CONSOL Energy Inc.
CNX Center
1000 CONSOL Energy Drive
Canonsburg, PA 15317-6506

phone: 724/485-3037
fax: 724/485-4932
e-mail: stevenbuffone@consolenergy.com
web: www.consolenergy.com

STEVEN A. BUFFONE, CHMM, QEP, GIT
COMPLIANCE & REGULATORY AFFAIRS

26 February 2018

Department of Environmental Protection,
Policy Office,
400 Market Street, P.O. Box 2063,
Harrisburg, PA 17105-2063

RE: *Comments on the Advance Notice of Proposed Rulemaking for Water Quality Standard for Manganese*

Dear Sir or Madam:

CONSOL Energy Inc. (CONSOL) appreciates the opportunity to submit comments on the Pennsylvania Department of Environmental Protection's (PADEP) Advance Notice of Proposed Rulemaking (ANPR) for the manganese water quality standard. CONSOL is a Canonsburg, PA based producer of high BTU bituminous thermal and crossover metallurgical coal. Our Pennsylvania Mining Complex, located in the southwestern part of the state, is home to some of the most productive underground longwall coal mining operations in the nation. In support of active and legacy mining operations throughout western Pennsylvania, PADEP has issued more than 30 National Pollutant Discharge Elimination System (NPDES) permits to CONSOL and its subsidiaries. Currently, these permits include manganese effluent limitations that were developed to be protective of the 1.0 mg/l specific water quality criteria for the Potable Water Supply (PWS) critical use (25 Pa. Code §93.7, table 3), regardless of the designated or protected use of each receiving stream prescribed by 25 Pa. Code §93.9.

On October 30, 2017, subsection (j) was added to section 1920-A of The Administrative Code of 1929 (the Code). This subsection directed the environmental quality board to, within ninety days of the effective date, *"promulgate regulations under… 'The Clean Streams Law'…that require the water quality criteria for manganese [to] be met, consistent with the exception in 25 Pa. Code §96.3(d)…."* The §96.3(d) exception clarifies that specific water quality criteria defined in §93.7 for protection of the PWS critical use, *"shall be met…at the point of all existing or planned surface potable water supply withdrawals…"* Similar to those parameters included in §93.6(d) exception, application of the manganese water quality criterion in §93.7 is also specific to the PWS critical use. Regulatory precedent supports the consistent application of the manganese water quality criterion at the point of withdrawal and therefore, inclusion of manganese in the §93.6(d) exception is appropriate.

Subsequently, on January 7, 2018, the Manganese ANPR was published in the Pennsylvania Bulletin. The ANPR clarifies that, in promulgating the rule, the Department must simultaneously consider the potential impacts to potable water suppliers, the potential detrimental effects that may occur between the point of discharge and point of intake as a result of the rule, environmental and social costs and benefits, and finally, savings to the regulated community. The ANPR further requests that stakeholders provide information and

scientific data related to these specific subjects, to assist in evaluation of the regulation under the Regulatory Review Act. In response to this request and in support of the subsection (j) addition to section 1920-A of the Code, CONSOL offers the following comments:

The change to the Code to reflect attainment of the Manganese water quality criterion at the point of intake will not result in a significant impact to the potable water suppliers, if implemented appropriately using existing regulatory mechanisms. PADEP should clarify that the change in the Code will not result in the complete elimination of manganese effluent limits in NPDES permits issued by the state. Rather, the rule should specify that the development of technology based manganese effluent limits would still apply at the point of discharge, such as in circumstances where the applicable jurisdiction of an overarching Federal Effluent Limit Guideline (ELG) applies, or where reasonable potential analysis completed as part of the permitting process indicates negative impact to a nearby potable water supply intake.

For instance, the federal ELG's for the coal mining industry 40 CFR §434 prescribe best available, technology based effluent limitations for various mine drainage categories. The federal ELG limitations of 2.0 mg/l monthly average and 4.0 mg/l daily maximum would apply. The PADEP, as the permitting authority, would maintain the right to define and reassess alternative criteria for facilities classified as post mining areas under 40 CFR §434.11(k).

In addition, reasonable potential analyses required under the federal NPDES regulations at 40 CFR §122.44 and incorporated at 25 Pa. Code § 92a.44 would continue to be completed. The existing PADEP Technical Guidance Document (TGD) for "Developing NPDES Permits for Mining Activities" (*see* PADEP document number 563-2112-115) recommends modeling using the Pentox software to evaluate the need for water quality based effluent limits. For manganese discharges, Pentox currently is programmed to compare effluent concentrations to the 1.0 mg/l criterion after immediate mixing in the receiving stream. However, for the parameters excepted by 25 Pa. Code §93.6(d), such as Phenolics, Fluoride, and Total Dissolved Solids, Pentox assumes complete mixing and uses the stream flow at the nearest downstream potable water supply intake, instead of the stream flow at the current discharge (*see* PADEP document number 391-2000-011, section 2.8). For these parameters, if the analysis indicates that the discharge is causing an exceedance above the water quality criterion at the point of intake, protective effluent limits are applied for the specific parameter. This reasonable potential analysis approach ensures that the responsibility for pollutant removal lies with the discharger, in cases where the effluent would cause an exceedance of the instream criterion. This approach shields the potable water suppliers from increased operational costs and responsibility. Conversely, if the reasonable potential analysis concludes that adequate assimilative capacity exists in the receiving stream, manganese effluent limits consistent with Federal ELGs would be assigned, if an applicable ELG exits. Because this approach has been effective for the other parameters whose water quality criteria are protective of the PWS critical use, a similar outcome is expected for manganese.

