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

Carbaryl

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 carbaryl to protect aquatic life in April 2012 (USEPA 2012). 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 2012 carbaryl 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 2.1 ug/L to protect aquatic life from acute exposures to carbaryl and a criterion continuous concentration (CCC) of 2.1 ug/L to protect aquatic life from chronic exposures to carbaryl.

Background

Carbaryl (1-naphthol-N-methylcarbamate; C₁₂H₂₂NO₂, CAS #63-25-2), also commonly known as Sevin®, is a broad-spectrum insecticide that is classified with other N-methyl

carbamate pesticides. In addition to being a board-spectrum insecticide, carbaryl is also registered for use as a mosquito adulticide, a molluscicide, in pet care products and to thin fruit in orchards to enhance fruit size and repeat bloom (USEPA 2012). It is available for use in the following formulations: baits; dusts; wettable powders; molasses, oil, and water suspensions; pellets; and granules.

Nationally, carbaryl ranked third among the most commonly used conventional pesticides in homes and gardens in 2009. Carbaryl usage was reported to range between 4 and 6 million pounds of active ingredient used annually in 2009. In 2012, carbaryl ranked fifth among the most commonly used conventional pesticides in homes and gardens. Carbaryl usage was reported to range between 2 and 4 million pounds (USEPA 2017b). Since carbaryl is moderately mobile in soils, it enters aquatic environments primarily through stormwater runoff from areas where it has been applied, including agricultural and urbanized areas.

Once in the aquatic environment, carbaryl typically degrades into other substances via hydrolysis or photolysis with the primary degradant being 1-naphthol. Hydrolysis is pH dependent and will occur more rapidly at higher pH. Photolysis occurs in waters that can be penetrated by sunlight and is generally limited to the upper water column of an aquatic system. Degradation of carbaryl and 1-naphthol by photolysis is rapid with half-lives of 1.8 days and less than an hour, respectively. It is important to note that 1-naphthol can result from a variety of natural and anthropogenic processes, so its presence does not indicate usage of carbaryl (USEPA 2012).

The Department reviewed water quality sample data for carbaryl 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 approximately 2100 sample results for carbaryl in Pennsylvania surface waters that were collected between 1973 and 2022 by USGS. Approximately 600 of the 2100 samples were collected during the past ten years (2012-2022). Most samples were analyzed for dissolved carbaryl, but a small number of samples were analyzed for total recoverable. Approximately 75% of the samples had non-detectable levels of carbaryl. Of the 25% of samples that had detectable amounts, the results ranged from 0.003 ug/L to 0.14 ug/L. If historical sample results are considered, there were three results above the proposed acute and chronic criteria recommendations. The highest values were 335 and 260 µg/L and both of these samples were collected in 1973. The third result was 2.41 ug/L, which only slightly higher than the proposed criteria of 2.1 ug/L. This sample was collected from the Little Neshaminy Creek at Valley Road in 2000.

Based on this analysis of available water quality data, the current levels of carbaryl found in Pennsylvania's surface waters are low when compared to USEPA's ambient water quality criteria recommendations for the protection of aquatic life. It is important to recognize there is potential for concentrations of carbaryl to become elevated if its use becomes more widespread and common. This potential increase in concentration could

be further exacerbated if some exotic pests become ubiquitous, as in the case of the spotted lanternfly (*Lycorma delicatula*). Carbaryl is an effective suppression agent against the spotted lanternfly, so as local populations of invasive spotted lanternfly surge, there would be an expected rise in the amount of carbaryl released into the environment (Penn State Extension 2021). 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 carbaryl.

Aquatic Life Toxicity and Carbaryl

Carbamate insecticides inhibit acetylcholinesterase in animals, which leads to a buildup of the neurotransmitter acetylcholine within the nervous system. This accumulation of acetylcholine triggers the nerve pulses to continue firing throughout the nervous system leading to uncontrolled movement, paralysis, convulsions, tetany and possibly death. Without proper neurological function, respiratory, circulatory, and other bodily functions fail. Most acetylcholinesterase inhibition effects are reversible upon removal of the exposure (USEPA, 2012).

