**COMMONWEALTH OF PENNSYLVANIA**
**DEPARTMENT OF ENVIRONMENTAL PROTECTION**
**BUREAU OF CLEAN WATER**

**TRIENNIAL REVIEW OF WATER QUALITY STANDARDS**

# RATIONALE FOR THE DEVELOPMENT OF AMBIENT WATER QUALITY CRITERIA FOR

# CHLORIDE

# PROTECTION OF AQUATIC LIFE

## Introduction

Section 303(c)(1) of the Clean Water Act (33 U.S.C.A § 1313(c)(1)) requires that states periodically, but at least once every three years, review and revise as necessary their water quality standards. Water quality standards are instream water quality goals that are implemented by imposing specific regulatory requirements (such as treatment requirements and effluent limits) on individual sources of pollution. As part of the current review, the chloride criterion is being evaluated.

Chloride occurs naturally in the aquatic environment, especially in waters flowing through geologic formations of marine origin. The major anthropogenic sources of chloride include deicing salt for roads, urban and agricultural runoff, treated industrial waste, discharges from municipal wastewater plants and the drilling of oil and gas wells (EPA, 1988). Elevated levels of chloride are toxic to aquatic life in freshwater environments. A state-wide aquatic life criterion for chloride would provide an appropriate level of protection for all of Pennsylvania's waters.

Pennsylvania's existing chloride criterion was developed primarily for the protection of potable water supplies (PWS). It is not applied in all waters of this Commonwealth, but rather only at the point of water supply intake, pursuant to 25 Pa. Code § 96.3(d) (relating to water quality protection requirements). The current PWS criterion for chloride is included in Table 3 at 25 Pa. Code § 93.7 (relating to specific water quality criteria) and establishes a maximum level of 250 milligrams of chloride per liter of water, applicable only at the point of all existing or planned surface PWS withdrawals, unless otherwise specified by regulation.

The Pennsylvania Department of Environmental Protection has developed draft water quality criteria for chloride for the protection of aquatic life. The draft criterion is based on current science that shows that the water hardness and sulfate concentrations affect chloride toxicity to aquatic organisms. This relationship is incorporated into the newly developed equation used for calculating the acute and chronic numeric criteria for chloride in Pennsylvania waters. The Department is recommending that this chloride criterion be applied in all waters for the protection of aquatic life.

## History

The U.S Environmental Protection Agency (EPA) published Ambient Water Quality Criteria (AWQC) for Chloride in February 1988, which summarized the published toxicity data that was available at that time for chlorides on freshwater plant and animal species. The acute and chronic effects of chlorides on aquatic animals were documented, along with the chronic effects of chloride on aquatic plants. The findings of 106 published scientific studies were considered in the development of the national aquatic life criteria for chloride. EPA developed the chloride criteria in 1988 for protection against adverse acute and chronic impacts on freshwater aquatic life based on the Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses, NTIS PB85-227049 (Stephan, et al., 1985). EPA determined the four-day (chronic) and one-hour acute average concentrations based upon how quickly some aquatic species reacted to higher concentrations of pollutants. The Criteria Continuous Concentration (CCC) and Criteria Maximum Concentration (CMC) values should not be exceeded more than once every three years on the average (US EPA, 1988).

**The 4-day average (CCC) criterion = 230 mg/l**

**The 1-hour average (CMC) criterion = 860 mg/l**

In 2005, the state of Iowa with the help of EPA Region 5 began an investigation into updating the existing chloride AWQC. The revised WQS was promulgated by Iowa in 2009. EPA Office of Research and Development scientists served to link the relationship of chloride toxicity to aquatic organisms with water hardness and sulfate concentration. This relationship provided the basis for the revised WQS promulgated in Iowa.

The Department has reviewed the equation-based aquatic life criteria for chloride as developed by EPA and successfully implemented in Iowa. The researchers at the Great Lakes Environmental Center (GLEC) in Columbus, OH and the Illinois Natural History Survey (INHS) in Champaign, IL worked collaboratively under a contract with the EPA to determine the toxicity of chloride in freshwater invertebrate species. The research demonstrated a strong correlation between chloride toxicity and hardness and to a lesser extent with sulfate. The final results of this toxicity testing were published in the report “Acute Toxicity of Chloride to Select Freshwater Invertebrates” US EPA, October 28, 2008. Iowa Department of Natural Resources (IDNR) selected the appropriate acute and chronic criteria equations after considering input from many sources and two equations were promulgated by Iowa. Both the one-hour acute and ninety-six hour chronic criteria values should not be exceeded more than once every three years on the average (personal communication: Connie Dou, IDNR, November 2011).

