EVALUATION OF WATER QUALITY CRITERIA FOR AQUATIC LIFE USE PROTECTION

CHLORIDE

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 in-stream 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.

A state-wide aquatic life criterion for chloride would provide an appropriate level of protection for all of Pennsylvania's waters and would circumvent the difficulties associated with the implementation of the current osmotic pressure (OP) criterion. The existing chloride criterion was developed primarily for the protection of potable water supplies. Although this criterion 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. Therefore, the Department is recommending additional chloride criteria to be applied in all waters for the protection of aquatic life. The current potable water supply (PWS) criterion for chloride is included in Table 3 at 25 Pa. Code § 93.7 (relating to specific water quality criteria), and reads as follows:

§ 93.7. Specific water quality criteria.
(a) Table 3 displays specific water quality criteria and associated critical uses. The criteria associated with the Statewide water uses listed in § 93.4, Table 2 apply to all surface waters, unless a specific exception is indicated in § § 93.9a—93.9z. Other specific water quality criteria apply to surface waters as specified in § § 93.9a—93.9z. All applicable criteria shall be applied in accordance with this chapter, Chapter 96 (relating to water quality standards implementation) and other applicable State and Federal laws and regulations.

TABLE 3

Parameter	*Symbol*	*Criteria*	*Critical Use**
		**********	
Chloride	Ch	Maximum 250 mg/l.	PWS
		**********	

*Critical Use: The designated or existing use the criteria are designed to protect. More stringent site-specific criteria may be developed to protect other more sensitive, intervening uses.

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

Pennsylvania's current criterion for chloride dates back to 1967, when the Sanitary Water Board (a predecessor of the Department) included it to prevent objectionable taste and odor in drinking water, based on recommendations in the United States Public Health Service (US PHS) Drinking Water Standards of 1962. The US PHS recommended that chloride should not exceed 250 mg/L in the water supply where other more suitable supplies were or could be made available. The limits were influenced primarily by considerations of taste. The Environmental Protection Agency's (EPA) Secondary Maximum Contaminant Levels (SMCL's) under the Federal Safe Drinking Water Act, which became effective in 1979, are set at the same 250 mg/L level. The Commonwealth's drinking water program incorporated the Federal standards into Chapter 109 (relating to safe drinking water).

In 1985, Chapter 93 was amended to provide for an exception to the statewide application of water quality criteria at all points instream after mixing for four parameters: total dissolved solids, fluoride, nitrite-nitrate and phenolics (PADER, 1985). As a result, the point of application of these criteria was moved to existing or planned surface potable water supply withdrawals. Amendments adopted on November 18, 2000, through the Regulatory Basics Initiative (RBI) triennial review, moved the provision, without change, to § 96.3(d) (relating to water quality protection requirements) of the newly created Chapter 96 (relating to water quality standards implementation) (PADEP, 2000). Chloride and sulfate were added on December 14, 2002 so that there are now six exceptions to the statewide application of water quality criteria (PADEP, 2002). The 250 mg/L potable water supply (PWS) standard for chloride is applicable only at the point of all existing or planned surface potable water supply withdrawals, unless otherwise specified. The 250 mg/L PWS chloride criterion value for Pennsylvania remained unchanged throughout this process.

The movement of the compliance point for total dissolved solids (TDS), chloride and sulfate criteria to the point of water supply intake was not expected to be detrimental to aquatic life because the statewide surface water criterion for osmotic pressure (OP = 50 mOsm/kg) was applied to protect aquatic life from the adverse effects of these other parameters throughout the waterbody. Unfortunately, there have been problems with the implementation of the Osmotic Pressure (OP) criterion. Most notably, OP is a measure of pressure, and, as such, it is not well suited to the mass-balance approach used to calculate Water Quality-Based Effluent Limitation (WQBELs). Additionally OP can only be evaluated at a single discharge point, which does not account for the cumulative loads of dissolved constituents added to a stream from multiple sources. Finally, limited

available laboratory capabilities for analysis of osmotic pressure adversely affect compliance monitoring.

TDS includes inorganic salts, organic matter and other dissolved materials in water. They can be naturally present in water or the result of mining or some industrial or municipal treatment of water. TDS contain minerals and organic molecules that provide benefits such as nutrients, but also may contain contaminants such as toxic metals and organic pollutants. The concentration and composition of TDS in natural waters is determined by the geology of the drainage, atmospheric precipitation and the water balance (evaporation/precipitation).

