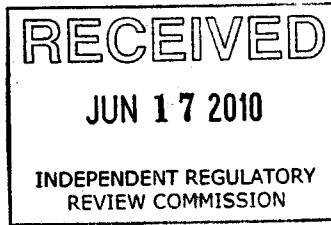




# University of Pittsburgh

*School of Law  
Environmental Law Clinic*

2841



(Use This Address for U.S. Mail)  
P.O. Box 7226  
Pittsburgh, PA 15213-0221

210 South Bouquet Street  
Sennott Square - Room 5207  
Pittsburgh, Pennsylvania 15260  
412-648-1300  
Fax: 412-648-1992

**Summary of Comments regarding the Chapter 93 Ambient Water Quality Criterion; Chloride (Ch) proposal, noticed in the May 1 2010 Pennsylvania Bulletin, submitted by The University of Pittsburgh Environmental Law Clinic, on behalf of our client, Clean Water Action, joined by the Sierra Club, Earthjustice, the Three Rivers Waterkeeper, the Delaware Riverkeeper Network, and the Pennsylvania Council of Trout Unlimited**

Overall, we support the adoption of revised water quality criteria for chloride to adequately protect aquatic life in Pennsylvania. However, we have a number of concerns with the proposed criteria. Our comment addresses the following concerns:

- DEP has the authority to adopt water quality criteria more stringent than the federal guidelines, and is obligated to consider "the state of scientific and technical knowledge" when making such determinations;
- The 1988 EPA criteria is based on outdated scientific data and methodologies;
- Adopting a set of criteria that would apply to all aquatic life uses fails to adequately protect those four aquatic life uses as defined in 25 PA. Code § 93.3 (2009);
- There is a need for more chronic exposure studies and for studies that reflect Pennsylvania's particular aquatic life;
- The majority of chloride criteria were developed using data on NaCl toxicity, which is the least toxic salt. However, continued Marcellus Shale exploration will expose Pennsylvania waters to more toxic salts, such as MgCl, KCl, and CaCl;
- The increasing Marcellus Shale industry activity will produce wastewater that will contribute high levels of chloride to streams and groundwater;
- The Commonwealth has already witnessed the devastating effect of high chloride concentrations on aquatic life, such as the Dunkard Creek kill;

In light of the legal requirement to protect all aquatic life uses by utilizing the most current science, implementing the British Columbia approach and criteria values is the only way to compensate for some gaps in the scientific knowledge and still ensure the protection of Pennsylvania's aquatic life uses. This conservative approach compensates for the lack of scientific data while still adequately considering the state of scientific knowledge and protecting all four aquatic life uses, but the Department must still work to fill in the gaps of scientific knowledge about chloride's impacts on aquatic life. The Department should address the imminent need for good criteria now by adopting the British Columbia values, and should move immediately to gather better toxicology data--especially on chronic exposures--and a better understanding of the effects of environmental variables like temperature and ion mixtures on chloride toxicity so that, at the next opportunity, the Department will be prepared to update the science, propose an even better set of criteria to protect aquatic life uses, and act as a leader in the field.



# University of Pittsburgh

*School of Law*  
*Environmental Law Clinic*

(Use This Address for U.S. Mail)  
P.O. Box 7226  
Pittsburgh, PA 15213-0221

210 South Bouquet Street  
Sennott Square - Room 5207  
Pittsburgh, Pennsylvania 15260  
412-648-1300  
Fax: 412-648-1992

June 15, 2010

Environmental Quality Board  
P.O. Box 8477  
Harrisburg, PA 17105-8477  
[RegComments@state.pa.us](mailto:RegComments@state.pa.us)

**Re: Chapter 93 Ambient Water Quality Criterion; Chloride (Ch)**

Dear Environmental Quality Board members,

Thank you for the opportunity to comment on the proposed revisions to Chapter 93 of the Pennsylvania Code noticed in the May 1, 2010 edition of the Pennsylvania Bulletin. The University of Pittsburgh Environmental Law Clinic respectfully submits these comments on behalf of our client, Clean Water Action, joined by the Sierra Club, Earthjustice, the Three Rivers Waterkeeper, the Delaware Riverkeeper Network, and the Pennsylvania Council of Trout Unlimited. Collectively, we commend the Environmental Quality Board (the "EQB" or the "Board") for recognizing the need to adopt revised water quality criteria for chloride that will protect aquatic life in Pennsylvania, and we strongly support the amendment of Chapter 93 to achieve that purpose.

However, the Board's proposal to adopt chloride criteria that are more than two decades old ("Proposed Chloride Criteria") is far weaker than the science and the law require. There are two major categories of problems with the Board's Proposed Chloride Criteria. **First**, since 1988, when the federal Environmental Protection Agency ("EPA") proposed its chloride criteria guidelines (the "1988 EPA Criteria"), which the Board has proposed to adopt unaltered, there have been significant new scientific studies about the toxicity of chloride and its effects on aquatic life, including some more recent studies by EPA. These studies not only offer more reliable data and more appropriate methodologies, but also reveal errors in the development of the 1988 EPA Criteria. **Second**, the 1988 EPA Criteria were not designed to account for Pennsylvania's water quality regulatory scheme or its characteristic aquatic life communities and chloride sources, and the Board's uncritical adoption of those standards necessarily replicates

those problems. The Proposed Chloride Criteria do not account for the fact that, with respect to water quality standards, Pennsylvania designates four categories of aquatic life as critical uses (cold water fishes, warm water fishes, trout stocking fishes, migratory fishes), each of which deserves distinct chloride criteria values. The Proposed Chloride Criteria do not account for the stream ecology of the Commonwealth, which consists of distinct aquatic life communities and stream parameters. Also, the Proposed Chloride Criteria do not account for those chloride sources that are especially significant to Pennsylvania (and adjacent states) such as wastewaters from Marcellus Shale development. Chloride criteria more stringent than the federal minima are amply justified by the need to protect Pennsylvania's aquatic life from elevated and more toxic species of chloride from gas development wastewaters.

Drawing upon the expertise of the Stroud Water Research Center (the "Stroud Center"), this comment, based on an expert report from the Stroud Center, recommends that the Board use different criteria development methodologies to set different criteria values that would actually protect all four aquatic life uses in Pennsylvania in accordance with the law, and we recommend that the Board act quickly to adopt more protective chloride criteria.

**I. The Stroud Water Research Center provides expert support for this comment.**

Clean Water Action, along with the University of Pittsburgh Environmental Law Clinic, Earthjustice, the Three Rivers Waterkeeper, the Sierra Club, the Delaware Riverkeeper Network, and the Pennsylvania Council of Trout Unlimited jointly retained the Stroud Center to evaluate whether the Proposed Chloride Criteria are adequately protective of aquatic life uses in Pennsylvania. The Stroud Center's expert report (the "Stroud Report"), which is annexed hereto as Appendix A, finds flaws with the 1988 EPA Criteria, evaluates alternative criteria values and criteria development methodologies, and recommends that the EQB propose chloride criteria that are different from the 1988 EPA Criteria and that are adequately protective of aquatic life uses in Pennsylvania in accordance with the law.

The Stroud Center is an internationally recognized research facility, specializing in the examination of the physical, chemical, and biological processes of streams and rivers, the life history of organisms, and the ecology of watersheds. The Stroud Center is staffed by experts in the fields of chemistry, microbial ecology, invertebrate biology, watershed ecology, and ecosystem modeling.

The scientists who prepared the appended expert report are nationally and internationally recognized as experts in the field. Those scientists are:

**Dr. David B. Arscott**, who is the Assistant Director and a Research Scientist at Stroud, specializes in aquatic invertebrate ecology, water resource monitoring program development, tropical river ecology, riparian and wetland ecology, ecohydrology, landscape ecology, and surface-groundwater interactions. He has published a large volume of scholarship on various topics within his field, including: the development of river flow ecology; molecular tracers of soot and sewage contamination; the relationship of major ions and nutrients to watershed conditions across a mixed-use, water-supply watershed; and riverine landscape diversity.

**Dr. John K. Jackson** serves as a Senior Research Scientist at Stroud. He has produced significant scholarship in the areas of sequential decision plans, benthic macroinvertebrates, and biological monitoring; climatic change and the life histories and biogeography of aquatic insects in eastern North America; freshwater biomonitoring and benthic macroinvertebrates; and the transport of *B.t.i.* and its effect on drift and benthic densities of nontarget macroinvertebrates in the Susquehanna River.

**Dr. William Eldridge**, an Assistant Research Scientist at Stroud, serves as the Principal Investigator of the Fish Molecular Ecology Division. His research and scholarship examines population viability of Chinook salmon following harvest selection; Fst interpretation, a measure of genetic distance; genetic diversity over multiple generations of supplementation: an example from Chinook salmon using microsatellite and demographic data; and long-term effects of translocation and release numbers on fine scale population structure among coho salmon (*Onchorhynchus kisutch*).

The Stroud Center evaluated various sets of chloride criteria in the U.S. and Canada; examined the available data and studies; and made several important observations, including:

- There is a paucity of studies on chronic, long-term exposures of aquatic life to chloride. Without more information on chronic exposures, setting an adequately protective chronic criterion is difficult.
- Taxa selection in toxicology studies is a major factor in good criteria development. Stroud notes that numerous studies utilized by the 1988 EPA Criteria were not truly random and did not include particularly sensitive species, yielding less protective criteria values.
- The majority of chloride criteria are dominated by data on NaCl toxicity, which is the least toxic salt. Such data does not represent well the contribution of more toxic non-NaCl salts from activities related to the coalbed methane and Marcellus natural gas industries.

- Without toxicology studies that are based on Pennsylvania's aquatic life and without a serious consideration of the role of temperature, it will be difficult to protect all four aquatic life uses in the Commonwealth (coldwater fishes, warmwater fishes, trout stocking, migratory fishes).
- The 1988 EPA Criteria are based on outdated data and methodologies.
- Various criteria development methodologies, like Iowa's and British Columbia's, have desirable elements that could yield better criteria than the 1988 EPA Criteria.

Stroud notes that since publication of the 1988 EPA Criteria, more data and methodologies have become available for use in developing criteria. At the same time, Stroud also notes that there are still studies to be done (for, e.g., chronic exposure and exposure to multiple salts), methodological considerations to be evaluated (for, e.g., better taxa selection for toxicology studies), and data to be collected. In light of the legal requirement to protect aquatic life uses by utilizing the most current science, Stroud concluded that the only way to compensate for some gaps in the scientific knowledge about chloride's impacts on Pennsylvania's aquatic life would be to propose the conservative approach implemented by British Columbia.

We incorporate the Stroud Report in this comment by reference.

## **II. The Board has the authority to adopt water quality criteria more stringent than those of the federal government.**

The EQB has the authority and duty to "formulate, adopt, and promulgate such rules and regulations as may be determined by the board for the proper performance of the work of the department [of environmental protection]..." 71 P.S. § 510-20(b). The Department of Environmental Protection ("DEP" or "Department") has the power to develop reasonable regulations implementing the stated policy of the Clean Streams Law, which provides that "[w]henver the department finds that any activity... creates a danger of pollution of the waters of the Commonwealth or that regulation of the activity is necessary to avoid such pollution, the department may... establish the conditions under which such activity shall be conducted..." 35 P.S. §§ 691.5(b)(1), 691.402 (2009). The conditions that the Department deems necessary to prevent water pollution and thereby to implement the provisions of the Clean Streams Law "become the rules and regulations of the department" upon adoption by the Board. 71 P.S. § 510-20(b); *see Dep't of Env'tl. Protection v. North American Refractories Co.*, 791 A.2d 461, 462 (Pa. Cmwlth. 2002).

Section 303(c) of the federal Clean Water Act requires states to submit newly adopted water quality standards to EPA for approval. 33 U.S.C. § 1313(c). EPA evaluates proposed water quality standards, such as the proposed chloride criteria, for consistency

with the requirements of the CWA. *Id.* § 1313(c)(3). A water quality standard should “provide water quality for the protection and propagation of fish, shellfish and wildlife and for recreation in and on the water and take into consideration their use and value of public water supplies, propagation of fish, shellfish, and wildlife, recreation in and on the water, and agricultural, industrial, and other purposes including navigation.” 40 C.F.R. § 131.2. Pennsylvania protects four aquatic life uses: cold water fishes (CWF); warm water fishes (WWF); migratory fishes (MF), and trout stocking (TSF). 25 Pa. Code § 93.3 (2009).

Section 304(a) of the CWA requires EPA to develop and publish water quality criteria that reflect the latest scientific knowledge “on the relationship that the effect of a constituent concentration has on particular aquatic species and/or human health.” 33 U.S.C. § 1314(a), 40 C.F.R. § 131.3(c). Water quality criteria comprise elements of state water quality standards and are expressed as constituent concentrations, levels, or narrative statements, representing a quality of water that supports a particular use. 40 C.F.R. § 131.3(b). Federal criteria are developed for the purpose of giving states guidance on developing the proper criteria to protect their waters. *Id.* § 131.3(c). Each aquatic life criterion consists of two components, which EPA defines as a criterion maximum concentration (CMC) for acute protection and a criterion continuous concentration (CCC) for chronic protection.<sup>1</sup> In Pennsylvania, each component is further defined in terms of magnitude, duration, and the maximum desired frequency of occurrence. 25 Pa. Code § 16.21.

DEP is free to adopt regulations that are more protective than federal standards. The Clean Streams Law empowers DEP to adopt regulations “as may be deemed necessary for the protection of the purity of the waters of the Commonwealth, or parts thereof, and to purify those now polluted, and to assure the proper and practical operation and maintenance of treatment works approved by it.” 35 P.S. § 691.304 (2009). The federal Clean Water Act specifically allows states to adopt and enforce “any standard or limitation respecting discharges of pollutants” or any other requirement to control pollution as long as the state rules are not “less stringent than the effluent limitation, or other limitation, effluent standard, prohibition, pretreatment standard, or standard of performance under [chapter 26]....” 33 U.S.C. § 1370(1) (2010).

### **III. Pennsylvania law requires protection of four distinct aquatic life uses.**

Whenever the Board proposes new water quality criteria, it must consider the Clean Streams Law prohibition against the introduction of pollutants that cause harm to “uses,” such as the aquatic life use of Commonwealth waters, in light of the current state

---

<sup>1</sup> EPA, WATER QUALITY HANDBOOK §3.1.2 (“Criteria for Aquatic Life Protection”) (last updated on Friday, November 9, 2009), available at <http://www.epa.gov/waterscience/standards/handbook/>.

of scientific knowledge on the impacts to such uses. *See* 35 P.S. § 691.1 (defining “pollution” as “contamination of any waters of the Commonwealth such as will create or is likely to create a nuisance or to render such waters harmful, detrimental or injurious to...uses, including...fish or other aquatic life, including but not limited to such contamination by alteration of the physical, chemical or biological properties of such waters”); *see also* 35 P.S. § 691.5(a)(4) (requiring consideration of the state of scientific knowledge in adopting rules and regulations). Section 93.3 of Title 25 of the Pennsylvania Administrative Code defines the protected water uses for the Commonwealth, which includes the aquatic life protected use. The Clean Streams Law does not define the term “aquatic life use,” so the agency has defined it as comprising four distinct uses: CWF, WWF, MF, and TSF.<sup>2</sup> There is no definition of aquatic life use that is independent of the four uses listed in Table 1 of section 93.3. The Commonwealth, therefore, must adopt acute and chronic criteria values for chloride that are specifically protective of those four aquatic life uses. Pennsylvania has already recognized the unique composition of each of these four aquatic ecosystems, and has accordingly set distinct water quality criteria values for dissolved oxygen and temperature that correspond to each use.<sup>3</sup>

There is a demonstrated correlation between temperature and chloride toxicity. The Stroud Center reviewed research that evaluated the relationship between NaCl and temperature on chironomid survival. The study concluded that chironomid survivals increased as temperatures decreased. The Stroud Report notes that “[a]s temperature increased, salt appeared to have an increasingly negative effect at decreasing concentrations, until at 22°C, any amount of salt depressed survival significantly.”<sup>4</sup>

Since Pennsylvania has already recognized that water bodies with specific protected aquatic life uses must maintain certain temperatures to support their ecosystems, and sound science supports a correlation between temperature and chloride, the Commonwealth must assign acute and chronic criteria values that adequately protect each individual aquatic life use.

In addition to temperature, the selection of certain species when conducting toxicology studies during the criteria development phase factors into the protection of different aquatic life uses. For example, the Stroud Report states that when developing criteria values for CWF and TSF streams, studies that include the more chloride-tolerant *Daphnia* species are not justified because they may expose rainbow trout to chloride concentrations that approach chronic levels.<sup>5</sup>

---

<sup>2</sup> 25 PA. CODE §93.3 (2009).

<sup>3</sup> *See* 25 PA CODE §93.7 (2009).

<sup>4</sup> Stroud Report at 17.

<sup>5</sup> *Id* at 20.

In other states with similar sets of aquatic life uses, the agencies have developed numerical water quality criteria that vary with different aquatic life uses. The following table consists of examples of states that have set use-specific criteria in correlation with their aquatic life designations.<sup>6</sup> In Iowa, for example, for each one-tenth change in pH, there is a different allowance of ammonia for the different cold water aquatic life types and the warm water aquatic life types. For example, at a pH level of 6.5, the acute criterion levels of ammonia are 48.8 (WW-1, WW-2, WW-3) and 32.6 (CW-1, CW-2). Determination of the chronic criterion is dependent upon both pH and temperature (in °C) and whether or not there are early life stages present.

State	Regulated Toxic	Aquatic life use designations/amount permitted
Nebraska <sup>7</sup>	Ammonia and metal/inorganics	Warmwater class A; warmwater class B; coldwater class A; coldwater class B
Ohio <sup>8</sup>	Ammonia, chlorine, pH	Exceptional warmwater; warmwater; limited warmwater; modified warmwater; seasonal salmonid; coldwater; limited resource water
Maine <sup>9</sup>	Bacteria	Class AA waters (as naturally occurs); Class A waters (as naturally occurs); Class B waters (64/100 ml(g.m.*) or 427/100 ml(inst.*); Class C waters (142/100 ml (g.m.*) or 949/100 ml (inst.*))
Arizona <sup>10</sup>	Suspended sediment	Aquatic and wildlife coldwater (80mg/L); aquatic and wildlife warmwater (80 mg/L); aquatic and wildlife ephemeral (no standard); aquatic and wildlife effluent-dependent (no standard)
Idaho <sup>11</sup>	Ammonia	Cold water; salmonid spawning; seasonal coldwater; warm water; modified
Kentucky <sup>12</sup>	Alkalinity	Cold water aquatic life; warm water aquatic life
Iowa <sup>13</sup>	Ammonia and other toxics	Cold Water aquatic life, type 1 (CW-1); Cold Water Aquatic Life, type 2 (CW-2); Warm water aquatic life, type 1 (WW-1); Warm water aquatic life, type 2 (WW-2); Warm water aquatic life, type 3 (WW-3)

\* g.m., geometric mean; inst., instantaneous level

<sup>6</sup> MEC Water Resources, Inc., *Review of Aquatic Life Use Designations for Select States* (Apr. 2008), available at [www.erc-env.org/Review of Aquatic Life Use Designations for Selected States\\_Final.pdf](http://www.erc-env.org/Review%20of%20Aquatic%20Life%20Use%20Designations%20for%20Selected%20States_Final.pdf) (appended hereto as Appendix B).

<sup>7</sup> 117 NEB. ADMIN CODE Ch. 4 §003.02B2a(2)(b) (2009).

<sup>8</sup> OHIO ADMIN. CODE 3745-1-01

<sup>9</sup> 38 ME. REV. STAT. ANN 465

<sup>10</sup> ARIZ. ADMIN. CODE R18-11-109.

<sup>11</sup> IDAHO ADMIN. CODE r. 58.01.02.250

<sup>12</sup> 401 KY. ADMIN. REGS. 10:031

<sup>13</sup> IOWA ADMIN.CODE 567-61.2(455B).



These examples demonstrate the feasibility of establishing numeric criteria specific to each aquatic life use. There is nothing about chloride that suggests a different approach.

In developing the 1988 EPA Criteria, the federal government did not consider the four-part aquatic life use scheme that Pennsylvania uses today. However, federal regulations specifically allow states to “adopt sub-categories of a use **and set the appropriate criteria to reflect varying needs of such sub-categories of uses, for instance, to differentiate between cold water and warm water fisheries.**” 40 C.F.R. § 131.10(c) (emphasis added). The EPA’s 1985 Handbook also encourages the development of use-specific criteria. The Handbook expressly states in the section on aquatic life designated uses that “[i]f subcategories of [aquatic life designated use] are adopted (e.g. to differentiate between coldwater and warmwater fisheries), then appropriate criteria should be set to reflect the varying needs of such subcategories.”<sup>14</sup> The table above demonstrates a series of states that have set appropriate criteria to reflect varying needs of multiple aquatic life uses; Pennsylvania, with respect to dissolved oxygen, has also adopted criteria specific to multiple aquatic life uses.<sup>15</sup>

If the Board believes that the 1988 EPA Criteria are sufficient, it must explain why, given that the 1988 EPA Criteria do not correspond to different aquatic life uses. Because EPA did not have Pennsylvania’s aquatic life uses in mind, and because the Stroud Report points out the flaws in the toxicology studies used in 1988 and the absence of consideration for temperature’s effects on chloride, the Board should address the lack of adequate protection for multiple aquatic life uses in one of two ways. After accounting for the varying degrees of chloride toxicity in CWF, WWF, TS and MF waters, the Board should either choose the lowest, most protective criteria values and apply them to all the aquatic life uses, or it should choose criteria values that correspond, based on the current science, to each aquatic life use. Anything less will not adequately protect all critical uses as required by law.

#### **IV. Both EPA and DEP must consider current science in developing water quality criteria.**

The Board is required to exercise sound judgment and discretion when implementing a declaration of policy, or when adopting rules and regulations. 35 P.S. § 691.5(a). When proposing water quality criteria, the Board must consider the following five factors:

- (1) Water quality management and pollution control in the watershed as a whole;

---

<sup>14</sup> EPA, WATER QUALITY HANDBOOK §3.2.2 (“Aquatic Life”) (last updated on Friday, November 9, 2009).

