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MEMORANDUM

To: Lower Willamette Group

From: John Toll, David DeForest, Brian Church

Subject: Derivation of Proposed Manganese PRG to Replace the Suter and Tsao (1996) Tier II Value in the Portland Harbor Feasibility Study

Date: August 1, 2014

SYNOPSIS

Measured manganese concentrations in the transition zone waters (TZW) of Portland Harbor, Oregon, exceeded the Tier II water quality benchmark developed at Oak Ridge National Laboratory (ORNL) (Suter and Tsao 1996). The Tier II value was derived following US Environmental Protection Agency (EPA) methods (EPA 1993) for chemicals that do not meet the minimum data requirements for development of ambient water quality criteria (AWQC). There is a high degree of uncertainty, associated with the use of this Tier II for decision making. Furthermore, the Tier II value was calculated almost 20 years ago, and sufficient manganese toxicity data are now available. For that reason, the Lower Willamette Group (LWG) and EPA agreed during a May 8, 2014, feasibility study (FS) meeting that the LWG would propose a new manganese water toxicity value. The purpose of this technical memorandum is to present the proposed alternative, hardness-based manganese "criterion."[1]

Studies published subsequent to Suter and Tsao (1996) have shown that hardness plays an important role in mitigating the bioavailability and toxicity of manganese to aquatic organisms (e.g., Stubblefield et al. 1997). At present, both New Mexico and Colorado have adopted hardness-based manganese water quality criteria which have been approved by EPA (CDPHE 2012; NMED 2011), and a biotic ligand model (BLM) for predicting chronic manganese toxicity was recently proposed by Peters et al. (2011).

Using the currently available toxicological data, hardness-based acute and chronic manganese criteria were calculated by Windward Environmental LLC (Windward) using EPA methods (Stephan et al. 1985). Those criteria are presented here. The acute and chronic manganese criteria developed and recommended by Windward are as follows:

$$\textbf{Acute criterion} = e^{(0.7424\,[\ln(\text{hardness})] + 5.092)}$$

[1] Note that the term "criterion" is used in this memorandum but, while EPA guidelines for AWQC development were followed, the "criterion" derived by Windward Environmental (Windward) have not been reviewed or endorsed by EPA's Office of Water.

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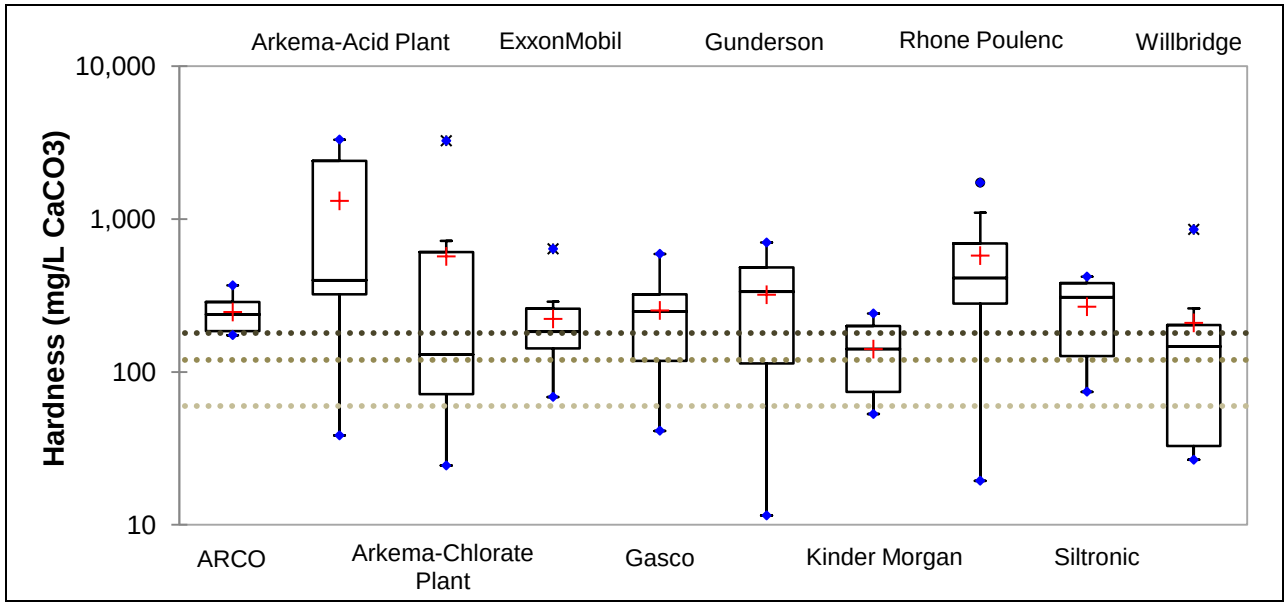
$$\text{Chronic criterion} = e^{(0.7424\,[\ln(\text{hardness})] + 4.220)}$$

CURRENT TIER II CRITERION

Chronic Tier II surface water guidelines were developed by Suter and Tsao (1996) as benchmarks for conducting screening-level risk assessments based on surface water chemistry; these guidelines were developed specifically for chemicals with insufficient toxicity data available to develop AWQC. The Tier II secondary chronic value (SCV) for manganese (120 µg/L) was selected as the toxicity reference value (TRV) for the baseline ecological risk assessment (BERA) for Portland Harbor. After reviewing the Tier II SCV value for manganese and the implications of its use in the assessment of risk associated with TZW in Portland Harbor, the benchmark has considerable uncertainty due to the limited dataset it was based upon, and is overly conservative for the hardness values measured in Portland Harbor TZW (Figure 1). Hardness alters manganese toxicity in aquatic systems (Reimer 1999; Stubblefield et al. 1997; Stubblefield and Hockett 2000; Davies 1980), as do several other water chemistry parameters (e.g., pH, free calcium ion, and free potassium ion) (Peters et al. 2011).



Notes: Hardness is shown on logarithmic scale. Dotted lines indicate thresholds between defined water hardness categories: soft (< 60 mg/L as calcium carbonate), moderately hard (60-120 mg/L as calcium carbonate), hard (120-180 mg/L as calcium carbonate), and very hard waters (> 180 mg/L as calcium carbonate). Additional plot symbols are as follows: blue points are minimums and maximums; red plus sign is the arithmetic mean; asterisks are extreme values.

Figure 1. Measured hardness in shallow (0-15-inch) Portland Harbor TZW

The Tier II value of 120 µg/L was calculated using acute toxicity data (i.e., median lethal concentrations [LC50s]) for *Asellus aquaticus* (isopod), *Crangonyx pseudogracilis* (amphipod), *Daphnia magna*, and fathead minnow (*Pimephales promelas*), which ranged from 19,200 to 694,000 µg/L. A chronic toxicity value was available for only fathead minnow; specifically, a chronic value of 1,775 µg/L was included in the dataset and used to calculate an acute-to-chronic ratio (ACR). The Tier II SCV for manganese of 120 µg/L was ultimately derived by dividing the lowest genus (geometric) mean acute value (GMAV) (19,350 µg/L) by an uncertainty factor (8.6)

and a mean ACR (18.24) (i.e., the geometric mean of the empirical ACR of 18.93 based on fathead minnow, and two generic ACRs of 17.9).

In the Portland Harbor BERA, TZW concentrations of manganese were compared to the Tier II SCV of 120 µg/L, regardless of other water chemistry parameters that may mediate toxicity in aquatic species (e.g., hardness). Based on the Tier II value, the average hazard quotients (HQs) (ratios of the TZW concentrations to the Tier II SCV) for manganese within Portland Harbor ranged up to 98 .

HARDNESS-BASED MANGANESE CRITERIA FOR NEW MEXICO AND COLORADO

Both New Mexico and Colorado have established hardness-based surface water quality criteria for the protection of aquatic life (CDPHE 2012; NMED 2011) based on a report by Stubblefield and Hockett (2000). The current EPA-approved acute and chronic criteria (expressed as µg/L manganese) in New Mexico/Colorado are as follows:

Acute criterion: $e^{(0.3331[\ln(\text{hardness})] + 6.4676)}$

Chronic criterion: $e^{(0.3331[\ln(\text{hardness})] + 5.8743)}$

RECOMMENDED HARDNESS-BASED MANGANESE CRITERION

This section describes the methods and data used to by Windward to develop the recommended hardness-based manganese criterion for the Portland Harbor remedial investigation (RI)/FS. The criterion is derived following EPA guidance (Stephan et al. 1985) using the New Mexico/Colorado manganese dataset plus additional manganese toxicity test data, many of which are more recent.

Ambient water quality criteria derivation

National AWQC for the protection of aquatic life are derived from empirical toxicity data, and are designed to be stringent enough to protect most sensitive species potentially exposed to a contaminant in any water body in the United States. Below these thresholds, no adverse effects on aquatic communities are anticipated, although because the AWQC concentrations are derived to protect all but the most sensitive species in the toxicity database, the most sensitive species could potentially be impacted. However, if data suggest that a commercially or recreationally important species is not protected at these concentrations, then an AWQC value can be adjusted to provide sufficient protection for these species as well.