TDS cause toxicity through increases in salinity, changes in the ionic composition of the water, and toxicity of individual ions. The composition of specific ions determines toxicity of elevated TDS in natural waters. Also, as the hardness increases, TDS toxicity may decrease. The major concern associated with high TDS concentrations relates to direct effects of increased salinity on the health of aquatic organisms.

Chlorides and Sulfates can be a significant source of TDS in wastewater discharges. During the fall of 2008, water quality issues related to these parameters emerged in the Monongahela River basin. While river flows reached seasonal lows, the concentrations of TDS and sulfates in the river increased to historic highs, exceeding the water quality standards at all of the seventeen Potable Water Supply (PWS) intakes from the border with West Virginia to Pittsburgh. Violations of water quality standards for TDS and Sulfates persisted in the river through November and December of 2008. Elevated Chloride levels were also observed in the Monongahela and at least one major tributary – South Fork Tenmile Creek. This sequence of events identifies a need to establish a chloride criterion for the protection of aquatic life at all locations on Pennsylvania surface waters.

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. These special protection waters received this designation because they have exceptionally high scenic, recreational, ecological, and/or water supply value. Special protection waters can either be classified as Outstanding Basin Waters or Significant Resource Waters. 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. Following is a list of the special protection waters from the DRBC Water Quality Regulations (3.10.3.A.2.g) (DRBC, 2008):

g. Classified Special Protection Waters
1) The following stream reaches are classified as Outstanding Basin Waters:
(a) The Upper Delaware Scenic and Recreational River (Delaware River between River Mile 330.7 and 258.4);
(b) Those portions of intrastate tributaries located within the established boundary of the Upper Delaware Scenic and Recreational River Corridor;
(c) The Middle Delaware Scenic and Recreational River (Delaware River between River Miles 250.1 and 209.5);
(d) Those portions of tributaries located within the established boundary of the Delaware Water Gap National Recreation Area.

2) The following stream reaches are classified as Significant Resource Waters:
(a) The Delaware River between River Miles 258.4 (the downstream boundary of the Upper Delaware Scenic and Recreational River) and 250.1 (the upstream boundary of the Delaware Water Gap National Recreation Area);
(b) The Lower Delaware River between River Miles 209.5 (the downstream boundary of the Delaware Water Gap National Recreation Area) and 134.34 (the Calhoun Street Bridge near the Head of Tide at Trenton, NJ).

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 ***Susquehanna River Basin Commission (SRBC), Interstate Commission on the Potomac River Basin (ICPRB)*** and the ***Great Lakes Commission (GLC)*** do not maintain or develop specific water quality criteria, and have not adopted chloride criteria for the protection of aquatic life.

The Great Lakes Water Quality Agreement, 1978 (GLWQA) is an international agreement between the United States and Canada that was first signed in 1972 and renewed in 1978. The GLWQA expresses the commitment of each country to restore and maintain the chemical, physical and biological integrity of the Great Lakes Basin Ecosystem and includes a number of objectives and guidelines, including water quality criteria to achieve these goals. This agreement is administered by the International Joint Commission (IJC), and by Pennsylvania's Office of the Great Lakes for the Commonwealth's portion of Lake Erie. Although the GLWQA does not contain specific chloride criteria for the protection of aquatic life, as described earlier and as adopted by ORSANCO, there are provisions to develop aquatic life criteria using the EPA Great Lakes Tier II approach. This approach could be used to develop site-specific chloride criteria for waters within the Great Lakes System, and may be applicable for other waters throughout the Commonwealth.

Discussion / Rationale for Chloride Criteria

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

The Department has reviewed the EPA ambient water quality criteria development document for chloride and agrees with the data analysis, interpretation, and methods used to develop the criteria. The Department recommends adopting these national chloride criteria for protection of aquatic life. Much research has been conducted subsequent to the US EPA 1988 national recommendation that continues to indicate the need for an aquatic life criterion for chloride. Scientists at the US EPA are currently conducting research to determine if the national criterion for chloride should be updated. The Department recommends adopting this current national aquatic life criteria (230 mg/L = chronic; 860 mg/L = acute) for chloride until new national aquatic life criteria are available for consideration.

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