<sup>15</sup> 25 PA CODE § 93.7 (Table 3, setting different sets of dissolved oxygen levels for TSF, WWF and HQ-CWF).

- (2) The present and possible future uses of particular waters;
- (3) The feasibility of combined or joint treatment facilities;
- (4) **The state of scientific and technological knowledge;**
- (5) The immediate and long-range economic impact upon the Commonwealth and its citizens.

*Id.* (emphasis added). The Department's regulations acknowledge that it may develop criteria for any substance not already included in the table of specific water quality criteria and associated critical uses that "is determined to be inimical or injurious to existing or designated water uses using the best available scientific information, as determined by the Department." 25 Pa. Code § 93.7(c).

The criteria development standards used by the federal agency in its Water Quality Handbook to ensure that a sound scientific rationale exists for the federal minimum criteria are also used during Pennsylvania's development of criteria.<sup>16</sup> Under the federal scheme, chloride is a nonconventional pollutant because it is neither a conventional nor a toxic pollutant.<sup>17</sup> 33 U.S.C. 1311(b)(2)(F). Chapter 3.4.2 of the Water Quality Handbook is entitled *Criteria for Nonconventional Pollutants*. It states in part that:

Criteria requirements applicable to toxicants that are not priority toxic pollutants (e.g. ammonia and chlorine), are specified in the 1983 Water Quality Standards Regulation (see 40 CFR 131.11). Under these requirements, States must adopt criteria based on sound scientific rationale that cover sufficient parameters to protect designated uses.

The relevant federal regulation, which embodies the policy stated in the Handbook, provides:

States must adopt those water quality criteria that protect the designated use. **Such criteria must be based on sound scientific rationale and must contain sufficient parameters or constituents to protect the designated**

---

<sup>16</sup> Phone conversation with DEP Attorney Tom Barron (Attorney, Div. of Water Quality Standards, Pennsylvania Dept. of Environmental Protection) (Monday, June 7 2010). Mr. Barron said that when the Commonwealth proposes water quality criteria that are identical to the federal guideline criteria, then the relevant federal criteria development standards apply.

<sup>17</sup> Under the federal scheme, there is a distinct set of criteria development standards that apply to conventional and toxic pollutants, and also to nonconventional pollutants like chloride. Currently, the DEP has no separate criteria development scheme for nonconventional pollutants, despite the fact that the term is defined in section 92.1 of Title 25 of the Pennsylvania Code ("a pollutant which is not a conventional or toxic pollutant"). The DEP should express clearly that when proposing criteria identical to those provided by the federal government, the applicable criteria development standards from the Clean Water Act would apply unless there are already Pennsylvania standards in place. In this case, because of the absence of a Pennsylvania regulatory scheme that governs nonconventional pollutants like chloride, the federal standards apply, but that is not stated anywhere in the DEP literature.

**use.** For waters with multiple use designations, the criteria shall support the most sensitive use.

40 C.F.R. § 131.11 (emphasis added). Federal regulations and the 1988 EPA Criteria documents specifically authorize states to use a range of scientifically defensible methods in establishing water quality criteria, including the adjustment of national criteria to reflect site-specific information.<sup>18</sup>

In 1988, EPA published a 304(a) criteria document entitled "Ambient Water Quality Criteria for Chloride – 1988." EPA 440-5-88-001. Under these federal criteria, levels of chloride at a minimum should be kept to an acute level of 860 mg/l and to a chronic level of 230 mg/l. EPA's water quality criteria represent the floor for state requirements. The 1988 EPA Criteria recognize, however, that "in many situations States might want to adjust water quality criteria developed under Section 304 to reflect local environmental conditions and human exposure patterns before incorporation into quality standards."<sup>19</sup> The Board must adjust the federal water quality criteria for chloride to address the four aquatic uses designated by Pennsylvania law and, in doing so, should ensure that proposed revisions to Chapter 93 accommodate local conditions in the Commonwealth consistently with the best available science.

#### **A. The current state of science does not support the 1988 EPA Criteria.**

Since 1988, the science on chloride toxicity has changed dramatically. Significant flaws are now apparent in the 1988 EPA Criteria studies, and more recent studies have been published in peer-reviewed literature that the Board must consider in determining the appropriate chloride criteria for Pennsylvania. As the Stroud Report demonstrates, EPA did not have the benefit of new toxicity studies or criteria development methodologies and did not adequately appreciate the need for safety factors for both acute and chronic criteria. In addition, EPA did not account for the synergistic effects of hardness, sulfate levels, or temperature, despite their well-documented influence on chloride toxicity.

Moreover, EPA repeatedly has admitted the shortcomings of the 1988 EPA Criteria. In 2003, the EPA published a document entitled "Draft Strategy: Proposed Revisions to the 'Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses.'" That document declares the need to rethink the 1985 water quality criteria development guidelines that were used to arrive

---

<sup>18</sup> 40 C.F.R. § 131.11(b); EPA, 1988 *Ambient Water Quality Criteria for Chloride – 1988*, EPA 440/5-88-001, pg 009.

<sup>19</sup> EPA, 1988 *Ambient Water Quality Criteria for Chloride – 1988*, EPA 440/5-88-001.

at the 1988 EPA Criteria.<sup>20</sup> Recently, EPA worked with at least one other state, Iowa, to assist in the development of better chloride criteria that more adequately protect aquatic life. In 2009, Charles Stephan, the scientist responsible for reviewing the chloride toxicology studies for EPA in 1985 and 1988, admitted that some of the studies used to develop the 1988 EPA Criteria are no longer reliable.<sup>21</sup> Whatever scientific value the 1988 EPA Criteria had in 1988, they no longer retain that value in 2010. Therefore, the Board may not simply adopt those criteria for future use in Pennsylvania.

**B. The current state of science requires that conditions specific to Pennsylvania be taken into account in developing chloride criteria**

Because of Pennsylvania's aquatic ecology and the various sources of chloride in the Commonwealth, any attempt to develop chloride criteria that protect the four aquatic life uses must consider a number of factors that were not considered by EPA in 1988. Only by considering the following factors would EQB be considering the state of scientific knowledge in 2010 and basing its criteria on sound scientific grounds:

*Non-NaCl salts and ion synergies due to Marcellus activities.*

When examining the 1988 EPA Criteria, the Stroud Center noted that although the EPA conceded that salts other than NaCl, (such as MgCl, KCl, and CaCl) might have more adverse effects on aquatic organisms, the EPA restricted itself to studies that evaluated only NaCl's impact. That limitation is especially relevant in Pennsylvania, where the Marcellus Shale wastewaters contain disproportionately high amounts of non-NaCl salts such as MgCl, CaCl, and KCl.<sup>22</sup> Not only are those non-NaCl salts often more toxic to aquatic life than is NaCl, they can react in solution in a manner that impacts the toxicity of chloride. Because the volume of Marcellus wastewaters is predicted to rise significantly in the next decade, and because there now is some science available on the toxicity of non-NaCl salts, EQB must take into account the contribution of the full range of chlorides from the Marcellus Shale activities.

*The relationship between chloride loadings in groundwater and chloride impairment in hydrologically connected surface waters.*

The United States Geological Survey authored a detailed report that evaluated the relationship between groundwater and surface water with respect to chloride levels.<sup>23</sup> The

---

<sup>20</sup> EPA, *Draft Strategy: Proposed Revisions to the 'Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses'* (2003), available at <http://www.epa.gov/waterscience/criteria/aqlife/>.

<sup>21</sup> Stroud Report at 10.

<sup>22</sup> *Id* at 20.

<sup>23</sup> USGS, *Chloride in Groundwater and Surface Water in Areas Underlain by the Glacial Aquifer System, Northern United States*, Scientific Investigations Report 2009-5086 (2009).

report noted that increases in chloride loads in both groundwater and surface waters are related to increases in road area and consequent deicing, increases in wastewater and septic-system discharges, recycling of chloride from drinking water, and leachate from landfills and salt storage areas. The report found a strong positive correlation between the amount of chloride in aquifers and elevated, impairment levels of chloride in hydrologically connected surface waters. Sites with maximum concentrations of chloride greater than 230 mg/l in surface streams had base-flow concentrations of chloride greater than 75 to 90 milligrams per liter, indicating that basins with high chloride concentrations in groundwater or wastewater discharge were **more likely to exceed the recommended chronic criteria.**<sup>24</sup> As the report mentions, some of the chloride loading in groundwater arrives very slowly in the form of saline plumes from landfill sites and salt and brine storage areas.<sup>25</sup> Considering the current state of scientific knowledge on the relationship between groundwater chloride loadings and surface water chloride levels, any development of chloride criteria to protect aquatic life uses in Pennsylvania must consider the chloride levels in the Commonwealth's aquifers both today and over time. Such a consideration should entail taking a more conservative approach to criteria development to compensate for both what is known and unknown about aquifers and chloride in Pennsylvania.

**V. Other states have adopted water quality criteria more stringent than the federal guidelines.**

Pennsylvania would not be the first state to recognize the need to exceed the federal standard. Subsequent to the release of the 1988 EPA Criteria, several states adopted state-specific chloride criteria that exceed EPA's recommended minimum. Wisconsin established acute and chronic chloride criteria of 757 and 395 mg/l, respectively, to protect fish and aquatic life. Wis. Admin. Code NR § 105.06. Illinois has a total chloride criterion of 500 mg/l. Ill. Admin. Code, tit. 35 § 302.208(f) (2009).

Iowa provides an example of a state working with the EPA to develop chloride criteria that are different from and more protective than the 1988 EPA Criteria and that take into consideration the state's particular needs. Iowa's Department of Natural Resources (IDNR) revised its water quality criteria for chloride in 2009. Prior to its rulemaking, IDNR, working closely with EPA, performed a literature search and discovered studies published after 1988, which indicated the need to collect additional data to determine if four species used for toxicity testing actually were sensitive to chloride. Consequently, EPA contracted with the Great Lakes Environmental Center in Columbus, OH and Illinois Natural History Survey at Champaign, IL to perform additional toxicity testing.<sup>26</sup> Iowa then recalculated the acute and chronic chloride

---

<sup>24</sup> *Id* at 32-33.

<sup>25</sup> *Id* at 32.

<sup>26</sup> EPA, *Acute Toxicity of Chloride To Select Freshwater Invertebrates*. (September 26, 2008).

criteria based upon the new data.<sup>27</sup> More details on the Iowa standard are available in the Stroud Report in § 3.4.

## **VI. Recent developments in Pennsylvania demonstrate the need for standards more stringent than the Proposed Chloride Criteria**

The Board has a duty to propose and eventually adopt water quality criteria for chloride that protect the four aquatic life uses for Pennsylvania. Pennsylvania already has some chloride-related problems, such as road salt runoff, that are common to most jurisdictions. However, Pennsylvania has chloride-related problems that are more particular to the region. First, activities related to the Marcellus Shale industry contribute significant amounts of chloride. Second, some of Pennsylvania's streams, such as Dunkard Creek, have recently suffered disastrous consequences of elevated chloride levels. Third, the EQB should consider groundwater contributions to chloride loading. Pennsylvania has a strong interest in adopting chloride criteria that are different and better than the 1988 EPA Criteria in order to address the chloride-related problems in the Commonwealth.

### **A. Marcellus Shale wastewater, which contains very high concentrations of chloride with more toxic speciations of salt than those studied for the 1988 EPA Criteria, must be taken into account when formulating Pennsylvania's chloride criteria for aquatic uses.**

Prior to recent development of hydraulic fracturing, the natural gas contained within Marcellus Shale underlying Pennsylvania was considered prohibitively expensive to access. However, technological development, along with the rising cost of natural gas, has led to increased interest in and development of the formation's resources. It is especially critical for Pennsylvania to develop adequate chloride criteria because of the unique impacts that gas drilling in the Marcellus Shale pose for the Commonwealth. The fracking fluids used for Marcellus Shale drilling operations and the resulting wastewater will contribute high levels of salts generally, and higher levels of the more toxic speciations of salt specifically, into Pennsylvania's waters.

The Marcellus shale is of marine origin and naturally contains high levels of salt. These salts are present in the formation brines that primarily consist of the chlorides of sodium, potassium, calcium and magnesium.<sup>28</sup> Most of these cations are essential nutrients for organisms. Different organisms, however, have different requirements and tolerances for these salts. Brines have elevated concentrations of these chloride salts,

---

<sup>27</sup> Iowa Department of Natural Resources, *Water Quality Standards Review: Chloride, Sulfate and Total Dissolved Solids*, (February 9, 2009), available at [http://www.iowadnr.gov/water/standards/files/ws\\_review.pdf](http://www.iowadnr.gov/water/standards/files/ws_review.pdf) (appended hereto as Appendix C).

<sup>28</sup> Soeder, D. J. and Kappel, W. M., May 2009, *Water Resources and Natural Gas Production from the Marcellus Shale*, USGS Fact Sheet 2009-3032, 5.

which have proven to be toxic to organisms at such high levels. For several aquatic species, potassium, calcium, and magnesium salts of chloride are more toxic as compared with sodium.<sup>29</sup>

The stratigraphic section of the Appalachian Basin possesses deep basinal saline brines. Oftentimes, potassium chloride, a metal halide salt composed of potassium and chlorine, is added to the fracturing fluid as a clay stabilizer to prevent the swelling and migration of formation clays, which could reduce pore space and subsequently reduce permeability.<sup>30</sup> Generally, between four to seven million gallons of the water,<sup>31</sup> along with sand and fracking fluids, are required to extract gas from a Marcellus Shale drilled well. Saline brine was observed in post-fracturing flowback fluids because of a breach into an area of the shale that contains mobile brine.<sup>32</sup> These brines possess total dissolved solids ("TDS") ranging from 9,990 to 343,000 mg/l and chloride concentrations much higher than seawater, ranging from 35,000 to 150,000 mg/l.<sup>33</sup> According to a study conducted in 2009 by the Society of Petroleum Engineers, wastewater from Marcellus Shale development has a salinity comparable to modern-day hypersaline evaporates, in terms of aqueous chemistry.<sup>34</sup>

The waste fluids generated by Marcellus Shale drilling and fracturing are considered industrial wastewater and are categorized as residual wastes. Generally, the water is treated or disposed of in five major ways. First, it may be treated in municipal waste treatment plants. However municipal waste treatment plants are usually not adequately prepared or do not have sufficient technological capability to sufficiently process the components of the solution. In addition, high chloride concentrations in fracturing wastewater could destroy the biological agents used to process municipal waste.<sup>35</sup> Usually, even if flowback water is treated through the typical municipal water

---

<sup>29</sup> Evans, M. and C. Frick. 2001. *The effects of road salts on aquatic ecosystems*. NWRI Contribution Series No. 02-308, National Water Research Institute and University of Saskatchewan, Saskatoon, SK, Canada. 53, 58.

<sup>30</sup> URS CORPORATION, WATER RELATED ISSUES ASSOCIATED WITH GAS PRODUCTION IN THE MARCELLUS SHALE: ADDITIVES USE; FLOWBACK QUALITY AND QUANTITIES; REGULATIONS; ON-SITE TREATMENT; GREEN TECHNOLOGIES; ALTERNATE WATER SOURCES; WATER WELL-TESTING (2009) (hereinafter "URS CORPORATION").

<sup>31</sup> Susquehanna River Basin Commission, Natural Gas Well Development in the Susquehanna River Basin (Information Sheet), 1 (Jan. 2010) (available at [http://www.google.com/url?sa=t&source=web&cd=5&ved=0CCkQFjAE&url=http%3A%2F%2Fwww.srb.bc.net%2Fprograms%2Fdocs%2FProjectReviewMarcellusShale\(NEW\)\(1\\_2010\).pdf&ei=7h4VTPKiD4HknQfmh\\_STDA&usq=AFQjCNFsnl9f9sYL5LaID3nbTHFHriW21A&sig2=gExim30HVVdkfDmj544UqQ](http://www.google.com/url?sa=t&source=web&cd=5&ved=0CCkQFjAE&url=http%3A%2F%2Fwww.srb.bc.net%2Fprograms%2Fdocs%2FProjectReviewMarcellusShale(NEW)(1_2010).pdf&ei=7h4VTPKiD4HknQfmh_STDA&usq=AFQjCNFsnl9f9sYL5LaID3nbTHFHriW21A&sig2=gExim30HVVdkfDmj544UqQ))

<sup>32</sup> URS CORPORATION at 12.

<sup>33</sup> Pettyjohn, W.A., THE OHIO JOURNAL OF SCIENCE 71(5): 257, September 1971, p-258

<sup>34</sup> Blaich, M.E., et. al. at 11.

<sup>35</sup> Wood, Michael & Sharon Ward. Responsible Growth: Protecting the Public Interest with a Natural Gas Severance Tax. April 2009. Page 18. Accessible at <http://www.pennbpc.org/sites/pennbpc.org/files/Responsible%20Growth%20-%20PA%20Severance%20Tax.pdf>.

process, the systems are not sufficient to eliminate the potentially toxic levels of chloride. Second, the solution can be disposed of in a deep injection well. This method is often utilized in Texas, where flowback is injected into depleted oil and gas wells. Pennsylvania's unique geological composition makes this option less viable. The limestone and shale underlying Pennsylvania contains naturally occurring fractures, increasing the likelihood that the fracturing wastewater could migrate into drinking water aquifers. Third, industrial wastewater treatment plants, such as crystallization and evaporation plants, may be utilized to treat the wastewater. Fourth, wastewater increasingly is being partially treated and reused as fracturing fluid. Finally, it may be stored in open evaporation pits. This option is also less viable in Pennsylvania because of the high annual rainfall.

There is a risk of contamination from these chemicals due to on-site storage of flowback in pits prior to treatment or reuse. Such storage could result in a leak or spill, contaminating surrounding surface waters. Similarly, inadequate well construction or fracturing "out of zone" can result in leaks from gas wellbores, allowing flowback to contaminate aquifers.<sup>36</sup>

The potential damage to aquatic habitats from unnatural chloride levels has been devastating in Pennsylvania. The Dunkard Creek kill in September 2009 poisoned innumerable fish and salamanders and completely eliminated mussels from the ecosystem.<sup>37</sup> Experts cite the presence of *P. parvum*, a type of golden algae that produces a potent toxin, as the main cause of the kill. Increased abundance of *P. parvum* is directly related to increased salinity.<sup>38</sup> As an even more recent example, the natural gas blowout that occurred on June 3, 2010 in Chester County released over a million gallons of brine and natural gas into the forest surrounding the well site. One expert analogized the damage to "spraying saltwater all over the surrounding vegetation because the water on site has a 'very, very high' content of salt and chloride."<sup>39</sup>

Another concern stems from the quantity of water necessary for gas extraction. Water management problems are increasing, especially during low flow months (July through October) when millions of gallons of water are extracted from surface waters and groundwater for use in the drilling and stimulating shale gas wells. Water usage during these low stream flow months could decrease the assimilative capacity of surface water for chloride and other toxics, thereby negatively affecting the aquatic life in those

---

<sup>36</sup> Tom Meyers, Review and Analysis of DRAFT Supplemental Generic Environmental Impact Statement on the Oil, Gas, and Solution Mining Regulatory Program Well Permit Issuance for Horizontal Drilling and High-volume Hydraulic Fracturing to Develop Marcellus Shale and Other Low-permeability Gas Reservoirs: September 2009. December 2009 at 14, 20 (on file with the authors).

<sup>37</sup> Reynolds, Louis. *Update on Dunkard Creek*. USEPA Region 3 Environmental Analysis and Innovation Division. November 23, 2009. Page 1.

<sup>38</sup> *Id.* At 3.

<sup>39</sup> Tim Puko. *Marcellus Blowout Sprays Gas in Clearfield County*. PITTSBURGH TRIBUNE REVIEW. Saturday, June 5, 2010.



streams.<sup>40</sup> Adding chemicals to waters with decreased in-stream flow prevents sufficient dilution and adds stress to an ecosystem already burdened by decreased water quantities.

Finally, unlike various other wastewaters, Marcellus Shale wastewaters contain not just NaCl, but also other salts like MgCl<sub>2</sub>, CaCl<sub>2</sub>, and KCl. These non-NaCl salts are more toxic to aquatic communities than is NaCl. The interactions among the cations of those salts (Ca, K, Mg and Na) have a demonstrated impact on the level of chloride's toxicity.<sup>41</sup> The fact that Marcellus Shale wastewaters contain non-NaCl salts could impact Pennsylvania's aquatic life in a fundamental way unless their presence is accounted for when developing chloride criteria for the Commonwealth.

## **B. Dunkard Creek conditions demonstrate existing chloride impacts on Pennsylvania's aquatic life.**

Dunkard creek is an example of the sort of havoc that elevated chloride levels can create. The Dunkard Creek watershed drains approximately 180 square miles in Monongalia County in West Virginia and Greene County in Pennsylvania.<sup>42</sup> Beginning on September 1, 2009, elevated levels of chlorides and other pollutants caused a massive fish kill that spanned approximately 43 miles of stream. The contamination killed high numbers of fish and salamanders, and completely eradicated the mussel population. After the incident, Region 3 of the Environmental Protection Agency, along with the West Virginia and Pennsylvania Departments of Environmental Protection and the Pennsylvania Fish and Boat Commission sampled the creek. Louis Reynolds, a Fisheries Biologist at Region 3 authored a report ("Dunkard Update") evaluating the fish kill generally and focusing ultimately on chloride's contributions to it.<sup>43</sup>

The cause of the fish kill was an elevated salinity level that facilitated a substantial bloom of a saltwater golden algae called *Prymnesium parvum* ("P. parvum"). P. parvum produces a toxin capable of killing aquatic life. While P. parvum usually resides in saltwater, it is now being found in brackish inland waters which elevated salinities are both natural and anthropogenic. Since its discover in 2001, P. parvum blooms have killed over 30 million fish in 33 water bodies.