EPA guidelines for AWQC development (Stephan et al. 1985) specify minimum study requirements for consideration in the development of acute and chronic criteria for the protection of aquatic life. For example, acute toxicity studies must have an exposure duration of 96 hours (although 48 hours is acceptable for more short-lived species, such as cladocerans and midges); organisms must not be fed during the study; and the endpoint must be mortality, immobilization, or a combination of the two. Chronic toxicity studies must be conducted using exposure durations that encompass the full life cycle or, for fish, early life stage (ELS) and partial life cycle. Although EPA guidelines recommend that ELS tests using fish have exposure durations of 28 to 32 days (60 days post-hatch for salmonids), testing has demonstrated that 7-day survival and growth tests with newly hatched fathead minnows (*Pimephales promelas*) are similar in sensitivity to ELS tests of longer duration (EPA 2002; Norberg and Mount 1985;

Naddy et al. 2007; Stubblefield and Hockett 2000) . Accordingly, 7-day survival and growth tests using *P. promelas* were included in this evaluation. EPA guidelines also stipulate that toxicant concentrations in the exposure solutions must be analytically verified in chronic studies (Stephan et al. 1985). Finally, under the Stephan et al. (1985) guidelines, toxicity studies that do not meet the specific study requirements may still be retained as "other data" if the study was otherwise scientifically valid. Such data are not used to calculate the criterion maximum concentration (CMC) and final chronic value (FCV), but may be used to justify lowering the acute or chronic criteria for a toxicant if the species and endpoint tested are considered to be "biologically or recreationally important," and if the CMC or FCV was determined to be inadequately protective of these species or endpoints.

To understand how AWQC are developed, it is useful to review the guidelines and terminology provided in Stephan et al. (1985); the general approach is briefly summarized below. The first step is to compile acute and chronic toxicity data from laboratory toxicity tests that meet the specific study type and duration requirements noted above. For each species with acceptable acute toxicity data, the species mean acute value (SMAV) is calculated as the geometric mean of the available 48- to 96-hour LC50s and EC50s (median effective concentrations) for each species. The GMAV is then calculated as the geometric mean of the available SMAVs for each genus. The 5th percentile of the distribution of available GMAVs is identified as the final acute value (FAV), which is divided by two (to estimate a low-effect concentration) to determine the CMC, or acute criterion. The 5th percentile is calculated based solely on the four most sensitive GMAVs and the total number of GMAVs (Stephan et al. 1985). AWQC are only developed if an eight family rule is met. When this rule not met, as is often the case for chronic toxicity data, the FCV, or chronic criterion, is derived by dividing the FAV by an ACR. However, if sufficient chronic toxicity data are available, the FCV is calculated in a manner similar to the FAV, using the four lowest genus mean chronic values (GMCVs) and the total number of GMCVs to calculate a 5th percentile value. In the current evaluation, sufficient chronic data were not available to use the latter method to derive a chronic criterion, so an ACR was applied.

Summary of new toxicity studies

An extensive search of available aquatic toxicity data in the literature and online (e.g., ECOTOX 2013) was conducted, and additional unpublished toxicity data used to support development of the manganese criteria adopted in New Mexico and Colorado were also obtained from the New Mexico Environment Department. Several studies were also obtained from Parametrix, Inc. that were sponsored by the International Manganese Institute (IMnI). All acceptable acute and chronic manganese toxicity data were compiled. Those data are presented in Tables 1 (acute data) and 2 (chronic data). Acute toxicity data were identified for 22 species and 21 genera, and the eight family rule was met. Chronic toxicity data were identified for 12 species and genera from 7 families, so the chronic data did not meet the eight family rule (data from a third family in the phylum Chordata were unavailable). Furthermore, chronic data for the amphipod *Hyalella azteca*, which represents one of the seven families with available chronic data, were considered highly unreliable (as discussed later). As such, reliable chronic data were available for only six families. Because the eight family rule was not met for the chronic toxicity dataset, the chronic criterion was developed using an ACR-based approach (EPA 1985). ACRs were identified for six species (Table 3), which meets EPA's minimum requirement of three species ACRs (Stephan et al. 1985).

The ranked GMAV values used to calculate the FAV and FCV (using the ACRs in Table 3 to obtain the FCV) are presented in Table 4.

Table 1. Acute manganese toxicity data

Species	Organism Lifestage/ Size	Exposure Type	Chemical Analysis	Duration (d)	Endpoint	Effect	Hardness (mg/L as $CaCO_3$)	Mn (µg/L)	Mn (µg/L) Adj. to 50 mg/L Hardness (µg/L)	Mn SMAV (µg/L)	Mn GMAV (µg/L)	Reference
Aeolosoma sp. (oligochaete worm)	<24 h	S	M	2	LC50	mortality	52	39,460	38,328	38,328	38,328	Parametrix (2009e)
Agosia chrysogaster (longfin dace)	juveniles	R	M	4	LC50	mortality	224	130,000	42,702	42,702	42,702	Lewis (1978)
Anodonta imbecillis (freshwater mussel)	6-8 days	NR	NR	NR	LC50	mortality	80	36,200	25,537	25,537	25,537	Wade et al. (1989) cited in Stubblefield and Hockett (2000)
Asellus aquaticus (isopod)	adults	R	U	4	LC50	mortality	50	333,000	333,000	333,000	333,000	Martin and Holdich (1986)
Bufo boreus (Western toad)	tadpoles	NR	NR	NR	LC50	mortality	95	339,842	211,027	211,027	211,027	ENSR (1996) cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	S	U	2	LC50	mortality	80	19,943	14,068	> 10,889	> 10,889	Hockett and Mount (1996)
Ceriodaphnia dubia (water flea)	neonates	S	U	2	LC50	mortality	172	16,921	6,762	--	--	Hockett and Mount (1996)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	NR	LC50	mortality	26	8,757	14,229	--	--	ENSR 1992 cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	NR	LC50	mortality	50	12,513	12,513	--	--	ENSR 1992 cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	NR	LC50	mortality	100	20,495	12,251	--	--	ENSR 1992 cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	NR	LC50	mortality	200	25,480	9,104	--	--	ENSR 1992 cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	NR	LC50	mortality	48	15,641	16,122	--	--	ENSR 1990 cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	NR	LC50	mortality	176	28,849	11,334	--	--	ENSR 1990 cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	NR	LC50	mortality	396	>45,000	>9,683	--	--	ENSR 1990 cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	NR	LC50	mortality	92	23,456	14,916	--	--	ENSR 1990 cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	R	M	4	LC50	mortality	26	6,700	10,887	--	--	Lasier et al. (2000)
Ceriodaphnia dubia (water flea)	neonates	R	M	4	LC50	mortality	92	14,500	9,221	--	--	Lasier et al. (2000)
Ceriodaphnia dubia (water flea)	neonates	R	M	4	LC50	mortality	184	15,900	6,044	--	--	Lasier et al. (2000)
Chironomus tentans (midge)	juveniles	NR	NR	NR	LC50	mortality	96	327,832	201,993	34,003	34,003	ENSR (1996) cited in Stubblefield and Hockett (2000)
Chironomus tentans (midge)	larvae	S	M	4	LC50	mortality	25	5,800	9,703	--	--	Reimer (1999)
Chironomus tentans (midge)	larvae	S	M	4	LC50	mortality	100	42,200	25,225	--	--	Reimer (1999)
Chironomus tentans (midge)	larvae	S	M	4	LC50	mortality	269	94,300	27,039	--	--	Reimer (1999)
Colisa fasciata (giant gourami)[a]	adults	S	U	4	LC50	mortality	120	1,040,000	542,969	542,969	542,969	Agrawal and Srivastava (1980)
Crangonyx pseudogracilis (amphipod)	adults	R	U	4	LC50	mortality	50	694,000	694,000	694,000	694,000	Martin and Holdich (1986)
Daphnia magna (water flea)	NR	NR	U	2	LC50	mortality	190	42,200	15,664	9,572	9,572	Cabejszek and Stasiak (1960)
Daphnia magna (water flea)	neonates	S	U	2	LC50	mortality	45.3	9,800	10,545	--	--	Biesinger and Christensen (1972)
Daphnia magna (water flea)	neonates	S	M	2	LC50	mortality	26.3	800	1,289	--	--	Reimer (1999)
Daphnia magna (water flea)	neonates	S	M	2	LC50	mortality	100	28,700	17,156	--	--	Reimer (1999)
Daphnia magna (water flea)	neonates	S	M	2	LC50	mortality	267	76,300	22,000	--	--	Reimer (1999)
Duttaphrynus melanostictus (Asian common toad)[a]	tadpole	R	M	4	LC50	mortality	18.6	39,000	81,261	81,261	81,261	Shuhaimi-Othman et al. (2012)
Hyalella azteca (scud)	larvae	S	M	4	LC50	mortality	27.2	3,600	5,657	6,416	6,416	Reimer (1999)
Hyalella azteca (scud)	larvae	S	M	4	LC50	mortality	100	22,200	13,270	--	--	Reimer (1999)
Hyalella azteca (scud)	larvae	S	M	4	LC50	mortality	272	31,000	8,816	--	--	Reimer (1999)
Hyalella azteca (scud)	2-3 mm	NR	NR	NR	LC50	mortality	96	6,630	4,085	--	--	ENSR (1996) cited in Stubblefield and Hockett (2000)
Hyalella azteca (scud)	2-3 mm	NR	NR	NR	LC50	mortality	94	10,169	6,364	--	--	ENSR (1996) cited in Stubblefield and Hockett (2000)
Hyalella azteca (scud)	7 d	R	M	4	LC50	mortality	26	3,000	4,875	--	--	Lasier et al. (2000)
Hyalella azteca (scud)	7 d	R	M	4	LC50	mortality	80	8,559	6,038	--	--	Lasier et al. (2000)
Hyalella azteca (scud)	7 d	R	M	4	LC50	mortality	164	13,700	5,672	--	--	Lasier et al. (2000)
Lymnaea stagnalis (pond snail)	3-4 weeks	R	M	4	LC50	mortality	172	255,530	27,989	27,989	27,989	Parametrix (2009a)

