Aquatic Life Water Quality Standards Technical Support Document for Nonylphenol and Ethoxylates

Triennial Water Quality Standard Amendments to Minn. R. chs. 7050 and 7052

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Minnesota Pollution Control Agency

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TECHNICAL SUPPORT DOCUMENT FOR NONYLPHENOL AND NONYLPHENOL ETHOXYLATES

Contents

Abstract

From the Minnesota *State Register*, Volume 33 (35), March 2, 2009:

Nonylphenol (NP) is an industrial chemical used primarily as an intermediary compound in the development of numerous commercial non-ionic surfactants. These surfactants are ingredients of detergents and emulsifyers found in household, industrial, agricultural, and other applications. The chemical makeup of the surfactants is largely in the form of nonylphenol and octylphenol ethoxylates, more broadly referred to as alkylphenol ethoxylates (APEs). Concentrations of these APEs primarily consist of nonylphenol ethoxylates (NPE) and have been reported from water samples collected from studies of the Mississippi River, smaller Minnesota streams, and wastewater effluents. Sources of NPEs to the environment include point and nonpoint discharges to surface waters. Under anaerobic conditions NPEs breakdown to NP.

Nonylphenol is toxic to aquatic organisms demonstrated, in part, through recent national criteria established by the EPA (AWQC– Nonylphenol 2007(EPA822R05005)). The need to develop national criteria was based both on concerns of NP toxicity and its presence in surface waters throughout the nation. The capacity of NP as an endocrine-disrupting compound is also documented in the EPA criteria document and in numerous reports in the scientific literature. Endocrine-disrupting chemicals (EDCs) are those compounds [human-made compounds or natural compounds at unnatural concentrations due to human activity] that exert an adverse effect through interaction with the endocrine system of mammals, birds, fish, amphibians and many invertebrates [from the MPCA's Legislative report on EDCs www.pca.state.mn.us/publications/reports/lrp-ei-1sy08.pdf].

The Minnesota Pollution Control Agency (MPCA) has reviewed the EPA AWQC and recent literature to develop draft numeric acute and chronic water quality criteria as the basis for future proposed Water Quality Standards (WQSs). Based on the available data on NP and NPEO, MPCA 's acute (FAV and MS) and chronic (CS) criteria were developed to be total NPE concentrations (NP plus two short chain ethoxylates, NP1E0 and NP2EO). MPCA reviewed EPA's conclusions on the EDC studies that suggest while the draft chronic criteria are not based specifically on EDC –mediated effects, would be protective of chronic adverse effects observed in aquatic species studies that impact aquatic communities.

Introduction

Nonylphenol (NP) is a mixture of isomers of branched and substituted structures within a nonyl (9 carbon) group formed in the process of petroleum distillation. Nonylphenol is produced in large quantities in the United States with estimates of over 200 million pounds produced per year. Commercial production limits the number of isomers to a few primary products dominated by the chemical 4(para)-nonylphenol (4-NP). Nonylphenol alone has limited use, but is an ingredient in the manufacture of a wide variety of alkylated products broadly described as nonylphenol ethoxylates (NPEO). These compounds have a primary use as non-ionic surfactants in commercial and household cleaning products, industrial materials processing, and additives to pesticide formulations and industrial lubricants. The focus of this discussion will be placed on 4-NP and two short-chain ethoxylates: nonylphenol mono-ethoxylate (NP1EO) and nonylphenol di-ethoxylate (NP2EO). For purposes of this document, the term nonylphenol ethoxylate (NPEO) will be used inclusive of the chemicals 4-NP (CAS #: 84852-15-3, NP1EO (CAS #: 27986-36-3) and NP2EO (CAS#: 20427-84-3).

Nonylphenol ethoxylates in the environment

Nonylphenol ethoxylates are often constituents of municipal or industrial wastes in effluent discharges to surface waters. In Minnesota, NPEO has been found in surface waters and sediments from around the state (Lee et al. 2004; Lee et al. 2008; MPCA 2009). Regular monitoring for NPEOs in Minnesota surface waters is limited due to lack of standardized analytical procedures and regulatory necessity. Nonylphenol ethoxylates inputs to surface waters and associated treatment facilities are a various mix of 1-20 carbon chain polyethoxylates. The short-chain (1 or 2 carbon) ethoxylates and 4-NP tend to be the most toxic to aquatic organisms (Servos 1999; Bistodeau *et al.* 2006), and are the most persistent forms in wastewater. Initial degradation of longer (3- 20) chain ethoxylates occurs through natural processes resulting in their breakdown to the less water soluble NP1EO, NP2EO and 4-NP (Soares 2008) . The two short chain intermediate compounds (NP1EO, NP2EO) may degrade further to 4-NP, but all three tend to resist degradation and are often found in sediments, wastewater sludge, and wastewater effluents.