CONSOL completed an analysis using four discharge locations in Indiana and Armstrong counties, to further demonstrate the availability and positive impact of receiving stream assimilative capacity between a permitted discharge and the point of potable water supply intake. For each location, CONSOL assumed no manganese was removed during the conventional treatment process. In other words, the discharge concentration was equal to the concentration measured in the raw, untreated water. CONSOL utilized the highest observed discharge flows and manganese concentrations to calculate a theoretical, worst case scenario discharge loading. Then, CONSOL calculated the flow that would be needed to reduce the instream manganese concentration to 0.90 mg/L and 0.05 mg/L, respectively. The 0.90 mg/L concentration was

selected because it represents a concentration below the 1.0 mg/L manganese water quality criterion that is protective of the PWS critical use. The 0.05 mg/L concentration was selected because it is equivalent to the Environmental Protection Agency (EPA) secondary drinking water quality criterion for manganese. The analysis indicates that, for these 4 discharges, after mixing with upstream flows ranging from 0.321 to 17.7 cfs, the instream manganese would be below the 1.0 mg/L criterion. Furthermore, after mixing with upstream flows ranging from 5.76 to 122 cfs, the instream manganese would be below the 0.05 mg/L criterion (Table 1). For these 4 locations, the nearest Potable Water Supply intake is the Pittsburgh Water Authority, in the Allegheny River. The theoretical dilution flows needed to achieve Manganese concentrations below the 1.0 mg/L criterion can be compared to flows measured at the United States Geologic Survey (USGS) gauge in the Allegheny River at Natrona Heights, PA (Table 2). In the Allegheny River, the minimum observed flow between October of 2016 and October of 2017 was 3,630 cfs. This flow is approximately forty times greater than the maximum theoretical flow required to achieve the secondary drinking water manganese standard of 0.05 mg/L at the point of intake. Therefore, an increase in the manganese concentrations at the discharge locations will not impact the instream water quality at the point of intake, and consequently, the potable water supplier would not need to adjust treatment methodologies or incur additional expenses as a result of the proposed change to the Code.

Table 1. Demonstration of Assimilative Capacity

Discharge Location	Theoretical Manganese Concentration at Point of Intake (mg/L)	Dilution Flow Downstream of Discharge Needed to Achieve Theoretical Manganese Concentration (cfs)
1 - Indiana County	0.90	5.06
	0.05	91.0
2 - Indiana County	0.90	6.76
	0.05	122
3 - Indiana County	0.90	0.321
	0.05	5.76
4 - Armstrong County	0.90	17.7
	0.05	82.9

Table 2. Minimum Discharge from (10/19/2016 - 10/18/2017) USGS 03049500 Allegheny River at Natrona, PA

Minimum Daily Discharge	00060, Discharge (cfs)
1/1/2016	3,630

Notes: Allegheny County, Pennsylvania
Latitude 40°36'55", Longitude 79°43'07" NAD27
Drainage area 11,410 square miles, Gage datum 736.36 feet above NGVD29

The regulatory analysis required under the Regulatory Review Act, completed in support of the change to the Code, should be limited to an evaluation of the PWS critical use. The ANPR and proposed change to the Code should not be expanded to develop new Manganese criteria for aquatic life, especially in the absence of criteria recommended by the EPA or surrounding Appalachian states. First, using the proposed rule as an opportunity to develop a separate or new water quality standard that is protective of aquatic life is outside of the scope of this rule making. There is no federal aquatic life standard for manganese, largely because the EPA acknowledged that there is not adequate science to support the development of such a standard.

Rather, EPA has only promulgated a Secondary Drinking Water standard for manganese. Secondary standards are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color). In the 2003 EPA publication, "Contaminant Candidate List Regulatory Determination Support Document for Manganese"[1], the EPA concludes that "Because manganese ingestion is not known to present adverse health effects at low levels, and because drinking water contributes only a small portion of normal oral intake, it is unlikely that regulation of manganese in drinking water would represent a meaningful opportunity for health risk reduction in persons served by public water systems. All CCL regulatory determinations and further analysis are formally presented in the Federal Register Notices (USEPA, 2002; 67 FR 38222, and USEPA, 2003a; 68 FR 42898)". In addition, manganese and manganese compounds are regulated by other federal programs, including the National Pollution Discharge Elimination System, the Clean Air Act Hazardous Air Pollutants list, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and the TRI, all related to drinking water protection and not aquatic life.

Consistent with EPA's conclusion, the proposed change to the Code should be limited to the manganese water quality criterion that existed at the time that subsection (j) was added. This standard was developed to be protective of potable water supply intakes and ultimately, the federal secondary drinking water standard. Including requests in this ANPR that are unrelated to the location of compliance for the manganese water quality criterion goes beyond the scope of the Code change.