Species	Organism Lifestage/ Size	Exposure Type	Chemical Analysis	Duration (d)	Endpoint	Effect	Hardness (mg/L as $CaCO_3$)	Mn (µg/L)	Mn (µg/L) Adj. to 50 mg/L Hardness (µg/L)	Mn SMAV (µg/L)	Mn GMAV (µg/L)	Reference
Lymnaea stagnalis (pond snail)	3-4 weeks	R	M	4	LC50	mortality	184	205,250	102,121	89,261	89,261	Parametrix (2009a)
Lampsilis siliquoidea (fatmucket clam)	<5 days	S	M	4	LC50	mortality	90	43,300	78,021	--	--	EPA (2010)
Megalonaias nervosa (washboard clam)	<5 days	S	M	4	LC50	mortality	92	31,500	20,032	20,032	20,032	EPA (2010)
Microhyla ornata (frog)[a]	tadpole	R	U	4	LC50	mortality	143.75	14,330	6,543	6,658	6,658	Rao and Madhyastha (1987)
Microhyla ornata (frog)[a]	tadpole	R	U	4	LC50	mortality	143.75	14,840	6,776	--	--	Rao and Madhyastha (1987)
Oncorhynchus kisutch (coho salmon)	juveniles	S	M	4	LC50	mortality	25.2	2,400	3,991	5,481	5,813	Reimer (1999)
Oncorhynchus kisutch (coho salmon)	juveniles	S	M	4	LC50	mortality	100	13,100	7,831	--	--	Reimer (1999)
Oncorhynchus kisutch (coho salmon)	juveniles	S	M	4	LC50	mortality	250	17,400	5,268	--	--	Reimer (1999)
Oncorhynchus mykiss (rainbow trout)	embryos	F	M	4	LC50	mortality	11.8	3,320	9,698	6,165	--	Davies and Brinkman (1994)
Oncorhynchus mykiss (rainbow trout)	NR	F	M	4	LC50	mortality	36	14,500	18,505	--	--	Davies (1980)
Oncorhynchus mykiss (rainbow trout)	NR	F	M	4	LC50	mortality	36	30,000	38,285	--	--	Davies (1980)
Oncorhynchus mykiss (rainbow trout)	NR	F	M	4	LC50	mortality	304	116,000	30,374	--	--	Davies (1980)
Oncorhynchus mykiss (rainbow trout)	juveniles	S	U	4	LC50	mortality	47.6	2,100	2,178	--	--	Reimer (1999)
Oncorhynchus mykiss (rainbow trout)	juveniles	S	U	4	LC50	mortality	100	20,700	12,374	--	--	Reimer (1999)
Oncorhynchus mykiss (rainbow trout)	juveniles	S	U	4	LC50	mortality	259	12,700	3,745	--	--	Reimer (1999)
Oncorhynchus mykiss (rainbow trout)	juveniles	NR	NR	NR	LC50	mortality	44	2,008	2,208	--	--	ENSR (1990) cited in Stubblefield and Hockett (2000)
Oncorhynchus mykiss (rainbow trout)	juveniles	NR	NR	NR	LC50	mortality	48	2,490	2,567	--	--	ENSR (1994) cited in Stubblefield and Hockett (2000)
Oncorhynchus mykiss (rainbow trout)	juveniles	NR	NR	NR	LC50	mortality	90	5,320	3,439	--	--	ENSR (1994) cited in Stubblefield and Hockett (2000)
Oncorhynchus mykiss (rainbow trout)	juveniles	NR	NR	NR	LC50	mortality	170	11,149	4,494	--	--	ENSR (1994) cited in Stubblefield and Hockett (2000)
Oncorhynchus mykiss (rainbow trout)	juveniles	NR	NR	NR	LC50	mortality	100	2,910	1,739	--	--	Birge et al. (1979) cited in Stubblefield and Hockett (2000)
Oncorhynchus mykiss (rainbow trout)	juveniles	NR	NR	NR	LC50	mortality	27.6	3,170	4,928	--	--	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)
Oncorhynchus mykiss (rainbow trout)	juveniles	NR	NR	NR	LC50	mortality	147.8	16,200	7,246	--	--	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	juveniles	NR	NR	NR	LC50	mortality	26	3,542	5,755	> 8,274	> 8,274	ENSR (1992) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	juveniles	NR	NR	NR	LC50	mortality	50	6,232	6,232	--	--	ENSR (1992) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	juveniles	NR	NR	NR	LC50	mortality	100	9,346	5,587	--	--	ENSR (1992) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	juveniles	NR	NR	NR	LC50	mortality	200	15,826	5,655	--	--	ENSR (1992) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	juveniles	NR	NR	NR	LC50	mortality	48	10,302	10,619	--	--	ENSR (1990) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	juveniles	NR	NR	NR	LC50	mortality	92	17,279	10,988	--	--	ENSR (1990) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	juveniles	NR	NR	NR	LC50	mortality	176	27,440	10,781	--	--	ENSR (1990) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	juveniles	NR	NR	NR	LC50	mortality	396	>45,000	>9,683	--	--	ENSR (1990) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	juveniles	NR	NR	NR	LC50	mortality	28	8,557	13,160	--	--	ENSR (1996) cited in Stubblefield and Hockett (2000)
Ptychocheilus oregonensis (northern pikeminnow)	juveniles	S	U	4	LC50	mortality	347	130,465	30,966	38,638	38,638	Beleau and Bartosz (1982)
Ptychocheilus oregonensis (northern pikeminnow)	post-larvae	S	U	4	LC50	mortality	316	189,482	48,210	--	--	Beleau and Bartosz (1982)
Salmo trutta (brown trout)	juveniles	F	M	4	LC50	mortality	10.9	9,060	28,070	16,490	16,490	Davies and Brinkman (1994)
Salmo trutta (brown trout)	juveniles	NR	NR	NR	LC50	mortality	48	15,973	16,464	--	--	ENSR (1994) cited in Stubblefield and Hockett (2000)
Salmo trutta (brown trout)	juveniles	NR	NR	NR	LC50	mortality	454	49,900	9,702	--	--	Davies and Brinkman (1995) cited in Stubblefield and Hockett (2000)
Salvelinus fontinalis (brook trout)	juveniles	NR	NR	NR	LC50	mortality	48	3,606	3,717	6,917	6,917	ENSR (1994) cited in Stubblefield and Hockett (2000)
Salvelinus fontinalis (brook trout)	juveniles	NR	NR	NR	LC50	mortality	31.3	5,120	7,249	--	--	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)
Salvelinus fontinalis (brook trout)	juveniles	NR	NR	NR	LC50	mortality	148.1	27,500	12,281	--	--	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)
Tubifex tubifex (tubificid worm)	NR	S	U	4	EC50	mortality	237	164,550	51,834	71,122	71,122	Rathore and Khangarot (2002)

Species	Organism Lifestage/ Size	Exposure Type	Chemical Analysis	Duration (d)	Endpoint	Effect	Hardness (mg/L as $CaCO_3$)	Mn (µg/L)	Mn (µg/L) Adj. to 50 mg/L Hardness (µg/L)	Mn SMAV (µg/L)	Mn GMAV (µg/L)	Reference
Tubifex tubifex (tubificid worm)	NR	S	U	4	EC50	mortality	237	239,270	75,372	--	--	Rathore and Khangarot (2002)
Tubifex tubifex (tubificid worm)	NR	S	U	4	EC50	mortality	237	239,390	75,410	--	--	Rathore and Khangarot (2002)
Tubifex tubifex (tubificid worm)	NR	S	U	4	EC50	mortality	237	275,700	86,847	--	--	Rathore and Khangarot (2002)

[a] Species not found in North America.

EC50 – median effective concentration
F – flow-through exposure
GMAV – genus mean acute value
LC50 – median lethal concentration
M – measured concentration
NR – not reported
R – renewal exposure
S – static exposure
SMAV – species mean acute value
U – unmeasured concentration

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Table 2. Chronic manganese toxicity data

Species	Organism Lifestage	Exposure Type	Chemical Analysis	Duration (days)	Endpoint	Effect	Hardness (mg/L CaCO3)	Mn (ug/L)	Mn (µg/L) Adj. to 50 mg/L Hardness (µg/L)	Mn SMAV (µg/L)	Mn GMAV (µg/L)	Reference
Aeolosoma sp. (oligochaete worm)	<24 h	R	M	14	EC20	population growth	48	3,630	3,742	3,742	3,742	Parametrix (2009f)
Carassius auratus (goldfish)	eggs	R	M	7	LC50	mortality	195	8,220	2,993	2,993	2,993	Birge (1978)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	7	EC20	growth	26	3,314	5,385	3,248	3,248	ENSR (1992) cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	7	EC20	growth	50	4,885	4,885	--	--	ENSR (1992) cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	7	EC20	growth	100	6,052	3,618	--	--	ENSR (1992) cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	7	EC20	growth	200	7,809	2,790	--	--	ENSR (1992) cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	NR	NR	7	EC20	growth	46	3,317	3,529	--	--	ENSR (1989) cited in Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	60	1,415.6	1,236	--	--	Parametrix (2010a)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	24	2,571.0	4,433	--	--	Parametrix (2010a)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	304	9,255.0	2,423	--	--	Parametrix (2010a)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	84	3,221.0	2,191	--	--	Parametrix (2010a)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	12	1,415.0	4,082	--	--	Parametrix (2010a)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	20	2,803.0	5,534	--	--	Parametrix (2010a)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	48	2,011	2,073	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	5,203	5,054	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	48	4,751	4,897	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	200	6,499	2,322	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	44	4,510	4,959	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	3,382	3,285	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	72	4,460	3,402	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	124	7,439	3,790	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	230	9,241	2,976	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	290	16,423	4,454	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	400	5,986	1,279	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	390	11,147	2,426	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	720	4,041	558	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	4,238	4,116	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	44	2,712	2,982	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	4,474	4,346	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	76	5,182	3,798	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	116	6,429	3,442	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	212	9,942	3,402	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	284	9,676	2,665	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	384	9,555	2,104	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	410	12,919	2,709	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	4,572	4,441	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	3,489	3,389	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	5,778	5,612	--	--	Parametrix (2010b)