P. parvum blooms are associated increased salinity. Research demonstrates that the dangerous toxin produced by P. parvum is dependent upon the availability of cations like Ca<sup>2+</sup> and Mg<sup>2+</sup> in the surrounding water<sup>44</sup>—the very cations that are

<sup>40</sup> M.B. Sweeney, McClure S., Chandler, S., Reber, C., Clark, P., Ferraro, J., Jacobs, P., Watta, D., Rogers, C., Bonnet, V., Shotts, A., Hess, S. Marcellus Shale Natural Gas: Environmental Impact. Marcellus Shale Natural Gas Extraction Study 2009-2010. Pages 1-15.

<sup>41</sup> Stroud Report at 16.

<sup>42</sup> Louis Reynolds (Fisheries Biologist, USEPA Region 3), Update on Dunkard Creek (Nov. 23, 2009) ("Dunkard Update" appended hereto as Appendix D).

<sup>43</sup> *Id.*

<sup>44</sup> *Id.* at 3.

disproportionately present in Marcellus Shale flowback, produced waters and wastewaters.<sup>45</sup>

Ultimately, the Dunkard Update focused on the contribution of chloride to the fish kill. The Dunkard Update considered the kill incident to be one of chronic exposure because chloride levels were elevated above the criteria (230 mg/L) for long periods of time. Chloride levels during the kill in the area of the kill were in the range of 400 to 4,000 mg/L.<sup>46</sup> In addition to chlorides, the Dunkard Update recognizes that the presence of ion matrices (multiple anions and cations that, when in combination, have synergistic properties and effects) contributed to the high dissolved solids load, ionic stress, and total ion toxicity.

Once *P. parvum* is in an aquatic environment it is nearly impossible to eradicate it since, with increasing total dissolved solids, freshwater algae that would otherwise compete with *P. parvum* are too stressed and debilitated to compete. The Dunkard Update concludes that the best way to avoid future fish kills as a result of *P. parvum* would be to decrease the levels of both TDS and chlorides. It adds that there should be more efforts to understand the effects of ion matrices present in Marcellus shale and coalbed methane brines that contain more chloride.

## Conclusion

We agree with the Department and the Board that an imminent need exists for the adoption of chloride water quality criteria that protect Pennsylvania's aquatic life uses. The Board can promptly meet that need by using the methodology developed by British Columbia<sup>47</sup> to calculate acute and chronic values as described in conclusion number five in the Stroud Report. The Stroud Center makes their recommendation by assessing the current state of scientific knowledge on acute and chronic chloride toxicity. The most recent acute toxicity studies were not considered in EPA's 1988 acute criterion, which makes the 1988 acute value the least protective of aquatic life out of all of the criteria considered by the Stroud Center. A distinct lack of chronic toxicity studies for chloride led the Stroud Center to conclude that a safety factor should be applied to chronic criteria derived from the use of an acute to chronic ratio to adequately protect the most sensitive aquatic species in Pennsylvania, such as trout and pollution-sensitive macroinvertebrate species characteristic of CWF waters. The state of scientific knowledge on adequate protection of aquatic life uses in Pennsylvania requires use of the British Columbia methodology to set chloride criteria.

---

<sup>45</sup> Stroud Report at 3, 7, 15-16, 20.

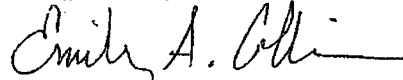
<sup>46</sup> Dunkard Update at 3.

<sup>47</sup> Ministry of Environment (British Columbia, Canada), Overview Report: Ambient Water Quality Guidelines for Chloride (2003), available at <http://www.env.gov.bc.ca/wat/wq/BCguidelines/chloride/chloride.html> (appended hereto as Appendix E).

The Department must implement a standard that is reflective of the current state of scientific knowledge. In order to provide adequate protection to aquatic life uses, individual criteria should be set to adequately protect each of Pennsylvania's four aquatic life use designations. In addition, the presence of Marcellus Shale development wastewater makes the Commonwealth more vulnerable than other states to high chloride loadings and greater chloride toxicity. The Dunkard Creek fish kill was a devastating example of the impact chloride has on aquatic life. Not only will chloride levels be higher because of Marcellus Shale wastewater, but it could also increase because of contributions from groundwater. The Commonwealth should use the British Columbia methodology described in the Stroud Report to adopt chloride criteria that will ensure protection of Pennsylvania's aquatic life uses. British Columbia acknowledged the lack of a full set of necessary data and reacted by building in safety factors to ensure the protection of aquatic life. In light of the legal requirement to protect all aquatic life uses by utilizing the most current science, implementing the British Columbia approach and criteria values is the only way to compensate for some gaps in the scientific knowledge and still ensure the protection of Pennsylvania's aquatic life uses. The Department can choose to use the British Columbia values of 600 mg/L (instantaneous maximum) and 150 mg/L (average of 5 weekly measurements taken over a 30 day period), or it can choose to use the Stroud Center's recalculations of the British Columbia methodology-based criteria that yield 564 mg/L (instantaneous maximum) and 91 mg/L ((average of 5 weekly measurements taken over a 30 day period). This conservative approach compensates for the lack of scientific data while still adequately considering the state of scientific knowledge and protecting all four aquatic life uses, but the Department must still work to fill in the gaps of scientific knowledge about chloride's impacts on aquatic life. The Department should address the imminent need for good criteria now by adopting the British Columbia values, and should move immediately to gather better toxicology data--especially on chronic exposures--and a better understanding of the effects of environmental variables like temperature and ion mixtures on chloride toxicity so that, at the next opportunity, the Department will be prepared to update the science, propose an even better set of criteria to protect aquatic life uses, and act as a leader in the field.

Once again, thank you for the opportunity to comment on the proposed water quality criteria for chloride. Please feel free to contact us at (412) 648-1300 with any questions or concerns.

Respectfully submitted,



Emily A. Collins  
Supervising Attorney



Megan Collelo  
Certified Legal Intern

*On behalf of:*

Myron Arnowitz  
Pennsylvania State Director  
Clean Water Action

Thomas Au  
Conservation Chair  
Sierra Club, Pennsylvania Chapter

Deborah Goldberg  
Managing Attorney  
Earthjustice

Patrick Greuter, Esq.  
Legal Director  
Three Rivers Waterkeeper

Dave Rothrock  
President  
Pennsylvania Council of Trout Unlimited

Joanne Spalding  
Managing Attorney  
Sierra Club

Maya K. van Rossum  
Delaware Riverkeeper  
Delaware Riverkeeper Network

**Stroud Water Research Center Expert Report on the Proposed  
Rulemaking by the Pennsylvania Environmental Quality Board  
[25 PA. CODE CH. 93] for Ambient Water Quality Criterion;  
Chloride (Ch) [40 Pa.B. 2264] [Saturday, May 1 2010]**

**Prepared by**

**William H. Eldridge, Ph.D.**

**David B. Arscott, Ph.D.**

**John K. Jackson, Ph.D.**



**970 Spencer Road**

**Avondale, PA 19311**

**Phone: 610-268-2153**

**[www.stroudcenter.org](http://www.stroudcenter.org)**

**Date: 14 June 2010**

**Stroud Report #: 2010004**

---

**Table of Contents**

<b>1</b>	<b>Report Goal and the Proposed Pennsylvania Chloride Criteria</b>	<b>1</b>
<b>2</b>	<b>Introduction</b>	<b>1</b>
2.1	Salt in nature	1
2.2	Sources and pathways of salt that enters aquatic ecosystems	2
2.3	Salinity trends in freshwaters	3
<b>3</b>	<b>Review of Existing Chloride Criteria</b>	<b>5</b>
3.1	EPA 1988 Criteria	5
3.2	Evans and Frick 2001	7
3.3	British Columbia 2003	8
3.4	Iowa 2009	9
3.5	Delaware, Maryland, New Jersey, New York, Ohio, Virginia, West Virginia	13
3.6	EPA Revision to the 1988 Chloride Criteria	14
3.7	Calculation of CMC and CCC criteria using 4 methods	14
<b>4</b>	<b>General Comments on Chloride Toxicity Literature</b>	<b>15</b>
<b>5</b>	<b>Examples of baseflow chloride concentrations in PA (EMAP survey 1993-96)</b>	<b>17</b>
<b>6</b>	<b>Stream Chloride Concentrations in Pennsylvania from EMAP Data and the Iowa Criteria</b>	<b>18</b>
<b>7</b>	<b>Conclusions</b>	<b>19</b>
<b>8</b>	<b>Literature Cited</b>	<b>23</b>
<b>Tables 1 - 3</b>		<b>26-28</b>
<b>Figures 1 - 8</b>		<b>29-36</b>

## **1 Report Goal and the Proposed Pennsylvania Chloride Criteria**

The Pennsylvania Environmental Quality Board has proposed to amend Table 3 in 25 Pa. Code § 93.7 (Specific Water Quality Criteria) which currently sets a Chloride ( $Ch_1$ ) criteria for Potable Water Supplies at a maximum concentration of 250 mg/l. The proposed amendment adds chloride criteria ( $Ch_2$ ) for Aquatic Life Uses for Cold Water Fishes (CWF), Warm Water Fishes (WWF), Migratory Fishes (MF), and Trout Stocking (TSF) for chronic conditions not to exceed a four-day average of 230 mg/l and for acute conditions not to exceed a one-hour average of 860 mg/l. Both chronic and acute criteria should not be exceeded more than once every 3 years on the average. These criteria are identical to those recommended by the US EPA (EPA 1988).

This report examines Pennsylvania's currently proposed ambient water quality criteria for chloride for the adequate protection of aquatic life uses in Pennsylvania. To that end, the report examines closely the scientific rationale behind the 1988 set of chloride criteria set by the EPA (which the Environmental Quality Board has decided to use as their criteria), and chloride criteria adopted by other states like Iowa, and the Canadian province of British Columbia. The report evaluates the methodologies utilized in formulating the various sets of chloride criteria to determine which methodologies best protect aquatic life uses of the Commonwealth's water resources. The report addresses the chloride problem in the Pennsylvania context in order to fashion a recommendation that will apply to the Commonwealth's particular issues. Finally, the report recommends that the Board propose a set of chloride criteria using the British Columbia approach that is based on scientifically sound rationale and will adequately protect aquatic life uses in Pennsylvania.

This report reflects the scientific opinion of three scientists at the Stroud Water Research Center, Drs. D.B. Arscott, W.H. Eldridge, and J.K. Jackson after their review of the proposed standard, existing standards (EPA, Iowa, Ohio, Canada), and a substantial proportion of the scientific literature on chloride in the environment and toxicity effects. This report was prepared during the 45-day review period starting on 1 May 2010.

## **2 Introduction**

### ***2.1 Salt in nature***

Salinity is the total concentration of salts in water. In chemistry, salts are ionic compounds that can result from the neutralization reaction of an acid and a base. Salts are composed of cations (positively charged ions) and anions (negatively charged ions). The component ions can be inorganic (such as chloride), as well as organic (such as acetate:  $CH_3COO^-$ ). There are several types of salt, but this report focuses on the chloride-containing salts which include (but are not limited to) sodium chloride (NaCl), calcium chloride ( $CaCl_2$ ), magnesium chloride ( $MgCl_2$ ), and potassium chloride (KCl). When dissolved in water, these salts dissociate into their free ions (i.e., the cations  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$  and the anion  $Cl^-$ ).

Aquatic organisms vary in their salt tolerance. Salt tolerance also varies depending on the specific cation involved. For example,  $Ca^{2+}$  is essential for algal growth. Most plants require  $Mg^{2+}$  since it is a component of the chlorophyll molecule.  $Na^+$  and  $K^+$  are involved in ion transportation and exchange across cell membranes in most organisms and chloride plays a role in the osmotic salinity balance and

the exchange ions. However, an organism's requirement for each of these varies from cation-to-cation and from species-to-species and this results in different toxicity thresholds for each cation specific to each organism of interest.

Organisms that tolerate a wide range of salinities are "euryhaline" and are typically present in estuaries where salinities can change hourly due to tidal fluctuations, or are diadromous species that migrate between fresh water and salt water. Stenohaline organisms can only tolerate a narrow range of salinities. Stenohaline species can be further subdivided into those that live in low-salinity environments (e.g., freshwaters) and those adapted to high salinity environments (e.g., marine systems). Prior to selecting organisms for assessment of the toxicity of chloride or other salt-derived ions, it is important to consider whether the organisms are known to be salt tolerant or salt sensitive or whether there are other known life stages that may be adapted to different saline conditions (e.g., anadromous fish like salmonids of the genus *Oncorhynchus*). Understanding general salt sensitivity is important because developing chemical criteria to protect a broad array of aquatic organisms will only be successful if the studies underpinning the criteria have focused on the proportion of taxa that will be the first to experience its toxic effects. Since chemical toxicity is primarily related to concentration, this would mean that the sensitive organisms would experience chemical stress at the lowest concentrations compared to more tolerant organisms. Understanding each organism's life history sensitivities is also important since negative impacts to any component of the life history will typically result in a decrease in survival of the population.

## ***2.2 Sources and pathways of salt that enters aquatic ecosystems***

Natural sources of salts to water resources include (1) the oceans; (2) the natural weathering of bedrock, surficial materials, and soils; (3) geologic deposits containing halite, or saline groundwater (brines); and (4) volcanic activity (Mullaney et al. 2009). Oceans typically contain about 19,000 mg/l of chloride resulting in the atmosphere above the oceans being dominated  $\text{Na}^+$  and  $\text{Cl}^-$ . This results in the deposition of  $\text{Na}^+$  and  $\text{Cl}^-$  being highest along the coast. The contribution of wet deposition to natural concentrations of  $\text{Cl}^-$  in streams in the northern US is estimated to be ~0.1 – 2.0 mg/l (Mullaney et al. 2009) varying with distance from the coast. In forested watersheds in the northern US, stream  $\text{Cl}^-$  concentrations typically ranged (as measured from 1991-2000 by USGS) from ~5-30 mg/l (approximated 25<sup>th</sup> and 75<sup>th</sup> percentile by eye from Fig. 15 in Mullaney et al. 2009). But in the snowy region of the U.S., natural sources represent only a fraction of the salt that enters the ground water and surface water.

Of the chloride salts discussed here ( $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , and  $\text{KCl}$ ), sodium chloride ( $\text{NaCl}$ ) is the most commonly produced and used in environmental applications. Its primary environmental use is as a deicing agent.  $\text{NaCl}$  is used to soften water in suburban and rural homes and  $\text{Cl}^-$  is then released to drainfields where it eventually flows to groundwater. Sodium chloride is also used as a food additive and condiment, in manufacturing pulp and paper, setting dyes in textiles and fabrics, and the production of soaps and detergents. In 2002, world production was estimated at 210 million metric tons (Feldman 2005). Magnesium chloride has many applications but its primary environmental use is as a deicing agent and as a dust and erosion control agent. It is also used in the manufacture of textiles, paper, fireproofing agents, cements, and refrigeration brine. Potassium chloride is primarily used as a fertilizer but is also used in food processing, and as a sodium-free substitute for table salt or as an alternative water softener.  $\text{KCl}$  is sometimes used in petroleum and natural gas operations. Calcium chloride is also



used as an ice-melting compound and is more effective than NaCl at lower temperatures. The Salt Institute states that the optimum temperature for ice melting by Na-, Mg-, and Ca-chloride is -6, -28, and -67 °F, respectively (Salt Institute 2004). Other environmental uses for CaCl<sub>2</sub> include use in fire extinguishers, in wastewater treatment as a drainage aid, in blast furnaces, in food processing (e.g., pickles), and in fabric softeners (as a thinner).

The common pathways through which salt enters ground and surface waters are atmospheric deposition, the dissolution of deicing salts from normal use on streets, parking lots, highways, and other paved surfaces; storage and handling of deicing salts; release of brines from oil and gas production; leaching from landfills; the treatment of drinking water and wastewater; and discharge of wastewater from treatments facilities and septic systems (Mullaney et al. 2009). The major anthropogenic sources of Cl<sup>-</sup> in surface waters of the US are deicing salt, urban and agricultural runoff, and discharges from municipal wastewater plants, industrial plants, and the drilling of oil and gas wells (EPA 1988). The use of salt in the US has increased from 42.9 million tons in 1975 to ~58.5 million tons in 2005. The major use of salt in 2005 was for deicing of roads, parking lots, and other impervious surfaces (Mullaney et al. 2009).

Prior to 2005, the largest use of salt had been in the chloralkali industry that produces chlorine and sodium hydroxide (Mullaney et al. 2009). Potassium and sodium chloride salts are also a common additive to hydraulic fracturing fluid used by the natural gas industry (GWPC 2009). The chemical composition of the fracturing fluid can change when injected in the geological formation by chemically dissolving other materials stored in the rock formation and the hydrocarbons being extracted. The concentration of salts in fracking fluid can increase substantially in geological formations containing large quantities of salt or formations derived from marine sediments, e.g., Marcellus Shales in NW and SW PA. Chloride salts dissolved into this fluid may contain KCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, NaCl and/or other metal chlorides. Unused fluid and the “flowback” fracking fluid is either reused or treated as waste. In some instances, the treated fracking fluid may be permitted to discharge to surface waters. In this case, permitted discharges of treated flowback from salt-laden geological formations may be of concern for their chloride content.

### ***2.3 Salinity trends in freshwaters***

The salinity of many streams, rivers, and lakes in the northeast United States has been increasing over the last couple of decades (Siver et al. 1996, Rosenberry et al. 1999, Kaushal et al. 2005b, Kelly et al. 2008, Gardner and Royer 2010). For example, Cl<sup>-</sup> concentrations in stream baseflow of a NY stream have increased by 1.5 mg/l/yr from ~15 to >40 mg/l Cl<sup>-</sup> over the 20-yr period 1985-2005 (Kelly et al. 2008). In these NY tributaries to the Hudson River, the average annual input of NaCl was 1.4 million kg/yr (Kelly et al. 2008). 83% was from road salt, 8% was from parking area salt, 4% was from sewage, and 3% was from water softeners. Natural sources (i.e., wet and dry deposition and weathering) accounted for <1% each. Minimally impacted watersheds in the NE U.S. probably typically had Cl<sup>-</sup> concentrations ≤ 30 mg/l with many streams ≤ 10 mg/l (estimated from Mullaney et al. 2009). Kaushal et al. (2005b) measured Cl<sup>-</sup> concentrations of up to 25% of the concentration of seawater in streams of Maryland, New York, and New Hampshire. Rosenberry et al. (1999) measured Cl<sup>-</sup> concentrations in a New Hampshire stream changing from 3.5 mg/l in 1970 to 53 mg/l in 1994. Chang and Carlson (2005) surveyed tributaries of Spring Creek (in PA) during spring snowmelt and documented peak Cl<sup>-</sup> concentrations of 362 and 551

mg/l Cl<sup>-</sup> in two of ten tributaries sampled during the winter-spring of 2001-2002. Studies of road-side wetlands have measured Cl<sup>-</sup> in ranging from 18–2700 mg/l (e.g., Benbow and Merritt 2004, Silver et al. 2009). The increases in Cl<sup>-</sup> concentrations in freshwater in the northeastern US threatens salt-sensitive biota and may result in the extirpation of certain species that may ultimately cause changes in community structure and function (e.g., loss of algae, invertebrates, and fish) of these stream ecosystems.

The type of water body has a significant impact on the chloride concentration. According to Evans and Frick (2001), the highest chloride concentrations in freshwater habitats are typically found in roadside ditches where melt-water is concentrated (up to 19,135 mg/L, full strength sea water is about 19,250 mg/L). The next highest levels are in rivers and streams in populated areas with significant road salt use (up to 4,310 mg/L). Small lakes and ponds typically have higher levels than larger lakes, but levels in small lakes were below 200 mg/L. Lakes and ponds that are large and/or have many streams flowing in and out have more dilution capacity than rivers and streams which keeps chloride concentrations low. More stagnant lakes and ponds may slowly accumulate chloride salts and develop a saltier hypolimnion (bottom strata) (Evans and Frick 2001).

There is a strong seasonal component to chloride concentrations. In 100 streams in the northern US that were sampled 10 or more times for chloride between 1991 and 2004, the highest values were generally found during the winter and spring months (Nov-April) coinciding with winter deicing activity (Mullaney et al. 2009). High concentrations of chloride that occurred in late spring and summer when there was no deicing activity may be due to the discharge of groundwater containing high concentrations of chloride or could be related to wastewater discharges containing chloride during a low-flow period.

In the same 100 streams as above, mean annual chloride loads were 6.4 tons/mi<sup>2</sup> from the forested basins, 15.4 tons/mi<sup>2</sup> from the agricultural basins, and 88 tons/mi<sup>2</sup> from the urban basins (Mullaney et al. 2009). The median baseflow chloride concentration was 3.5 mg/L for forested basins, 21 mg/L for agricultural basins, and 81 mg/L for urban basins (Mullaney et al. 2009). The maximum measured chloride concentrations exceeded the EPA chronic criterion (230 mg/L) in 13 sites with urban land use and 2 sites with agricultural land use. Six sites had concentrations greater than the EPA 230 mg/L in 10 % or more of the samples collected. At three sites, samples were greater than the acute criterion (860 mg/L). Significant terms explaining variability of chloride yield were highway density, number of major discharges upstream of the monitoring site in the USEPA PCS database, potential evapotranspiration, and the difference between the percent urban and agricultural land. Major discharges included municipal wastewater treatment facilities with discharges greater than 1 million gallons per day, and other facilities that the EPA rates as major based on volume and type of pollutants and type of receiving waters.

Data were available to test for temporal trends in chloride loading for 19 sites (Mullaney et al. 2009). At three urban sites, increases in chloride load over time could be attributed to changes in the application of deicing salts, the expansion of the road network and impervious surfaces that needed deicing, increases in the number of septic systems, increases in the volume of wastewater discharge, and the arrival of saline groundwater plumes from landfills and salt-storage facilities over time.

Increased chloride concentration in groundwater is beginning to raise the baseline chloride concentration in streams in rural areas. During the period 1986-2005, chloride concentration increased 1.5 mg/L per year and chloride export increased 33,000 kg/year in tributaries to the Hudson River (Kelly et al. 2008). Road salt use and increased population density were not sufficient to account for the increased Cl<sup>-</sup>. Increase in streamwater concentration was more likely due to a lag effect of long-term road salt use and subsurface buildup.

