMC and four days for the CCC for aquatic life criteria based on standard laboratory toxicity tests. These recommendations can be found in USEPA's *Water Quality Standards Handbook* (USEPA 2017).

Table 1. Summary of Freshwater Aquatic Life Criteria for TBT.

	Magnitude	Duration	Frequency
Acute	0.46 µg/L	One-hour average	Once every 3 years on average
Chronic	0.072 µg/L	Four-day average	Once every 3 years on average

Complete details regarding the specific derivation for both the acute and chronic components of the TBT aquatic life criteria are described in USEPA's *2003 Ambient Aquatic Life Water Quality Criteria for Tributyltin (TBT)* (USEPA 2003).

The criteria recommendations were derived using the peer-reviewed procedures defined in USEPA's *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (the 1985 guidelines, Stephan et al. 1985). Therefore, comprehension of these guidelines will be necessary to understand the process used by USEPA to derive this aquatic life criterion recommendation. Ambient water quality criteria derived using these guidelines will protect the aquatic organisms and aquatic life uses specified by states in their water quality standards regulations.

The 1985 guidelines require that a minimum of eight phylogenetically different families are represented in the toxicity data set that is used to derive criteria values for aquatic life and describe which eight phylogenetically different families are required to be in the dataset. The minimum data requirements were met for TBT such that a final acute criterion value could be calculated. Freshwater genus mean acute values (GMAVs) were available for 13 species representing 12 genera (see Appendix – Table A-1). As described in the previous section, the least sensitive organism to acute exposure was a freshwater clam, *E. complanatus,* which was more than 20,000 times less sensitive than the most sensitive organism. The final acute value (FAV) for freshwater aquatic organisms was calculated based on all twelve available GMAVs and is 0.9177 ug/L (*E. complanatus* is included in the FAV calculation for freshwater organisms). The CMC is derived by dividing the FAV by 2 and results in a recommendation of 0.4589 ug/L.

Depending on the data that are available concerning chronic toxicity to aquatic animals, the final chronic value might be calculated in the same manner as the FAV or by dividing the final acute value by the final acute-chronic ratio (FACR). In some cases, it may not be possible to calculate a final chronic value. For TBT, species mean chronic values (SMCV) were not available for eight families. When sufficient chronic toxicity data is not available, acute-to-chronic ratios can be calculated using a minimum of three different aquatic life families provided that at least one species is a fish, one species is an invertebrate and one species is an acutely sensitive freshwater species. If this data is not available, a final chronic value cannot be calculated. For TBT, chronic toxicity data was not available for eight families. However, sufficient data was available to calculate an FACR (see Appendix – Table A-2). The FACR was calculated to be 12.69 and is equal to the geometric mean of the acute to chronic ratios for *Daphnia magna* (36.60), *Pimephales promelas* (10.01), *Acanthomysis sculpta* (4.664), and *Eurytemora affinis* (15.17). The CCC was derived by dividing the FAV by the FACR and results in a recommendation of 0.072 ug/L.

USEPA 304(a) national criteria recommendations developed using the 1985 guidelines are based on the premise that toxicological data for the species used to derive the national criteria recommendations are representative of the sensitivities of other untested species (USEPA 2013). Based on this premise, 304(a) criteria recommendations are designed to protect the various freshwater and saltwater aquatic communities found across the United States.

Development of TBT Water Quality Criteria

The Department has evaluated USEPA's 304(a) acute and chronic freshwater criteria recommendations for TBT to determine if the recommendations are appropriate for this Commonwealth. The Department's evaluation included consideration of the available toxicological data and the aquatic organisms used in these studies, the methodology used to derive the national recommendation (i.e., the 1985 guidelines), and the Department's policies and regulations found in 25 Pa. Code Chapters 93 and 16. The USEPA 304(a) criteria recommendations for TBT are consistent with the Department's regulations and policies for developing aquatic life criteria found at §§ 93.8a (relating to toxic substances), 93.8c (relating to human health and aquatic life criteria for toxic substances), and 16.21 – 16.24 (relating to guidelines for development of aquatic life criteria).

Calculation of Ambient Water Quality Criteria for TBT

Final Acute Value (FAV) = 0.9177 μg/L

Criterion Maximum Concentration (CMC) = FAV ÷ 2

= (0.9177 μg/L) ÷ 2

= 0.4589 μg/L

= 0.46 ug/L

Final Acute-Chronic Ratio (FACR) = 12.69

Final Chronic Value = FAV ÷ FACR

= (0.9177 μg/L) ÷ 12.69

= 0.0723 μg/L

= 0.072 ug/L

Conclusion

The Department recommends the Board adopt USEPA's 304(a) ambient water quality criteria recommendations for TBT as described in this rationale document. Statewide application of these nationally-recommended water quality criteria will provide an appropriate level of protection for freshwater aquatic organisms from the toxic effects of TBT.

Literature Cited

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Appendix A

Table A-1. This table was taken from USEPA 2003 and shows the ranked GMAVs that were used in the derivation of the nationally recommended freshwater aquatic life criteria for TBT.

Rank	Genus Mean Acute Value (µg/L)	Species	Species Mean Acute Value (µg/L)
12	24,600	Freshwater clam, *Elliptio camplanatus*	24,600
11	12.73	Lake trout, *Salvelinus naymaycush*	12.73
10	10.2	Mosquito, *Culex* sp.	10.2
9	8.3	Bluegill, *Lepomis macrochirus*	8.3
8	5.5	Channel catfish, *Ictalurus punctatus*	5.5
7	5.4	Annelid, *Lumbriculus variegatus*	5.4
6	4.571	Rainbow trout, *Oncorhynchus mykiss*	4.571
5	4.3	Cladoceran, *Daphnia magna*	4.3
4	3.7	Amphipod, *Gammarus pseudolimnaeus*	3.7
3	2.6	Fathead minnow, *Pimephales promelas*	2.6
2	1.80	Hydra, *Chlorohydra viridissmia*	1.80
1	1.170	Hydra, *Hydra littoralis*	1.201
		Hydra, *Hydra oligactis*	1.14

Table A-2. This table is taken from USEPA 2003 and it shows the acute to chronic ratios obtained in the derivation of the nationally recommended freshwater criteria for TBT.

Acute-Chronic Ratios

Species	**Hardness (mg/L as $CaCO_3$)**	**Acute Value (µg/L)**	**Chronic Value (µg/L)**	**Ratio**	**Reference**
Cladoceran, *Daphnia magna*	51.5	4.3	0.1414	30.41	Brooke et al. 1986
Cladoceran, *Daphnia magna*	160-174	11.2	0.2542	44.06	ABC Laboratories, Inc. 1990d
Fathead minnow, *Pimephales promelas*	51.5	2.6	0.2598	10.01	Brooke et al. 1986
Copepod, *Eurytemora affinis*	-	2.2	<0.088	>25.00	Hall et al. 1987;1988 a
Copepod, *Eurytemora affinis*	-	2.2	0.145	15.17	Hall et al. 1987;1988 a
Mysid, *Acanthomysis sculpta*	-	0.61[a]	0.1308	4.664	Davidson et al. 1986a,1986b
Snail, *Nucella lapillus*	34-35[b]	72.7	0.0143	5,084	Harding et al. 1996

[a] Reported by Valkirs et al. (1985).
[b] Salinity (g/kg).