Species	Organism Lifestage	Exposure Type	Chemical Analysis	Duration (days)	Endpoint	Effect	Hardness (mg/L CaCO3)	Mn (ug/L)	Mn (µg/L) Adj. to 50 mg/L Hardness (µg/L)	Mn SMAV (µg/L)	Mn GMAV (µg/L)	Reference
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	8,002	7,772	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	48	7,260	7,483	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	4,111	3,993	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	2,331	2,264	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	48	3,319	3,421	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	1,638	1,591	--	--	Parametrix (2010b)
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC25	reproduction	92	5,200	3,307	--	--	Lasier et al. (2000)
Chironomus tentans (midge)	larvae	F	M	54	EC20	mortality	89	17,830	11,621	11,621	11,621	Parametrix (2009g)
Danio rerio (zebrafish)	eggs	F	M	35	EC20	mortality	95	5,121	3,180	3,180	3,180	Parametrix (2009d)
Daphnia magna (water flea)	NR	R	M	21	EC16	reproduction	45.3	4,100	4,412	3,373	3,373	Biesinger and Christensen (1972)
Daphnia magna (water flea)	neonates	S	M	21	IC25	reproduction	100	5,400	3,228	--	--	Reimer (1999)
Daphnia magna (water flea)	neonates	S	M	21	IC25	reproduction	269	9400	2,695	--	--	Reimer (1999)
Hyalella azteca (amphipod)	7-9 day juveniles	F	M	35	EC20	mortality	104	513	361	--[a]	--[a]	Parametrix (2009b)
Lymnaea stagnalis (pond snail)	<24 h	R	M	30	EC20	growth	174	9,040	3,582	3,582	3,582	Parametrix (2009c)
Oncorhynchus mykiss (rainbow trout)	embryos	F	M	121.76	MATC	mortality	36.8	1,570	1,971	1,665	1,665	Davies and Brinkman (1994)
Oncorhynchus mykiss (rainbow trout)	embryos	F	M	121.76	MATC	mortality	36.8	790	992	--	--	Davies and Brinkman (1994)
Oncorhynchus mykiss (rainbow trout)	embryos	NR	NR	NR	EC20	growth	29	1,398	2,095	--	--	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)
Oncorhynchus mykiss (rainbow trout)	embryos	NR	NR	NR	EC20	growth	151	4,259	1,875	--	--	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	embryos	NR	NR	NR	EC20	growth	30	2,550	3,726	2,659	2,659	ENSR (1996) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	larvae	NR	NR	NR	EC20	growth	26	1,338	2,174	--	--	ENSR (1992) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	larvae	NR	NR	NR	EC20	growth	50	5,490	5,490	--	--	ENSR (1992) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	larvae	NR	NR	NR	EC20	growth	100	5,120	3,061	--	--	ENSR (1992) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	larvae	NR	NR	NR	EC20	growth	200	13,152	4,699	--	--	ENSR (1992) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	larvae	NR	NR	NR	EC20	growth	46	3,417	3,635	--	--	ENSR (1989) cited in Stubblefield and Hockett (2000)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	3,117	4,341	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	104	8,010	4,651	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	3,145	4,380	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	60	6,222	5,434	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	100	9,525	5,694	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	192	8,828	3,251	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	244	7,861	2,423	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	292	7,742	2,089	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	400	6,991	1,493	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	372	1,928	435	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	672	8,287	1,204	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	204	1,573	554	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	396	1,776	382	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	2,137	2,976	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	52	1,333	1,295	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	1,186	1,652	--	--	Parametrix (2010c)

Species	Organism Lifestage	Exposure Type	Chemical Analysis	Duration (days)	Endpoint	Effect	Hardness (mg/L CaCO3)	Mn (ug/L)	Mn (µg/L) Adj. to 50 mg/L Hardness (µg/L)	Mn SMAV (µg/L)	Mn GMAV (µg/L)	Reference
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	36	2,147	2,740	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	52	2,388	2,319	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	430	599	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	92	8,587	5,461	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	200	12,860	4,595	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	2,648	3,688	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	2,463	3,430	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	100	5,099	3,048	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	100	8,501	5,082	--	--	Parametrix (2010c)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	60	2,985.0	2,607	--	--	Parametrix (2010d)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	24	2,068.0	3,566	--	--	Parametrix (2010d)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	312	27,604.0	7,090	--	--	Parametrix (2010d)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	88	7,054.0	4,636	--	--	Parametrix (2010d)
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	12	1,078.0	3,110	--	--	Parametrix (2010d)
Salmo trutta (brown trout)	juveniles	F	M	121.76	MATC	mortality	37.5	2,700	3,343	4,104	4,104	Davies and Brinkman (1994)
Salmo trutta (brown trout)	juveniles	F	M	121.76	MATC	mortality	37.5	4,190	5,188	--	--	Davies and Brinkman (1994)
Salmo trutta (brown trout)	eyed eggs	F	M	62	IC25	survival and weight	30.9	4,670	6,675	--	--	Stubblefield et al. (1997)
Salmo trutta (brown trout)	eyed eggs	F	M	62	IC25	survival and weight	151.8	5,590	2,451	--	--	Stubblefield et al. (1997)
Salvelinus fontinalis (brook trout)	embryos	NR	NR	NR	EC20	growth	32	2,104	2,930	2,157	2,157	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)
Salvelinus fontinalis (brook trout)	embryos	NR	NR	NR	EC20	growth	156	3,695	1,588	--	--	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)

[a]*H. azteca* SMAV and GMAV excluded from evaluation (see text).

EC – effective concentration
F – flow-through exposure
GMAV – geometric mean acute value
IC – inhibitory concentration
LC – lethal concentration
LOEC – lowest-observed-effects concentration
M – measured concentration
MATC – maximum acceptable toxicant concentration
na – not applicable
NOEC – no-observed-effects concentration
NR – not reported
R – renewal exposure
S – static exposure
SMAV – species mean acute value
U – unmeasured concentration

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Table 3. Acute-to-chronic ratios

Species	Hardness (mg/L)	Acute Value (µg/L)	Chronic Value (µg/L)	ACR	Species Mean ACR	Reference
Ceriodaphnia dubia (water flea)	26	8,757	3,314	2.642	3.153	Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	50	12,513	4,885	2.562	--	Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	100	20,495	6,052	3.386	--	Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	200	25,480	7,809	3.263	--	Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	48	15,641	3,317	4.715	--	Stubblefield and Hockett (2000)
Ceriodaphnia dubia (water flea)	92	14,500	5,200	2.788	--	Lasier et al. (2000)
Daphnia magna (water flea)	45.3	9,800	4,100	2.390	4.689	Biesinger and Christensen (1972)
Pimephales promelas (fathead minnow)	"HARD"	33,603	1,770	18.98	18.98	Kimball (1978)
Salmo trutta (brown trout)	48	15,973	4,670	3.4203	3.42	Stubblefield and Hockett (2000)
Salvelinus fontinalis (brook trout)	31.3	5,120	2,104	2.4335	4.26	Stubblefield and Hockett (2000)
Salvelinus fontinalis (brook trout)	148.1	27,500	3,695	7.4425	--	Stubblefield and Hockett (2000)
Oncorhynchus mykiss (rainbow trout)	27.6	3,170	1,398	2.2675	2.94	Stubblefield and Hockett (2000)
Oncorhynchus mykiss (rainbow trout)	147.8	16,200	4,259	3.8037	--	Stubblefield and Hockett (2000)
Geometric mean ACR					4.78	

ACR – acute-to-chronic ratio
AWQC – ambient water quality criteria
EPA – US Environmental Protection Agency
na – not applicable

Table 4. Ranked acute manganese toxicity data with FAV and CMC Values

Rank	Mn GMAV (µg/L)[a]	Species	Mn SMAV (µg/L)[a]
22	694,000	*Crangonyx pseudogracilis* (amphipod)	694,000
21	542,969	*Colisa fasciata* (giant gourami)[b]	540,902
20	333,000	*Asellus aquaticus* (isopod)	333,000
19	211,027	*Bufo boreus* (Western toad)	210,438
18	89,261	*Lymnaea stagnalis* (pond snail)	88,769
17	81,261	*Duttaphrynus melanostictus* (Asian common toad)[b]	81,612
16	71,122	*Tubifex tubifex* (tubificid worm)	70,641
15	42,702	*Agosia chrysogaster* (longfin dace)	42,424
14	38,638	*Ptychocheilus oregonensis* (northern pikeminnow)	38,321
13	38,328	*Aeolosoma* sp. (oligochaete worm)	38,321
12	34,003	*Chironomus tentans* (midge)	33,917
11	27,989	*Lampsilis siliquoidea* (fatmucket clam)	27,917
10	25,537	*Anodonta imbecillis* (freshwater mussel)	25,485
9	20,032	*Megalonaias nervosa* (washboard clam)	19,979
8	16,490	*Salmo trutta* (brown trout)	16,474
7	> 10,889	*Ceriodaphnia dubia* (water flea)	> 10,859
6	9,572	*Daphnia magna* (water flea)	9,547

Rank	Mn GMAV (µg/L)[a]	Species	Mn SMAV (µg/L)[a]
5	> 8,274	*Pimephales promelas* (fathead minnow)	> 8,255
4	6,917	*Salvelinus fontinalis* (brook trout)	6,911
3	6,658	*Microhyla ornata* (frog)[b]	6,628
2	6,416	*Hyalella azteca* (scud)	6,402
1	5,813	*Oncorhynchus kisutch* (coho salmon)	5,468
--	--	*Oncorhynchus mykiss* (rainbow trout)	6,156
FAV			**5,940**
CMC			**2,970**

[a] Acute toxicity values were normalized (within species) to a standard hardness (50 mg/L as calcium carbonate) prior to averaging following EPA methods (Stephan et al. 1985).