## Test Compound Determination

Chloride is one of the major anions commonly found in surface and wastewater. It is a constituent of naturally occurring minerals; it readily dissolves in water, and is important to living systems. As a solid, chloride is typically found as a salt bonded with a cation such as calcium, sodium, magnesium, or potassium. The salinity of a water body is measured by its total salt composition. Freshwater lakes are dominated by the cations: $Ca^{2+}$, $Mg^{2+}$, $K^+$ and $Na^+$ and the anions $HCO3^-$ , $SO_4^{2-}$ and $Cl^-$. (Wetzel, 1983) Data obtained from stream surveys of Pennsylvania waters confirmed this determination: the ionic composition is >40% $HCO3^-$/ $Ca^{2+}$, followed by $SO_4^2$, $Mg^{2+}$, $Na^+$, $K^+$ and $Cl^-$. Pennsylvania waters are calcium/bicarbonate dominant.

Chloride toxicity tests have been conducted through the addition of chloride salts such as sodium chloride (NaCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$) and potassium chloride (KCL). Results of tests with potassium and magnesium chloride suggest toxic effects observed can be due to the potassium and magnesium cation, rather than the chloride ion. It has been observed that the toxic effects of calcium chloride and sodium chloride are due to the chloride anion. In establishing the effect concentrations of the chloride ion, exposure to KCL and $MgCl_2$ salts are lower (more toxic) than the effect concentration of the exposures to $CaCl_2$ and NaCl salts (Canadian Council of Ministers of the Environment, 2011). Therefore the approximate order of chloride salt toxicity to freshwater organisms is KCL > $MgCL_2$ > $CaCl_2$ > NaCl (Mount et al 1997). Based on this information, chloride toxicity to freshwater organisms was evaluated using tests dosed with NaCl to ensure the effect concentrations were derived from tests where effects were based on the chloride anion, not the associated cations.

**Other Modifying Factors**

A long term study by Elphick et al. indicates that increased hardness may have an effect on the toxicity of chloride. GLEC and INHS (2008) also conducted some short-term exposure tests indicating that a hardness-chloride toxicity relationship exists for the water flea *Ceriodahpnia dubia*, the fingernail clam *Sphaerium simile*, the Oligochaete *Tubifex tubifex* and the aquatic snail *Gyraulus parvus*. (CCME, 2011)

EPA contracted with the GLEC and the INHS (2009) to perform toxicity testing for chloride. The results showed that chloride toxicity is heavily dependent on water hardness, and to a lesser degree, sulfate levels in water. PA Department staff has been monitoring sulfate and hardness levels at Water Quality Network (WQN) stations throughout PA. This data confirms that PA source waters have a varied amount of hardness and sulfate concentrations. As an example, the Aughwick Creek watershed is located in southcentral Pennsylvania. In this single watershed, the hardness values range from 10 mg/l in the small freestone streams to 250 mg/l in areas of limestone geology. There is a full range of hardness values between the 10 mg/l and 250 mg/l as the tributaries flowing through various geologies coalesce and mix. This is not an unusual situation as there are extensive limestone deposits in the Commonwealth. Pennsylvania has a legacy of abandoned coal mines that can discharge high levels of sulfate. Instream sulfate levels are elevated where there are concentrations of these abandoned discharges. Where there is a legacy of abandoned coal mines the sulfates often range between 100 to 500 mg/l and sometimes higher. In contrast, the streams in the less affected parts of the state have sulfate values less than 50 mg/l. Urban streams often have sulfate between 50 mg/l and 100 mg/l. The variation in the hardness and sulfate concentrations throughout the state confirms that it is appropriate to develop an equation based criterion that includes a modification for hardness and sulfate.