Increases in water temperature, pH and hardness can increase carbaryl toxicity in the aquatic environment. However, there is generally a lack of sufficient trend data to warrant the need to adjust the carbaryl water quality criteria for these parameters.

It is also important to consider whether the degradants of carbaryl, such as 1-naphthol, are inimical to aquatic life. The primary effect of 1-naphthol exposure is thought to be narcosis which is a reversible anesthetic effect. It is caused by chemicals partitioning into cell membranes and nervous tissue which results in disruption of cell functions including those in the central nervous system. Toxicity test results indicate that 1- naphthol is toxic to aquatic life with the most sensitive endpoint being larval growth and development of fathead minnows when chronic exposure exceeds 100 µg/L (USEPA 2012). With that in mind, the highest estimated sample result for 1-naphthol found in the Water Quality Portal for Pennsylvania surface waters was more than 2,000 times lower than the levels that seem to have any effect on aquatic life. The observed low levels of 1-naphthol are likely because of its rapid degradation. USEPA indicated that the available aquatic life toxicity data for 1-naphthol is inconclusive and recommended additional studies involving fish and invertebrates to address uncertainties surrounding toxicity and effects from 1-naphthol (USEPA 2012).

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 carbaryl, toxicity test data was available for 47 freshwater genera (60 species). The first, second, third, fourth,

and seventh most sensitive tested species were stoneflies with SMAVs ranging from 3.175 ug/L to 9.163 ug/L. The species included *Isogenus sp., Skwala sp., Pteronarcys californica, Claassenia sabulosa,* and *Pteronarcella badia.* Cladocerans (*Daphnia carinata* and *Ceriodaphnia dubia*) were the next most sensitive taxon followed by amphipods (*Gammarus pseudolimnaeus, Gammarus lacustris,* and *Hyalella azteca*). The ten most sensitive freshwater genera are in the classes Insecta and Crustacea, which is expected given that carbaryl is an insecticide (USEPA 2012).

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). Carbaryl has been shown to negatively affect survival, growth and reproduction in Fathead Minnows (*Pimephales promelas*). Negative effects on reproduction were observed in a waterflea (*Daphnia magna*), and negative effects on growth were observed in Colorado Pikeminnow (*Ptychochelius lucius*) and Bonytail Chub (*Gila elegans*).

No acceptable data on bioaccumulation of carbaryl in freshwater are available, but due to its low octanol/water partition coefficient, carbaryl is not expected to bioconcentrate to a significant extent (USEPA 2012).

Guidelines for Carbaryl

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

The current federal recommendations are designed to protect aquatic life in freshwater from the acute and chronic effects of carbaryl (USEPA 2012). 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 2017a).

	Magnitude	Duration	Frequency
Acute	2.1 µg/L	One-hour average	Once every 3 years
			on average
Chronic	2.1 µg/L	Four-day average	Once every 3 years
			on average

Table 1. Summar	y of Freshwater	Aquatic Life	Criteria for	Carbaryl.
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Complete details regarding the specific derivation for both the acute and chronic components of the carbaryl aquatic life criteria are described in USEPA's 2012 Ambient Aquatic Life Water Quality Criteria for Carbaryl (USEPA 2012).

The criteria recommendations were derived using the peer-reviewed procedures defined in EPA'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 the 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 CMC was developed by first assembling available acute test data and it was determined that the minimum data requirements prescribed in the 1985 guidelines were met.

There were 47 genera (60 species) included in the dataset for the derivation of the nationally recommended acute freshwater criteria (see Appendix – Table A-1). The Species Mean Acute Values (SMAVs) were calculated by taking the geometric mean of the acute data for each species in the data set. Genus Mean Acute Values (GMAVs) are either (1) the calculated geometric mean for all of the SMAVs included in that genera; or (2) if there is only one SMAV in that genera, then the GMAV was set equal to the SMAV. The Final Acute Value (FAV) was derived through regression analysis on the four most sensitive GMAVs. The CMC was calculated by dividing the FAV by 2. The four most sensitive genera were within a factor of 1.8 of one another. The freshwater FAV (the 5th percentile of the species sensitivity distribution) for carbaryl is 4.219 ug/L. The CMC is derived by dividing the FAV by 2 and results in a recommendation of 2.1 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. 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. There were 5 genera (5 species) in the chronic freshwater dataset for carbaryl (see Appendix; Table A-2). The minimum data requirements for eight phylogenetically different families as specified in the 1985 guidelines were not met, so the CCC calculation relied on the acute to chronic ratios (ACRs). There were 4 valid ACRs that were considered in this approach. The