Second, Pennsylvania's development of a manganese criterion that is protective of the PWS critical use and no other stream uses or classifications is consistent with the approach utilized in neighboring Appalachian states. The fact that Virginia, West Virginia, Ohio, and Kentucky, all have regulations that address the secondary constituent manganese and potable water supply intakes in a similar manner, and which were all passed review by the Federal EPA is worth noting. A comparison of regional Appalachian State and Commonwealth standards are provided in Table 3 below. In a memo, the Virginia Department of Environmental Quality, Water Division even stated that when public drinking water plants treat natural river water; the initial step is to remove the suspended soil particles, which include the suspended manganese, so this should not be an issue for the typical drinking water plant treating surface water. This is not a health issue. Manganese is an essential nutrient and the recommended daily intake of manganese ranges from 2,000 to 10,000 micrograms per day. DEQ staff has concluded that this manganese criterion has been inappropriately applied to Virginia's natural waters and it is not needed (Davenport 2014).

Even with the change to the addition of subsection (j) to the Code, through the use of Reasonable Potential Analysis, PA would still have the ability to enforce standards as strict as, or stricter than, neighboring states. Given the discrepancy in regulation between Pennsylvania and its neighboring states, the economic impact of the current manganese regulation on industry and jobs in the Commonwealth should be considered.

1. United States Environmental Protection Agency. (2003) Contaminant Candidate List Regulatory Determination Support Document for Manganese. EPA-815-R-03-12, United States Environmental Protection Agency, Office of Water (4607M) Standards and Risk Management Division Washington, DC 20460

Table 3. Comparison of State Water Quality Standards		
State	**Secondary Drinking Water Standards (mg/L)**	**Clean Water Act Water Quality Standards Protective of Designated Uses (mg/L)**
West Virginia	0.05	*Use Designation - Human Health* 6.2.d. All other surface water intakes where the water is used for human consumption. (See Appendix B for partial listing of Category A waters; see section 7.2.a.2, herein for additional requirements for Category A waters.) The manganese human health criterion (1.0 mg/L) shall only apply within the five-mile zone immediately upstream above a known public or private water supply used for human consumption.
	West Virginia Bureau for Public Health	47CSR2
Virginia*	0.05	Not regulated
	9 VAC 25-260 Virginia Water Quality Standards	9 VAC 25-260
Ohio	0.05	Not regulated
	(OAC 3745-82)	(OAC 3745-1)

As stated above, the scope of the ANPR should be limited to the PWS intake analysis. Expanding the scope of the analysis beyond the PWS intake will delay the timeframe for implementation of the proposed rule, as mandated by Section 1920-A, Subsection (j) of The Code. However, as requested, CONSOL is providing a summary of peer reviewed, scientific studies to support the conclusion that the updated rule will not cause additional impacts to the water uses protected under Chapter 93, including human health, other water supply uses, recreational uses, or aquatic life. The following scientific evidence demonstrates that manganese toxicity is only of concern at high concentrations or in waters of very low hardness. Consistent with the ANPR request, these published aquatic life toxicity studies were selected because they are representative of Pennsylvania species and water bodies (Table 4). For tests conducted in waters of hardness in excess of 100 mg/L as CaCO3, toxic manganese concentrations ranged from 4.7 to 49.9 mg/L, depending on the endpoint and organism tested. Regardless of test circumstance, these concentrations indicate that the minimal increase in downstream manganese concentrations that may result from moving the point of compliance with the manganese water quality criterion from the discharge to the PWS intake are unlikely to impact Pennsylvania's aquatic life.

Table 4. Summary of Manganese Ecotoxicity Data				
Reference	**Organism**	**Endpoint**	**Hardness (mg/L as CaCO3)**	**Manganese Concentration (mg/L)**
Khangarot (1991)	Sludge worm (*Tubifex)*	48-h LC50	230-250	208.1
		96-h LC50	230-250	170.6
Blesinger & Christensen (1972)	Daphnid (*Daphnia magna)*	48-h LC50	43	9.8
		21-d LC50	43	5.7

Baird et. al. (1991)	Daphnid (*Ceriodaphnia dubia)*	48-h EC50	160-180	4.7-56.1
Boucher & Watzin (1999)	Daphnid (*Daphnia magna)*	48-h LC50	75-100	9.1
Lasier et al. (2000)	Daphnid (*Daphnia magna)*	48-h LC50	26	5.7
			92	14.5
			184	14.5
Lasier et al. (2000)	Amphipod (*Hyaltelia azteca)*	96-h LC50	26	3.0
			80	8.6
			164	13.7
Martin & Holdich (1986)	Isopod (*Asetlius aquaticus)*	48-h LC50	45-55	771
		96-h LC50	45-55	333
Martin & Holdich (1986)	Isopod (*Asetlius aquaticus)*	48-h LC50	45-55	1389
		96-h LC50	45-55	694
USEPA 905-R-10-002 (2010)	Mussel (*Lampsitis stilquoideo)*	96-h LC50	152	43.3
	Mussel (*Megalonaias nervosa)*	96-h LC50	112	31.5
Stubblefeild et al. (1997)	Brown trout (*Salmo trutta)*	62-d ELS – LOEC	30	7.38
			150	8.81
			450	16.21
		62-d ELS – IC25	30	4.67
			150	5.59
			450	8.68
Davies & Brinkman (1994)	Brown trout (*Salmo trutta) - fingerling*	96-h LC50	38	3.77
			38	9.06
			454	49.9
Davies & Brinkman (1994)	Brown trout (*Salmo trutta) - fingerling*	4-m chronic growth/ survival	37.5	2.70
			37.5	4.19
Davies & Brinkman (1994)	Rainbow trout (*Oncorhynchus mykiss)*	96-h LC50	34.0	4.83
			34.0	3.31
Davies & Brinkman (1994)	Rainbow trout (*Oncorhynchus mykiss)*	4-m chronic growth/ survival	36.8	0.79
			36.8	1.57