HOW AND WHY WATER QUALITY STANDARDS ARE DEVELOPED

U.S. EPA National Clean Water Act 304(a) Aquatic Life Criteria

The MPCA is required by federal law to assess and revise its rules that protect the designated, beneficial uses of state surface water and groundwater. Mandates under the Clean Water Act maintain a state's requirement to develop water quality standards (WQSs) for the protection of aquatic life communities. The U.S. Environmental Protection Agency (EPA) is responsible for developing these 304(a) *Ambient Water Quality Criteria* (AWQC) on a national basis, and it is up to the state to use or modify criteria based on more local and scientifically defensible data that are still as protective as national criteria. Concern for the protection of aquatic life prompted the to develop national aquatic life AWQC for nonylphenol, centering on the compound 4-nonylphenol (EPA 2005). The national criteria for freshwater aquatic life are based on evaluation of toxicity endpoints of nonylphenol to aquatic organisms. This document pursues the development of numeric standards derived for the combined concentrations of the three most toxic and persistent nonylphenol ethoxylate compounds, 4-NP, NP1EO and NP2EO as the basis for draft acute and chronic WQSs.

Development of aquatic life criteria for nonylphenol ethoxylates

Toxicity data for NPEO used to develop a numeric standard was evaluated through national guidance provided by the EPA (USEPA 1985) and requirements in Minn. R. chs. 7050 and 7052. Briefly, studies from the scientific literature are assembled, acceptable toxicity endpoints and taxonomic categories are compiled, and a species sensitivity distribution is calculated that assumes protection of about 95% of aquatic communities. Effects of NPEO on aquatic organisms were assessed for survival endpoints reported from short-term (acute) laboratory exposures. The primary mode of action of NPEO on the whole organism is generally considered a narcotic effect. Toxicity tests are described as the lethal or effect concentration of 50% of the (test) population, referred to as LC50 or EC50, respectively. These endpoints serve as the basis for developing the species sensitivity distribution as described in the EPA guidance.

Scientific studies were evaluated for acceptable data based primarily on information provided in the 1985 EPA Guidelines and ASTM methodologies (ASTM, 2009). Toxicity information used for development of this numeric standard included those data published in the EPA national AWQC document augmented with additional reports from studies published over the past ten years. Development of a numeric standard combined toxicity results of the three related nonylphenol compounds: 4-NP, NP1EO and NP2EO. Most toxicity information is based on tests using the compound 4-NP. Additional literature includes studies that reported results for six aquatic species in exposures to NP1EO and NP2EO (Table 1). Results of three of these studies could not be used as two were from species of a non-native frog, and one used a mixture of unreported nonylphenol ethoxylates (NPEO).

Studies with acceptable NPEO data provided values used to calculate a numeric standard for 23 freshwater genera comprising 28 species from 81 acute toxicity endpoints. Data sources for these endpoints were combined from sources of the existing EPA AWQC document and the open literature (Table 2). Species acute sensitivity to NPEO ranged from 55.72 micrograms/liter (µg/l) for *Hyalella* to 4108.6 µg/L for *Xenopus*. Use of *Xenopus* extends the convention of developing an aquatic life standard from toxicity test using only native species. However, *Xenopus* is an accepted laboratory test species demonstrated, in part, through its use in toxicity testing using FETAX methods (ASTM 2004) and methods employed by the EPA to examine endocrine disrupting compounds. A comparison of reported endpoints between NPEO and 4-NP tend to show that the short chain ethoxlylates are slightly less toxic than 4-NP for the species tested. This observation has been reported from other sources (EPA 2005; Servos 1999). Studies reporting toxicity endpoints for short-chain ethoxylates are few, and these toxicity values are disbursed throughout the range of endpoints for all NPEO. As such, values reported for toxicity endpoints of 4-NP, NP1EO and NP2EO are considered together as equally toxic and deemed appropriate for inclusion in deriving the numeric standards. Additional information on the combined toxicity of NP, NP1EO and NP2EO to aquatic life may be available following actions of rulemaking recently proposed by the EPA (Federal Register 2009).

Table 3 provides a summary of the Minnesota Pollution Control Agency's (MPCA) draft WQSs. The calculated Final Acute Value (FAV) of 59.78 µg/L for NPEO compares to the national criterion FAV for freshwater of 55.49 µg/L for 4-NP. This difference can be explained in part as both the total number of geometric mean acute values (GMAV) and the GMAVs for the four lowest taxa are slightly higher in development of this numeric standard compared to the national criteria. Developing numeric standards that includes effects of NPEO is reasonable because: 1) short-chain ethoxylates are expected to be the most common form of NPEO in surface waters. They are the most recalcitrant form in the ethoxylated chain degradation, and are most likely to be a

component of effluent discharges, 2) These short-chain NP ethoxlylates degrade further to 4-NP under anaerobic conditions found in many aquatic sediments. A numeric standard for NPEO serves to reduce the total amounts of 4-NP present in the environment by also reducing the potential release of the short-chain ethoxylates.