In the New York City drinking water supply watersheds, groundwater is a major contributor to streams. Groundwater discharge accounts for at least 60% of total annual stream flow in the Croton watershed (Heisig 2000). Chloride concentration in groundwater supplies exhibits a relatively linear relationship to road-salt application rate or two-lane road density throughout the year. In surface-water supplies, chloride concentration depends on salting intensity, soil type, climate, topography, and water volume, with larger water bodies exhibiting lower concentrations through the process of dilution (Heisig 2000). Deicing salts applied to roads during winter have been the primary source of solutes to groundwater in the Croton watershed, where chloride concentrations in baseflow of sampled streams ranged from 18 to 280 mg/l (Heisig 2000).

Baseline chloride levels are also increasing in rural streams of the northeast that have not seen an increase in road density (Baltimore MD, Hudson Valley NY, and Hubbard Brook NH) (Kaushal et al. 2005a). Possible causes are increased use of road salt and higher concentrations of chloride in groundwater.

### **3 Review of Existing Chloride Criteria**

#### **3.1 EPA 1988 Criteria**

The PA DEP has proposed criteria that are the same as those derived by the EPA in 1988. Therefore we will use the EPA 1988 criteria as a starting point for this review.

In 1988, the EPA published a recommended Ambient Water Quality Criteria for Chloride (EPA 1988). To prepare the criteria, they reviewed the available chloride toxicity studies in August 1985, and included some more recent literature. The EPA acknowledged that the chlorides of potassium, magnesium, and calcium were generally more toxic to aquatic organisms than sodium chloride, but they limited their analyses to sodium chloride because the most data was available for this salt, and because most of the anthropogenic salt in the environment is likely to be sodium chloride (EPA 1988). All of these other forms of Cl<sup>-</sup> salts are typically found in Marcellus Shale waste water effluent. They noted that there was not sufficient data to indicate that toxicity would change with hardness, alkalinity, or pH.

To generate the Criterion Maximum Concentration (CMC), the EPA relied on studies by independent labs that identified the concentration of contaminant that caused mortality or a sub-lethal fitness effect to 50% of the individuals in a 96-hour exposure (LC<sub>50</sub> or EC<sub>50</sub>, respectively) to establish the acute criteria. Rules that the EPA followed when selecting studies are outlined in the "Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses" (Stephan et al. 1985) (hereinafter "1985 guidelines"). These EPA recommended rules require them to give preference to studies that used a flow of fresh water through the system (flow-through) over

studies that used static water or that recycled water through a biofilter (renewal). EPA's review included 45 values for the 96-hr LC<sub>50</sub>, or EC<sub>50</sub> from 15 species representing 13 genera. Of these 45 values, 23 were dropped because the salt used was not NaCl. Of the remaining 22 values, 4 were dropped because the study was not conducted in flow-through water and a value for the same species using flow-through water was available. The species mean acute value (SMAV) was the geometric mean of tests on the same species. The genus mean acute value (GMAV) was the geometric mean of tests on the same species. In 1988, there were 12 GMAVs.

The EPA used a procedure detailed in the 1985 Guidelines to calculate the Final Acute Value (FAV). The FAV is used to calculate the criterion maximum concentration (CMC). EPA's procedure to calculate the FAV is designed to protect 95% of the species, as there is a 95% confidence interval in their formula (however, it is not clear if this is intended to protect 95% of species in the environment or 95% of the species used in determining the criteria (EPA 1985)). First, the four lowest GMAVs are identified. In 1988, the four lowest GMAVs were 1974 (*Daphnia*, a water flea), 2540 (*Physa*, a snail), 2950 (*Lirceus*, an isopod), and 3795 (*Cricotopus*, a midge) in mg/L Cl<sup>-</sup>. From these values, and the count of the total number of GMAV available (in this case 12), they calculated the FAV to be 1720 mg/L. The FAV is then divided in half (i.e., a safety factor of 2 is applied) to determine the CMC of 860 mg/L.

The same approach can be used to calculate the criteria continuous concentration (CCC) if there is sufficient data from chronic exposure studies, but in 1988 sufficient data did not exist. Rather, the EPA took advantage of the fact that there was a great deal more information on acute toxicity than there was on chronic toxicity to use the acute-to-chronic ratio (ACR) approach. Chronic studies had been conducted on three species: fathead minnows, rainbow trout, and *Daphnia pulex*. The chronic value for these species was calculated as the geometric mean between the lowest observed effect concentration (LOEC) and the no observed effect concentration (NOEC). The ACR for a given species was the ratio of the acute LC<sub>50</sub> or EC<sub>50</sub> to the chronic value. In 1988, the EPA determined the ACR for fathead minnows (15.17), rainbow trout (7.308), and *Daphnia pulex* (3.952). The EPA then calculated the geometric mean of the three species' ACRs, which was 7.594. The CCC is then determined to be the FAV divided by the ACR. The CCC was determined to be 230 mg/L (1720/7.594 rounded to the nearest ten). The data from the chronic studies were used only to set the ACR, and did not factor in the determination of the CCC in any other way. The ACR approach is acceptable when there are animals in at least three different families, provided that 1) at least one is a fish, 2) at least one is an invertebrate, and 3) at least one is an acutely sensitive freshwater species (EPA 1985). The Final Acute-to-Chronic Ratio geometric mean ACR was 7.594.

There are three factors in the derivation of the CMC, or acute criterion, which make the EPA approach protective. First, the EPA uses data from 96-hour exposure experiments to derive a CMC which is not to be exceeded for more than one hour every three years. The toxicity of chloride is time dependent. Chloride levels that are lethal over 96-hours may not have an impact when exposure is less than one day (Evans and Frick 2001). The second factor that makes the EPA approach protective is in the equations used to calculate the FAV, which are designed to protect 95% of the species represented in the testing. These equations may result in a FAV that is lower than the lowest observed GMAC. Finally, the EPA applies what appears to be a safety factor of two to the FAV to arrive at the CMC. This safety factor may be used to account for the fact that the FAV reflects a value at which acute mortality will occur in some species, but the aim of the criterion is to prevent chloride levels from reaching these toxic levels. One

concern, however, is that the FAV equations are sensitive to the number of genera for which there are GMAVs, but not necessarily to their toxicity values. The artifact arises because the equations for FAV are designed to account for the precision with which one knows the variance among the GMAVs (W. Eldridge, personal observation<sup>1</sup>). When there are few studies, one is less sure of the true distribution of the GMAVs, and the equations have a correction factor which lowers the FAV. As studies are added, the precision should increase. Therefore, adding an additional GMAV that is larger than the lowest four will increase the FAV. Only by finding a GMAV that is more sensitive than the fourth lowest will the FAV become lower.

On the other hand, the derivation of the criteria continuous concentration (CCC; or the chronic criteria) does not include any additional protections that we could see. For instance, the CCC is determined from the FAV before the safety factor is applied. In addition, the chronic values used by the EPA are the geometric mean of the NOEC (no observable effect concentration) and the LOEC (lowest observable effect concentration). Therefore, one cannot be certain that no effect will occur. In addition, the chronic value is completely dependent upon the derivation of the FAV and the ACR. For a given FAV, dividing by a smaller ACR will result in a higher CCC. And the lack of protections comes despite chronic studies having been conducted for only three species. The ACRs varied from 3.9 (*Daphnia*) to 15.17 (fathead minnow). These chronic studies were limited in “sensitive” life history components (i.e., embryonic, eggs, juvenile fish). In addition, no plant, algae or amphibian toxicity data were included. *Spirogyra setiformis* was extremely sensitive (71 mg/l produced inhibition of growth, chlorophyll, and C fixation). Plants and algae are foundational resources for stream food webs. The loss of taxa or their abundance may have impacts to higher trophic levels such as invertebrates and fish.

The EPA 1988 criteria also do not account for the synergistic effects of hardness, sulfate, or temperature. Since 1988, each of these variables have been shown to significantly influence chloride toxicity (Iowa DNR 2009). Current efforts by the EPA (as reflected in the Iowa criteria described below) attempt to address hardness and sulfate interactions but not temperature. The 1988 criteria also were derived only from NaCl toxicity studies despite data cited in that study indicating greater toxicity to Cl<sup>-</sup> derived from KCl and MgCl<sub>2</sub>. The study (EPA 1988) also states specifically that the criterion probably will not be adequately protective when the chloride is associated with potassium, calcium, or magnesium, rather than sodium. If PA adopts the 1988 federal chloride criteria, PA should acknowledge that the criteria is not protective when the chloride is associated with potassium, calcium, or magnesium, as there is sufficient evidence that acute and chronic values for Cl<sup>-</sup> derived from KCl and MgCl<sub>2</sub> would be considerably lower than the 1988 acute criterion (there is just not enough data to calculate acute criteria). Currently, the Commonwealth does not regulate Mg, K, or Ca, but should consider adding Mg<sup>2+</sup> to the metal concentration criteria.

### **3.2 Evans and Frick 2001**

In 2001, Evans and Frick (2001) published a review of the available chloride toxicity data, which included a unique method to derive chloride criteria for aquatic life. They were tasked with evaluating the impact of road salt on aquatic life in Canada. Evans and Frick (2001) present a different method of deriving the criteria. The Canadian method involves a three tier approach. The first and second tiers

---

<sup>1</sup> Authors observations on the result of the formula after adding or subtracting studies from the equation.

provide for the determination that the substance under consideration reaches levels in the environment that could have an adverse impact. Tier three assessments provide for the analysis of the likelihood that the substance under consideration will have a harmful impact on the environment. It does so by considering the distribution of exposures or effects among organisms (Evans and Frick 2001). Evans and Frick (2001) reviewed the available chloride toxicity data and the criteria for other jurisdictions. From all the acute studies (less than 7 days), they used just those involving a 2-4 day exposure. They normalized the 2-day and 3-day exposures studies to a 4-day exposure by using a correction factor based on Cowgill and Milazzo (1990) who investigated LD<sub>50</sub> responses of two species of cladocerans to sodium chloride at daily intervals over a 7-day period (Evans and Frick 2001). They noted the lack of chronic studies, and therefore relied on the EPA 1988 ACR (7.59) to calculate a chronic value for the same species for which they had acute data. They used these chronic data to prepare a cumulative distribution curve of the % of taxa that would be affected for a given concentration of chloride. They fit a sigmoid function through that curve and calculated 95% confidence intervals around that regression. The procedure for choosing the sigmoid function was not described. Several options exist for fitting sigmoid curves (e.g., 3, 4, or 5 parameters, logistic, Weibull, Gompertz, Hill, or Chapman equations). Differences in these equations can result in considerable variations in the fit (particularly at the tails of the regression where chloride criteria would be derived). Also, compared to data available in 2010, the available data (acute data forming their 96 hr curve) for their review were limited; therefore the distribution begins at 10% of species affected with a mean of 240 mg/L Cl<sup>-</sup>.

One strength of this approach is that the authors were able to generate confidence intervals for their distribution. The lower bound to the 95% confidence interval (for their chronic curve) at which 10% of species were affected was 194 mg/L and the upper bound was 295 mg/L (Evans and Frick 2001). However, their approach was heavily dependent upon the ACR, as was the EPA 1988 approach. Their approach is also sensitive to the derivation of the sigmoid curve. Curve fitting is sensitive to the equation for the curve as well as the data that is being fitted. SigmaPlot, which Evans and Frick used to fit the sigmoid curve, has three different equations for the sigmoid curve: a 3-, 4-, or 5- parameter equation. It is not apparent which version they used, or even what their rationale was for fitting a sigmoid curve. There are other equations for the sigmoid curve that might also be appropriate. The amount, distribution and transformation of these data (Evans and Frick log transformed their data before fitting) will also affect the fit of the curve. Using a different equation for the curve or not transforming the data would result in a slightly different predicted value for the 5% species cutoff, which makes this approach less robust than other approaches for calculating criteria.

### **3.3 British Columbia 2003**

The British Columbia Ministry of Environment adopted an Ambient Water Quality Guideline for Chloride in 2003 (Nagpal et al. 2003). Their guideline for Freshwater and Aquatic Life states that the average of 5 weekly measurements taken over a 30-day period should not exceed 150 mg/L with an instantaneous maximum not to exceed 600 mg/L. British Columbia considered the available scientific literature, existing guidelines from other jurisdictions, and environmental conditions in British Columbia. In British Columbia, background chloride concentrations are 1-100 mg/L Cl<sup>-</sup> with maximum concentrations from 13-140 mg /L Cl<sup>-</sup>. Most of the chloride that enters the environment in British Columbia is from the storage and application of road salt for accident prevention, which is predominantly NaCl. Their standards are based on two reviews – Evans and Frick (2001) and Bright and Addison (2002). British

Columbia considered the scientific literature on chloride toxicity to be “not always conclusive because it is usually based on laboratory work that, at best, only approximates field conditions.” British Columbia invoked a “precautionary principle” to incorporate built-in safety factors that are conservative relative to the EPA 1988 guidelines, but considered natural and background conditions in the province.

The acute and chronic rationales were as follows:

*Acute rationale:* The guideline for maximum chloride concentration was derived by applying a **safety factor of two** to the 96-h EC<sub>50</sub> of 1204 mg/L for the tubificid worm, *Tubifex tubifex* (Khangarot 1991), and rounding the number to the nearest tenth. A safety factor of two is applied to the acute data because of the relative strength of the acute data set (28 values, 20 species, 15 studies).

*Chronic rationale:* The recommended water quality guideline was derived by **dividing the lowest LOEC** (lowest observed effect concentration) from a chronic toxicity test **by a safety factor of 5**. The lowest LOEC for a chronic toxicity test was 735 mg/L for *Ceriodaphnia dubia* (DeGreave et al. 1992). That chloride concentration resulted in a 50% reduction in reproduction over the 7 day test duration. Utilizing this value and following the application of a safety factor of five, the chronic guideline is 150 mg/L (rounded to the nearest tenth place). The safety factor of 5 in the derivation of the chronic guideline was justified as follows: (a) chronic data available from the literature were scant; (b) in a recent study, Diamond et al. (1992) found a LOEC/NOEC ratio for reproduction of 3.75 in *C. dubia* exposed to NaCl for 7 days. Also, LC<sub>50</sub>/LC<sub>0</sub> of 3 and LC<sub>100</sub>/LC<sub>0</sub> of 4 were obtained by Hughes (1973), whereas the DeGreave et al. (1992) data yielded LC<sub>50</sub>/NOEC ratios that ranged from about 1.0 to 6.9; (c) additional protection may be required for those species that are more sensitive but have not yet been tested in the literature.

The guidelines are used to set site-specific objectives. In most cases, the objectives are the same as the guidelines, but they could be higher or lower depending upon background levels and the value and significance of the waterbody. The guidelines and objectives have no legal standing, but they can be used to develop waste management permits, orders and approvals that do have legal standing.

### **3.4 Iowa 2009**

In 2009, Iowa adopted new chloride criteria for the protection of aquatic life after consultation with the EPA and the publication of new data produced by the Great Lakes Environmental Center (GLEC) and the Illinois National History Survey (INHS) on chloride toxicity to four invertebrate species (Iowa DNR 2009). Those studies assessed the water flea (*Ceriodaphnia dubia*), planorbis snail (*Gyraulus parvus*), tubificid worm (*Tubifex tubifex*), and fingernail clam (*Sphaerium simile*) sensitivity to chloride under varying hardness concentrations. (For purposes here, hardness is a measure of the concentration of dissolved calcium carbonate – CaCO<sub>3</sub>). Results indicated that the water flea, clam, and worm had decreased sensitivities to chloride with increasing hardness. The water flea was tested for the influence of sulfate concentrations on chloride sensitivity and was found to be negatively influenced by SO<sub>4</sub> concentrations. As a result, the State of Iowa proposed 12 options (both acute and chronic) for setting chloride criteria

with 8 of those options varying with hardness and sulfate concentrations, 4 varying with hardness only, and 4 flat criteria. Ultimately, Iowa adopted two of the options that vary with hardness and sulfate: acute chloride criteria =  $287.8 * [\text{hardness}]^{0.205797} * [\text{sulfate}]^{-0.07452}$  and chronic chloride criteria =  $177.87 * [\text{hardness}]^{0.205797} * [\text{sulfate}]^{-0.07452}$ . Figure 1 illustrates how the chloride criteria vary with hardness assuming a constant sulfate concentration of 37.9 mg/l (an average of PA streams from an EPA EMAP study, see below). The Iowa DNR states that if no hardness or sulfate data are available, the statewide default values will be used but there is no further guidance in that document that present the default values (Iowa DNR 2009). However, the Iowa fact sheet states that background hardness and sulfate concentrations are 200 mg/l as CaCO<sub>3</sub> and 63 mg/l SO<sub>4</sub> ([http://www.iowadnr.gov/water/standards/files/ws\\_fact.pdf](http://www.iowadnr.gov/water/standards/files/ws_fact.pdf)).

Iowa worked with the EPA to develop their chloride criteria. Iowa instituted three major changes from the 1988 EPA Criteria. The first was to add acute and chronic studies and to remove what were determined to be questionable studies. In the end, the Iowa DNR increased the number of genera used to calculate the FAV and CMC from 13 in 1988 to 29 (Stephan 2009a). Another change was to develop a pair of criterion equations rather than a pair of criterion values. The equations were to account for the secondary interactions of hardness and sulfate to chloride toxicity. The third major change was in the way they calculated the criterion chronic concentration (CCC). Rather than use the ACR method used by the EPA in 1988, they used the ACR and genus mean acute value (GMAV) to calculate a predicted genus mean chronic value (pGMCV). They then used the pGMCV to calculate a final chronic value (FCV) using the same equations used for the FAV. These changes resulted in a lower CMC but higher CCC for most observed values of hardness and sulfate. The Iowa approach is better able to account for site specific conditions, but the method to determine the CCC is still reliant on the ACR and therefore will be subject to the same criticism.

The review and analysis of existing toxicity studies was presented in a series of draft letters and amendments written by Charles Stephan of the EPA in Duluth, MN dated Jan. 15, 2009 (Stephan 2009b) and Feb. 3, 2009 (Stephan 2009c, a) and in the Water Quality Standards Review (Iowa DNR 2009). According to Stephan (2009b), some studies that were used in 1988 were no longer appropriate. Short acute tests were not used because they sometimes give higher LC<sub>50</sub>s than standard tests (Stephan 2009b). Data from Dowden (1960) and Kostecki and Jones (1983) were not used because, according to Stephan (2009), there were problems with the source of the dilution water. Hamilton et al. (1975) was not used because the midges were not adequately acclimated (according to Stephan 2009b). Acute tests where organisms were fed were not used in EPA 1988 criteria, but these tests were used by Stephan in 2009 and are given preference over unfed acute tests when the test organisms were cladocerans. In addition, tests that were conducted in static or renewal water were not used by the EPA in 1988. But Stephan (2009c, a) thought that "for chloride, as long as the concentration of dissolved oxygen is sufficiently high, it seemed appropriate to give static and renewal acute tests the same weight as flow-through acute tests in the derivation of the SMAV for a species."

Since the 1988 review by the EPA, a study by Wurtz and Bridges (1961) was uncovered, which included six species including two species suspected of being sensitive to chloride (Iowa DNR 2009). A second study (Khangarot 1991) included acute toxicity data for the tubificid worm (*Tubifex tubifex*), which indicated that this species might also be highly sensitive to chloride, but these data were considered unacceptable because the test temperature was high and the acute value for *Daphnia magna* in the



same water was unusually low (Stephan 2009). Given the importance of these data, and the lack of verification by other laboratories, the IDNR and EPA determined that more toxicity data were warranted to independently determine if those species were indeed sensitive to chloride (Iowa DNR 2009). The 1985 guidelines for deriving water quality criteria (Stephan 1985) also allow for the use of a criteria equation rather than a criteria value if there is sufficient evidence that toxicity varies in a predictable manner with one or more environmental variables.

EPA contracted with the GLEC in Columbus, OH and the INHS at Champaign, IL to perform the additional toxicity testing of potentially sensitive species, and to evaluate the impact of hardness or sulfate to chloride toxicity. They evaluated the acute toxicity of chloride to four freshwater invertebrate species: water flea (*Ceriodaphnia dubia*), fingernail clam (*Sphaerium simile*), planorbid snail (*Gyraulus parvus*), and tubificid worm (*Tubifex tubifex*). The experiments were conducted under different levels of water hardness (all four species) and sulfate concentrations (*C. dubia* only). Rank order of sensitivity to acutely lethal chloride at a given water hardness is in order (most to least): *S. simile*>*C. dubia*>*G. parvus*>*T. tubifex*.

The addition of the new studies indicated that the EPA 1988 criterion maximum concentration (CMC) was too high. Incorporating new toxicity values for sensitive taxa resulted in a final acute value (FAV) of 1364 mg/L Cl<sup>-</sup>, which was divided by 2 to arrive at a CMC of 682 mg/L. This value is lower than the 1988 EPA CMC (860 mg/L). Although Iowa did not use this value for their CMC, they did present it as an option (Iowa DNR 2009).

The studies by the GLEC and INHS demonstrated that the toxicity of chloride varied with both hardness and sulfate (Stephan 2009b). Stephan (2009b) used regression of log transformed hardness and LC<sub>50</sub>s from four species to determine how acute responses varied with hardness. Three of the four species showed a strong positive relationship with hardness; i.e., as hardness increased, more chloride was needed to achieve an acute response. The fourth species, the snail *Gyraulus parvus*, showed no response. One species, *C. dubia*, showed a negative relationship with sulfate, although the effect was less than had been observed with hardness. Stephan (2009b) noted that the average of the exponents (describing the hardness response) for three species (*S. simile*, *G. parvus*, *T. tubifex*) was similar to that of *C. dubia*, which he used to justify exclusive use of *C. dubia* to derive the exponents used in the Iowa criteria. Multiple regression was used to determine the exponents for hardness and sulfate using log transformed *C. dubia* LC<sub>50</sub>'s, hardness, and sulfate.