**PA Site Specific Research/Literature Review**

The Department contracted with the Stroud Water Research Center, in Avondale, Pennsylvania to perform chloride toxicity testing. The study was designed to provide the additional information needed to support the development of a chloride criterion that is protective across the range of aquatic habitats and species found in Pennsylvania waters. Benthic macroinvertebrates were used in this eco-toxicity study of chloride because they are an ecologically important group of aquatic organisms and are common components of the Pennsylvania bio-monitoring multi-metrics used in standard water quality assessment protocols (e.g., PA IBI; PADEP 2013)

The following mayfly species were included in the study: *Neocloeon triangulifer*, previously classified as *Centroptilum* (Jacobus and Wiersema, 2014), *Anafromtilum semirufum*, *Procloeon fragile*, *Ephemerella invaria*, *Maccaffertium modestum* and *Leptophlebia cupida*. All six species were evaluated for short term (acute) exposures to chloride. Chloride sensitivities were determined using sodium chloride because sodium is known to have little effect on the toxicity of chloride (Stroud 2015). Four species (*N. triangulifer*, *A. semirufum*, *P. fragile*, *M. modestum*) were subjected to a whole-life (chronic) toxicity test. The chronic test began with newly hatched larvae and ended when all larvae had emerged as adults (i.e., 20-48 days). The development time for a complete life cycle of *M. modestum* is 60-80 days. The experiment was ended before the adult emergence; therefore the chronic study of *M. modestum* was omitted.

The acute and chronic data obtained from the Stroud study was incorporated into the data set used to determine Pennsylvania-specific chloride criteria. It has been shown that some aquatic organisms show significantly more sensitivity when tested in reconstituted laboratory water compared to natural waters (CCME, 2011). The Stroud study was conducted in water from three source water streams: Spruce Run, a soft water stream (hardness 6 mg/L) in Union County, PA; House Run, a moderately hard water stream (hardness 94 mg/L) in Greene County, PA and Cedar Run, a hard water (hardness 212 mg/L) stream in Union County, PA. The reference stream was White Clay Creek which is a moderately hard water stream (hardness 89 mg/L) located at the Stroud Water Research Center in Chester County, PA, where all the study species were originally collected. (Stroud, 2015)

**Other toxics data sources used:**

Toxics data that was compiled by Charles Stephan, November 06, 2007 – This document contains acceptable acute and chronic data obtained from several significant studies (Birge et al., 1985; Spehar 1987; Cowgill and Milazza 1990; and Wisloh 2007). It also contains a list of the studies reviewed previous to 2007 that were not approved and the reasons for the disapproval.

Data from Canadian Council of Minister of the Environment, 2011 – This document contained additional studies (Harmon et al 2003; Collins & Russell 2009; Gillis 2011, GLEC & INHS 2008; Elphick et al 2011; Wang and Ingersoll 2010; US EPA 2010, Valenti et al 2007; Bringolf et al 2007) In particular, the Valenti et al, Bringolf et al and Gillis studies contained valuable data on sensitive and endangered mussels. This document also contains studies that have relevant chronic toxicity data.

US EPA, 2015 – EPA's data set contained additional peer reviewed studies. (GLEC and INHS 2010; Wang et al 2013; Garner and Royer 2010; Soucek 2012, 2013; Environ 2009; Sanzo and Hecnar 2006; Garibay and Hall 2004).

In addition, PA DEP staff evaluated Maryland's Freshwater Chloride Development Methodology and reviewed the data used in their chloride criteria development. (MDE, 2013)

**Acute criteria determination**

Acute values were used from all acceptable data contained in the reports listed above. This resulted in 219 acute toxicity results for aquatic species (51 genera). The LC50's are in mg/L for all acceptable data, including Stroud mayfly data. The four genera most sensitive to acute testing were *Epioblasma* (freshwater mussel); *Sphaerium* (fingernail clam); *Neocloeon* (mayfly); and *Lampsilis* (freshwater mussel). The genus mean acute value (GMAV) for the most sensitive organism (*Epioblasma*) was 698 mg/L. This value was lower than the calculated final acute value (FAV) of 874.8 mg/L. In order to protect for this sensitive freshwater mussel, the species mean acute value (SMAV) for the *Epioblasma* (698 mg/L) was used as the FAV. The final acute value is 349 mg/L, which will be incorporated into the hardness/sulfate modifying equation to determine the final acute chloride criterion.