Calculation of chronic standard (CS) values can be achieved in one of two ways. Given sufficient chronic toxicity data to fulfill the Tier I taxonomic categories, a chronic value can be calculated in the same manner as the acute value. With insufficient chronic toxicity data, an acute to chronic ratio can be used. The latter method was used to compute the acute to chronic ratios (ACR) available for three freshwater species. National freshwater AWQC are based on an ACR for an estuarine species, which was not used for this numeric standard development. National guidelines suggest that choice of an ACR be determined using either 1) the geometric mean of three or more ACRs if there is no apparent trend between ACR values and acute toxicity values, or 2) the ACR for the study pair that had a GMAV closest to the calculated FAV. The former method was selected as no apparent trend could be discerned from the data. It was observed that fish appear to have large differences between their acute and chronic endpoints, so it was important that the one ACR available for fish (rainbow trout) be included in the calculations of the final ACR (8.023). Also, as fish appear to have greater chronic sensitivity and rainbow trout are an important aquatic species in Minnesota, a chronic standard for cold-water (class 2A) uses was calculated using the ACR (28.11) for rainbow trout. The chronic standard for all other class 2 waters was calculated using the geometric mean ACR for the three species shown in Table 2.
Studies have reported chronic effects of NPEO on aquatic organisms using conventional endpoints that represent effects on populations of aquatic animals (i.e., survival and growth), but were not sufficient for Tier 1 assessment. The national AWQC document provides an examination of chronic effects reported from the literature through 2005.

Endocrine-active endpoints for nonylphenol ethoxylates

Nonylphenol is documented as an endocrine active compound (EAC) described in part through its estrogenic activity in aquatic organisms, particularly vertebrates (EPA 2005). Endocrine Active Compounds are broadly described as chemicals that exert effects attributed to disruption of the endocrine system, which regulates critical growth, developmental and reproductive aspects of an organism's life cycle. These sorts of compounds are also referred to as endocrine disrupting compounds, but the term EAC serves to better describe the activity of these compounds in biological systems. Current understanding of EACs characterize them through both activational (e.g., vitellogenin production) and organizational (e.g., intersex) endpoints, and a variety of measured responses through histological, physiological, molecular (i.e., protein, gene) and other observations. This document, however, will not be developing aquatic life WQSs based on endocrine-active endpoints. The challenge with developing numeric standards based on EAC endpoints is the scientific information gap, specific to NPEOs, that precludes a connection of these endpoints to effects at the population level[1].

Research with NPEO has documented effects of estrogenic exposure in organisms to responses measured through chemical reproductive proteins (e.g., vitellogenin induction) and their cellular precursors (e.g., m-RNA induction) (Vazquez-Duhalt 2005). These chemical biomarkers also have been associated with internal effects (e.g., gonadal deformities), external effects (anatomical deformities, secondary sex characteristics), and some limited reproductive (fecundity, hatching success), behavioral (spawning success) and other effects (growth,

[1] Other environmental pollutants that have relevant ecological effects data for evaluating population level effect are discussed in the MPCA's 2008 Legislative Report, *Endocrine Disrupting Compounds* (at http://www.pca.state.mn.us/publications/reports/lrp-ei-1sy08.pdf).

survival). Absolute outcomes of toxicity tests using NPEO, however, have yet to report definitive dose-response and endpoint calculations that are critical to development of numeric standards for aquatic life. As NPEO comes from entirely anthropogenic sources, surveys of wastewater effluents and ambient waters have detected these compounds in a number of sites in Minnesota (Lee et al. 2004 and 2008). In conjunction with this analysis, laboratory studies have examined organism responses to exposures of whole effluent dilutions and aqueous solutions spiked with relevant concentrations of nonylphenols (Bistodeau *et al.* 2006, Schoenfuss *et al.* 2002). Outcomes from these tests did not produce any absolute connections to reproductive effects. Recently, Schoenfuss (2008) showed that chronic exposures of fathead minnow to nonylphenols in wastewater effluent affected spawning behavior of males. Results of these tests do not include conclusive dose-response characteristics, but serve to provide additional information of possible population-level effects in connection with wastewater effluents containing measurable amounts of NPEO. Numerous studies have examined behavioral and reproductive-related effects following exposure to whole effluents, mixtures and treatments containing nonylphenol and octylphenol ethoxylates. Dr. Scheonfuss is currently engaged with the agency in efforts that include assessing reproductive effects in female fathead minnows.

The intent of this standards development is to ensure additional protection to aquatic organisms from exposure to the broader suite of nonylphenol ethoxylates through attempting to keep the most toxic compounds (4-NP, NP1EO and NP2EO) from entering the environment. A cursory examination of the recent literature (i.e., ECOTOX database search) suggest that many studies reporting chronic effects of NPEO focused more on assessing endocrine active endpoints. These too were reported in the national criteria document as other endpoints (US EPA 2005; Table 6). From these (Table 6) data, a species sensitivity distribution was created (Figure A) that offers a relative comparison between this range of endpoints and the chronic value of NPEO developed for the draft CSs. The species sensitivity distribution was plotted using the online EPA program CADDIS (US EPA 2000). This exercise was not meant to prescribe any definitive measure of effect on the aquatic community, but it may serve to provide some insight toward the relative protection offered by the draft Minnesota chronic standard to aquatic life.