Iowa explored four different options for accounting for changing toxicity as a result of site-specific hardness and sulfate concentrations. Under Option A, acute values were not normalized for either hardness or sulfate and the criteria were not dependent upon either hardness or sulfate (a fixed standard similar to the EPA 1988). Under Options B, C, and D the acute values were either not normalized for hardness and sulfate (Option B) or were normalized (Options C and D), and were either dependent upon both hardness and sulfate (Options B and C) or just hardness (Option D). In the end, Iowa elected to go with Option C, but the CMC and CCC equations were updated to reflect additional data that became available between the time the draft criteria were published and the time the final rule was presented. The final rule was still based on Option C but with the new values (constants) that represented an increase in the values for the CMC and the CCC.

Stephan (2009c, a) also determined the ACR to be lower than the one used by the EPA in 1988. In 1988, the EPA calculated a geometric mean ACR of 7.594 based on two studies of three species: fathead minnows [ACR=15.17], *Daphnia pulex* [ACR= 3.951] (Birge et al. 1985), and rainbow trout [ACR=7.308] (SPEHAR 1987). But the acute and chronic tests with the fathead minnow were performed in different waters and Stephan (2009) determined that the ACR should not be used. Five additional ACRs were available from the scientific literature in 2009 for species for which both acute and chronic values were calculated in the same water. The additional ACRs were all from invertebrate cladocerans and were much smaller than the ACR for fathead minnow and rainbow trout: three ACRs for *Ceriodaphnia dubia* (1.508, >3.841, and 2.601), one for *Daphnia ambigua* (4.148) and one for *Daphnia magna* (1.974) (presented in Stephan 2009). For a given acute value, a smaller ACR will result in a higher CCC. As a result of the smaller ACRs used in 2009, the Iowa CCC (417 mg/L) is higher than the EPA 1988 value (230 mg/L).

The ACR has a large influence over the CCC value; therefore, Iowa explored four different methods of selecting the ACR. CCC1 was derived using ACR = 4.826 which is the geometric mean of the ACRs for rainbow trout (7.308) and the geometric mean of the three *Daphnia* species (3.187). CCC1 was determined to be too high for species at the 5<sup>th</sup> percentile (Iowa DNR 2009). CCC2 was derived using ACR = 3.187 which is the geometric mean of the ACRs for the three *Daphnia* species. CCC2 was determined to be appropriate for species at the 5<sup>th</sup> percentile (Iowa DNR 2009). The IDNR document did not state the exact value of CCC3 but claims that "CCC3 was derived from predicted Genus Mean Chronic Values that were calculated using ACR = 7.308 of Rainbow Trout for vertebrates and ACR = 3.187 of *Daphnia* for invertebrates." This statement implies that the ACR for CCC3 was the average of those two values or 5.248. However, we calculated CCC3 to be 3.357 after dividing 1148 (the FAV in the review document) by 342 (342 is the CCC3 value given for Option A in the review document). The review document provides no additional insight into how Iowa derived the ACR of 3.357, but the arithmetic mean of the three ACRs for *D. ambigua*, *D. magna*, and *D. pulex* equals 3.357. There appears to be an additional issue in the CCC3 equation under Option C. If the ACR of 3.357 for CCC3 is correct, then the multiplier would not be 161.5, which is the value in their Table 4 (Iowa DNR 2009) but rather should be 151.5 (i.e.,  $2 * \text{CMC} / \text{CCC3} - \text{ACR} = \text{CCC3}$ , or  $2 * 254.3 / 3.357 = 151.5$ ). This formula is appropriate for Options A, B, and D and we expect that the formula for Option C would be the same. If we are correct that the CCC should be 151.5, the resulting chronic criteria would be reduced by 10-30 mg/l Cl<sup>-</sup> at a sulfate concentration of 37.9 mg/l. Iowa selected Option C for the acute criterion and CCC3 under Option C as their final proposed chloride criteria after input from the EPA and a special Technical Advisory Committee "based on the scientific justification" (Iowa DNR 2009).

If trout were indeed not used in the selection of the CCC3-ACR value for the Iowa chronic criteria, then it follows that this ACR was derived from three different *Daphnia* studies. The Stephan (2009b) report suggests that these three studies were Harmon et al. (2003), Cowgill and Milazzo (1990), and Birge et al. (1985). One of these studies had a very low ACR for *Daphnia magna* (i.e., resulting from a high chronic value relative to other studies) (Cowgill and Milazzo 1990). *D. magna* is known to be atypical of cladocerans because of its high salinity tolerance (Ebert 2005).

The fourth approach that Iowa explored to determine the CCC was not presented in the Water Quality Standards Review dated Feb. 9, 2009, which contained the final proposed chloride criteria, but was presented in a March 2, 2009 update to their proposed chloride criteria (Stephan 2009a, c). It was in this

new document that the method of calculating the CCC fundamentally changed from what the EPA had done in 1988. Rather than use the ACR from four species to calculate the CCC (Iowa DNR 2009), this approach relied on the predicted GMCV from 29 genera (Stephan 2009a). This method still relied on the ACR, but changed how it was used (Stephan 2009a). In addition, the predicted GMCV did not represent new research, but rather were derived from the existing GMAVs and ACRs. Stephan (2009a) divided the GMAV for each species by the ACR to calculate a genus mean chronic value (GMCV). The GMCVs were then used to calculate a FCV using the same equations that were used to calculate the FAV. Stephan (2009a) noted that the ACR for vertebrates appeared to be large (rainbow trout 7.308 and fathead minnow 15.17) relative to the ACR for invertebrates (*Daphnia* geometric mean ACR 3.187). Therefore, he applied the rainbow trout ACR to all vertebrates and the *Daphnia* geometric mean ACR to all invertebrates, and arrived at a FCV=CCC of 417.0 mg/L Cl<sup>-</sup>. Using two ACRs had a substantial effect on the CCC value when compared to a single geometric mean ACR. With an ACR of 4.826 the FCV=CCC would have been 282.6 mg /L Cl<sup>-</sup> (Stephan 2009a).

Stephan (2009a) justified the alternative approach based on the “good science” clause in section XII.B of the 1985 guidelines. This approach is based on the fact that the four low SMACRs for chloride were obtained with invertebrates, whereas the single high acceptable SMACR was obtained with a vertebrate, and another unacceptable SMACR for fathead minnows was also high (Stephan 2009a). This can be interpreted to mean that vertebrates have a higher ACR on the average than invertebrates (Stephan 2009a).

### **3.5 Delaware, Maryland, New Jersey, New York, Ohio, Virginia, West Virginia**

New Jersey, Virginia, and West Virginia have already adopted the EPA (1988) recommended criteria. New York State has chloride criteria set at 250 mg/l for protecting surface and ground water designated as a water supply for drinking. Ohio, Maryland, and Delaware do not have water quality criteria protecting aquatic life from chlorides. However, Ohio has a statewide aquatic life criterion for total dissolved solids of 1,500 mg/l and human health criteria for the Ohio River main stem at 250 mg/l Cl<sup>-</sup>.

The Delaware River Basin Commission (DRBC) has classified certain waters for “special protection” because they have exceptionally high scenic, recreational, ecological, and/or water supply value. Accordingly, the DRBC has stated that those “special protection” waters (SPW) shall have no measurable change in their existing water quality (2008). The DRBC defines a “Measurable Change to Existing Water Quality” as an actual or estimated change in a seasonal or non-seasonal mean (for SPW waters upstream of and including River Mile 209.5) or median (for SPW waters downstream of River Mile 209.5) in-stream pollutant concentration that is outside the range of the two-tailed upper and lower 95 percent confidence intervals that define existing water quality. All of these waters requiring special protection had median chloride levels less than 50 mg/l Cl<sup>-</sup> which suggested that increases over 50 mg/l would near violation of the rule. This example is similar to PA’s Antidegradation Law that protects biota and water quality of each stream within its designated and existing use in PA (e.g., EV = exceptional value streams, HQ = high quality streams). (PADEP defines a measurable if the instream concentration of a pollutant exceeds the upper 95 percent confidence limit of the median value in the data set used to determine the instream water quality objective). The DRBC documented the location of the “Outstanding Basin

Waters” and “Significant Resource Waters” as reaches along the Upper Delaware (river miles 330.7-250.1), portions of intrastate tributaries, the Middle Delaware (river miles 250.1-134.34), and portions of tributaries located within the Delaware Water Gap National Recreation Area. Furthermore, the DRBC established specific aquatic life use criteria for chloride based on the naturally dilute background levels of the Delaware River for two zones river mile 133.4-108.4 where maximum 15-day average  $\text{Cl}^-$  is 50 mg/l and from river mile 108.5 to 95.0 where maximum 30-day average concentrations of  $\text{Cl}^-$  is 180 mg/l.

### ***3.6 EPA Revision to the 1988 Chloride Criteria***

The US EPA is currently reviewing the 1988 chloride criteria (see Stephan 2009b) and has considered revising their 1985 “Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses” (EPA 2003). The most recent analyses by the EPA (Stephan 2009a, b, c), which were used by Iowa to set their criteria in 2009, do not explicitly propose new EPA chloride criteria. However, the indication from Stephan (2009b) is that the new EPA guidelines will shift to a weight of evidence approach. It is our impression based on Stephan (2009a, b, c) that one fundamental change in the guidelines will be in the rules for determining which studies to include and how information will be used (i.e., which studies are used to calculate FAV, ACR and FCV, and which studies will be used as guidance). Another possible shift will be in the method that chronic criteria are generated, although the justification behind Stephan (2009a) adopting the FCV approach has yet to be critically reviewed. The use of criterion equations in Iowa does not reflect a fundamental shift from the 1985 guidelines, however this was a new approach for chloride regulation in the US. The implication is that the EPA may consider environmental variables, such as hardness and sulfate that are likely to affect chloride toxicity when they update their criteria.

### ***3.7 Calculation of CMC and CCC criteria using 4 methods***

The criteria described above were determined with different sets of data, therefore **we explored which criteria would arise from the different methods if the same data set was used**. The four methods that we explored were EPA 1988, Evans and Frick 2001, British Columbia 2003, and Iowa 2009. **All methods were re-calculated using the GMAVs from the Stephan 2009a report, and are presented in Tables 1 and 2**. For each method, we calculated or determined the FAV, CMC, FCV and CCC using what we think best represents the method. For the methods that relied on an ACR, we used three different values to demonstrate the sensitivity of the CCC value to the ACR. For the Iowa 2009 method, we determined the criterion values (i.e., ignoring hardness or sulfate), not the equations, for better comparison with the other methods.

All methods indicate that the FAV and CMC would be less than 830 mg/L, which is the EPA value and the value proposed by PA (Table 2). The Evans and Frick 2001 method resulted in the most similar value (824 mg/L) and the British Columbia method resulted in the smallest value (564 mg/L). The EPA 1988 and Iowa 2009 methods resulted in the same value (640 mg/L) because the same set of equations were used.

The four methods resulted in slightly different values for the FCV but vastly different values for the CCC (Table 2). The Evans and Frick and British Columbia methods resulted in lower values than the proposed

criterion; the EPA 1988 and Iowa methods resulted in higher values. The most conservative method, by far, was British Columbia's, which resulted in a CCC of 91 mg/L. The reason the Evans and Frick method gave a lower value than EPA 1988 and Iowa was because of the ACR. We used an ACR of 7.59 for Evans and Frick. Iowa used two ACRs, one for vertebrates (7.308) and another for invertebrates (3.187), which we would have expected to result in a lower FCV; but in this case, the value for FCV using this approach is only slightly smaller than the value derived using the EPA 1988 approach, which used just the 3.187 value. The probable reason the change is slight is that the Iowa method relied on only the four lowest predicted GMCVs to calculate the FCV, and in this case only one vertebrate was among those four.

It is not clear which method works best. All methods make a number of assumptions, and each is sensitive to the data used. There is less discrepancy among the values for the CMC but the CCC values are particularly sensitive to the method used. In the face of such uncertainty, it would be best to err on the side of caution and use a safety factor when deriving the CCC criterion.

#### **4 General Comments on Chloride Toxicity Literature**

There are several reviews of the chloride toxicity literature that provide greater detail than we will go into here (see EPA 1988, Evans and Frick 2001, Iowa DNR 2009, Stephan 2009a,b,c). Based on our inspection of these reviews and a limited search of the relevant literature we have attempted to identify limitations to the general body of literature and to point out potential gaps in knowledge.

The quantification of the impact of chloride concentrations on aquatic organisms has been primarily approached from a toxicological perspective where laboratory studies are used to isolate organisms of interest and subject them to varying concentrations of chloride in the form of NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, or KCl. The majority of studies has been limited to the use of NaCl but Evans and Frick and to some extent Stephan (2000B) summarize those studies. In addition, the majority of studies has conducted short-term or acute studies (1 week or less; typically 96 hrs but 24 and 48 hrs studies are common) where concentrations of salt vary dramatically and the primary response variable is mortality (lethality). As such, acute studies primarily result in the documentation of LC<sub>50</sub> values (lethal concentrations where 50% mortality occurs). There are a limited number of longer-term or chronic studies and even fewer studies that have conducted both acute and chronic studies using the same organisms as part of the same study. Chronic studies typically involve other life stages that may vary in toxicity response. Non-lethal response variables include % hatching success, growth rate, metabolic rate, or size at maturity, for example. The limited nature of both acute and chronic information produced within a study for the same organism is very important to the derivation of ACRs (see Iowa Criteria above and through this report) used in nearly all of the proposed criteria in the United States and is also extensively discussed in the Canadian review conducted by Evans and Frick (2001).

As mentioned previously, there are far fewer studies examining CaCl<sub>2</sub>, MgCl<sub>2</sub>, or KCl toxicity to aquatic organisms than for NaCl toxicity. Evans and Frick (2001) and Stephan (2009b) summarize most of those studies. In 1988, the EPA presented acute toxicity data for CaCl<sub>2</sub>, MgCl<sub>2</sub>, and KCl, but limited the derivation of the acute and chronic criteria to only NaCl toxicity studies. Both reviews found that KCl tends to be the most toxic salt followed by MgCl<sub>2</sub>, CaCl<sub>2</sub>, and then NaCl. The majority of chloride criteria developed to date are limited to or dominated by data on NaCl chloride toxicity, the least toxic salt. This

point is routinely justified by the fact that NaCl is the most anthropogenically abundant of these four salts. Marcellus shale discharges constitute an example of anthropogenic contributions of other salts.

One of the more intriguing studies we reviewed was a study conducted on Eastern Australia's aquatic macroinvertebrate fauna (Dunlop et al. 2007). Dunlop et al. (2007) collected 102 species from 4 regions in E. Australia and conducted acute (72 hr) chloride toxicity tests. They observed regionally-specific salinity tolerances and suggested that local ambient conditions influenced sensitivities within species. They also provided exemplary analysis that ranked the acute toxicity of the major taxonomic groups studied. The only other study we reviewed that attempted to do this was Evans and Frick (2001), but they used information from many disparate studies and did not find several representatives within each major taxonomic group to parallel Dunlop et al. (2007). The rank order reported in Dunlop et al. (2007) indicated that the known evolutionary invasions of various taxonomic groups to freshwater tended to groups of organisms predisposed to salinity tolerances. For example, decapods (primarily crayfish) invaded freshwater directly from salt water environments; out of all of the groups tested, they had the highest salinity tolerances. Ephemeroptera, on the other hand, were the most sensitive and were among the first insects to invade freshwaters millions of years ago from the terrestrial environment. It was interesting to note that Australian aquatic taxa may be better adapted to more saline conditions than North American taxa (logically following that the Australian continent is very dry and consequently inland waters have elevated salt concentrations due to evaporative losses and subsequent concentration of salts in residual pools of water). It was also intriguing to note that no comparable study has been conducted in the US (i.e., no single study has so exhaustively included so many taxa from an extensive geographical range).

Two studies on chloride toxicity in the embryonic survivorship of the spotted salamander suggest that these eggs are sensitive to low chloride concentrations (perhaps as low as 150 mg/l Cl<sup>-</sup>) (Turtle 2001, Karraker et al. 2008). However, both studies were field studies where pollutants other than chloride may have influenced survivorship, and the Karraker et al. (2008) study only measured specific conductivity as a surrogate for salinity. Other amphibian studies (Dougherty and Smith 2006, Sanzo and Hecnar 2006) document chloride impacts to larval stages of various frogs, and one study (Dougherty and Smith 2006) observed lower LC<sub>50</sub>s for MgCl<sub>2</sub> derived Cl<sup>-</sup> (as low as 116 mg/l Cl<sup>-</sup>) compared to NaCl derived Cl<sup>-</sup> (as low as 406 mg Cl<sup>-</sup>/l) for *Rana clamitans*. The EPA 1988 criteria do not include data from amphibians and the recent EPA review by Stephan (2009) only includes two acute amphibian studies (Bullfrog tadpole and Chorus frog). Evans and Frick (2001) provide a fairly comprehensive review and include amphibians in their acute and chronic chloride risk characterization. Amphibian species in Pennsylvania that occur in streams or in water bodies immediately adjacent to streams are listed in Table 3. Not including stream dwelling or stream-side wetland dwelling amphibians may ultimately yield a less protective criteria.

There have been a very limited number of studies on the synergistic effects of salt cations on chloride toxicity. Evans and Frick (2001) point out that those salt solutions that contain different salts (particularly Na, Ca, Mg, and K) in certain proportions can be physiologically-balanced to neutralize or reduce the specific toxicity of each through antagonistic action. This can lead to reduced toxicity of cations to aquatic organisms. Evans and Frick (2001) cite three studies that have investigated this ion synergy: Garrey (1916) using minnows; Grizzle and Mauldin (1995) using juvenile striped bass, red drum, and channel catfish; and Borgmann (1996) using a freshwater amphipod. A common thread appears to be that, at the right concentration, **Ca tends to reduce the toxicity of NaCl**. The GLEC and INHS studies

(see Iowa DNR 2009, Stephan 2009b) quantified the influence of hardness on Cl<sup>-</sup> toxicity in 4 species known to be sensitive to Cl<sup>-</sup> and also the influence of sulfate on *Ceriodaphnia* Cl<sup>-</sup> toxicity (see analysis of Iowa criteria below). Those studies found that 3 of the 4 taxa studied had increased tolerances of chloride with increasing CaCO<sub>3</sub> hardness; *Ceriodaphnia* had decreased tolerance of Cl<sup>-</sup> with increasing SO<sub>4</sub> concentrations. All of the studies on the ion synergies and chloride toxicity are for acute tests only. **We have found no studies that have evaluated these relationships on a chronic basis.**

Silver et al. (2009) studied chironomid larvae (non-biting midges) responses to road deicing salt in two constructed wetlands in NE Pennsylvania. Specific conductivity (as an indicator of salt concentration) during runoff events in winter approached that of seawater (30 mS/cm). Conductivity remained high during winter (4 mS/cm) and returned to 1 mS/cm in spring. They conducted laboratory tests using NaCl to test the influence of NaCl and temperature on chironomid survival and found that lower temperatures resulted in higher survivorship. In fact, at low temperature, survival appeared to be higher in the presence than in the absence of salt. As temperature increased, salt appeared to have an increasingly negative effect at decreasing concentrations, until at 22°C, any amount of salt depressed survival significantly. Silver et al. (2009) suggested that at low temperatures, NaCl uptake by midge larvae may help induce supercooling and external NaCl may depress the freezing point to prevent inoculative freezing. Also, at lower temperatures, midges may enter diapause and be physiologically inactive, so metabolic costs of osmoregulation are lowered. These data suggest that seasonal changes in temperature may be an important factor to consider with regard to chloride toxicity, especially higher summer temperatures associated with warm water fisheries.

Meador and Carlisle (2007) examined distributions of 105 stream fish species from 773 sites throughout the US for relationships with 10 chemical and physical variables measured by the USGS National Water Quality Assessment Program. They calculated tolerance indicator values for all physical-chemical variables based on changes in fish community patterns. Chloride tolerance indicator values were relatively low. For example, Brook Trout and Cutthroat Trout had a calculated tolerance value of 3.1 and 4.4 mg/l Cl<sup>-</sup>, respectively. A classification of Tolerant, Moderate, and Intolerant was developed for each physicochemical variable. Chloride tolerance categories were 35-42 mg/l Cl<sup>-</sup> (tolerant), 23-31 mg/l Cl<sup>-</sup> (moderate), and 10-24 mg/l Cl<sup>-</sup> (intolerant). The remaining fish taxa were associated with each group. Several other physicochemical variables were correlated with Cl<sup>-</sup> concentrations (e.g., suspended sediments and total phosphorus). Other unmeasured variables may be influencing these patterns; and at such a broad spatial scale, the ultimate factors and mechanisms responsible for fish distributions are likely to be complex. These results suggest that changes in chloride concentrations that are less than the EPA 1988 (and the proposed PA criteria) chronic criteria value may still influence fish distributions and ultimately alter site-specific fish community structure.

## 5 Examples of baseflow chloride concentrations in PA (EMAP survey 1993-96)

From 1993-1996, the USGS collected water chemistry samples from 246 streams in Pennsylvania as part of a national Environmental Assessment and Monitoring Program (EMAP). Concentrations of major anions, cations, major nutrients, and organic and inorganic carbon are available online<sup>2</sup> along with other

<sup>2</sup> [http://oaspub.epa.gov/emap/webdev\\_emap.show\\_frames?entry\\_id\\_in=275](http://oaspub.epa.gov/emap/webdev_emap.show_frames?entry_id_in=275)

related datasets<sup>3</sup>. Hardness (mg CaCO<sub>3</sub>/L) was calculated from Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations using Standard Method 2340B (Standard Methods 1998).

Sample sites were located throughout the state but were primarily from the Appalachian Plateau and Ridge and Valley physiographic provinces (Fig. 2). The average chloride, sulfate, and hardness concentrations ( $\pm$  95% confidence intervals) were 7.7 (6.3-9.1), 37.9 (21.6-54.2), and 68.6 (54.3-82.9) mg/l, respectively. Only 19 of 246 sites had Cl<sup>-</sup> concentrations > 20 mg/l, and 4 sites were >50 mg/l Cl<sup>-</sup> (Fig. 3). The concentrations of chloride, sulfate, and hardness varied by aquatic use designation (Fig. 4) such that EV and HQ streams had the lowest concentrations and WWF and TSF had the highest concentrations. All four approaches to set acute and chronic criteria would result in chloride concentrations at least several times greater than base flow concentrations commonly observed in Pennsylvania streams in their most natural condition (i.e., Exceptional Value and High Quality waters).