[b] Species not found in North America.

CMC – criterion maximum concentration
EPA – US Environmental Protection Agency
FAV – final acute value
GMAV – genus mean acute value
SMAV – species mean acute value

Hardness-toxicity relationships

Method

The relationship between hardness and manganese toxicity values was determined following EPA methods for AWQC development (Stephan et al. 1985). The general approach to derive hardness-dependent criteria entails the use of an analysis of covariance to derive a log-linear slope that quantitatively relates standard toxicity values (e.g., LC50s) to water hardness (see Table 1 for available data). To evaluate whether there is a significant statistical relationship between hardness and toxicity, there must be definitive toxicity values (i.e., undefined "less than" or "greater than" toxicity values may not be used) from toxicity studies that expose organisms over a range of water hardness values; the highest hardness must be at least three times greater than the lowest, and the highest hardness must also be at least 100 mg/L (as calcium carbonate) greater than the lowest.

The pooled slope of the relationship between hardness-normalized acute toxicity data[2] and logarithmically transformed hardness was calculated as 0.7424. Data were too limited to develop a separate hardness slope for chronic toxicity, so the acute hardness slope of 0.7424 was assumed. This is consistent with EPA guidance (Stephan et al. 1985).

The following sections describe the acute and chronic hardness-dependent criteria determined by Windward.

Acute criterion

The acute manganese toxicity values were normalized to a common hardness of 50 mg/L (as calcium carbonate) using the pooled slope of 0.7424, and the GMAVs were calculated based on

[2] Standard toxicity values (e.g., LC50s) were normalized within species and then pooled across species when developing the hardness-toxicity relationship slope. Species slopes were not statistically different.

the hardness-normalized values (Table 1). The GMAVs were then ranked from high to low, and a FAV of 5,940 µg/L was calculated based on the four lowest GMAVs (Table 4). The FAV was then divided by two in order to derive a CMC (acute criterion) of 2,970 µg/L. This CMC is based on a hardness of 50 mg/L, but the following equation can be used to derive the CMC at the hardness of interest:

$$\textbf{Acute criterion} = e^{(0.7467[\ln(\text{hardness})] + 5.092)}$$

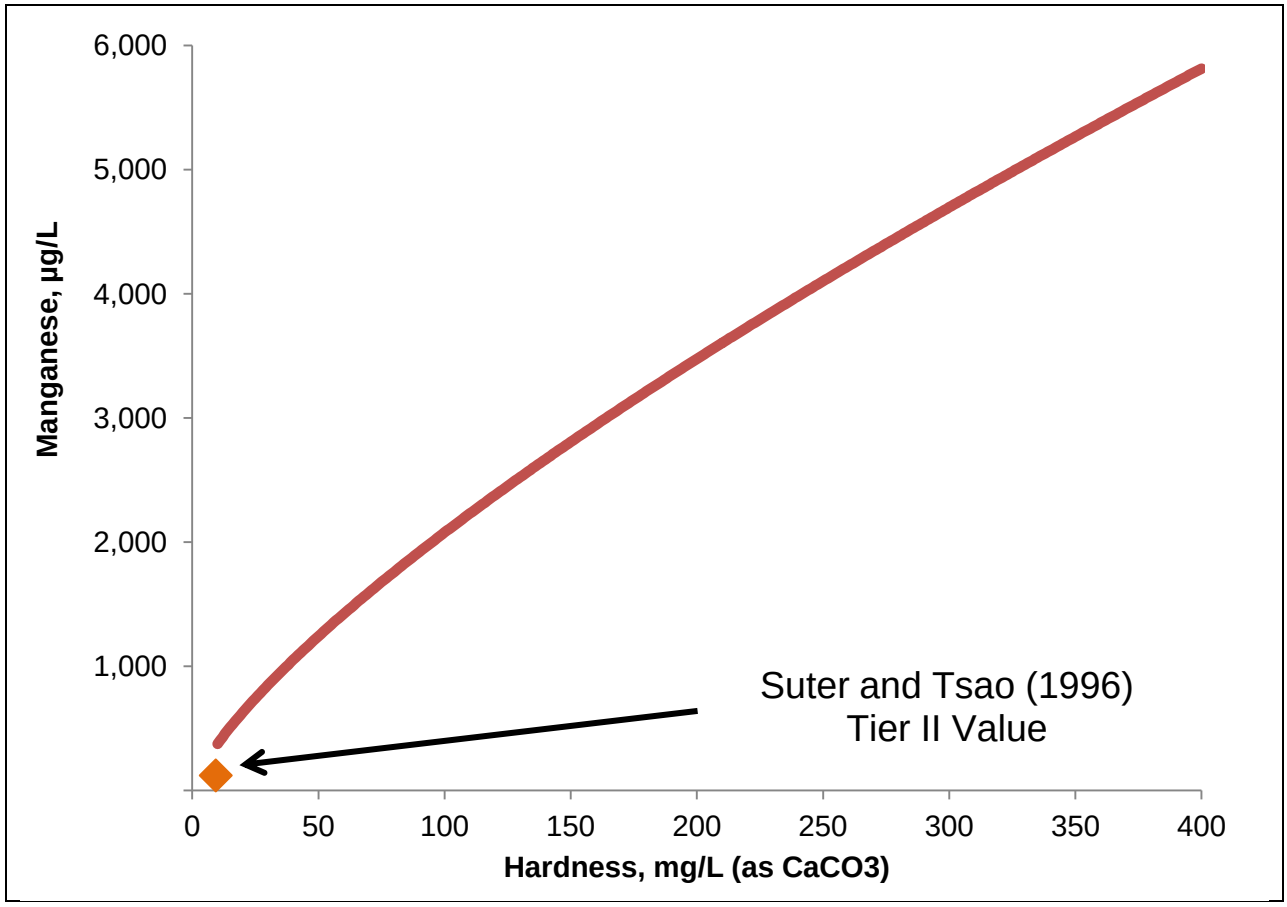
Chronic criterion

In order to derive a FCV (chronic criterion), the FAV of 5,940 µg/L at a hardness of 50 mg/L (as calcium carbonate) was divided by the final ACR of 4.78 (Table 3). The resulting FCV was 1,241 µg/L (based on a hardness of 50 mg/L). The following equation can be used to derive the FCV at the hardness of interest:

$$\textbf{Chronic criterion} = e^{(0.7424[\ln(\text{hardness})] + 4.220)}$$

The recommended chronic criterion is plotted as a function of hardness in Figure 2.

Because the chronic manganese criteria discussed in this evaluation were derived using acute hardness slopes and ACRs, the empirical chronic value (e.g., 20th percentile effective concentration [EC20], etc.) were compared to the corresponding hardness-based chronic criteria at the reported test hardness in order to ensure that the chronic criteria are appropriately protective. The ratio of each individual chronic value to its corresponding hardness-based criterion was calculated, and a ratio of < 1 indicated that the criterion would not have been protective of that particular chronic toxicity value. In some instances, use of the Windward chronic criterion was found to produce potentially under-protective individual toxicity values for rainbow trout (*Oncorhynchus mykiss*) (1 of 4 test results [25%]), *Ceriodaphnia dubia* (2 of 43 test results [5%]), and fathead minnow (*Pimephales promelas*) (5 of 36 test results [15%]); otherwise, use of the Windward chronic criterion produced toxicity values sufficiently protective of these species on average across all tests (Table 5). The chronic criterion would not produce the available chronic toxicity value protective of *H. azteca*, which was the lowest toxicity value identified. However, as discussed in the following section, there is considerable uncertainty in the chronic manganese value for *H. azteca*, and that value was excluded from this evaluation (i.e., consistent with EPA guidance it was not deemed necessary to lower the recommended chronic manganese criterion in order to ensure protection of this species).



Note: Orange diamond represents current Tier II manganese value (Suter and Tsao 1996) applied in the BERA. The Tier II hardness value of approximately 9.3 mg/L (as calcium carbonate) was calculated by setting the Windward criterion equal to the Tier II value of 120 µg manganese/L and solving for the hardness. This hardness value is less than the minimum observed hardness in Portland Harbor TZW samples (11.5 mg/L as calcium carbonate).