**Acute Data**

| Genus | GMAV (mg/L) | Genus | GMAV (mg/L) | Genus | GMAV (mg/L) |
|---|---|---|---|---|---|
| *Epioblasma* | 698 | *Physa* | 2667 | *Aciperser* | 5903 |
| *Sphaerium* | 785 | *Rana* | 2680 | *Cyprinella* | 5956 |
| *Neocloeon* | 959 | *Pseudacris* | 2882 | *Lepidostoma* | 6000 |
| *Lampsilis* | 991 | *Lirceus* | 2950 | *Lepomis* | 6634 |
| *Anafroptilum* | 1090 | *Macaffertium* | 3052 | *Carassius* | 6959 |
| *Ambystoma* | 1178 | *Planorbella* | 3731 | *Gambusia* | 7786 |
| *Ceriodaphnia* | 1197 | *Ephemerella* | 3759 | *Oncorhynchus* | 8379 |
| *Elliptio* | 1437 | *Limnodrilus* | 3761 | *Libellulidae* | 9671 |
| *Procloeon* | 1449 | *Bufo* | 3926 | *Fundulus* | 9706 |
| *Megalonaisas* | 1517 | *Caecidotea* | 4049 | *Gasterosteus* | 10200 |
| *Lasmigona* | 1577 | *Lumbriculus* | 4254 | *Cambarus* | 10557 |
| *Margaritifera* | 1577 | *Nephelopsis* | 4310 | *Anguilla* | 11929 |
| *Brachionus* | 1645 | *Erpobdella* | 4550 | *Agria* | 14255 |
| *Daphnia* | 1765 | *Ameriurus* | 4849 | | |
| *Isonychia* | 1880 | *Pimephales* | 5010 | | |
| *Musculium* | 1930 | *Tubifex* | 5311 | | |
| *Villosa* | 2215 | *Chironomus* | 5371 | | |
| *Gyraulus* | 2430 | *Leptophlebia* | 5473 | | |
| *Diaptomus* | 2571 | *Lithobates* | 5846 | | |

| Rank | Genus/ Species | GMAV mg/L |
|---|---|---|
| 4 | *Lampsilis (freshwater mussel)* | 991 |
| 3 | *Neocloeon (mayfly)* | 959 |
| 2 | *Sphaerium (fingernail clam)* | 785 |
| 1 | *Epioblasma (freshwater mussel)* | 698 |

**Chronic criteria determination**

The chronic toxicity data set included 10 aquatic species. *Pimephales promelas*, *Oncorhynchus mykiss*, *Daphnia ambigua*, *Daphnia magna*, *Daphnia pulex*, *Ceriodaphnia dubia*, *Lumbriculus variegatus*, *Neocloeon triangulifer*, *Anafroptilum semirufum* and *Procloeon fragile*. The final calculated acute/chronic ratio (FACR) from the acceptable data is 6.2. The final chronic value is 112.7 mg/L (113 mg/L), which will be incorporated into the hardness/sulfate modifying equation to determine the final chronic chloride criterion.

| Species | SCV mg/L | SAV (mg/L) | GM ACR | Source |
|---|---|---|---|---|
| *Pimephales promelas* | 433.1 | 6570 | 10.2 | Birge et al 1985 |
| | 598 | 4079 | | Elphick et al. 2011 |
| *Oncorhynchus mykiss* | 922.7 | 8379 | 9.1 | Stephan 2007 |
| *Daphnia ambigua* | 259 | 1213 | 5.4 | Harmon et al 2003 |
| *Daphnia magna* | 2382 | 4731 | | Stephan 2007 |
| | 421 | 3630 | | Elphick et al. 2011 |
| *Daphnia pulex* | 372 | 1470 | | Stephan 2007 |
| *Ceriodaphnia dubia* | 925 | 1395 | 2.6 | Stephan 2007 |
| | 425 | 1677 | | Stephan 2007 |
| | 454 | 1068 | | CCME, 2011 |
| *Lumbriculus variegatus* | 825 | 3100 | 3.8 | Elphick et al. 2011 |
| *Neocloeon triangulifer* | 109 | 704 | 8.4 | Stroud, 2015 |
| | 175 | 2141 | | Stroud, 2015 |
| | 188 | 1420 | | Stroud, 2015 |
| *Anafroptilum semirufum* | 114 | 107 | 8.3 | Stroud, 2015 |
| | 279 | 1827 | | Stroud, 2015 |
| | 128 | 1336 | | Stroud, 2015 |
| *Procloeon fragile* | 168 | 472 | 6.1 | Stroud, 2015 |
| | 332 | 2110 | | Stroud, 2015 |
| | 245 | 1765 | | Stroud, 2015 |
| | | Final ACR | **6.2** | |