Draft Water Quality Standards for Nonylphenol and Ethoxylates

Minnesota aquatic life WQSs for nonylphenol ethoxylates

The MPCA has decided to adopt criteria values for nonylphenol ethoxylates best described as 4-nonylphenol (CAS number 84852-15-3), NP1EO (CAS number 104– 35–8) and NP2EO (CAS number 27176– 93–8). Development of a state standard for this suite of NPEO serves both as a means to adopt water quality standards that fulfill the Clean Water Act mandate and provide better protection for aquatic life uses in the state. Adopting these standards for NPEO versus standards for 4-NP alone is better suited because the realistic environmental exposure to aquatic organisms is not restricted to a single chemical.

Sources used to gather information needed for the development of aquatic life criteria were retrieved from a search of academic databases. Primary databases were Scirus (www.scirus.com), Google Scholar (scholar.google.com), University of Minnesota library, MPCA library resources, U.S. EPA ECOTOX and other sources. The national criteria document (US EPA 2005) provided the majority of the toxicity data used for the Minnesota criteria development.

The Aquatic Life Summary Sheets (Table 3) presents the technical detail for the Class 2 Final Acute Value (FAV) and Chronic Standard (CS) value of 59.78 µg/L, rounded to 60 µg/L, and 7.4 µg/L, respectively. Additionally, a separate chronic value for cold water uses (Class 2A) of 2.4 µg/L was developed for the protection of cold-water fish. Development of these Minnesota standards considered additional data from the scientific literature that expanded upon studies using 4-NP, NP1EO and NP2EO. Results of those tests did not show 4-NP to be considerably more toxic than NP1EO or NP2EO, and the addition of toxicity test endpoints for more species serves to better reflect a broader aquatic community response. Inclusion of one study using the amphibian *Xenopus*, though not particularly sensitive, offers a broader perspective of surrogate test species. Minnesota standard calculations also added to the calculation of an acute to chronic ratio (ACR). In efforts to better reflect the freshwater focus of Minnesota criteria, the national ACR using a saltwater species was not included in the final ACR used for deriving a chronic value.

Considerations of Human health in aquatic life criteria

The national AWQC for nonylphenol (US EPA 2005) only developed aquatic life acute and chronic standards and did not include a review of human health-based chronic criterion. EPA has also not published toxicological values for use in risk assessment in the Integrated Risk Information System (IRIS). Developing water quality standards also include review of available data to evaluate the beneficial uses of drinking water, fish consumption, and recreational primary contact. MPCA works closely with the Minnesota Department of Health (MDH) on toxicological evaluations and had requested a human health review to ensure that the chronic standard being developed will be protective for both aquatic communities and human health (MDH 2009). MDH provides toxicological data reviews used by MPCA since the 1990 adoption of human health-based methods and standards. Prior to recommending toxicological values for use by MPCA, the dataset has to meet their criteria for sufficient and acceptable data (e.g. MDH HBV level- reference doses and appropriate drinking water intake rates). At this time, MDH did not develop a final reference dose or provide human health risk assessment advice (RAA) for nonylphenol. However, a survey of available secondary literature revealed sources of information about the mammalian toxicity of nonylphenol to suggest that the human health-based WQS would not be as stringent as the chronic standard developed to protect aquatic life. As a review of primary information sources was not possible, the presentation of these results could not be used in the development of NPE standards. MPCA will continue to evaluate the availability of final toxicological assessments by EPA's IRIS and MDH for future consideration in WQSs.

Implementation

WQSs are expected to be assessed and updated every three years according to provisions in the Clean Water Act. The MPCA has the responsibility for assessing existing water quality standards and for considering any new or existing national criteria for surface waters to develop WQSs. Developing Minnesota WQSs for nonylphenol ethoxylates is based on lack of existing criteria or WQSs for these chemicals and availability of National AWQC to provide guidance only for 4-nonylphenol. Based on additional research data, MPCA augmented the National criteria values by adding the two short-chain ethoxylates (NP1EO, NP2EO) when developing protective values for the three most toxic nonylphenol ethoxylates. A study of selected surface waters in Minnesota found nonylphenol ethoxylates present in many lakes and streams, and not always associated with wastewater sources (Lee et al. 2009). Setting values protective of aquatic life for NPEOs offers a better assurance that these anthropogenic chemicals are less likely to be released to the environment.

Methods for chemical analysis of nonylphenol ethoxylates are available through select laboratory procedures and draft guidance documents under review by the American Society for Testing and Materials (ASTM). A standard method for the analysis of surface water and wastewater is anticipated to be complete by 2012. Current practices of sample analysis are on a project basis (see Zaugg et al. 2006), which provide for quantifying concentrations of total NPEO1, NPEO2 and 4- NP.

Table 1. Acute toxicity values considered in development of numeric aquatic life standards. Notes: n – not used for standard development: (marine) – marine species; (short test) – test length unacceptable; (chemical) – exposure chemical not reported or unacceptable; (non-native) – not native species; (methods) – unacceptable methods used. ACR – data used to calculate acute to chronic ratio.