Kleinmann and Watzlaf also summarized the results of manganese tolerances on aquatic life, reporting that tolerance limits in reviewed literature varied considerably and that the low tolerances have all been associated with one watershed that contains very low levels of hardness. They also reported that researchers found that a hardness as low as 10 mg/L prevented trout mortality. Tolerances rates for other invertebrates ranged even higher. They went on to say that it appears that manganese is only toxic to fish at low concentrations when the stream water is exceptionally soft and pure. Except in such rare instances, manganese can be considered to be about as toxic to aquatic life as potassium. They concluded that manganese effluent limits should be reexamined in light of this information and that if the stream water has sufficient hardness to protect sensitive fish, and if sufficient dilution is available to avoid adverse effects on downstream users, then it would appear that more lenient effluent limits could be substituted without adverse consequences (Kleinmann and Watzlaf, 1988).

Additional specific information about these studies is provided as an attachment to this letter.

In accordance with the Regulatory Review Act, PADEP must consider the environmental costs and benefits of the proposed rule. Conventional methods employed for Manganese removal in the water treatment process may negatively impact aquatic life. Application of the rule will limit or minimize the amount of harmful chemicals utilized, thus having a positive environmental benefit. In natural waters, dissolved manganese is predominately undersaturated at the plus 2 oxidation state. As a result, manganese is in equilibrium with other natural water constituents present in measurable concentrations, such as iron and carbonate. To overcome this equilibrium and attain the minimum plus 4 oxidation state required to render manganese compounds insoluble, significant chemical treatment is needed (Mozley, 1989). Chemical facilitation of manganese removal may consist of alkaline pH adjustment through the use of sodium hydroxide or hydrated lime. However, depending on the co-precipitation and presence of other natural species in the water, the addition of an oxidant such as sodium permanganate may also be required.

Both mechanisms introduce aquatic toxicity with the potential to impact aquatic life. First, in order to precipitate manganese using alkaline pH adjustment alone, chemical addition sufficient to raise the pH above 9.1 s.u. is required. At this high pH, no co-precipitation with other chemical constituents occurs. However, EPA water quality standards specify that at discharge pH's must be between 6.0 and 9.0 s.u., to limit toxicity to freshwater fish.

Some NPDES permittees have been granted approval to discharge effluent of pH greater than 9.0 s.u. in order to facilitate manganese removal, even in the absence of an aquatic life water qulity criterion for manganese. In addition, natural waters also contain Aluminum compounds that have a limited range of insolubility, approximately between pH 5.5 and 8.5 s.u.. In other words, at the pH levels above 8.5 s.u. that are required for manganese removal, aluminum is soluble or dissolved in the water (Gensemer et. al., 2017). Dissolved aluminum is more toxic to aquatic life, especially under circumstances of low hardness and high dissolved organic carbon. Consequently, raising the pH to facilitate manganese removal also resolubilizes aluminum, creating a species that is toxic to aquatic life at low concentrations.

Finally, to limit the alkaline pH adjustment required to facilitate manganese removal, an oxidant chemical may also be employed. Although addition of oxidant chemicals is effective at catalyzing manganese oxidation and precipitation, strong oxidizers also threaten aquatic life in high concentrations by increasing biological oxygen demand.

Consequently, complete removal or reduction in chemical treatment required for manganese treatment as a result of the proposed rule could provide an environmental benefit by limiting the impact to aquatic toxicity. Furthermore, this benefit of removal or reduction of manganese treatment chemicals outweighs the related

minimal impact to instream concentrations of manganese. In locations where adequate instream assimilative capacity exists, and the designated use of the receiving stream is not PWS, the minimal increase in concentrations is negligible. To demonstrate this fact, Table 5 below compares the average manganese concentrations measured downstream of CONSOL discharges in West Virginia located more than five miles upstream of potable water supply intakes, before and after eliminating chemical treatment for Manganese removal. As stipulated by West Virginia regulation and policies for post mining discharges, these locations were granted variances that eliminated manganese from the subject NPDES permits. Due to the assimilative capacity of the respective receiving streams, there was minimal increase in downstream manganese concentrations after removal of chemicals. There was no negative impact to water quality, while the receiving streams benefitted from the elimination of chemicals that are harmful to aquatic life. Upon promulgation of the proposed rule in Pennsylvania, a similar outcome should be expected.