difference between the lowest and highest ACR is a factor of 22, and the ACR increases as the SMAV increases. As such, the 1985 guidelines state that the final acute to chronic ratio (FACR) should be calculated from the geometric mean of the ACRs for species whose SMAVs are close to the FAV. Following this recommendation, the FACR would be the geometric mean of 1.094 (*C. dubia*) and 1.581 (*D. magna*), which is 1.315. The guidelines stipulate that if the most appropriate species mean ACRs are less than 2.0 then the FACR should be equal to 2.0. The CCC was given by dividing the FAV by the FACR of 2.0 and results in a recommendation of 2.1 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, the national criteria recommendations are designed to protect the various freshwater and saltwater aquatic communities found across the United States.

Development of Carbaryl Water Quality Criteria

The Department has evaluated USEPA's 304(a) acute and chronic freshwater criteria recommendations for carbaryl to determine if the recommendations are appropriate for this Commonwealth. The Department's evaluation included consideration of the toxicological studies and the aquatic organisms used in these studies along with the methodology used to derive the national recommendation (i.e., the 1985 guidelines). These 304(a) criteria recommendations are consistent with the Department's regulations and policies for developing aquatic life criteria found at §§ 93.8a, 93.8c, and 16.21—16.24.

Calculation of Ambient Water Quality Criteria for Carbaryl

Final Acute Value (FAV) = 4.219 μ g/L Criterion Maximum Concentration (CMC) = FAV ÷ 2 = (4.219 μ g/L) ÷ 2 = 2.1095 μ g/L = 2.1 μ g/L Final Acute-Chronic Ratio (FACR) = 2.0 Final Chronic Value = FAV ÷ FACR = (4.219 μ g/L) ÷ 2.0 = 2.1095 μ g/L = 2.1 μ g/L

Conclusion

The Department recommends the Board adopt USEPA's 304(a) ambient water quality criteria recommendations for carbaryl 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 carbaryl.

Literature Cited

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APPENDIX

Table A-1. This table was taken from USEPA 2012 and shows the freshwater GMAVs used in the derivation of the current national aquatic life recommendation for carbaryl. They are ranked from most resistant to most sensitive based on Genus Mean Acute Value.

	Genus Mean Acute		Species Mean Acute
Rank	Value (µg/L)	Species	Value (µg/L)
47	27,609	Walking catfish,	27,609
		Clarias batrachus	
46	>27,000	Snail,	>27,000
		Aplexa hypnorum	
45	24,632	Mussel,	24,632
		Anodonta imbecillis	
44	20,000	Black bullhead,	20,000
		Ameiurus melas	
43	16,700	Goldfish,	16,700
		Carassius auratus	
42	16,296	Green frog,	16,296
		Rana clamitans	
41	12,400	Channel catfish,	12,400
		Ictalurus punctatus	
40	12,310	Boreal toad,	12,310
		Bufo boreas	
39	9,039	Green sunfish,	9,460
		Lepomis cyanellus	
	-	Redear sunfish	11,200
		L. microlophus	
	-	Bluegill,	6,970
		L. macrochirus	
38	8,656	European chub,	8,656
		Leuciscus cephalus	
37	8,200	Oligochaete worm,	8,200
		Lumbriculus variegatus	
36	8,012	Fathead minnow,	8,012
		Pimephales promelas	
35	6,400	Largemouth bass,	6,400
		Micropterus salmoides	
34	4,350	Razorback sucker,	4,350
		Xyrauchen texanus	
33	4,153	Common carp,	4,153
		Cyprinus carpio	
32	>3,000	Gila topminnow,	>3,000
		Poeciliopsis occidentalis	