**Chronic Data Ranked**

| Rank | Species | SMCV mg/L |
|---|---|---|
| 4 | *Daphnia ambigua* (water flea) | 259 |
| 3 | *Procloeon fragile* (mayfly) | 248 |
| 2 | *Anafroptilum semirufum* (mayfly) | 174 |
| 1 | *Neocloeon triangulifer* (mayfly) | 157 |

| | |
|---|---|
| **FAV** | 874.8 |
| **FAV for lowest GMAV** | 698 |
| **FACR** | 6.2 |
| **CMC based on FAV for lowest GMAV** | 349 |
| **CCC** | 112.7 |

**Chloride Criteria Development**

The hardness and sulfate values used to derive the appropriate chloride criteria shall be determined by instream measurements, statewide water quality network (WQN) or other values as approved by the Department. The proposed chloride criterion is calculated using the following equations that incorporate the hardness and sulfate modifiers based on the GLEC studies:

**Acute Chloride Criterion Equation – One hour average concentration should not exceed**

$$\text{Acute Criterion (mg/L)} = \mathbf{349}(\text{Hardness})^{0.2058}(\text{Sulfate})^{-0.0745}$$

**Chronic Chloride Criterion Equation – 4 day average concentration should not exceed**

$$\text{Chronic Criterion (mg/L)} = \mathbf{113}(\text{Hardness})^{0.2058}(\text{Sulfate})^{-0.0745}$$

## Recommendation

On April 17, 2012 the EQB adopted a proposed rulemaking for the promulgation of an aquatic life criterion for chloride. Based on the comments received during the public comment period, which ended August 8, 2012, the Department, in this new proposed rulemaking has re-evaluated and incorporated Pennsylvania-specific data into the determination of the chloride criterion. The Department has developed a state-specific equation-based aquatic life criterion for chloride. It incorporates additional state-specific aquatic toxicity data, as related to the ion composition of our waterbodies, and the necessary adjustment for the effects of hardness and sulfate on the toxicity of chloride.

The Department recommends adopting the Pennsylvania-specific equation-based aquatic life criterion for chloride.

## Literature Cited

Canadian Council of Ministers of the Environment (CCME) 2011. Canadian Water Quality Guidelines : Chloride Ion. Scientific Criteria Document. Winnipeg, Canada.

Patricia L. Gillis, Feb 24, 2011. Assessing the toxicity of sodium chloride to the glochidia of freshwater mussels: Implications for salinization of surface waters. Environmental Pollution vol. 159 (2011) 1702-1708.

Iowa Department of Natural Resources. Feb 9, 2009. Water Quality Standards Review: Chloride, Sulfate, and Total Dissolved Solids. (Also available from: http://www.iowadnr.gov/portals/idnr/uploads/water/standards/ws_review.pdf)

JAMES R.F. ELPHICK, KELLI D. BERGH, and HOWARD C. BAILEY, 2010. Chronic Toxicity of Chloride to Freshwater Species: Effects of Hardness and Implications for Water Quality Guidelines. Environmental Toxicology and Chemistry, Vol. 30, No. 1, pp. 239–246, 2011.

Maryland Department of the Environment (MDE), August, 2013. Freshwater Chloride Criterion Development Methodology.

PADEP. 2002. Water quality standards implementation – chloride and sulfate (final rulemaking). Pennsylvania Bulletin, 32PaB6101.

Stephan, Charles 2007. US EPA Personal Communication, Data cl study.

Stephan, Charles. 2009. Environmental Scientist United States Environmental Protection Agency. Personal Communication

STEPHAN, C.E., D.I.MOUNT, D.J. HANSEN, J.H. GENTILE, G.A. CHAPMAN, AND W.A. BRUNGS. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. PB85-227049.

STROUD WATER RESEARCH CENTER. January 29, 2015. Ecotoxological responses of stream mayflies exposed to elevated chloride in source waters that differ in hardness. Pub Number 20140.

US EPA. 1988. Ambient water quality criteria for chloride. EPA 440/5-88-001. (available from: <http://www.epa.gov/waterscience/criteria/library/ambientwqc/chloride1988.pdf>).

US EPA. 1995. Water quality guidance for the Great Lakes system. Federal Register Vol. 60, No. 56, Pg. 15387.

US EPA. October 28, 2008. Acute Toxicity of Chloride to Select FW Invertebrates. EPA Contract Number: 68-C-04-006, Work Assignment 4-34 Sub-task 1-15. (Prepared for the USEPA by the GLEC and the INHS. http://www.dnr.mo.gov/env/wpp/rules/rir/so4-cl-GLEC-INHSchloriderpt.pdf)

US EPA. December 2010. Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses.

US EPA. 2015. Chloride Toxicity Data Set.