Table 5. Comparison of WV Locations receiving Mn Waiver

Site Location	Average Downstream Manganese Concentration During Chemical Treatment (mg/L)	Average Downstream Manganese Concentration After Removal of Chemical Treatment (mg/L)
1 – WV	0.699	0.74
2 – WV	0.87	1.87
3 – WV	1.20	1.95
4 – WV	0.44	0.74
5 – WV	0.75	1.22
6 – WV	0.17	0.22

The ANPR requests information related to the potential savings to the regulated community, as a result of the proposed rule. As requested, CONSOL completed an analysis to demonstrate the annual cost savings that would be possible as a result of the rule. In order to complete the analysis, CONSOL selected a variety of locations in Pennsylvania where either passive or active treatment methodologies are utilized to achieve compliance with manganese effluent limitations of 1.0 mg/L or less (Table 5). For locations where active chemical treatment is utilized, the savings are comprised of chemical, utilities, operation, and monitoring costs. For the sites where passive treatment is currently employed, manganese is the only parameter that currently does not meet Pennsylvania's water quality standards without chemical treatment. In these situations, upon promulgation of the rule, CONSOL would pursue complete release of the associated permit, allowing the sites to be utilized for the pastureland, habitat, forestry, or other post mining land uses approved by the Department. In these cases, the costs savings assume elimination of all operational costs at the site.

It should be noted that these estimates do not take into the account the added benefits to the Commonwealth associated with minimizing electricity usage, transportation of hazardous chemicals, or regulation and inspection of chemical storage tanks. Furthermore, the Commonwealth should complete a similar evaluation of abandoned mine land water treatment facilities to which the Commonwealth must unnecessarily dedicate resources for manganese chemical treatment. The benefit associated with the elimination or reduction of chemical treatment to facilitate return of these properties to their intended post mining land use is immeasurable.

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Table 5. Annual Cost Savings Related to Moving Measurement of the Manganese Water Quality Criterion to the Point of Intake	
Treatment Site Location	**Yearly Site Total**
Treatment Site 1 - Greene County	$55,565
Treatment Site 2 - Indiana County	$44,555
Treatment Site 3 - Indiana County	$16,218
Treatment Site 4 - Indiana County	$22,476
Treatment Site 5 - Greene County	$108,600
Treatment Site 6 - Indiana County	$3,500
Treatment Site 7 - Armstrong County	$1,000
Treatment Site 8 - Indiana County	$4,366
Treatment Site 9 - Indiana County	$837
Total Potential Yearly Cost Savings	**$257,117**

Notes: 1. Assumes shutdown and discontinuing treatment activities at Treatment Plants 1 through 4.
2. Assumes a reduction in chemical treatment at Treatment Plants 5 through 9.
3. Costs are based on 2017 actuals.
4. All treatment site locations are in PA.
5. Total potential yearly saving is based on current costs.

CONSOL appreciates the opportunity to comment on the PADEP's Advanced Notice of Proposed Rulemaking for Water Quality Standard for Manganese. To summarize the comments above, CONSOL supports the inclusion of manganese in the exception for PWS critical uses defined at 25 Pa. Code §93.6(d). Most importantly, adopting this change will not negatively impact the potable water suppliers, because existing regulatory mechanisms such as Federal Effluent Limitation Guidelines and the Reasonable Potential Analyses will continue to be utilized to regulate manganese discharges permitted under the NPDES program. In addition, no unanticipated consequences to aquatic life or other designated uses are expected as a result of the proposed rule. In fact, the environmental benefits associated with the reduction in use and transport of hazardous chemicals, as well as the increased opportunity for mine lands to be utilized as intended by their post mining land uses, is considerable. Finally, in accordance with the October 2017 update to subsection (j) of the Code, CONSOL respectfully requests that PADEP limits the update to §93.6(d) and the associated evaluations to the application of the manganese water quality criterion at the point of intake only, on an expedited timeframe.

If you have any questions, or require additional supporting information, please do not hesitate to contact me at stevenbuffone@consolenergy.com.

My best regards,

Steven A. Buffone

Steven A. Buffone, CHMM, QEP, GIT
Compliance & Regulatory Affairs
CONSOL Energy Inc.

Attachments: 1

Peer reviewed Scientific Studies and Journals

This document was prepared by a third-party consultant for CONSOL in response to a request from the Pennsylvania Department of Environmental Protection (Department) for available information regarding whether the existing 1.0 mg/L standard established for the PWS use is protective of aquatic life in Pennsylvania surface waters. To achieve that goal, this document presents the results of a literature review conducted to examine the effects of Mn to freshwater species that potentially inhabit Pennsylvania streams, or are closely related species within the same taxonomic group (e.g., salmonids).

Manganese toxicity to aquatic life is evaluated in relation to manganese concentrations and hardness levels observed within Pennsylvania streams and rivers where PWS are typically located. Lastly, difficulties in assessing whether impacts to biological communities are attributable to manganese is discussed, because when manganese is present above normal background concentrations, other more-toxic metals such as aluminum are also likely elevated and/or the pH is significantly depressed.

1.0 Literature Review

1.1 Methods for Accessing Information and Locations of Reference Documents

A search was conducted on the Internet to locate journal articles, reports, and associated references dealing with the toxicity of manganese to aquatic organisms. The Concise International Chemical Assessment Document 63 entitled, *Manganese and its Compounds: Environmental Aspects* published by the World Health Organization in 2004 provided a comprehensive list of references that was used to identify pertinent references to address the objectives of this search. Journal articles were obtained through search libraries including BioOne, JSTOR, and Elsevier. Other on-line sources such as the National Technical Reports Library (NTRL), U.S. EPA National Service Center for Environmental Publications (NSCEP), and Colorado Parks and Wildlife website were accessed to obtain pertinent reports.

