

**COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF ENVIRONMENTAL PROTECTION
BUREAU OF POINT AND NON-POINT SOURCE MANAGEMENT**

**RATIONALE FOR THE DEVELOPMENT OF
AMBIENT WATER QUALITY CRITERIA FOR**

CHLORIDE

PROTECTION OF AQUATIC LIFE USE

Introduction

A state-wide aquatic life criterion for chloride would provide an appropriate level of protection for all of Pennsylvania's waters. The existing chloride criterion was developed primarily for the protection of potable water supplies. Although this criterion, a maximum of 250 mg/l, may be protective of instream aquatic life uses when applied, it is not applied in all waters of the 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). Elevated levels of chloride are toxic to aquatic life in freshwater environments.

Pertinent scientific literature and historical data were reviewed and are discussed in detail in the following sections. This document presents the rationale and results of analyses conducted by the Pennsylvania Department of Environmental Protection (Department) during development of an aquatic life criterion for chloride.

Background of Chloride Criteria

The need for chloride criteria is clearly demonstrated by the characteristics of flow back water used in gas well drilling. Chloride is the dominant anion in nearly all formation waters associated with petroleum and with most conventional natural gas (Kharaka and Rice, 2004).

In addition to being conservative (by virtue of its non-volatile, non-sequestering, nonreactive property), chloride is usually present in relatively high concentrations ranging from 10,000 to 200,000 mg/l, ten to a hundred times the concentration of most inorganics and more than a million times the levels of most volatile and semivolatile organic constituents (Hays, 2009).

Characteristics of Chloride

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).

Freshwater fish and aquatic communities cannot survive in elevated concentrations of chlorides. Maintaining a proper salt-to-water balance in a fresh water environment challenges most aquatic life and, in particular, aquatic insects. Macroinvertebrates maintain an internal ionic concentration that is higher than the surrounding environment by actively transporting ions in and out of their bodies through osmoregulation (Buchwalter and Luoma 2005). Osmoregulation can be disrupted by large increases in certain ions (including chloride). This disruption in water balance and ion exchange is capable of causing stress or death to the organism (Pond, et al. 2008).

Pennsylvania River Basin Commissions -- Chloride Criteria

Pennsylvania's water quality regulations require the application of any more stringent water quality standards developed by other agencies under interstate compacts or international agreements.

The *Delaware River Basin Commission (DRBC)* has classified certain waters as special protection. According to DRBC's regulations, there shall be no measurable change in the existing water quality of special protection waters. A measurable change is defined as a statistically significant change in the concentration of pollutants. Existing water quality is defined by a set of parameters in Tables 1 and 2 of the DRBC Water Quality Regulations. All referenced median chloride levels are less than 50 mg/L.

In addition to the previously described special protection waters, DRBC has established specific aquatic life use criteria for chloride based on the naturally dilute background levels of the Delaware River for two zones (DRBC, 2008).

- **ZONE 2** is that part of the Delaware River extending from the head of tidewater at Trenton, New Jersey, R.M. (River Mile) 133.4 (Trenton-Morrisville Toll Bridge) to R.M. 108.4 below the mouth of Pennypack Creek, including the tidal portions of the tributaries thereof. **Maximum 15-day average 50 mg/l.**
- **ZONE 3** is that part of the Delaware River extending from R.M. 108.4 to R.M. 95.0 below the mouth of Big Timber Creek, including the tidal portions of the tributaries thereof. **Maximum 30-day average concentration of 180 mg/l.**

The *Ohio River Valley Water Sanitation Commission (ORSANCO)* has established human health criteria for the Ohio River main stem at 250 mg/L for chloride. The Commission has also adopted the Tier I and Tier II methodologies (ORSANCO's Pollution Control Standards, Appendix D) as the mechanisms for Great Lakes states and tribes to derive aquatic life criteria (including chloride). The Tier I methodology (eight family approach) is equivalent to the *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses*, PB85-227049 (Stephan et al., 1985). If the minimum data requirements for the Tier I methodology are not met, aquatic life values can be calculated based upon the Tier II approach, as outlined in Appendix D and the US EPA *Water Quality Guidance for the Great Lakes System* published in the Federal Register on March 23, 1995 (US EPA, 1995).