Species Scientific Name	Endpoint Conc. (ug/L)	Chemical exposure	Author	Notes
Acipenser oxyrhynchus	80	4 - NP	Dwyer et al. 2000	n (marine)
Acipenser oxyrhynchus	80	4 - NP	Dwyer et al. 2000	n (marine)
Alosa sapidissima	50	4 - NP	Dwyer et al. 2000	n (short test)
Bufo boreas	120	4 - NP	Dwyer et al. 1999	y
Ceriodaphnia	210	NPEO	Isidori et al. 2006	y; ACR
Ceriodaphnia	220	NPEO	Isidori et al. 2006	y; ACR
Ceriodaphnia	70	NPEO	Isidori et al. 2006	n (chemical)
Ceriodaphnia	92.4	NPEO	TenEcyck and Markee 2007	y
Ceriodaphnia	328	NPEO	TenEcyck and Markee 2007	y
Ceriodaphnia	716	NPEO	TenEcyck and Markee 2007	y
Chironomus	160	4 -NP	England 1993	y
Crinia insignifera	6400	NPEO	Mann and Bidwell 2000	n (non-native)
Crinia insignifera	4500	NPEO	Mann and Bidwell 2000	n (non-native)
Daphnia magna	104	4 - NP	Brooke 1993	y; ACR
Daphnia magna	190	4 - NP	Comber 1993	y; ACR
Daphnia magna	180	4 -NP	Hirano et al. 2004	y
Etheostoma	190	4 - NP	Dwyer 1999	y
Etheostoma	110	4 - NP	Dwyer 1999	y
Etheostoma lepidum	220	4 - NP	Dwyer et al. 1999	y
Etheostoma lepidum	200	4 - NP	Dwyer et al. 1999	y
Etheostoma lepidum	190	4 - NP	Dwyer et al. 1999	y
Etheostoma rubrum	110	4 - NP	Dwyer et al. 1999	y
Etheostoma rubrum	170	4 - NP	Dwyer et al. 1999	y
Etheostoma rubrum	130	4 - NP	Dwyer et al. 1999	y
Gila elegans	310	4 - NP	Dwyer 1995	y
Gila elegans	270	4 - NP	Dwyer 1995	y
Gila elegans	290		Sappington et al. 2001	y
Hyallela	20.7	4 - NP	Brooke 1993	y
Hyallela	150	4 -NP	England 1995	y
L. variegatus	342	4 - NP	Brooke 1993	y
Lampsilis cardium	1190	4 -NP	Milam et al. 2005	n (methods)
Lampsilis siliquoidea	490	4 -NP	Milam et al. 2005	n (methods)
Lepomis	209	4 - NP	Brooke 1993	y
Leptodea fragilis	570	4 -NP	Milam et al. 2005	n (methods)

Ligumia subrostrata	1040	4 -NP	Milam et al. 2005	n (methods)
Litoria adelaidensis	9200	NPEO	Mann and Bidwell 2000	n (non-native)
Litoria adelaidensis	8800	NPEO	Mann and Bidwell 2000	n (non-native)
Litoria adelaidensis	8800	NPEO	Mann and Bidwell 2000	n (non-native)
Megalonaias nervosa	560	4 -NP	Milam et al. 2005	n (methods)
Onchorhynchus	221	4 - NP	Brooke 1993	y; ACR
Onchorhynchus	190	4 - NP	Dwyer 1995	y
Onchorhynchus	260	4 - NP	Dwyer 1995	y
Onchorhynchus	140	4 - NP	Dwyer 1995	y
Onchorhynchus	270	4 - NP	Dwyer 1995	y