1.2 Criteria used to include (or exclude) studies in this presentation.

The Department's Advance Notice of Proposed Rulemaking specifically asked for published aquatic life toxicity studies that are representative of Pennsylvania species and waterbodies. To that effect, aquatic toxicity studies performed using marine organisms or invertebrate and fish species that are not native to, or unlikely to inhabit Pennsylvania surface waters, were not included in this review. The brook trout (*Salvelinus fontinalis*), which is a native species in Pennsylvania, has apparently not been used for aquatic toxicity tests to assess the effects of manganese. No aquatic toxicity studies using brook trout or other sensitive species (e.g., darters) with manganese as the toxicant were found during this literature search. Brook trout have been used for toxicity studies to assess the effects of other metals such as aluminum, cadmium, iron, and zinc. Therefore, this review relied on studies of two surrogate salmonid species (rainbow trout, *Oncorhynchus mykiss* and brown trout, *Salmo trutta*), which are raised in hatcheries in Pennsylvania and stocked in Pennsylvania streams during trout fishing season.

1.3 Summary of studies/ reports excluded from consideration with reasons for exclusion

The aquatic toxicity testing results from the Reimer (1999) Master's Thesis (Table 1) have been excluded from this evaluation. These toxicity tests were conducted by The Pacific Environmental Science Centre, Aquatic Toxicity Laboratory. There were several questionable results generated from

these tests. First, the very low acute LC_{50} value (0.8 mg Mn/L) reported for *Daphnia magna* at the test hardness of 25 mg/L is potentially due to effects from soft water rather than manganese. Mortality of 70% was observed in the control groups at hardness < 50 mg/L after 5 days of the chronic *Daphnia magna* 21-day test, which had to be discontinued. Although the acute test was only 48-hours duration, it is uncertain whether the low LC_{50} was attributable to Mn exposure only, rather than contributory effects from low hardness. This LC_{50} value (0.8 mg Mn/L) is much lower than the LC_{50} (9.8 mg Mn/L) reported for *Daphnia magna* by Biesinger and Christensen (1972) at a hardness of 43 mg/L.

Secondly, the results for the acute 96-hour rainbow trout toxicity test did not follow the trend of decreasing manganese toxicity with increasing water hardness. The LC_{50} value for the 250 mg/L hardness test concentration was lower than the value for the 100 mg/L hardness test concentration. Additionally, it does not appear that initial and final Mn concentrations were measured in the test vessels for all of these static tests, particularly the 96-hour rainbow trout toxicity test.

Reimer (1999) concluded that the toxicity testing program commissioned by the British Columbia Ministry of Environment, Lands and Parks (BCMELP) and conducted by Pacific Environmental Science Centre, Aquatic Toxicity Laboratory were not comprehensive enough to permit derivation of full guidelines for manganese. To meet BCMELP full guideline requirements, an additional chronic study on a non-planktonic species would be required, and either flow-through tests or confirmation of Day 0 and final day manganese concentrations in the test water would be required. Additional studies on rainbow trout would also be required since the data generated did not fit the pattern of increasing manganese concentration (decreased toxicity) with increasing water hardness.

Lewis (1976) reported results for a 29-day toxicity test where rainbow trout eggs were exposed to $MnSO_4$ at concentrations of 1, 5, and 10 mg/L. Test results indicated statistically significant (p value <0.001) mortality noted as low as 1 mg Mn/L. However, this test was conducted at a very low hardness of 5.0 mg/L as $CaCO_3$, which would not be representative of the hardness of a larger-order stream or river in Pennsylvania where a public water supply would likely be located. Additionally, 7% mortality was reported in the control group, with 12% mortality for eggs exposed to 1 mg Mn/L. No data was presented in the Lewis article to evaluate the differences in survival between the three replicate groups of 150 eggs in each test concentration, but the article stated there were no significant differences in mortality between the three groups. In view of the very low hardness used to conduct this test and the potential for high natural mortality of fish eggs, combined with the minor 5% difference in survival between the control group and lowest Mn concentration, we do not believe the data presented is relevant considering expected hardness levels in Pennsylvania surface waters supporting PWS intakes.

The studies performed by Davies and Brinkman (1994, 1995) at the aquatic toxicity lab of the Fish Research Section of the Colorado Division of Wildlife appear to have been flow-through toxicity tests performed by experienced investigators using acceptable test methods. Results from these studies were summarized by the investigators as Job Progress Reports under Federal Aid Projects #F-243R-1 and #F-243R-2. Therefore, although they are not formally published aquatic toxicity reports as requested by the Department, they appear to provide usable scientific data and appear to have been used by the Colorado Water Quality Control Commission in the development of acute and chronic aquatic life water quality criteria for manganese.

2.0 Presentation of Reviewed Journals

Freshwater Fish

2.1 Peer reviewed journal publication

Stubblefield WA, Brinkman SE, Davies PH, Garrison TD (1997). Effects of water hardness on the toxicity of manganese to developing brown trout (*Salmo trutta*). *Environmental Toxicology and Chemistry*, 16(10):2082–2089.