Figure 2. Recommended hardness-based chronic manganese criterion

Table 5. Ratio of hardness-based manganese criteria to empirical chronic toxicity data

Species	Organism Lifestage	Exposure Type	Chemical Analysis	Duration (days)	Endpoint	Effect	Hardness (mg/L CaCO3)	Mn (ug/L)	Reference	Windward Criterion	New Mexico/ Colorado Criterion	Chronic Value-to-Windward Criterion Ratio	Chronic Value-to-New Mexico/ Colorado Criterion Ratio
Aeolosoma sp. (oligochaete worm)	<24 h	R	M	14	EC20	population growth	48	3,630	Parametrix (2009f)	1,205	1,292	3.0	2.8
Carassius auratus (goldfish)	eggs	R	M	7	LC50	mortality	195	8,220	Birge (1978)	3,411	2,061	2.4	4.0
Ceriodaphnia dubia (water flea)	neonates	NR	NR	7	EC20	growth	26	3,314	ENSR (1992) cited in Stubblefield and Hockett (2000)	764	1,053	4.3	3.1
Ceriodaphnia dubia (water flea)	neonates	NR	NR	7	EC20	growth	50	4,885	ENSR (1992) cited in Stubblefield and Hockett (2000)	1,242	1,309	3.9	3.7
Ceriodaphnia dubia (water flea)	neonates	NR	NR	7	EC20	growth	100	6,052	ENSR (1992) cited in Stubblefield and Hockett (2000)	2,077	1,650	2.9	3.7
Ceriodaphnia dubia (water flea)	neonates	NR	NR	7	EC20	growth	200	7,809	ENSR (1992) cited in Stubblefield and Hockett (2000)	3,475	2,078	2.2	3.8
Ceriodaphnia dubia (water flea)	neonates	NR	NR	7	EC20	growth	46	3,317	ENSR (1989) cited in Stubblefield and Hockett (2000)	1,167	1,274	2.8	2.6
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	60	1,415.6	Parametrix (2010a)	1,422	1,391	**< 1.0**	1.0
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	24	2,571.0	Parametrix (2010a)	720	1,025	3.6	2.5
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	304	9,255.0	Parametrix (2010a)	4,743	2,389	2.0	3.9
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	84	3,221.0	Parametrix (2010a)	1,825	1,557	1.8	2.1
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	12	1,415.0	Parametrix (2010a)	430	814	3.3	1.7
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	20	2,803.0	Parametrix (2010a)	629	965	4.5	2.9
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	48	2,011	Parametrix (2010b)	1,205	1,292	1.7	1.6
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	5,203	Parametrix (2010b)	1,278	1,327	4.1	3.9
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	48	4,751	Parametrix (2010b)	1,205	1,292	3.9	3.7
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	200	6,499	Parametrix (2010b)	3,475	2,078	1.9	3.1
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	44	4,510	Parametrix (2010b)	1,129	1,255	4.0	3.6
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	3,382	Parametrix (2010b)	1,278	1,327	2.6	2.5
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	72	4,460	Parametrix (2010b)	1,628	1,479	2.7	3.0
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	124	7,439	Parametrix (2010b)	2,437	1,772	3.1	4.2
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	230	9,241	Parametrix (2010b)	3,855	2,177	2.4	4.2
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	290	16,423	Parametrix (2010b)	4,579	2,352	3.6	7.0
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	400	5,986	Parametrix (2010b)	5,814	2,618	1.0	2.3
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	390	11,147	Parametrix (2010b)	5,706	2,596	2.0	4.3
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	720	4,041	Parametrix (2010b)	8,995	3,184	**0.4**	1.3
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	4,238	Parametrix (2010b)	1,278	1,327	3.3	3.2
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	44	2,712	Parametrix (2010b)	1,129	1,255	2.4	2.2
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	4,474	Parametrix (2010b)	1,278	1,327	3.5	3.4
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	76	5,182	Parametrix (2010b)	1,694	1,505	3.1	3.4
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	116	6,429	Parametrix (2010b)	2,319	1,733	2.8	3.7
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	212	9,942	Parametrix (2010b)	3,629	2,119	2.7	4.7
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	284	9,676	Parametrix (2010b)	4,509	2,335	2.1	4.1
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	384	9,555	Parametrix (2010b)	5,641	2,582	1.7	3.7
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	410	12,919	Parametrix (2010b)	5,922	2,639	2.2	4.9
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	4,572	Parametrix (2010b)	1,278	1,327	3.6	3.4
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	3,489	Parametrix (2010b)	1,278	1,327	2.7	2.6
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	5,778	Parametrix (2010b)	1,278	1,327	4.5	4.4

Species	Organism Lifestage	Exposure Type	Chemical Analysis	Duration (days)	Endpoint	Effect	Hardness (mg/L CaCO3)	Mn (ug/L)	Reference	Windward Criterion	New Mexico/ Colorado Criterion	Chronic Value-to-Windward Criterion Ratio	Chronic Value-to-New Mexico/ Colorado Criterion Ratio
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	8,002	Parametrix (2010b)	1,278	1,327	6.3	6.0
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	48	7,260	Parametrix (2010b)	1,205	1,292	6.0	5.6
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	4,111	Parametrix (2010b)	1,278	1,327	3.2	3.1
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	2,331	Parametrix (2010b)	1,278	1,327	1.8	1.8
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	48	3,319	Parametrix (2010b)	1,205	1,292	2.8	2.6
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC20	reproduction	52	1,638	Parametrix (2010b)	1,278	1,327	1.3	1.2
Ceriodaphnia dubia (water flea)	neonates	R	M	7	EC25	reproduction	92	5,200	Lasier et al. (2000)	1,953	1,604	2.7	3.2
Chironomus tentans (midge)	larvae	F	M	54	EC20	mortality	89	17,830	Parametrix (2009g)	1,905	1,587	9.4	11.2
Danio rerio (zebrafish)	eggs	F	M	35	EC20	mortality	95	5,121	Parametrix (2009d)	2,000	1,622	2.6	3.2
Daphnia magna (water flea)	NR	R	M	21	EC16	reproduction	45.3	4,100	Biesinger and Christensen (1972)	1,154	1,267	3.6	3.2
Daphnia magna (water flea)	neonates	S	M	21	IC25	reproduction	100	5,400	Reimer (1999)	2,077	1,650	2.6	3.3
Daphnia magna (water flea)	neonates	S	M	21	IC25	reproduction	269	9,400	Reimer (1999)	4,331	2,294	2.2	4.1
Hyalella azteca (amphipod)	7-9 day juveniles	F	M	35	EC20	growth	104	513	Parametrix (2009b)			**0.2**	**0.3**
Lymnaea stagnalis (pond snail)	<24 h	R	M	30	EC20	growth	174	9,040	Parametrix (2009c)	3,134	1,984	2.9	4.6
Oncorhynchus mykiss (rainbow trout)	embryos	F	M	121.76	MATC	mortality	36.8	1,570	Davies and Brinkman (1994)	989	1,182	1.6	1.3
Oncorhynchus mykiss (rainbow trout)	embryos	F	M	121.76	MATC	mortality	36.8	790	Davies and Brinkman (1994)	989	1,182	**0.8**	**0.7**
Oncorhynchus mykiss (rainbow trout)	embryos	NR	NR	NR	EC20	growth	29	1,398	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)	829	1,092	1.7	1.3
Oncorhynchus mykiss (rainbow trout)	embryos	NR	NR	NR	EC20	growth	151	4,259	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)	2,821	1,892	1.5	2.3
Pimephales promelas (fathead minnow)	embryos	NR	NR	NR	EC20	growth	30	2,550	ENSR (1996) cited in Stubblefield and Hockett (2000)	850	1,105	3.0	2.3
Pimephales promelas (fathead minnow)	larvae	NR	NR	NR	EC20	growth	26	1,338	ENSR (1992) cited in Stubblefield and Hockett (2000)	764	1,053	1.8	1.3
Pimephales promelas (fathead minnow)	larvae	NR	NR	NR	EC20	growth	50	5,490	ENSR (1992) cited in Stubblefield and Hockett (2000)	1,242	1,309	4.4	4.2
Pimephales promelas (fathead minnow)	larvae	NR	NR	NR	EC20	growth	100	5,120	ENSR (1992) cited in Stubblefield and Hockett (2000)	2,077	1,650	2.5	3.1
Pimephales promelas (fathead minnow)	larvae	NR	NR	NR	EC20	growth	200	13,152	ENSR (1992) cited in Stubblefield and Hockett (2000)	3,475	2,078	3.8	6.3
Pimephales promelas (fathead minnow)	larvae	NR	NR	NR	EC20	growth	46	3,417	ENSR (1989) cited in Stubblefield and Hockett (2000)	1,167	1,274	2.9	2.7
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	3,117	Parametrix (2010c)	892	1,129	3.5	2.8
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	104	8,010	Parametrix (2010c)	2,139	1,671	3.7	4.8
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	3,145	Parametrix (2010c)	892	1,129	3.5	2.8
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	60	6,222	Parametrix (2010c)	1,422	1,391	4.4	4.5
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	100	9,525	Parametrix (2010c)	2,077	1,650	4.6	5.8
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	192	8,828	Parametrix (2010c)	3,372	2,050	2.6	4.3
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	244	7,861	Parametrix (2010c)	4,028	2,220	2.0	3.5
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	292	7,742	Parametrix (2010c)	4,603	2,357	1.7	3.3
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	400	6,991	Parametrix (2010c)	5,814	2,618	1.2	2.7
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	372	1,928	Parametrix (2010c)	5,509	2,555	**0.3**	**0.8**
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	672	8,287	Parametrix (2010c)	8,546	3,112	**< 1.0**	2.7
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	204	1,573	Parametrix (2010c)	3,527	2,092	**0.4**	**0.8**
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	396	1,776	Parametrix (2010c)	5,771	2,609	**0.3**	**0.7**
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	2,137	Parametrix (2010c)	892	1,129	2.4	1.9
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	52	1,333	Parametrix (2010c)	1,278	1,327	1.0	1.0