Species Scientific Name	Endpoint Conc. (ug/L)	Chemical exposure	Author	Notes
Onchorhynchus	180	4 - NP	Dwyer 1995	y
Onchorhynchus	180	4 - NP	Dwyer 1995	y
Onchorhynchus	160	4 - NP	Dwyer 1995	y
Onchorhynchus	150	4 - NP	Dwyer 1995	y
Onchorhynchus	140	4 - NP	Dwyer 1995	y
Onchorhynchus	220	4 - NP	Dwyer 1995	y
Oncorhynchus clarkii stomias	150		Sappington et al. 2001	y
Oncorhynchus gilae apache	170		Sappington et al. 2001	y
Oncorhynchus mykiss	190		Sappington et al. 2001	y
Ophiogomphus	596	4 - NP	Brooke 1993	y
Oryzias latipes	870	4 - NP	Kashiwada et al. 2002	n (test spp.)
Oryzias latipes	850	4 - NP	Kashiwada et al. 2002	n (test spp.)
Oryzias latipes	130	4 - NP	Kashiwada et al. 2002	n (test spp.)
Oryzias latipes	850	4 - NP	Kashiwada et al. 2002	n (test spp.)
Physella	774	4 - NP	Brooke 1993	y
Pimephales promelas	128	4 - NP	Brooke 1993	y
Pimephales promelas	210	4 - NP	Dwyer 1995	y
Pimephales promelas	360	4 - NP	Dwyer 1995	y
Pimephales promelas	310	4 - NP	Dwyer 1995	y
Pimephales promelas	330	4 - NP	Dwyer 1995	y
Pimephales promelas	170	4 - NP	Dwyer 1995	y
Pimephales promelas	290	4 - NP	Dwyer 1995	y
Pimephales promelas	140	4 -NP	Holcombe et al. 1984	y
Pimephales promelas	270		Sappington et al. 2001	y
Pimephales promelas	323	NPEO	TenEcyck and Markee 2007	y
Pimephales promelas	136	NPEO	TenEcyck and Markee 2007	y
Pimephales promelas	218	NPEO	TenEcyck and Markee 2007	y
Poeciliopsis occidentalis	250	4 - NP	Dwyer et al. 1999	y
Poeciliopsis occidentalis	250	4 - NP	Dwyer et al. 1999	y
Poeciliopsis occidentalis	230	4 - NP	Dwyer et al. 1999	y
Ptychocheilus lucius	270	4 - NP	Dwyer 1995	y
Ptychocheilus lucius	240	4 - NP	Dwyer 1995	y
Ptychocheilus lucius	260		Sappington et al. 2001	y
Rana sphenocephala	340	4- NP	Bridges et al. 2002	y
Scaphirhynchus platorynchus	200	4 - NP	Dwyer et al. 1999	n (short test)
Scaphirhynchus platorynchus	130	4 - NP	Dwyer et al. 1999	n (short test)
Scaphirhynchus platorynchus	130	4 - NP	Dwyer et al. 1999	y
Thamnocephalus platyurus	4.82	NP form	Brausch and Smith 2007	n (chemical)
Thamnocephalus platyurus	2.6	NP form	Brausch and Smith 2007	n (chemical)
Thamnocephalus platyurus	3.68	NP form	Brausch and Smith 2007	n (chemical)
Utterbackia imbecilis	770	4 -NP	Milam et al. 2005	y

Xenopus laevis	5400	NPEO	Mann and Bidwell 2000	y
Xenopus laevis	2800	NPEO	Mann and Bidwell 2000	y
Xenopus laevis	3300	NPEO	Mann and Bidwell 2000	y
Xenopus laevis	4600	NPEO	Mann and Bidwell 2000	y
Xenopus laevis	3900	NPEO	Mann and Bidwell 2000	y
Xenopus laevis	4600	NPEO	Mann and Bidwell 2000	y
Xenopus laevis	4800	NPEO	Mann and Bidwell 2000	y
Xiphophorus helleri	205.98		Kwak et al. 2001	y
Xyrauchen texanus	190	4 - NP	Dwyer 1995	y
Xyrauchen texanus	160	4 - NP	Dwyer 1995	y
Xyrauchen texanus	170		Sappington et al. 2001	y

Table 2. Calculations of aquatic life numeric standard for 4-NP, NP1EO and NP2EO.

Genus name			GMAV	Rank	P		ACR		
Xenopus			4108.6	18					
Physella			774.0	17					
Ophiogomphus			596.0	16					
Lumbriculus			342.0	15					
Rana			340.0	14					
Gila			289.5	13					
Ptychocheilus			256.4	12					
Ceriodaphnia			251.3	11			9.08		
Pimephales			225.9	10					
Lepomis			209.0	9					
Onchorhynchus			181.4	8			28.11		
Xyrauchen			172.9	7					
Chironomus			160.0	6					
Etheostoma			159.8	5	0.26				
Daphnia			152.6	4	0.21		2.02		
Scaphirhynchus			130.0	3	0.16				
Bufo			120.0	2	0.11				
Hyallela			55.7	1	0.05				
				GMAV	P	ln GMAV	(ln GMAV)	Sq Rt P	
		Daphnia magna		152.6	0.21	5.0281	25.2820	0.4588	
		Scaphirhynchus plato		130.0	0.16	4.8675	23.6929	0.3974	
		Bufo boreas		120.0	0.11	4.7875	22.9201	0.3244	
		Hyallela azteca		55.7	0.05	4.0204	16.1635	0.2294	
						Genus		ACR	
s2 Num	0.6029					Ceriodaphnia		9.08	
s2 Denom	0.0293					Onchorhynchus		28.11	
S2	20.6093					Daphnia		2.02	
Sqrt S2	4.5397					Mysis		8.40	
L	3.0756								
A	4.0907								
FAV	59.7808								
									GeoMean
CC: Chronic Calc(Mysis)			**7.1**			**ACR (Mysis; EPA Crit.)**			8.40
CC: Chronic Calc #1			**7.5**			**ACR (RBT, D.m., C.d., Mysis):**			7.95
CC (2A Salmonid):			**2.1**			**ACR (2A salmonid):**			28.11
CC (FW ACR):			**7.5**			**ACR FW (RBT, C.d., D.m.)**			8.02