2.1.1 General Description of Study

An early life stage (ELS) toxicity test was performed using brown trout (*Salmo trutta*), which were exposed over three life stages, which included embryo (egg), larva (sac fry), and alevin (swim-up fry). A continuous-flow proportional dilution system delivered seven test concentrations of manganese and a dilution water control to the test chambers. Tests were conducted using laboratory dilution/control water with hardness of 30 mg/L (low), 150 mg/L (medium), and 450 mg/L (high hardness) as $CaCO_3$. Mean exposure concentrations of manganese in the 30 mg/L hardness test ranged from 0.51 to 15.5 mg/L. Mean exposure concentrations of Mn in the 150 mg/L hardness test ranged from 2.78 to 74.90 mg/L, while Mn concentrations in the 450 mg/L hardness test ranged from 2.54 to 100.82 mg/L. Fifteen embryos were initially placed in an egg cup in each test chamber and four replicates were tested per treatment. Upon hatching, fish were released from the egg cup into the test chamber. The number of live eggs, hatches, partial hatches, and live fish were counted in each test chamber daily, and dead organisms were removed using a siphon. At test termination (62 days), live fish in each chamber were counted and sacrificed using isopropyl alcohol, then blotted dry and weighed.

Findings

- Brown trout hatching success ranged from 86.6 to 98.2% and was generally not affected by manganese exposure over the range of concentrations and hardness levels tested.
- Larval survival decreased with increasing manganese concentrations and mortality was observed sooner in higher manganese concentrations than lower concentrations for all three hardness tests.
- Lowest Observable Effects Concentration (LOEC), expressed in terms of trout survival were 7.38, 8.81, and 16.21 mg Mn/L, respectively in the 30 mg/L, 150 mg/L, and 450 mg/L hardness tests.
- Growth was a more sensitive endpoint for detecting manganese toxicity than survival, as the LOECs for trout weight (excluding survival) were 4.41 and 8.68 mg Mn/L, respectively for the 150- and 450-mg/L hardness tests.
- Chronic IC_{25} values of 4.67, 5.59, and 8.68 mg Mn/L were reported at hardness levels of 30 mg/L, 150 mg/L, and 450 mg/L
- The current study demonstrated a definite relationship (decreasing toxicity with increasing hardness) between manganese toxicity and water hardness for brown trout.

2.1.2 Applicability

The author states that the study, "provides a basis upon which to estimate the potential adverse effects of chronic manganese exposure to salmonid species." The author also states, "early-life stage (ELS) studies test organisms at more sensitive life stages, measure more sensitive endpoints, and employ exposure conditions that may more closely resemble natural environmental exposures..." Although the brown trout is not native to Pennsylvania streams, the brook trout (*Salvelinus fontinalis)* is a native salmonid species. The Stubblefield data suggests LOEC and IC_{25} values obtained for these sensitive endpoints at low-hardness water of 7.37 and 4.67 mg/L Mn, respectively, which are significantly greater than the 1.0 mg/L water quality criterion for manganese suggested for the PWS intake location, at a PA default hardness value of 100 mg/L.

2.2 Unpublished Federal Aid Project, Job Progress Reports from Fish Research Section of Colorado Division of Wildlife

Davies PH, Brinkman SF (1994). *Acute and chronic toxicity of manganese to exposed and unexposed rainbow and brown trout*. Federal Aid in Fish and Wildlife Restoration. Job Progress Report #F-243R-1, Colorado Division of Wildlife, Fort Collins, Colorado, USA.

2.2.1 General Description of Study

Two sets of acute toxicity tests were conducted for both exposed and unexposed rainbow trout (*Oncorhynchus mykiss*) and brown trout (*Salmo trutta*). Eyed rainbow trout eggs and fingerling brown trout were first acclimated to relatively soft water for a period of four days and two weeks, respectively before initiating exposure to manganese. The exposed groups were exposed to increasing Mn concentrations up to five days, after which they were exposed to a final acclimation concentration of 0.80 mg Mn/L for four months. The acute brown trout test was conducted at Mn concentrations of 30, 22.5, 16.8, 9.6, 5.4, 3.0, and 0.0 mg/L. The 96-hour LC_{50} was calculated for exposed and unexposed test organisms for both trout species.

Chronic tests consisted of four, four-month experiments using unexposed and exposed (acclimated) rainbow and brown trout. Twenty rainbow trout from the unexposed and exposed groups and 20 exposed and 20 unexposed brown trout were placed in the testing aquaria. All test organisms were exposed to Mn concentrations of 6.00, 4.50, 3.36, 1.92, 1.08, 0.60, and 0 mg/L. Mean lengths of exposed and unexposed rainbow trout used for the chronic test were 89.5 mm and 87.1 mm, respectively. Mean lengths of exposed and unexposed brown trout used for the chronic test were 154.3 mm and 151.4 mm, respectively.

3.2.2 Findings

- Unexposed brown trout had a lower LC_{50} value (3.77 mg Mn//L) than the exposed group (LC_{50} value = 9.06 mg Mn/L) suggesting prior acclimation of exposed test organisms to 0.80 mg Mn/L for four months increased their resistance to acute Mn toxicity.
- However, rainbow trout that were embryonically exposed as eggs to Mn had a slightly lower LC_{50} value (3.32 mg/L) compared to unexposed test organisms (4.83 mg/L).

- Chronic test results indicated higher chronic values for the manganese-exposed groups for both rainbow trout and brown trout with an approximate 2 times increase in tolerance of exposed rainbow trout eggs and 1.6 times for brown trout fingerlings when compared to unexposed fish.
- Data served as basis of statement by Reimer (1999) that, "…organisms inhabiting surface waters may be more naturally tolerant of or acclimated to the manganese levels present in those waters."