Species	Organism Lifestage	Exposure Type	Chemical Analysis	Duration (days)	Endpoint	Effect	Hardness (mg/L CaCO3)	Mn (ug/L)	Reference	Windward Criterion	New Mexico/ Colorado Criterion	Chronic Value-to-Windward Criterion Ratio	Chronic Value-to-New Mexico/ Colorado Criterion Ratio
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	1,186	Parametrix (2010c)	892	1,129	1.3	1.1
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	36	2,147	Parametrix (2010c)	973	1,174	2.2	1.8
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	52	2,388	Parametrix (2010c)	1,278	1,327	1.9	1.8
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	430	Parametrix (2010c)	892	1,129	**0.5**	**0.4**
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	92	8,587	Parametrix (2010c)	1,953	1,604	4.4	5.4
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	200	12,860	Parametrix (2010c)	3,475	2,078	3.7	6.2
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	2,648	Parametrix (2010c)	892	1,129	3.0	2.3
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	32	2,463	Parametrix (2010c)	892	1,129	2.8	2.2
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	100	5,099	Parametrix (2010c)	2,077	1,650	2.5	3.1
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	100	8,501	Parametrix (2010c)	2,077	1,650	4.1	5.2
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	60	2,985.0	Parametrix (2010d)	1,422	1,391	2.1	2.1
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	24	2,068.0	Parametrix (2010d)	720	1,025	2.9	2.0
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	312	27,604.0	Parametrix (2010d)	4,835	2,410	5.7	11.5
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	88	7,054.0	Parametrix (2010d)	1,889	1,581	3.7	4.5
Pimephales promelas (fathead minnow)	larvae	R	M	7	EC20	growth	12	1,078.0	Parametrix (2010d)	430	814	2.5	1.3
Salmo trutta (brown trout)	juveniles	F	M	121.76	MATC	mortality	37.5	2,700	Davies and Brinkman (1994)	1,003	1,190	2.7	2.3
Salmo trutta (brown trout)	juveniles	F	M	121.76	MATC	mortality	37.5	4,190	Davies and Brinkman (1994)	1,003	1,190	4.2	3.5
Salmo trutta (brown trout)	eyed eggs	F	M	62	IC25	survival and weight	30.9	4,670	Stubblefield et al. (1997)	869	1,116	5.4	4.2
Salmo trutta (brown trout)	eyed eggs	F	M	62	IC25	survival and weight	151.8	5,590	Stubblefield et al. (1997)	2,832	1,896	2.0	2.9
Salvelinus fontinalis (brook trout)	embryos	NR	NR	NR	EC20	growth	32	2,104	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)	892	1,129	2.4	1.9
Salvelinus fontinalis (brook trout)	embryos	NR	NR	NR	EC20	growth	156	3,695	Davies and Brinkman (1998) cited in Stubblefield and Hockett (2000)	2,890	1,913	1.3	1.9

Note: Chronic value-to-criterion ratios equal the manganese concentration (for the given endpoint) divided by the hardness-based criterion (at the test hardness). **Bold** ratios indicate an instance where the criterion would be under-protective (i.e., ratio < 1.0).

EC – effective concentration
F – flow through exposure
IC – inhibitory concentration
LC – lethal concentration
M – measured concentration
MATC – maximum acceptable toxicant concentration
nr – not reported
R – renewal exposure
S – static exposure
U – unmeasured concentration

SENSITIVITY OF *HYALELLA AZTECA* TO MANGANESE: VARIABILITY AND UNCERTAINTY

As noted above, the amphipod *Hyalella azteca* is the species most sensitive to manganese in chronic exposures, based on a 42-day life cycle test (Parametrix 2009b). However, there are several uncertainties relating to the toxicity value(s) that can be derived from this test, in large part related to issues associated with the toxicity test method, specifically the standard test diet. Due to these uncertainties, chronic manganese data for *H. azteca* were excluded from manganese "criteria" development in this evaluation. The following documents chronic data available for *H. azteca* and the associated uncertainties.

In the 42-day life cycle test using *H. azteca*, test organisms are exposed to the test solution in chambers containing sediment for 28 days, at which point live and dead organisms are recovered. Amphipods from a subset of replicates are measured for growth. Live organisms among the remaining replicates are then placed back in the chambers for the remaining 14 days of exposure (with sediment excluded), which represents the reproductive phase of the test. Overall, the endpoints measured are 1) survival and growth after 28 days; 2) survival and reproduction after 35 days; and 3) survival, growth, and reproduction after 42 days. The test is considered acceptable if control survival is ≥ 80% after 28 days. Although not specifically a test acceptability requirement, the test method also notes that reproduction from days 28 to 42 generally results in more than two young per female (EPA 2000). In the Parametrix (2009b) test, control survival was 91% after 28 days and decreased to 81 and 51% after 35 and 42 days, respectively. Control reproduction after 42 days was 1.55 young per female. Therefore, the test met acceptability requirements based on control survival after 28 days, but survival had decreased substantially (to 51%) by day 42 of the test. Control reproduction was less than the typically desired level.

Various manganese effects concentrations for *H. azteca* can be derived from Parametrix (2009b) based on the different endpoints and time points. As available, EC20s were the preferred statistic for the purpose of this evaluation. The EC20s for survival after 28, 35, and 42 days were 753, 513, and 256 µg/L, respectively. Because control survival decreased substantially from 81% at day 35 to 51% at day 42, the EC20 of 513 µg/L on day 35 was considered the most reliable for the survival endpoint. Growth, in terms of both biomass (dry weight per original organism) and dry weight (per surviving organism), was considered a less sensitive endpoint than survival, with 28-day EC20s of 1,610 and 1,949 µg/L, respectively (EC20s could not be determined based on day 42 data due to lack of a concentration-response relationship). Parametrix (2009b) noted that one replicate in the 1,403 µg Mn/L treatment had high dry weights (i.e., greater than the majority of control replicates). When this replicate was excluded, the biomass and dry weight EC20s decreased to 1,249 and 203 µg/L, respectively. The latter is less than the survival EC20 of 513 µg/L based on day 35, and also less than the day 42 growth (dry weight) no-observed-effects concentration (NOEC) of > 285.9 µg/L. Accordingly, the dry weight EC20 with the one replicate removed was not considered a reliable toxicity threshold for growth effects. Finally, no significant effects ($p > 0.05$) on reproduction were observed at day 42, and an EC20 could not be determined (and, as discussed above, control reproduction was less than the typically desired level). Overall, the most reliable manganese EC20 from this test was determined to be the day 35 EC20 of 513 µg/L for survival.

For comparison to the Parametrix (2009b) *H. azteca* test, Norwood et al. (2007) tested the effects of manganese on *H. azteca* survival and growth following 28-day exposures in two different test containers (glass and high-density polyethylene [HDPE]). They reported manganese LC25s (25% lethal concentrations) of 532 and 8,076 µg/L for amphipods exposed to manganese in glass and HDPE containers, respectively, and IC25s (25% inhibition concentrations) of 116 and 7,032 µg/L for growth of amphipods exposed in glass and HDPE containers, respectively. The LC25 for amphipods in glass containers was comparable to the EC20 for survival in the Parametrix (2009b) test, while the IC25 for growth was less than that observed in the Parametrix (2009b) test. However, the much greater LC25 and IC25 in the HDPE container compared to the glass container are puzzling, as manganese concentrations in the test waters were analytically verified (i.e., the difference does not appear to be an artifact of manganese binding to the walls of one container type much more than the other). Furthermore, manganese concentrations were measured in the amphipods following the 28-day exposure, and concentrations appeared to be comparable in both exposure systems (again suggesting that the manganese exposures were comparable between the two types of containers). This suggests that the differences in the toxicity values between the two container types may be due to a factor other than manganese. However, this is uncertain; Norwood et al. (2007), likewise, did not have an explanation.

The chronic studies conducted by Parametrix (2009b) and Norwood et al. (2007) each contained uncertainties. The former included poor 42-day survival and low reproduction, while the latter resulted in large differences in effects between exposure container types. In addition to these uncertainties, there has recently been much discussion on the importance of diet in *H. azteca* tests, further raising questions as to the organism's chronic sensitivity to manganese. The EPA laboratory in Duluth, Minnesota, has recently been conducting research relative to diet in the 42-day *H. azteca* toxicity test. Hockett et al. (2011) conducted several 42-day tests using various diets, including diatoms, wheatgrass, TetraMin, YCT (Yeast, Cerophyl®, and Trout Chow), and several of these foods in combination. They found that the standard fixed ration of 1 ml YCT/chamber-day (the diet used by Parametrix (2009b)) limited amphipod growth and reproduction in the latter portions of the 42-day exposure, and they observed greater growth and reproduction with a variety of alternate foods or feeding schedules. For example they observed the reproduction of more than 10 young per female, while Parametrix (2009b) observed only 1.55 young per female in the controls fed the 1 mL YCT diet. As an result of these same studies, David Mount (EPA-Duluth) recommended that the Great Lakes National Program Office consider the diet and water used in testing with *H. azteca* adequate if 42-day survival is ≥ 80%, weights are > 0.3 mg dry weight (dw)/individual at 28 days and > 0.5 mg dw/individual at 42 days, and mean reproduction is more than 4 young per female (Mount 2011). None of these parameters were achieved in the Parametrix (2009b) study based on the standard 1 mL YCT diet.

For all of the above reasons, chronic manganese toxicity data for *H. azteca* were excluded from the derivation of a chronic manganese "criterion."