	Genus Mean Acute		Species Mean Acute
Rank	Value (µg/L)	Species	Value (µg/L)
31	2,930	Nile tilapia,	2,930
		Oreochromis niloticus	
30	2,655	Bonytail chub,	2,655
		Gila elegans	
29	2,600	Black crappie,	2,600
		Pomoxis nigromaculatus	
28	2,515	Guppy,	2,515
		Poecilia reticulate	
27	2,480	Yellow perch,	2,480
		Perca flavescens	
26	2,470	Gray tree frog,	2,470
		Hyla versicolor	0.070
25	2,462	Crayfish,	2,870
			0.110
	-	Crayfish,	2,112
0.1	0.070	O. VIIIIS	0.1.10
24	2,079	Greenthroat darter,	2,140
			0.000
	-	Fountain darter,	2,020
		E. IONICOIA	
22	2 005	(formarly aguawfish)	2.005
23	2,005	(IOIIIIeIIy Squawiisii),	2,005
22	1 910	Apacho trout	1.540
22	1,010	Apache trout, Oncorhynchus apacho	1,540
			1.654
	-	O kisutch	1,054
		Chinook salmon	2 690
		O tshawytscha	2,000
	-	Cutthroat trout	3 300
		O clarkii	0,000
	-	Rainbow trout.	860
		O. mvkiss	
21	1.810	Shortnosed sturgeon.	1.810
	.,	Acipenser brevirostrum	.,
20	1.730	African clawed frog,	1.730
	,	Xenopus laevis	
19	1,322	Striped bass,	1,322
		Morone saxatilis	
18	1,269	Brook trout,	1,629
		Salvelinus fontinalis	
	-	Lake trout,	988.1
		S. namaycush	
17	1,000	Crayfish,	1,000
		Procambarus clarkia	

Rank	Genus Mean Acute Value (µg/L)	Species	Species Mean Acute Value (ug/L)
16	889.0	Atlantic salmon,	1.129
		Salmo salar	, -
	-	Brown trout,	700
		S. trutta	
15	839.6	Crayfish,	839.6
		Cambarus bartoni	
14	280	Aquatic sowbug,	280
		Asellus brevicaudus	
13	250	Amphipod,	250
		Pontoporeia hoyi	
12	230	Mysid,	230
		Mysis relicta	
11	200	Backswimmer,	200
		Notonecta undulate	
10	15.2	Amphipod,	15.2
		Hyalella azteca	
9	13.78	Amphipod,	18.76
		Gammarus lacustris	
	-	Amphipod,	10.12
		G. pseudolimnaeus	
8	11.90	Cladoceran,	35
		Daphnia carinata	
	-	Cladoceran,	7.521
		D. magna	
	-	Cladoceran,	6.4
		D. pulex	
7	9.163	Stonefly,	9.163
		Pteronarcella badia	
6	8.781	Cladoceran,	8.781
		Simocephalus serrulatus	
5	5.958	Cladoceran,	5.958
		Ceriodaphnia dubia	
4	5.6	Stonefly,	5.6
		Claassenia sabulosa	
3	4.8	Stonefly,	4.8
		Pteronarcys californica	
2	3.6	Stonefly,	3.6
		Skwala sp.	
1	3.175	Stonefly,	3.175
		Isoaenus sp.	

Table A-2. This table was taken from USEPA 2012 and shows the freshwater GMCVs used in the derivation of the current national aquatic life recommendation for carbaryl. They are ranked from most resistant to most sensitive based on Genus Mean Chronic Value.

Rank	Genus Mean Chronic Value (µg/L)	Species	Species Mean Chronic Value (µg/L)
5	897.8	Bonytail chub, <i>Gila elegans</i>	897. 8
4	636.8	Fathead minnow, Pimephales promelas	636. 8
3	620.8	Colorado pikeminnow (formerly squawfish), <i>Ptychochelius Lucius</i>	620. 8
2	10.6	Cladoceran, Ceriodaphnia dubia	10.6
1	3.770	Cladoceran, Daphnia magna	3.77 0