3.2.3 Applicability

The results suggest that fish exposed to low levels of manganese in surface waters may be more naturally tolerant to or become acclimated to manganese, thereby reducing toxicity at higher manganese concentrations. The minimum LC50 values for the study were in the range of 3.32 to 3.77 mg Mn/L.

Freshwater Mussels

3.3 Published USEPA Report

U.S. Environmental Protection Agency. November 2010. A 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. USEPA Region 5.

3.3.1 General Description of Study

Specific toxicity tests of interest conducted by Illinois Natural History Survey (INHS) included separate 96-hour static acute tests to determine the toxicity of manganese on <5-day old juveniles of two freshwater mussel species, *Lampsilis siliquoidea* (fatmucket) and *Megalonaias nervosa* (washboard). Fatmucket juveniles were exposed to test concentrations of 150, 75, 37, 18.8, 9.4, and 4.7 mg Mn/L. Washboard juveniles were exposed to test concentrations of 300, 150, 75, 37.5, and 18.8 mg Mn/L. Five juveniles were placed in each 50-ml beaker containing 40-ml test solution, with four test vessels per treatment, for a total of 20 organisms per treatment. The LC_{50} value for each test was calculated using the Spearman-Karber method.

3.3.2 Findings

- The LC_{50} value for *L. siliquoidea* was determined to be 43.3 mg/L Mn.
- The LC_{50} value for *M. nervosa* was determined to be 31.5 mg/L Mn.
- The hardness value in the test concentration (37 mg Mn/L) closest to the LC_{50} value for *L. siliquoidea* was 152 mg/L as $CaCO_3$.
- The hardness value in the test concentration (37.5 mg Mn/L) closest to the LC_{50} value for *M. nervosa* was not reported due to interference, but the hardness for the 18.8 mg/L test concentration was reported as 112 mg/L.

3.3.3 Applicability

The fatmucket is a common mussel species that is found within streams in the Lake Erie and Ohio River drainage basins in Pennsylvania. Therefore, acute toxicity test results regarding this

mussel species' sensitivity to manganese present in Pennsylvania streams are pertinent and the current acute toxicity data suggests that a water quality criterion for manganese significantly higher than 1.0 mg/L would be protective for juvenile freshwater mussels. The washboard mussel is not found in Pennsylvania Rivers, but is found primarily in the Ohio River and Mississippi River in the Midwest.

Freshwater Invertebrates

3.4 Peer reviewed journal publications

Lasier, P.J., P.V. Winger and K.J. Bogenrieder (2000). Toxicity of Manganese to *Ceriodaphnia dubia* and *Hyalella azteca*. *Archives of Environmental Contamination and Toxicology*, 38, pp. 298-304.

Martin, T.R. and D.M. Holdich (1985). The Acute Lethal Toxicity of Heavy Metals to Peracarid Crustaceans (With Particular Reference to Fresh-Water Asellids and Gammarids). Wat. Res., Vol. 20, No. 9, pp. 1137-1147.

3.4.1 General Description of Studies

Lasier (2000) performed both acute and chronic toxicity tests using the daphnid *Ceriodaphnia dubia* and the amphipod *Hyalella azteca.* Acute 48-hour tests and chronic three-brood tests were performed using *Ceriodaphnia dubia* <24 hours old and between 24-48 hours old at hardness levels ranging from 26 to 184 mg/L as $CaCO_3$. Acute 96-hour toxicity tests were performed with 7-day old *Hyalella azteca* organisms at comparable hardness levels (26, 80, and 164 mg/L).

3.4.2 Findings

- Lasier (2000) observed decreasing toxicity to *Hyalella azteca* as hardness increased, with LC_{50} values increasing from 3.0 to 8.6 to 13.7 mg Mn/L as hardness increased from 26 to 80 to 164 mg/L as $CaCO_3$.
- Lasier (2000) observed a similar effect with *Ceriodaphnia dubia*, with acute LC_{50} values increasing from 6.2 to 14.5 to 15.2 mg Mn/L as hardness increased from 26 to 92 to 164 mg/L, respectively.
- Chronic IC_{50} values were lower than acute LC_{50} values averaging 3.9, 8.5, and 11.5 mg Mn/L over this same range of water hardness values.
- Martin and Holdrich (1985) reported much higher acute 48-hour and 96-hour LC_{50} values for the isopod *Asellus aquaticus* and amphipod *Crangonyx pseudogracilis* with values of 771 and 333 mg Mn/L, and 1,389 and 694 mg Mn/L, respectively at a hardness of 50 mg/L.

3.4.3 Applicability

Daphnids are found in surface waters of Pennsylvania so their use as a test organism is appropriate. Similarly, aquatic isopods of the family Asellidae (genus *Asellus* redesignated as genus *Caecidotea)* can also be found in Pennsylvania streams, as can amphipods of both *Crangonyx* and *Hyallela*. According to the test data, LC50 and IC50 values for moderate hardness water for *Ceriodaphnia dubia* are 14.5 mg/L and 8.5 mg/L; for *Hyallela* are 8.6 mg/L, and for *Asellus* and *Crangonyx* are all greater than 300 mg/L.

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