It is also instructive to note that the range of concentration of hardness in Pennsylvania was considerably lower than that found in Iowa. For example, the Iowa DNR report (2009) provides a map of hardness concentrations mostly ranging from 200 to 400 mg/l CaCO<sub>3</sub> compared to 29 of the 246 EMAP sites in PA >150 mg/l CaCO<sub>3</sub> and 18 of 246 sites >200 mg/l CaCO<sub>3</sub>. Within Pennsylvania, the streams in southwest PA tended to have higher hardness and sulfate concentrations than elsewhere in the state (Fig. 5).

## 6 Stream Chloride Concentrations in Pennsylvania from EMAP Data and the Iowa Criteria

EMAP data were used to calculate acute and chronic chloride criteria based on the Iowa formulation. Those data indicate that the Iowa criteria would lower the acute chloride criteria from the proposed 860 mg/l to an average of 500.9  $\pm$  10.6 mg/l (95% CI), and raise the chronic standard from the proposed 230 mg/l to 309.6  $\pm$  6.5 mg/l (Fig. 6). The range of values calculated for the 246 EMAP sites using the acute and chronic Iowa criteria were 342.8 – 742.0 and 211.8 – 458.6 mg/l Cl<sup>-</sup>, respectively and the full distribution of data are shown in the middle and lower panels of Fig. 6.

EMAP data were paired with information on the PA designated use assigned to each sampling site. The site-specific criteria derived using the Iowa criteria equations were then partitioned based on the designated use (Fig. 7). Based on those data, EV and HQ designations would have lower chloride criteria applied to those sites (if they were to be included in a chloride criteria; currently Antidegradation Criteria protect EV and HQ streams) compared to CWF, WWF, and TSF.

Finally, EMAP data were used to calculate Iowa chloride criteria (chronic and acute) over the range of hardness or sulfate occurring in the database (Fig. 8). The resulting panels in Fig. 8 illustrate the relationship between the chronic and acute chloride criteria and either hardness or sulfate over the entire range of hardness and sulfate conditions occurring in the EMAP PA dataset (left panels) and for the majority of sites (right panels; i.e., x-axis concentrations range over the 95% confidence intervals for either sulfate [upper right panel] and hardness [lower right panel] in the EMAP dataset).

<sup>3</sup> <http://www.epa.gov/emap/html/data/surfwatr/data/mastreams/9396>



## 7 Conclusions

After reviewing four different approaches for deriving water quality chloride criteria to protect aquatic life (Stephan et al. 1985, Evans and Frick 2001, Nagpal et al. 2003, Iowa DNR 2009) and the data underpinning PA's proposed criteria (EPA 1988) and the Iowa criteria (Stephan 2009a,b,c), it is clear that:

- 1) All approaches set chloride criteria that are at least several times greater than natural baseline chloride concentrations, and therefore represent a measurable and significant change in the chemical composition of freshwater ecosystems in the NE United States. The question that the current evidence is unable to answer is: will these criteria result in significant biological change? There is limited evidence of the biological impact of previous elevated chloride levels in aquatic ecosystems in the U.S. or Canada. Past monitoring efforts (see introduction) suggest that some streams regularly reach the acute criterion, but there has not been a noted change in biota following these pulses, largely because of a dearth of biological data following these episodic events. One study has demonstrated that macroinvertebrate drift increases in response to pulsed chloride input (Blasius and Merritt 2002). Another study has demonstrated losses of species in stream fish communities with small changes in chloride levels across a regional-scale analysis (Meador and Carlisle 2007), and the composition of algal species has been observed to change when chloride concentrations increase (Evans and Frick 2001). Nonetheless, there are limited data on biological changes accompanying changing chloride concentrations in the natural environment. We could not find any studies evaluating the influence of chloride on vital stream functions such as primary production, stream metabolism, or nutrient uptake or processing, all of which are important indicators of water quality for aquatic ecosystems.
- 2) All of these criteria are based on data for invertebrate and fish species that are not a random subset of stream invertebrate and fish species. Rather, most of the species with chloride data are known to be not especially sensitive to changes in environmental condition, which is one reason they survived well in the laboratory and became standards in laboratory bioassay protocols. The most recent iteration of the taxa that qualify based on EPA standards (in Stephan 2009a,b,c) doesn't include any classically sensitive stream invertebrate species such as stoneflies, mayflies, and caddisflies, all of which are important indicators of stream condition and are integral in the regulatory definition of stream impairment. Our concern is that criteria intended to protect most (e.g., 90% or 95%) of the species with chloride data might actually protect a much smaller proportion of all species that occur in a natural community because the natural community includes many species known to be sensitive to environmental change while the laboratory studies are biased toward species known to be at least moderately tolerant of environmental change. This is one reason to approach the acute and chronic criteria with a strong safety factor.
- 3) Data available are primarily from acute toxicity studies, but the chronic criterion may be more important for long-term structuring stream communities and maintaining designated use for aquatic life. For example, fish tend to be moderately tolerant of acute chloride stress relative to macroinvertebrates, but they are one of the more sensitive taxa to chronic chloride stress. For example, fat head minnows (Birge et al. 1985) experienced the greatest mortality between days

9 and 21 and therefore had one of the highest acute-to-chronic ratios examined. The dearth of chronic studies on both invertebrates and fish is troubling. It is likely that, like some amphibians (e.g., spotted salamander), embryonic and early life stages of some fish will be more sensitive than is currently recognized.

- 4) The majority of chloride criteria developed to date are limited to or dominated by data on NaCl chloride toxicity, the least toxic salt. This point is routinely justified by the fact that NaCl is the most anthropogenically abundant of these four salts. However, no special guidance is given for permitting salt applications or industrial effluents known to include significant amounts of chloride derived from the more toxic non-sodium salts, including Marcellus Shale wastewater.
- 5) Using the data provided in Stephan 2009a (Table 2 herein), we have calculated both the acute (CMC) and chronic (CCC) criteria using the methods of the EPA (Stephan et al. 1985, EPA 1988), Evans and Frick (Evans and Frick 2001), British Columbia (Nagpal et al. 2003), and Iowa (Iowa DNR 2009) and have compared the range of values with the proposed PA values (Table 3). The range of acute values is 564 – 830 mg/l Cl<sup>-</sup> and the range of the chronic values is 91 – 428 mg/l Cl<sup>-</sup>. This comparison eliminates the variability in the choices each of the authors have made with regard to studies included or excluded. We note that the PA proposed acute value is the least protective criterion, primarily because it is not based on more recent acute toxicity studies. We recommend that PA adopt an acute criterion that is reflective of these new data. The method adopted by British Columbia is the most protective of aquatic life among these approaches. BC invoked a precautionary principle that acknowledged both the uncertainty of the available data and analyses and the importance of protecting their aquatic life. Since BC adopted their criteria, only new acute datasets have become available and the values in Table 3 utilize those data but use the BC approach to arrive at a final value (i.e., lowest SMAV/2[safety factor]). The BC use of a safety factor of 2 for the acute criteria was also consistent with what the EPA had done. However, BC was the only entity to apply a safety factor for the chronic criterion (5). We feel that the use of a safety factor for chronic criteria derived from the use of an ACR is clearly justified given the very limited number of chronic toxicity studies, and the desire to protect species that may be more sensitive than those used in the standard laboratory bioassays. We recommend that PADEP adopt the same methodology that BC has used for calculating both acute and chronic data. We feel that this is particularly important for the chronic criteria, as there is the potential for permitted discharges (particularly from the Marcellus Shale gas drilling industry) to raise chloride concentrations in streams to near the chronic criteria level. Given the paucity of data determining thresholds for chronic effects, this approach is warranted. At the very least, a safety factor should be applied to any of the other methods producing a chronic criterion.

We have a number of concerns that are specific to the actions and options available for PADEP:

- 6) Protecting CWFs and TSFs based on ACRs that included more chloride-tolerant *Daphnia* is not justified when it may expose rainbow trout to chloride concentrations approaching their chronic levels (1,324 mg/l Cl<sup>-</sup> killed 46% of individuals in an early life stage test and at 643 mg/l Cl<sup>-</sup> killed <4%). Trout are an integral component in the definition of these two aquatic life uses. The proposed chronic value of 230 mg/l is potentially a concern for biotic assemblages in

Pennsylvania. For example, Meador (2007) suggests that optimum  $\text{Cl}^-$  values are low (3-35 mg/l) and we infer that if those  $\text{Cl}^-$  concentrations are exceeded it may result in changes in fish community structure. Similarly, not having a temperature component also seems to invite season-specific impairments of macroinvertebrates in TSFs and WWFs based on the recent findings of Silver et al. (2009), based on the seasonal movement of organisms into and out of various life history stages, and based on variation in their metabolic rates in response to seasonal changes in water temperature. Adding a temperature component to the chloride criteria would require further research on temperature effects.

- 7) The Evans and Frick (2001) method has the benefit of being reproducible and open to interpretation. Their use of nearly all of the valid acute  $\text{LC}_{50}$  data in Fig. 7-2 (Evans and Frick 2001), and the calculation of a sigmoid curve function (including 95% confidence intervals) that describes the percent of genera affected versus chloride concentration, is readily digestible by the public. However, the sigmoid curve function can be generated using various numbers of terms (parameters) in the equation and/or various equations (e.g., sigmoid, logistic, Weibull). The result of choosing a slightly different function can result in differences in acute and chronic values. To use this approach requires a valid justification for the choices made in fitting the curve to these data. Furthermore, these data still represented a small subset of aquatic species, and were biased towards lab friendly species that are easiest to culture (e.g., *Daphnia*). Since the selection of taxa was not a random subset of the aquatic species at large, most criteria based on the animals selected are primarily protective of those species tested (e.g., being protective of 95% of those taxa might only be protective of 50% of all species). This point is not limited to Evans and Frick but is valid for all of the approaches we have reviewed. This is the primary reason that the application of a safety factor is needed. The Evans and Frick (2001) study did not apply a safety factor to either their acute  $\text{LC}_{50}$  relationship or the derived chronic relationship.
- 8) More data is generally better, but there is a need for more consideration of how data gets incorporated. The Stephan (2009a,b,c) approach of calculating a predicted genus mean chronic value from the species mean acute values does not seem justified in this case. The GMCVs are not much better than guesses, and there is no attempt to correct for this inherent uncertainty. Adding GMCV values above the lowest four gives the false sense of increased precision of the true distribution of the GMCV, which has the result of increasing the final chronic value (FCV). We feel it would be appropriate to apply a safety factor to the chronic criteria to acknowledge the uncertainty in the FCV.
- 9) The use of hardness and sulfate equations (Iowa DNR 2009) in PA will improve protections and application of the chloride criteria only to a limited extent since the range of criteria in PA would be narrow (based on EMAP site values for hardness and sulfate in PA). Secondly, the hardness and sulfate exponents in the Iowa criteria were based on data from an acute toxicity study of only one species (*C. dubia*), although four species were studied and three were sensitive to hardness. No data were available on the relationship between hardness or sulfate and chronic toxicity. In the end, Iowa uses a default value for hardness and sulfate if no other data are available. This is akin to setting a fixed criterion value but allowing site-specific deviations if one

gathers the appropriate data. Clearly, more species-specific data are needed to better understand the relationship between chloride toxicity and hardness or sulfate.

- 10) As noted above, previous reviews of chloride considered only NaCl and considered road salt to be the most likely source of chloride. We feel that the current proposed standard should explicitly acknowledged that these criteria are specific to NaCl derived chloride, and guidance should be given to address cases when significant chloride is derived from salts (i.e., KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub>) that have proven to be more toxic sources of chloride.

Our review of four approaches (Stephan et al. 1985, Evans and Frick 2001, Nagpal et al. 2003, Iowa DNR 2009) for deriving chloride criteria to protect aquatic life identified a number of weaknesses in the available data and the analyses used to derive criteria. We were especially concerned with (1) the near absence of important stream-inhabiting and stream-classifying species such as mayflies, stoneflies, and caddisflies, (2) the dependence on relatively few chronic studies, and (3) the choice of excluding some studies that were very important (e.g., fat head minnow Birge et al. 1985). We believe these weaknesses justify using a very conservative approach to assigning criteria. All four approaches to set acute and chronic criteria would result in chloride concentrations at least several times greater than base flow concentrations commonly observed in Pennsylvania streams in their most natural condition (i.e., Exceptional Value and High Quality waters). The lowest criteria for chloride were derived by the Canadian Province of British Columbia (Nagpal et al. 2003) – they acknowledged the weaknesses in available data, and applied safety factors of 2 for the acute criterion and 5 for the chronic criterion. Given the limits in the available data, and the potential that treated wastewaters from Marcellus Shale drilling may result in near-criterion chloride concentrations 356 days per year (versus the 30 days of a standard chronic bioassay), we believe the British Columbia criteria (either the originally adopted criteria or our re-calculated criteria in Table 2) would be the most protective of aquatic life for Pennsylvania streams, especially for the trout and many pollution-sensitive macroinvertebrate species that characterize Cold Water Fishes streams.

## 8 Literature Cited

- Benbow, M. E. and R. W. Merritt. 2004. Road-salt toxicity of select Michigan wetland macroinvertebrates under different testing conditions. *Wetlands* 24:68-76.
- Birge, W. J., J. A. Black, A. G. Westerman, T. M. Short, S. B. Taylor, D. M. Bruser, and E. D. Wallingford. 1985. Recommendations on numerical values for regulating iron and chloride concentrations for the purpose of protecting warmwater species of aquatic life in the Commonwealth of Kentucky. University of Kentucky, Lexington, KY.
- Blasius, B. J. and R. W. Merritt. 2002. Field and laboratory investigations on the effects of road salt (NaCl) on stream macroinvertebrate communities. *Environmental Pollution* 120:219-231.
- Borgmann, J. 1996. Systematic analysis of aqueous ion requirements of *Hyallela azteca* - A standard artificial medium including the essential bromide ion. *Archives of Environmental Contamination and Toxicology* 30:356-363.
- Bright, D. A. and J. Addison. 2002. Derivation of Matrix Soil Standards for Salt under the British Columbia Contaminated Sites Regulation. Addendum A: Technical Options Analysis for a Soil Chloride Standard for Drinking Water Protection (Aesthetic). Report to the British Columbia Ministry of Water, Land and Air Protection, Ministry of Transportation and Highways, British Columbia Buildings Corporation, and the Canadian Association of Petroleum Producers, Applied Research Division, Royal Roads University, Victoria, BC, Canada.
- Chang, H. J. and T. N. Carlson. 2005. Water quality during winter storm events in Spring Creek, Pennsylvania USA. *Hydrobiologia* 544:321-332.
- Cowgill, U. M. and D. P. Milazzo. 1990. The sensitivity of two cladocerans to water quality variables: salinity and hardness. *Archiv für Hydrobiologie* 120:185-196.
- DeGreave, G. M., J. D. Cooney, B. H. Marsh, T. L. Pollock, and N. G. Reichenbach. 1992. Variability in the performance of the 7-d *Ceriodaphnia dubia* survival and reproduction test: an intra- and interlaboratory study. *Environmental Toxicology and Chemistry* 11:851-866.
- Diamond, J. M., E. L. Winchester, D. G. Mackler, and D. Gruber. 1992. Use of the mayfly *Stenonema modestum* (Heptageniidae) in subacute toxicity assessments. *Environmental Toxicology and Chemistry* 11:415-425.
- Dougherty, K. T. and G. R. Smith. 2006. Acute effects of road de-icers on the tadpoles of three anurans. *Applied Herpetology* 3:87-93.
- Dowden, B. F. 1960. Cumulative toxicities of some inorganic salts to *Daphnia magna* as determined by median tolerance limits. *Proceedings of the Louisiana Academy of Sciences* 23:77-85. (A:915).
- DRBC. 2008. Administrative Manual - Part III. Water Quality Regulations, with amendments through July 26, 2008. 18 CFR Part 410. Delaware River Basin Commission. West Trenton, New Jersey.
- Dunlop, J. E., N. Horrigan, G. McGregor, B. J. Kefford, S. Choy, and R. Prasad. 2007. Effect of seasonal variation on salinity tolerance of macroinvertebrates in Eastern Australia and implications for ecosystem protection trigger values. *Environmental Pollution* doi:10.1016/j.envpol.2007.03.020.
- Ebert, D. 2005. Ecology, Epidemiology, and Evolution of Parasitism in *Daphnia* [Internet]. National Library of Medicine (US), National Center for Biotechnology Information, Bethesda, MD.
- EPA. 1988. Ambient aquatic life water quality criteria for chloride-1988. EPA 440/5-88-001, U.S. Environmental Protection Agency, Duluth, Minnesota.

- EPA. 2003. Draft strategy: Proposed revisions to the "Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. U.S. Environmental Protection Agency.
- Evans, M. and C. Frick. 2001. The effects of road salts on aquatic ecosystems. NWRI Contribution Series No. 02-308, National Water Research Institute and University of Saskatchewan, Saskatoon, SK, Canada.
- Feldman, S. R. 2005. Sodium Chloride. Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc. Published online, 2005 doi:10.1002/0471238961.1915040902051820.a01.pub2.
- Gardner, K. M. and T. V. Royer. 2010. Effect of Road Salt Application on Seasonal Chloride Concentrations and Toxicity in South-Central Indiana Streams. *Journal of Environmental Quality* 39:1036-1042.
- Garrey, W. E. 1916. The resistance of freshwater fish to changes of osmotic and chemical conditions. *American Journal of Physiology* 39:313-329.
- Grizzle, J. M. and A. C. Mauldin II. 1995. Effect of calcium on acute toxicity of sodium chloride to larval and newly transformed juvenile striped bass. *Journal of Aquatic Animal Health* 7:298-303.
- GWPC, U. 2009. Modern shale gas development in the United States: a primer. Work Performed Under DE-FG26-04NT15455, Ground Water Protection Council and U.S. Department of Energy, Oklahoma City, OK.
- Hamilton, R. W., J. K. Buttner, and R. G. Brunetti. 1975. Lethal levels of sodium chloride and potassium chloride for an Oligochaeta, a chironomid midge, and a caddisfly of Lake Michigan. *Environmental Entomology* 4:1003-1006.
- Harmon, S. M., W. L. Specht, and G. T. Chandler. 2003. A comparison of the daphnids *Ceriodaphnia dubia* and *Daphnia ambigua* for their utilization in routine toxicity testing in the southeastern United States. *Archives of Environmental Contamination and Toxicology* 45:79-85.
- Heisig, P. M. 2000. Effects of residential and agricultural land uses on the chemical quality of baseflow of small streams in the Croton watershed, Southeastern New York. WRIR 99-4173, U.S. Geological Survey.
- Hughes, J. S. 1973. Acute Toxicity of Thirty Chemicals to Striped Bass (*Morone saxatilis*). Louisiana Wild Life and Fisheries Commission (A:2012).
- Iowa DNR. 2009. Water quality standards review: chloride, sulfate, and total dissolved solids. Iowa Department of Natural Resources.
- Karraker, N. E., J. P. Gibbs, and J. R. Vonesh. 2008. Impacts of road deicing salt on the demography of vernal pool-breeding amphibians. *Ecological Applications* 18:724-734.
- Kaushal, S. S., P. M. Groffman, G. E. Likens, K. T. Belt, W. P. Stack, V. R. Kelley, L. E. Band, and G. T. Fisher. 2005a. Increased salinization of fresh water in the northeastern United States. *Proceedings of the Academy of Natural Sciences of Philadelphia* 102:13517-13520.
- Kaushal, S. S., P. M. Groffman, G. E. Likens, K. T. Belt, W. P. Stack, V. R. Kelly, L. E. Band, and G. T. Fisher. 2005b. Increased salinization of fresh water in the northeastern United States. *Proceedings of the National Academy of Science of the United States of America* 102:13517-13520.
- Kelly, V. R., G. M. Lovett, K. C. Weathers, S. E. G. Findlay, D. L. Strayer, D. J. Burns, and G. E. Likens. 2008. Long-term sodium chloride retention in a rural watershed: legacy effects of road salt on streamwater concentration. *Environmental Science and Technology* 42:410-415.
- Khangarot, B. S. 1991. Toxicity of metals to a freshwater tubificid worm, *Tubifex tubifex* (Muller). *Bulletin of Environmental Contamination and Toxicology* 46:906-912. (A:2918).