RECOMMENDATION

Several studies have shown a relationship between manganese toxicity and water hardness (Stubblefield et al. 1997; Reimer 1999; Peters et al. 2011). We recommend that the hardness-based criterion we have derived be used to replace the Tier II value of 120 µg/L derived by

Suter and Tsao (1996). The manganese chronic criterion developed in this memorandum and recommended for the ecological PRG is calculated according to EPA's methods (Stephan et al. 1985) and is based on a larger and more up-to-date toxicity database that existing hardness-based criteria. Therefore, as per the direction received from EPA at the May 8, 2014 LWG-EPA FS meeting, Windward recommends that the chronic, hardness-based criterion developed herein replace the Tier II value as the ecological PRG for use in the Portland Harbor FS.

REFERENCES

Agrawal SJ, Srivastava AK. 1980. Haematological responses in a fresh water fish to experimental manganese poisoning. Toxicol 17(1):97-100.

Beleau MH, Bartosz JA. 1982. Acute toxicity of selected chemicals: data base. Colorado River Fishery Project final report contracted studies, Report No. 6. US Fish and Wildlife Service, Salt Lake City, UT.

Biesinger KE, Christensen GM. 1972. Effects of various metals on survival, growth, reproduction, and metabolism of *Daphnia magna*. J Fish Res Bd Can 29:1691-1700.

Birge WJ. 1978. Aquatic toxicology of trace elements of coal and fly ash. In: Thorp JH, Gibbons JW, eds, Energy and environmental stress in aquatic systems: papers from symposium, Augusta, Georgia, November 1977. Technical Information Center, US Department of Energy, Washington, DC, pp 219-240.

Cabejszek I, Stasiak M. 1960. Investigation on the influence of some metals on the biocoenosis of water with the use of daphnia magna as an indicator (Part I). Roczyn Zabl Hig Warsaw 11:303-312.

CDPHE. 2012. The basic standards and methodologies for surface water (5 CCR 1002-31). Regulation No. 31. Colorado Department of Public Health and Environment, Denver, CO.

Davies PH. 1980. Water pollution studies. Investigations on the toxicity of metals to fish. Job progress report No. F-33-R-15. Federal Aid in Fish and Wildlife Restoration, Colorado Division of Wildlife, Fort Collins, CO.

Davies PH, Brinkman SF. 1994. Acute and chronic toxicity of manganese to exposed and unexposed rainbow and brown trout. Job progress report No. F-243R-1. Federal Aid in Fish and Wildlife Restoration, Colorado Division of Wildlife, Fort Collins, CO.

ECOTOX. 2013. ECOTOXicology database [online database]. US Environmental Protection Agency, Available from: http://cfpub.epa.gov/ecotox/ecotox_home.cfm.

EPA. 1985. Ambient aquatic life water quality criteria for cadmium-1984. EPA440/5-84-032. US Environmental Protection Agency, Washington, DC.

EPA. 1993. Water quality guidance for the Great Lakes system and correction; proposed rules. 40 CFR Parts 122 et al. Federal Register volume 58 (72) 20802-21047. US Environmental Protection Agency, Washington, DC.

EPA. 2000. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates. Second Edition. EPA/600/R-99/064. US Environmental Protection Agency, Washington, DC.

EPA. 2002. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to marine and estuarine organisms. Third edition. EPA/821-R-02-014. Office of Water, US Environmental Protection Agency, Washington, DC.

EPA. 2010. Final report on acute and chronic toxicity of nitrate, nitrite, boron, manganese, fluoride, chloride and sulfate to several aquatic animal species. EPA 905-R-10-002. US Environmental Protection Agency, Chicago, IL.

Hockett JR, Mount DR. 1996. Use of metal chelating agents to differentiate among sources of acute aquatic toxicity. Environ Toxicol Chem 15(10):1687-1693.

Hockett JR, Highland TL, Hoff DJ, Mount DR, Norberg-King TJ, Valenti T. 2011. Modifying foodsand feeding regimes to optimize the performance of *Hyalella azteca* during chronic toxicity tests. Society of Environmental Toxicology and Chemistry North America 32nd Annual Meeting, Boston, MA, November 13-17, 2011. SETAC.

Kimball GL. 1978. The effects of lesser known metals and one organic to fathead minnows (*Pimephales promelas*) and *Daphnia magna*. Department of Entomology, Fish and Wildlife, University of Minnesota, Minneapolis, MN.

Lasier PJ, Winger PV, Bogenrieder KJ. 2000. Toxicity of manganese to *Ceriodaphnia dubia* and *Hyalella azteca*. Arch Environ Contam Toxicol 38:298-304.

Lewis M. 1978. Acute toxicity of copper, zinc and manganese in single and mixed salt solutions to juvenile longfin dace, Agosia chrysogaster. Fish Biol 13(6):695-700.

Martin TR, Holdich DM. 1986. The acute lethal toxicity of heavy metals to peracarid crustaceans (with particular reference to fresh-water asellids and gammarids). Wat Res Bull 20(9):1137-1147.

Mount D. 2011. Personal communication (memorandum from D. Mount, EPA, to Great Lakes National Program Office regarding the demonstration of food/water suitability for *Hyaella azteca)*. US Environmental Protection Agency, Duluth, MN. November 2011.

Naddy RB, Rehner AB, McNerney GR, Gorsuch JW, Kramer JR, Wood CM, Paquin PR, Stubblefield WA. 2007. Comparison of short-term chronic and chronic silver toxicity to fathead minnows in unamended and sodum chloride-amended waters. Environ Toxicol Chem 26(9):1922-1930.

NMED. 2011. State of New Mexico standards for interstate and intrastate surface waters. 20.6.4 NMAC. New Mexico Environmental Department, Santa Fe, NM.

Norberg TJ, Mount DI. 1985. A new fathead minnow (*Pimephales promelas*) subchronic toxicity test. Environ Toxicol Chem 4:711-718.

Norwood WP, Borgmann U, Dixon DG. 2007. Chronic toxicity of arsenic, cobalt, chromium and manganese to *Hyalella azteca* in relation to exposure and bioaccumulation. Environ Pollut 147:262-272.

Parametrix. 2009a. Acute toxicity of manganese to the great pond snail, *Lymnaea stagnalis*. Parametrix, Albany, OR.

Parametrix. 2009b. Chronic toxicity of manganese to the amphipod, *Hyalella azteca,* under flow-through conditions. Parametrix, Albany, OR.

Parametrix. 2009c. Chronic toxicity of manganese to the great pond snail, *Lymnaea stagnalis*. Parametrix, Albany, OR.

Parametrix. 2009d. Early life-stage toxicity of manganese to the zebrafish (*Danio rerio*) under flow-through conditions. Parametrix, Albany, OR.

Parametrix. 2009e. Evaluation of acute manganese toxicity to the aquatic oligochaete, *Aeolosoma* sp. Parametrix Environmental Research Lab, Albany, OR.

Parametrix. 2009f. Evaluation of chronic toxicity of manganese to the aquatic oligochaete, *Aeolosoma sp*. Parametrix, Albany, OR.

Parametrix. 2009g. Life-cycle toxicity of manganese to the midge, *Chironomus tentans*. Parametrix, Albany, OR.

Parametrix. 2010a. Chronic toxicity of manganese to the cladoceran, *Ceriodaphnia dubia*, in natural waters. Parametrix, Corvallis, OR.

Parametrix. 2010b. Chronic toxicity of manganese to the cladoceran, *Ceriodaphnia dubia*: framework for the development of a biotic ligand model (BLM). Parametrix, Corvallis, OR.

Parametrix. 2010c. Chronic toxicity of manganese to the fathead minnow (*Pimephales promelas*): framework for the development of a biotic ligand model (BLM). Parametrix, Corvallis, OR.

Parametrix. 2010d. Chronic toxicity of manganese to the fathead minnow, *Pimephales promelas*, in natural waters. Parametrix, Corvallis, OR.

Peters A, Lofts S, Merrington G, Brown B, Stubblefield W, Harlow K. 2011. Development of biotic ligand models for chronic manganese toxicity to fish, invertebrates, and algae. Environ Toxicol Chem 30(11):2407-2415.

Rao IJ, Madhyastha MN. 1987. Toxicities of some heavy metals to the tadpoles of frog, *Microhyla ornata* (dumeril & bibron). Toxicol Let 36(2):205-208.

Rathore RS, Khangarot BS. 2002. Effects of temperature on the sensitivity of sludge worm *Tubifex tubifex Müller* to selected heavy metals. Ecotox Environ Saf 53(1):27-36.

Reimer PS. 1999. Environmental effects of manganese and proposed guidelines to protect freshwater life in British Columbia. Master of Science in the Faculty of Graduate studies. Chemical & Bio-Resource Engineering, University of British Columbia, Vancouver, BC. 123 pp.

Shuhaimi-Othman M, Nadzifah Y, Umirah NS, Ahman AK. 2012. Toxicity of metals to tadpoles of the common Sunda toad, *Duttaphrynus melanostictus*. Toxicol Environ Chem 94(2):364-376.

Stephan CE, Mount DI, Hansen DJ, Gentile JH, Chapman GA, Brungs WA. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. PB85-227049. Office of Research and Development, US Environmental Protection Agency, Washington, DC.

Stubblefield WA, Hockett JR. 2000. Derivation of a Colorado State manganese table value standard for the protection of aquatic life. ENSR Corporation, Fort Collins, CO.

Stubblefield WA, Brinkman SF, Davies PH, Garrison TD, Hockett JR, McIntyre MW. 1997. Effects of water hardness on the toxicity of manganese to developing brown trout (*Salmo trutta*). Environ Toxicol Chem 16(10):2082-2089.

Suter GW, Tsao CL. 1996. Toxicological benchmarks for screening potential contaminants of concern for effects on aquatic biota: 1996 revision. Prepared for U.S. Department of Energy Office of Environmental Management. Risk Assessment Program, Health Sciences Research Division.