The Current National Aquatic Life Criteria for Chloride

EPA published *Ambient Water Quality Criteria for Chloride* in February 1988, which summarized the published toxicity data 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*, PB85-227049 (Stephan, et al., 1985). EPA determined the four-day and one-hour chronic and 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 current national aquatic life criterion for chloride is given here:

The Iowa
Based

The 4-day average (CCC) criterion = 230 mg/l
The 1-hour average (CMC) criterion = 860 mg/l

Equation-
Aquatic Life

Chloride Criteria

The Great Lakes Environmental Center (GLEC) in Columbus, OH and the Illinois Natural History Survey (INHS) at Champaign, IL worked collaboratively under a contract with the EPA to determine the toxicity of chloride on four freshwater invertebrate species: water flea (*Ceriodaphnia dubia*), fingernail clam (*Sphaerium simile*), planorbid snail (*Gyraulus parvus*), and tubificid worm (*Tubifex tubifex*). The toxicological results obtained using these species are applicable in Pennsylvania waters as this collection of species is representative of Pennsylvania. The research demonstrated a strong correlation between chloride toxicity and hardness. The ambient sulfate concentration was also determined to be influential on the toxic effects of the chloride, albeit notably less so than the influence from hardness. The final results of this toxicity testing were published in the report "Acute toxicity of Chloride To Select Freshwater Invertebrates, October 28, 2008". Iowa Department of Natural Resources (IDNR) selected the appropriate acute and chronic criteria equations after considering input from the EPA, Iowa's Technical Advisory Committee, and internal discussions among IDNR employees (IDNR, 2009). The equations that were promulgated by Iowa for the acute and chronic chloride criteria for the protection of aquatic life are given below. In calculating the value of the chloride criteria, the Department will use the specific hardness of the receiving stream prior to mixing with the waste discharge. Both the one-hour and ninety-six hour acute and chronic criteria values should not be exceeded more than once every three years on the average (personal communication: Connie Dou, IDNR, November 2011). Iowa adopted these criteria in 2009 and they were approved by the EPA on May 19, 2010.

$$\begin{aligned} \text{Acute criteria value (mg/L)} &= 287.8(\text{Hardness})^{0.205797}(\text{Sulfate})^{-0.07452} \\ \text{Chronic criteria value (mg/L)} &= 177.87(\text{Hardness})^{0.205797}(\text{Sulfate})^{-0.07452} \end{aligned}$$

Pennsylvania has Reconsidered Its Determination to Promulgate the 1988 Federal Aquatic Life Criteria for Chloride in Favor of the Iowa Equation-Based Criteria

The EQB adopted a proposed rulemaking for the promulgation of the current national aquatic life criteria for chloride at its March 16, 2010 meeting. The Department recommended adopting the current national aquatic life criteria (230 mg/L = chronic; 860 mg/L = acute) for chloride. The proposed rulemaking was published at 40 Pa.B. 2264 (May 1, 2010) with a comment period that closed on June 15, 2010.

Prior to proposing the current national aquatic life criteria (USEPA, 1988), Pennsylvania DEP had considered several options in the determination of the most appropriate aquatic life criteria for chloride, including the equation-based aquatic life criteria for chloride that was successfully promulgated by Iowa and has since been approved by the EPA. The federal approval of Iowa's standard occurred during the public comment period on Pennsylvania's proposal for the 1988 federal aquatic life criteria.

The Department has reviewed the equation-based aquatic life criteria for chloride as developed by EPA and successfully implemented in Iowa. The Department recommends adopting the Iowa equation-based aquatic life criteria for chloride.

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