- Kostecki, P. T. and J. J. Jones. 1983. The effect of osmotic and ion-osmotic stresses on the mortality of Rainbow Trout (*Salmo gairdneri*). *Comparative Biochemistry and Physiology* 74A:773-775.
- Meador, M. R. and D. M. Carlisle. 2007. Quantifying tolerance indicator values for common stream fish species of the United States. *Ecological Indicators* 7:329-338.
- Mullaney, J. R., D. L. Lorenz, and A. D. Arntson. 2009. Chloride in groundwater and surface water in areas underlain by the glacial aquifer system, northern United States. Scientific Investigations Report 2009-5086, U.S. Geological Survey.
- Nagpal, N. K., D. A. Levy, and D. D. MacDonald. 2003. Water Quality: Ambient water quality guidelines for chloride - Overview report. Ministry of Environment, British Columbia, Canada (online <http://www.env.gov.bc.ca/wat/wq/BCguidelines/chloride/chloride.html>), British Columbia, Canada.
- Rosenberry, D. O., P. A. Bukaveckas, D. C. Buso, G. E. Likens, A. M. Shapiro, and T. C. Winter. 1999. Movement of road salt to a small New Hampshire Lake. *Water Air and Soil Pollution* 109:179-206.
- Salt Institute. 2004. Highway salt and our environment. Salt Institute, Alexandria, VA.
- Sanzo, D. and S. J. Hecnar. 2006. Effects of road de-icing salt (NaCl) on larval wood frogs (*Rana sylvatica*). *Environmental Pollution* 140:247-256.
- Silver, P., S. M. Rupprecht, and M. F. Stauffer. 2009. Temperature-dependent effects of road deicing salt on chironomid larvae. *Wetlands* 29:942-951.
- Siver, P. A., R. W. Canavan, IV, C. K. Field, L. J. Marsicano, and A.-M. Lott. 1996. Historical Changes in Connecticut Lakes Over a 55-Year Period. *Journal of Environmental Quality* 25:334-345.
- Spehar, R. L. 1987. Memorandum to C. Stephan. U.S. EPA. U.S. EPA, Duluth, MN.
- Standard Methods. 1998. Standard Methods for the Examination of Water and Wastewater. 20<sup>th</sup> edition. L.S. Clesceri, A.E. Greenberg, A.D. Eaton editors.
- Stephan, C. E. 2009a. Calculation of aquatic life criteria for chloride. 09FebChlorideCriteria.wpd, U.S. Environmental Protection Agency, Duluth, MN.
- Stephan, C. E. 2009b. Draft, Calculation of aquatic life criteria for chloride. Draft Report 1-15-2009, U.S. Environmental Protection Agency, Duluth, MN.
- Stephan, C. E. 2009c. Summary data concerning the acute toxicity of sodium chloride to aquatic animals. 09FebChlorideAcute.wpd, U.S. Environmental Protection Agency, Duluth, MN.
- 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. U.S. Environmental Protection Agency Office of Research and Development, Duluth, MN.
- Turtle, S. L. 2001. Embryonic survivorship of the spotted salamander (*Ambystoma maculatum*) in roadside and woodland vernal pools in southeastern New Hampshire. *Journal of Herpetology* 34:60-67.
- Wurtz, C. B. and C. H. Bridges. 1961. Preliminary results from macro-invertebrate bioassays. *Proceeding of the Pennsylvania Academy of Sciences* 35:51-56.

Expert Report on the Proposed Ambient Water  
Quality Criteria for Chloride in PA Waters



**Table 1:** Chloride genus mean acute values (GMAV in mg Chloride/L) ranked highest to lowest. The GMAV is the geometric mean of the species mean acute values (SMAV). Table reproduced from Stephan 2009a.

Rank	GMAV	Genus	Species	Species	SMAV
29	17161	<i>Anguilla</i>	American eel	<i>Anguilla rostrata</i>	17,160.6
28	16203	<i>Cambarus</i>	Crayfish	<i>Cambarus sp.</i>	16,203.2
27	14897	<i>Fundulus</i>	Plains killifish	<i>Fundulus kansae</i>	14,897.1
26	14843	<i>Libellulidae</i>	Dragonfly	<i>Libellulidae</i>	14,843.4
25	13453	<i>Gasterosteus</i>	Threespine stickleback	<i>Gasterosteus aculeatus</i>	13,452.6
24	>11860	<i>Poecilia</i>	Guppy	<i>Poecilia reticulata</i>	>11,860
23	9933	<i>Gambusia</i>	Mosquitofish	<i>Gambusia affinis</i>	9,933.4
22	9157	<i>Lepomis</i>	Green sunfish	<i>Lepomis cyanellus</i>	9,974.9
			Bluegill	<i>Lepomis macrochirus</i>	8,406.5
21	8971	<i>Notropis</i>	Red shiner	<i>Notropis lutrensis</i>	8,971.1
20	8043	<i>Oncorhynchus</i>	Rainbow trout	<i>Oncorhynchus mykiss</i>	8,042.6
19	7442	<i>Ameiurus</i>	Black bullhead	<i>Ameiurus melas</i>	7,442.4
18	6515	<i>Pimephales</i>	Fathead minnow	<i>pimephales promelas</i>	6,515.3
17	6219	<i>Tubifex</i>	Tubificid worm	<i>Tubifex tubifex</i>	6,218.6
16	6111	<i>Cyprinella</i>	Bannerfin shiner	<i>Cyprinella leedsii</i>	6,111
15	6072	<i>Chironomus</i>	Midge	<i>Chironomus dilutus</i>	6,072
14	5897	<i>Rana</i>	Bullfrog (tadpole)	<i>Rana catesbeiana</i>	5,897
13	5444	<i>Lumbriculus</i>	Aquatic worm	<i>Lumbriculus variegatus</i>	5,444
12	5078	<i>Hyalella</i>	Amphipod	<i>Hyalella azteca</i>	5,077.7
11	4686	<i>Pseudacris</i>	Chorus frog	<i>Pseudacris sp.</i>	4,686
10	4369	<i>Nepheleopsis</i>	Leech	<i>Nepheleopsis obscura</i>	4,369
9	3946	<i>Diaptomus</i>	Copepod	<i>Diaptomus clavipes</i>	3,946.1
8	3891	<i>Lirceus</i>	Isopod	<i>Lirceus fontinalis</i>	3,890.7
7	3728	<i>Gyraulus</i>	Snail	<i>Gyraulus parvus</i>	3,727.7
6	3350	<i>Physa</i>	Snail	<i>Physa gyrina</i>	3,350
5	3086	<i>Villosa</i>	Mussel	<i>Villosa delumbis</i>	3,821.1
				<i>Villosa iris</i>	2,491.6
4	2835	<i>Lampsilis</i>	Mussel	<i>Lampsilis fasciola</i>	2,907.1
				<i>Lampsilis siliquoidea</i>	2,764.4
3	2326	<i>Daphnia</i>	Cladoceran	<i>Daphnia ambigua</i>	1,649.7
				<i>Daphnia magna</i>	3,773.1
				<i>Daphnia pulex</i>	2,020.5
2	1542	<i>Ceriodaphnia</i>	Cladoceran	<i>Ceriodaphnia dubia</i>	1,542.3
1	1128	<i>Sphaerium</i>	Fingernail clam	<i>Sphaerium simile</i>	1,127.9



## Expert Report on the Proposed Ambient Water Quality Criteria for Chloride in PA Waters



**Table 2:** The chloride criterion maximum concentration (CMC or acute criterion in mg Chloride/L) and criterion chronic concentration (CCC or chronic criterion in mg Chloride/L) calculated using four different methods based on the 29 GMAV values in Table 2 (GMAV values from Stephan 2009a). The CMC is calculated by dividing the final acute value (FAV) by the safety factor, and the CCC is calculated by dividing the final chronic value (FCV) by the safety factor. Three of the methods relied on the acute-to-chronic ratio (ACR) to convert the FAV into an FCV.

Method		FAV	Safety factor	CMC
PA Proposed				<b>860</b>
EPA 1988 <sup>a</sup>		1,364	2	682
E&F 2001 <sup>b</sup>		1,648	2	824
BC 2003 <sup>c</sup>		1,128	2	564
Iowa 2009 <sup>d</sup>		1,364	2	682

Method	ACR	FCV	Safety factor	CCC
PA Proposed				<b>230</b>
EPA 1988 <sup>a</sup>	3.187	428	1	428
E&F 2001 <sup>b</sup>	7.59	217	1	217
BC 2003 <sup>c</sup>	-	455	5	91
Iowa 2009 <sup>d</sup>	7.308 & 3.187	422	1	422

<sup>a</sup> The EPA's 1985 equations were used to calculate the FAV. The ACR is the geometric mean of 3 *Daphnia* species and was taken from Stephan 2009a. The FCV is the FAV/ACR.

<sup>b</sup> E&F = Evans & Frick 2001. A 3-parameter sigmoid curve was fit to the cumulative percentage of genera lost as a function of the natural log transformed GMAVs using the nls function in R. The equation was % genera lost =  $a / (1 + \exp(-(\ln(\text{GMAV}) - c) / b))$  and the fitted values were  $a = 1.035$ ,  $b = 0.431$ ,  $c = 8.692$ . The FAV is the value at which 5% of genera are predicted to be lost. Evans & Frick (2001) did not specify a safety factor for the CMC, so a safety factor of 2 was assumed. The ACR is the same one used by the EPA in 1988 based on fathead minnow, rainbow trout and *Daphnia pulex*. The FCV is the FAV/ACR.

<sup>c</sup> The FAV is the lowest observed GMAV (1128 mg/L for *Sphaerium simile*) and the FCV is the lowest observed effect concentration (LOEC, 455 mg/L for *Ceriodaphnia dubia* by Aragao and Pereira (2003) reported in Stephan 2009b).

<sup>d</sup> The EPA's 1985 equations were used to calculate the FAV. The FCV was calculated using the same equations with the predicted GMCVs which were calculated by dividing the GMAV by the ACR of 7.308 for vertebrates or 3.187 for invertebrates.

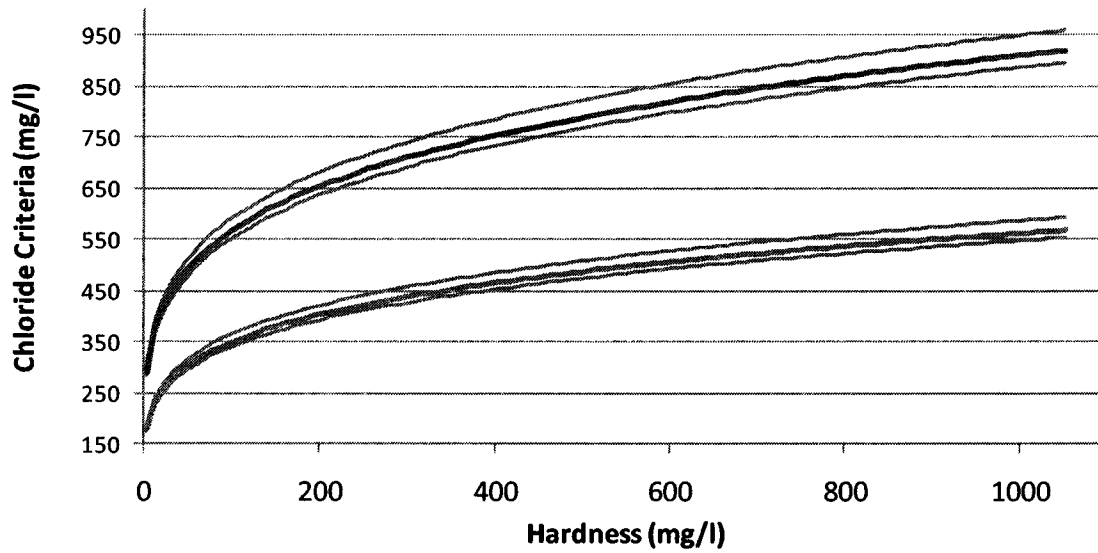
# Expert Report on the Proposed Ambient Water Quality Criteria for Chloride in PA Waters



**Table 3: Amphibian species in Pennsylvania associated with streams or stream-side pools. Data from PA Fish and Boat Commission ([http://www.fish.state.pa.us/amp\\_rep.htm](http://www.fish.state.pa.us/amp_rep.htm)).**

Species	Common name	Habitat	Egg	Larva	Juvenile	Adult
<i>Acris crepitans crepitans</i>	Northern Cricket frog	streamside (occasionally)	submerged grasses	yes	no	no
<i>Bufo americanus americanus</i>	Eastern American Toad	eggs and larva sometimes in slow moving streams	yes (sometimes)	yes (sometimes)	no	yes - streamside
<i>Bufo woodhousii fowleri</i>	Fowler's Toad	streamside (occasionally)	yes (sometimes)	yes (sometimes)	no	yes - streamside
<i>Cryptobranchius alleganiensis alleganiensis</i>	Easem Hellbender	Large order stream Fast moving	yes under rocks or logs	yes	yes	yes
<i>Desmognathus fuscus fuscus</i>	Northern dusky salamander	Headwaters and seeps	eggs are laid near water	yes	yes	yes - streamside
<i>Desmognathus monticola monticola</i>	Appalachian seal salamander	Streamside and headwaters	Eggs attached to moist rocks	yes	streamside	streamside
<i>Desmognathus ochrophaeus</i>	Mountain dusky salamander	Lotic	near water	yes	streamside	streamside
<i>Eurycea bislineata bislineata</i>	Northern two-lined salamander	streamside and stream rocky brooks	submerged rocks/logs	yes	yes	yes - streamside
<i>Eurycea longicauda longicauda</i>	Longtail salamander	associated with caves; shale and limestone creeks	swallow water	yes	yes	yes - streamside
<i>Gyrinophilus porphyriticus porphyriticus</i>	Northern Spring salamander	springs	under rocks	yes	yes	yes
<i>Hemidactylium scutatum</i>	Four-toed salamander	seeps and boggy areas	single eggs on streamside moss above water	yes	yes/no	no
<i>Necturus maculosus maculosus</i>	Mudpuppy salamander	Lotic (most orders of streams) and lentic	Streamside nest points to water	yes	yes	yes
<i>Notophthalmus viridescens viridescens</i>	red-spotted newt	Lotic (headwaters) and lentic	yes, attached to vegetation	yes	No, terrestrial	yes
<i>Pseudacris brachyphona</i>	Mountain Chorus Frog	mountains streamside	yes	yes	streamside	streamside
<i>Pseudacris feriarum feriarum</i>	Upland Chorus Frog	riparian floodplains	yes	yes	streamside	streamside
<i>Pseudacris feriarum kalmi</i>	New jersey Chorus frog	Rare frog Woodland frog	yes	yes	streamside	streamside
<i>Pseudacris triseriata</i>	Western chorus frog	famland grasslands near water	yes	yes	streamside	streamside
<i>Pseudotriton montanus montanus</i>	Eastern mud salamander	muddy springs and mucky areas along streams, swamps, and bogs	yes	yes	streambank/ mud	streambank/ mud
<i>Pseudotriton ruber ruber</i>	Northern red salamander	clean small streams, springs	yes	yes	yes	yes
<i>Rana catesbeiana</i>	Bullfrog	mainly large bodies of water; large slowmoving- heavy vegetative streams	yes	yes	yes	yes
<i>Rana clamitans melanota</i>	Northern Green Frog	Smaller streams shallow water (occasionally) (reproduction)	yes	yes	yes	yes
<i>Rana palustris</i>	Pickereel frog	Smaller streams shallow water (occasionally) (reproduction)	yes	yes	streamside	streamside
<i>Rana pipiens</i>	Northern Leopard frog	Smaller streams shallow water (occasionally) (reproduction)	yes	yes	streamside	streamside
<i>Rana sphenoccephala*</i>	Coastal Plain Leopard frog	Smaller streams shallow water (occasionally) (reproduction)	yes	yes	streamside	streamside
<i>Rana sylvatica</i>	Wood Frog	Smaller streams shallow water (occasionally) (reproduction)	yes	yes	streamside/ terrestrial	streamside/ terrestrial

All *Ambystoma* species excluded typically breed in vernal pools  
 All *Plethodon* species excluded because of terrestrial habits  
*Hyla crucifer crucifer*, *Hyla versicolor versicolor* and *Pseudacris crucifer crucifer* excluded typically breed in vernal pools



**Figure 1:** Iowa acute (red = upper line) and chronic (orange = lower line) chloride criteria at constant sulfate concentration of 37.9 mg/l (average  $\text{SO}_4$  concentration of 246 sites in PA from the EMAP database 1991-2000). Grey lines are 95% confidence intervals for sulfate concentrations from 246 sites in PA.

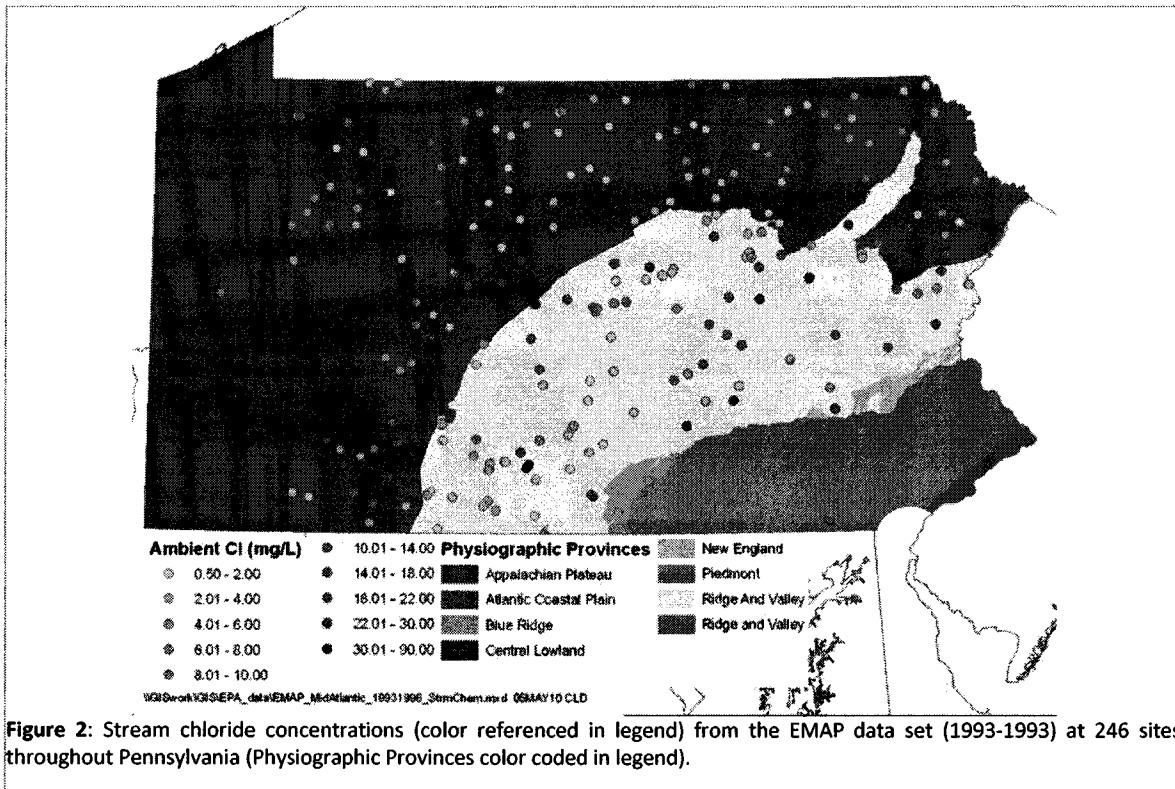
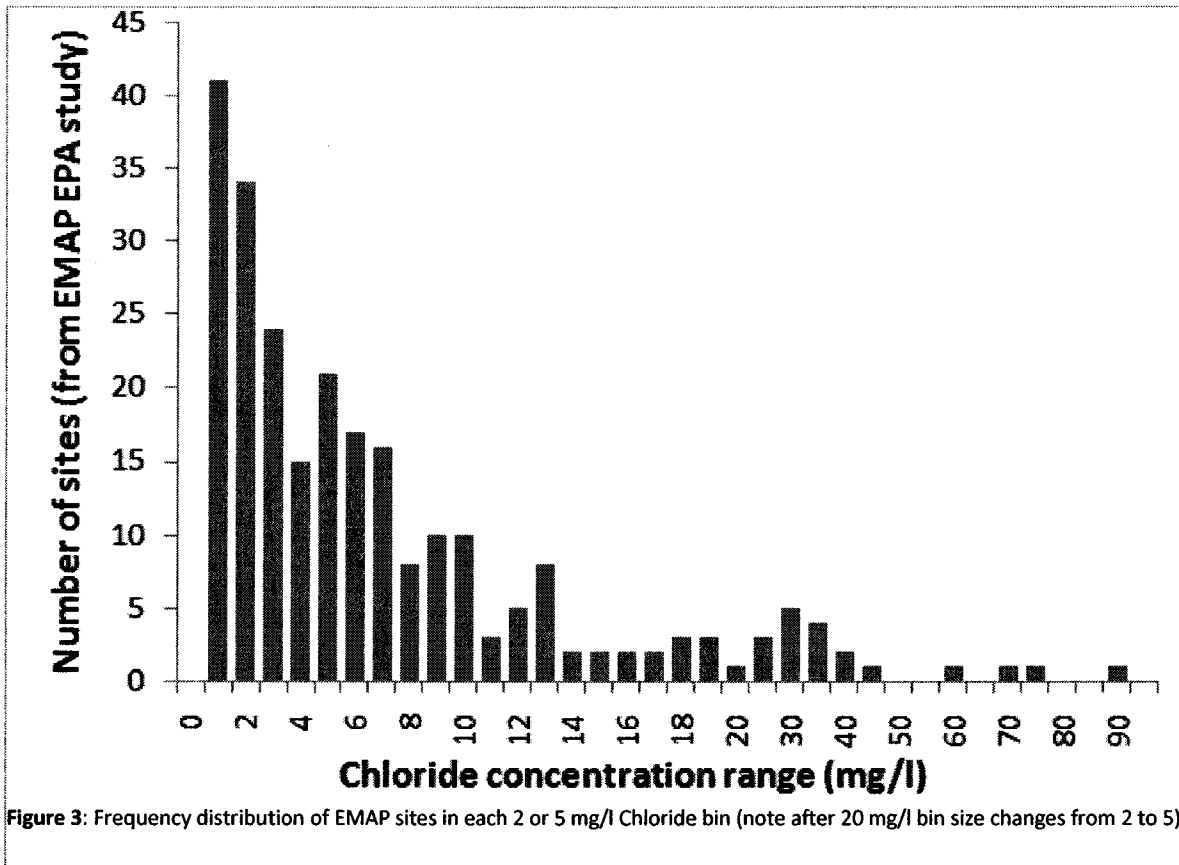
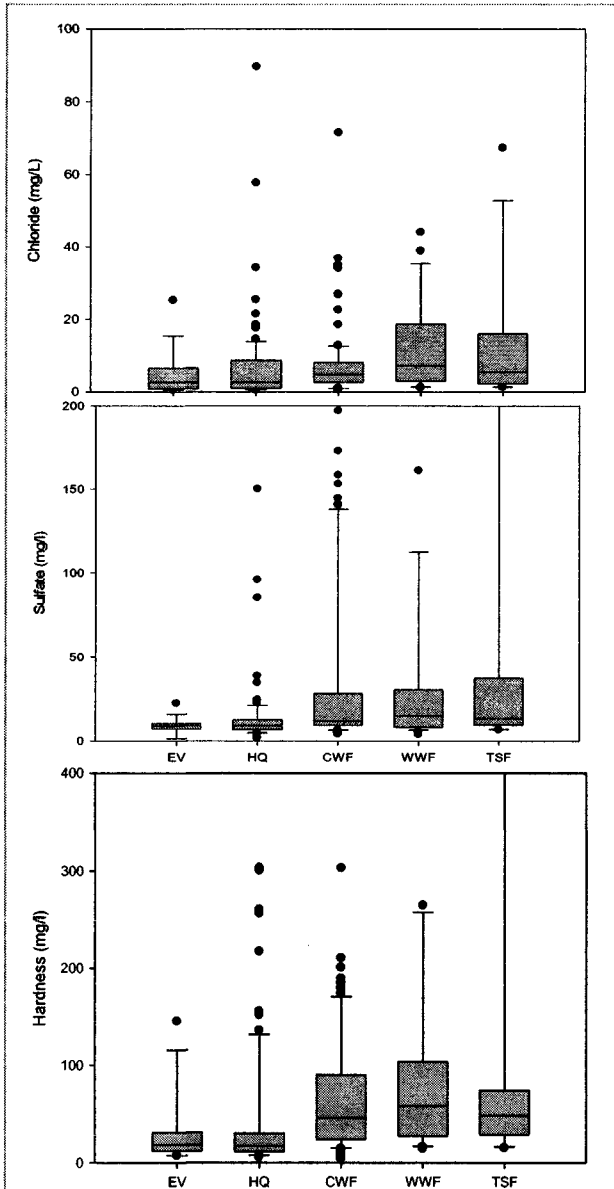


Figure 2: Stream chloride concentrations (color referenced in legend) from the EMAP data set (1993-1993) at 246 sites throughout Pennsylvania (Physiographic Provinces color coded in legend).