Table 3 Draft Water Quality Standards

A. Chemical: **Nonylphenol ethoxylates**	CAS#	Date **January 2010**

B. Minnesota Criterion: ug/l (unless noted otherwise)					
Water Class	**Use**	**CS**	**MS**	**FAV**	**Basis[2]**
1,2A	DW, Salmonid	2.4	30	59.78	PCAT1
1,2Bd	DW, NonSalmonid	7.4	30	59.78	PCAT1
2B, 2C, 2D	NonSalmonid	7.4	30	59.78	PCAT1
	Other			Round to 60	

Are Minnesota numeric standards modified from existing EPA criteria? **Yes**
Is toxicity related to water quality characteristic?: **No**
If yes, above standard values determined for:
Slope: Acute:
Chronic:

Formulas:	**MPCA**	**EPA**
CS:		
MS:		
FAV:		

Notes: Chronic criteria lowered for 2A waters to protect Rainbow Trout

C. EPA Criterion:	ug/l	
Date: Dec 2005	CCC: 6.6	Basis: EPA T1 (4- nonylphenol)
	MC: 28	Basis: EPA T1 (4- nonylphenol)
	FAV: 55.49	Basis: EPA T1 (4- nonylphenol)
D. Other Criteria ug/l		**Source**

E. Notes: U.S. EPA Aquatic Life for Nonylphenol available at:
www.epa.gov/waterscience/criteria/nonylphenol

[2] Criteria basis codes for part B:
EPA = From EPA criterion
PCA = Criterion developed by Minnesota Pollution Control Agency staff
T1 = Direct aquatic life toxicity, EPA national criteria procedures used
T2 = Direct aquatic life toxicity, EPA advisory procedures used
Hs = Human health systemic effects
Hc = Human health carcinogenic effects
R = Tissue residue (bioaccumulation)
W = Wildlife effects
O = Organoleptic (taste and odor)
Other = Criterion based on other end point

MINNESOTA POLLUTION CONTROL AGENCY
DRAFT AQUATIC LIFE NUMERIC STANDARD
Determination of Numeric Standard from Aquatic Life Toxicity Values

A. Chemical: **Nonylphenol ethoxylates**	CAS#	Date **January 2010**

B. EPA National Method				
1. Data requirements:	Salmonid (2A water only):		Onchorhynchus	
	Osteichthyes (fish):		Scaphirhynchus, Pimephales	
	Chordata (fish, amphibian):		Bufo, Rana.	
	Planktonic crustacean:		Daphnia, Ceriodaphnia	
	Benthic crustacean:		Hyalella azteca	
	Aquatic insect:		Chironomus, Ophiogomphus.	
	Phylum other than Arthropoda or Chordata:		Physella	
	Second insect or phylum not already rep.:		Lumbriculus	
2. GMAVs	Lowest 4(2A):	152.65 (Daphnia magna)	Lowest 4(2B,2C, 2D):	same
ug/l		130.0 (Scaphirhynchus platorynchus)		same
	N: 23	120.0 (Bufo boreas)	N:	same
		55.7 (Hyalella azteca)		same
3. FAV:	2A: 59.78		2B, 2C, 2D: 59.78	
4. Adjustments to FAVs: None				

5. Chronic data:	No.	Species:
mean values		

6. ACR Measured:	Acute value	Chronic value	ACR
Ceriodaphnia	214.94	23.66	9.083
Onchorhynchus	221	7.861	28.11
Daphnia (Geomean)	140.57	69.50	2.023
GeoMean ACR:			7.795 Note: Onchorhynchus ACR (28.11) used for class 2A chronic criterion calculation.
7. Final Plant Value: **Not Determined**			
C. EPA Advisory Method **Not Determined**			

D. Notes: **Nonyphenol ethoxylates are described as combined aqueous concentrations of 4-nonylphenol, nonylphenol mono-ethoxylate (NP1EO) and nonylphenol di-ethoxylate (NP2EO).**

MINNESOTA POLLUTION CONTROL AGENCY
DRAFT AQUATIC LIFE NUMERIC STANDARD
HUMAN HEALTH – To Be Determined

A. Chemical: **Nonylphenol ethoxylates**	CAS#	Date 30 June 2009

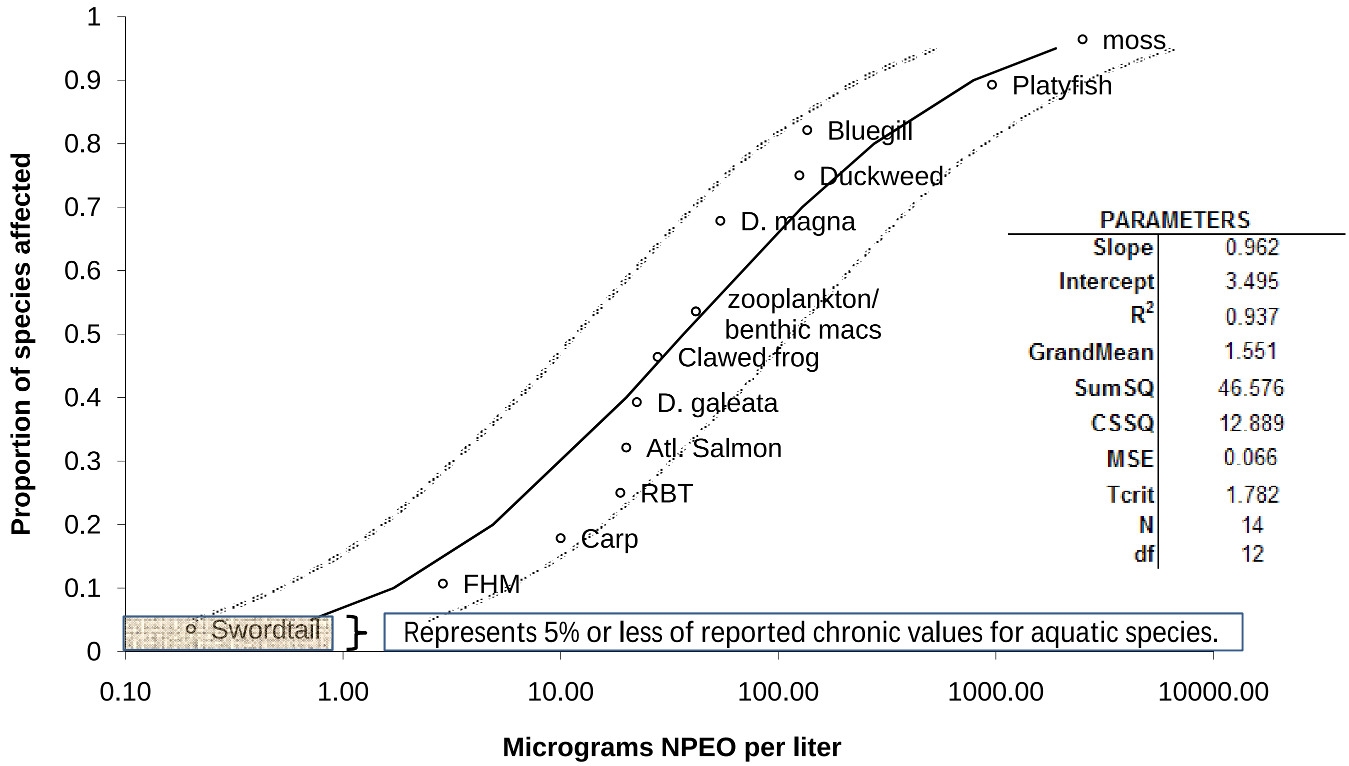
B. EPA Human Health Criterion: ug/l	DW and fish: none	fish only: none	DW only: none
ADI/Ref.dose: mg/kg/day	Cancer Potency Slope: $(mg/kg\text{-}d)^{-1}$		
Final BCF:	%lipid:		
RSC:			

C. Minnesota Human Health Criterion			
1. Ref.dose: mg/kg/day	Source:		
RSC:	Source:		
2. Cancer Potency Slope: $(mg/kg\text{-}d)^{-1}$	Source:		
3. Measured BAFs: Species/Tissue	BAF	%lipid	Norm BAF
1.			
2.			
Geo mean:			
4. Measured BCFs: Species/Tissue	BCF	%lipid	Norm. BCF
1.			
2.			
Geo mean:			
5. Edible portion BAF or BCF	BAF		BCF
Cold water: 6.0 % lipid			
Warm water: 1.5 % lipid			
6. Geo mean unadjusted for lipid:			
7. log Kow: adjust. for % lipid:	meas.	QSAR:	Est. BCF:
8. Parachor:			
9. Food Chain Multiplier:			
10. Final BAF: 2A:	2B,2C, 2D:		
11. Criteria: ug/l	2A:	2Bd:	2B/2C, 2D:	HRL/HBV:

D. Organoleptic: ug/l	Source:

E. Notes: Sufficiently reviewed human health toxicological values were not available from U.S. EPA's Integrated Risk Information System or Minnesota Department of Health (MDH 2009) to develop a human health-based CS. EPA's 304 (a) AWQC also did not provide final recommended national bioaccumulation factors.

Figure A. Data summarized from US EPA (2005), Table 6 as plotted using a species sensitivity distribution performed by CADDIS (US EPA 2000).



Taxa	Micrograms NPEO per liter	Standard Deviation	Proportion Taxa	Number of Observations
Swordtail	0.20		4%	1
FHM	2.88	0.17	11%	4
Carp	10.00		18%	2
RBT	18.80	0.73	25%	18
Atl. Salmon	20.00		32%	1
D. galeata	22.40		39%	1
Clawed frog	27.87	0.15	46%	2
zooplankton	41.80		54%	1
benthmacs	41.80		54%	1
D. magna	54.14	0.11	68%	3
Duckweed	125.00		75%	1
Bluegill	135.90		82%	1
Platyfish	960.00		89%	1
moss	2500.00		96%	1

Plotted data summarized from EPA 2005, Table 6.

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