**Figure 4:** Box plots (middle line = mean; upper and lower box limits = 25<sup>th</sup> and 75<sup>th</sup> percentiles, error bars = 5<sup>th</sup> and 95<sup>th</sup> percentiles, and black circles are outliers) of stream concentrations of chloride (upper left), sulfate (upper right), hardness (bottom) in mg/l by Pennsylvania designated use (EV = Exceptional Value, HQ = High Quality, CWF = Cold Water Fishery, WWF = Warm Water Fishery (WWF), and TSF = Trout Stock Fishery, note now MF or Migratory Fishery site in EMAP dataset). Data from EMAP dataset 1993-1996.

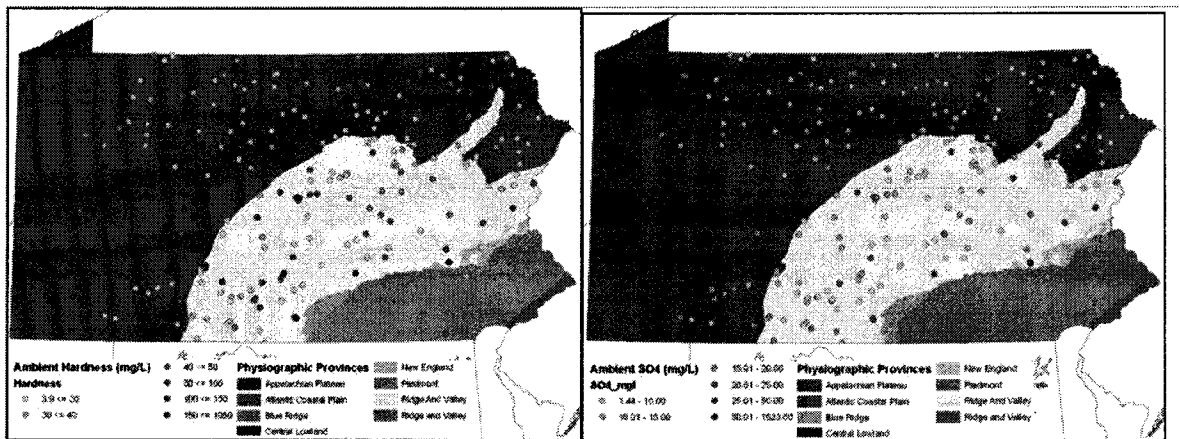
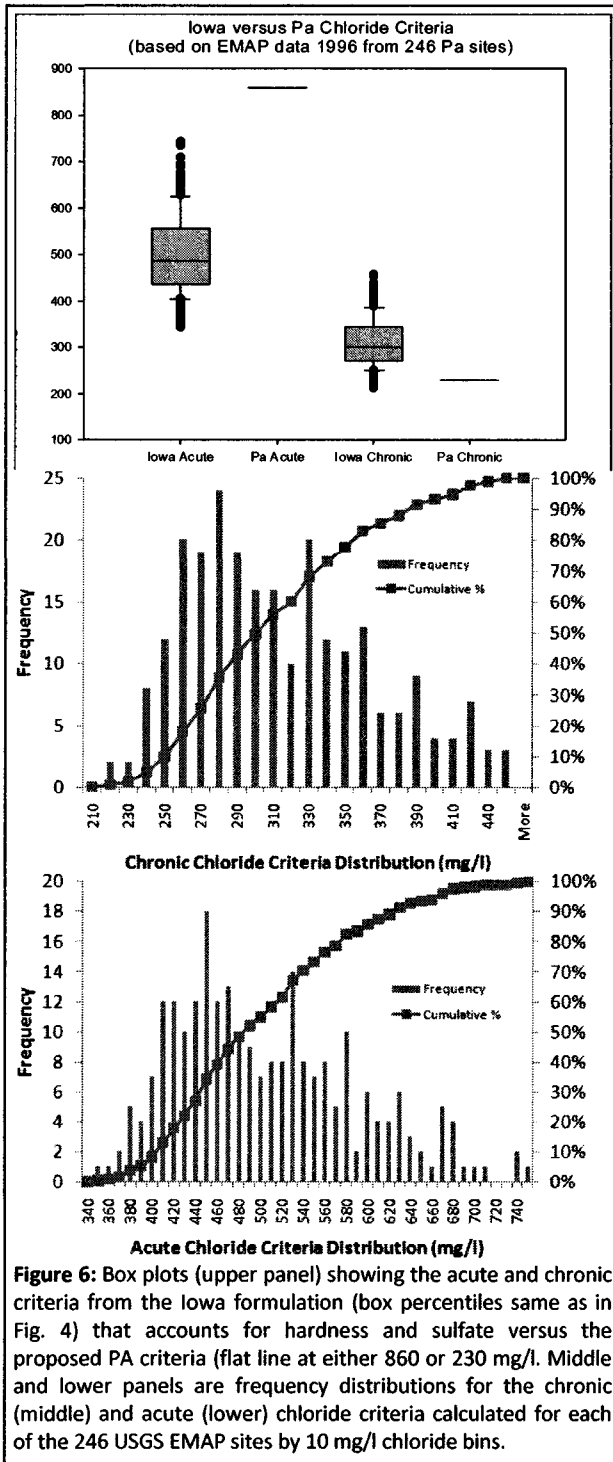


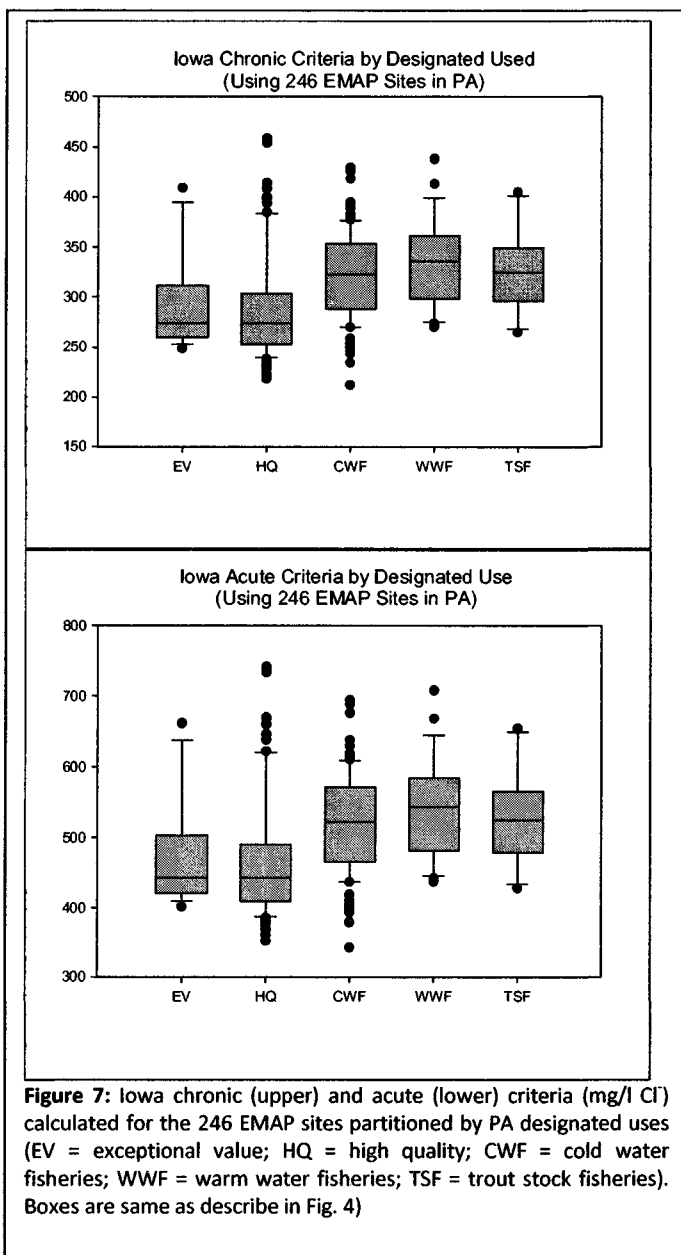
Figure 5: Hardness (left) and sulfate (right) concentrations (color coded yellow = low to red = high) measured at the 246 EMAP sites from 1993-96.

# Expert Report on the Proposed Ambient Water Quality Criteria for Chloride in PA Waters

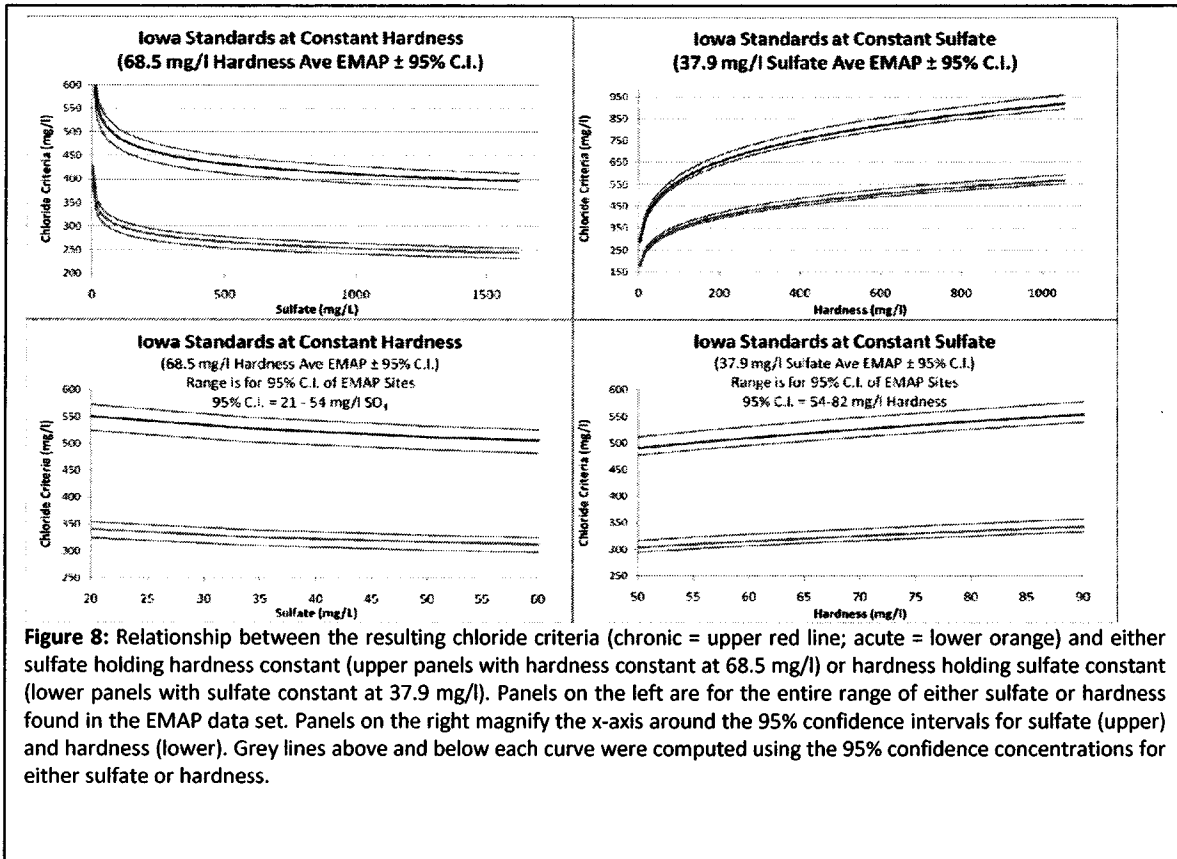


**Figure 6:** Box plots (upper panel) showing the acute and chronic criteria from the Iowa formulation (box percentiles same as in Fig. 4) that accounts for hardness and sulfate versus the proposed PA criteria (flat line at either 860 or 230 mg/l). Middle and lower panels are frequency distributions for the chronic (middle) and acute (lower) chloride criteria calculated for each of the 246 USGS EMAP sites by 10 mg/l chloride bins.





**Figure 7:** Iowa chronic (upper) and acute (lower) criteria (mg/l Cl<sup>-</sup>) calculated for the 246 EMAP sites partitioned by PA designated uses (EV = exceptional value; HQ = high quality; CWF = cold water fisheries; WWF = warm water fisheries; TSF = trout stock fisheries). Boxes are same as describe in Fig. 4)



## **Review of Aquatic Life Use Designations for Select States**

**PREPARED FOR:**

**Environmental Resources Coalition**  
3118 Emerald Lane  
Jefferson City, MO 65109

**Missouri Department of Natural Resources**  
Water Protection Program  
P.O. Box 176  
Jefferson City, MO

April 2008

**PREPARED BY:**

**MEC Water Resources, Inc.**  
1123 Wilkes Blvd., Suite 400  
Columbia, MO 65201

---

TABLE OF CONTENTS

1.0 PROJECT BACKGROUND	1
2.0 TIERED AQUATIC LIFE USES	1
2.1 The TALU Approach in Ohio	4
2.2 The TALU Approach in Maine	6
3.0 REVIEW DISCUSSION	7
3.1 Missouri Aquatic Life Use Designations	8
3.2 Use Designation Approaches in Other States	8
3.3 Review Summary	9
4.0 CONCLUSIONS	9
5.0 REFERENCES	10

LIST OF APPENDICIES

APPENDIX A: States Aquatic Life Use Designation Summaries

LIST OF TABLES

TABLE 1: Biological Condition Gradient Attributes.  
TABLE 2: Dissolved Oxygen Criteria in Ohio.  
TABLE 3: Tier-Specific Aquatic Life Use Criteria in Maine.  
TABLE 4: States Evaluated for Aquatic Life Use Designations.  
TABLE 5: Predominant Aquatic Life Use Types for Selected States.

LIST OF FIGURES

FIGURE 1: Conceptual Diagram of the Biological Condition Gradient.  
FIGURE 2: Warmwater Aquatic Life Use Designations in Ohio.  
FIGURE 3: Results from TALU Designation Evaluation Performed by CABB.  
FIGURE 4: Tiered Aquatic Life Use Designations in Maine.

## 1.0 PROJECT BACKGROUND

In September 2000, U.S. EPA Region VII (EPA) issued a formal review of Missouri's Water Quality Standards to the Missouri Department of Natural Resources (MDNR). Within the review, EPA noted that emphasis on recreationally important fish species within Missouri's beneficial use definitions may not fully address the biologic integrity goal of the Federal Clean Water Act of 1972 (CWA). EPA identified Tiered Aquatic Life Uses (TALUs) as a possible approach to resolve this concern.

In spring 2006, the Missouri Clean Water Commission directed MDNR to form several Clean Water Policy Workgroups, including the Tiered Aquatic Life Use Advisory Group. As part of the Ecological and Water Resources Assessment Project (EWRAP), the Environmental Resources Coalition (ERC) and MEC Water Resources Inc. (MEC) provided the following technical support to the Missouri Tiered Aquatic Life Use Advisory Group:

- Evaluation of aquatic life use frameworks implemented by States having established bioassessment programs;
- Tiered Aquatic Life Use presentations; and
- Attendance of Advisory Group meetings to provide technical support.

The following sections include an overview of TALU concepts and a summary of aquatic life uses for selected States. Appendix A includes an individual summary of the aquatic life uses in each state that was reviewed. A TALU presentation authored by MEC and ERC, and an Advisory Group Progress presentation authored by MDNR are also available by request.

## 2.0 TIERED AQUATIC LIFE USES

Protection of biologic integrity is a principle goal of the Federal Clean Water Act. Nationally and within Region VII, EPA supports the implementation of Tiered Aquatic Life Uses (TALU) to provide accurate aquatic life use protection (Jackson 2003, USEPA 1994). TALUs are biologically-based determinations of the expected aquatic condition in a waterbody. They are separate and specific designated uses that are differentiated or 'tiered' along a Biological Condition Gradient (BCG).

The BCG is a conceptual model used for interpreting the biological response of the aquatic community in response to increasing stressors. The BCG model is divided into six tiers that represent the condition of the biological community (Figure 1). It describes the complete range of aquatic conditions from the healthiest, most undisturbed community in the first tier to severely altered communities in tier 6 (USEPA 2005, Davies and Jackson 2006).

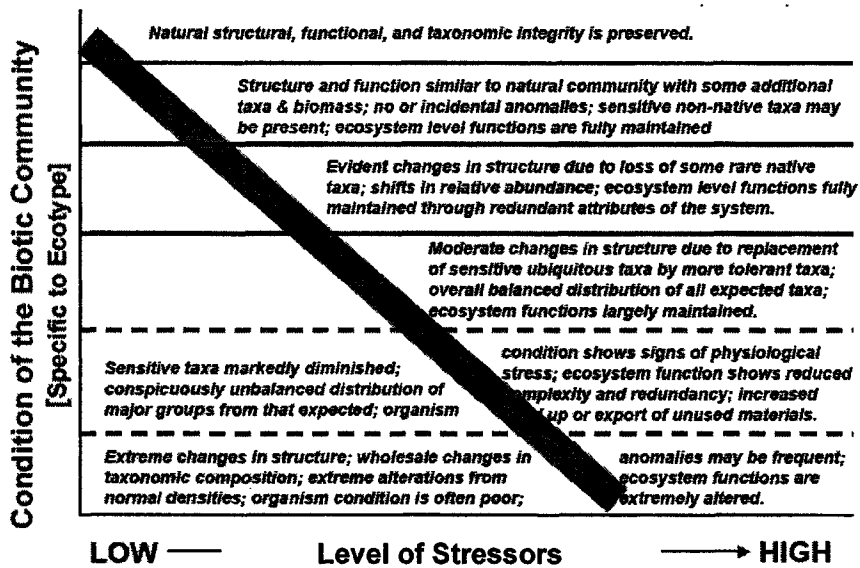


FIGURE 1. Conceptual Diagram of the Biological Condition Gradient. (Adapted from Jackson 2003).

Streams are assigned to one of the six tiers based on the quality of the aquatic condition as measured by 10 system attributes (Table 1). These 10 attributes measure community structure and function, organism condition and system performance, and the interactions between physical habitat and the biota (USEPA 2005). If enough biological monitoring data is available, the conceptual BCG model can be “calibrated” to describe the tiers in terms of the biota specific to a region or state. With a properly calibrated model, states can better describe the change in the composition of the aquatic community with increasing levels of stressors across the BCG tiers (USEPA 2005). The ability to accurately predict the change in the aquatic community in response to disturbance is fundamental to the TALU approach of beneficial use development.

The degree of human disturbance in the watershed is not the only determinant of the quality of the aquatic community. Physiogeographic differences also dictate the distribution and composition of aquatic communities (Barbour et al. 1996). This is especially relevant in Missouri where 19 distinct ecological drainage units (EDUs) have been identified (MDNR 2002, Sowa et al. 2004). An EDU is a geographical area that contains relatively distinct assemblages of aquatic organisms (Sowa et al. 2004). In order to accurately protect aquatic life, a TALU system must consider the natural spatial variability that is present in aquatic communities.

An important determinant of BCG model calibration with respect to regional differences is the ability to describe regional reference conditions. The reference condition reflects the highest attainable aquatic condition for the region and acts as the benchmark by which to judge impairment in other waterbodies (Barbour et al. 1996, USEPA 2005).

Because natural habitats do not exist, acceptable reference conditions are those in which habitat is of sufficient quality to support a minimally disturbed aquatic community (Barbour et al. 1996). The regional reference condition can be identified directly through reference site evaluations, or indirectly through a combination of historical data, simulation modeling, and best professional judgment (Barbour et al. 1996).

TABLE 1. Biological Condition Gradient Attributes.

Measured Response	BCG Attribute	Attribute Description*
Taxonomic Composition/ Structure	1	Endemic Species
	2	Sensitive Rare Taxa
	3	Sensitive Ubiquitous Taxa
	4	Taxa of Intermediate Tolerance
	5	Tolerant Taxa
	6	Introduced Taxa
Organism Condition/ System Performance	7	Organism Condition
	8	Ecosystem Function
Habitat/Biota Interactions	9	Spatial/Temporal Stressors
	10	Ecosystem Connectance

\* - See Jackson (2005) for further discussion of biological attributes.

To quantify the minimally disturbed aquatic communities associated with regional reference conditions, States must have an established biomonitoring program. The data collected through routine biological assessments of reference streams aid in the development of numeric thresholds, or biocriteria, which are used to quantitatively define the acceptable reference conditions. Biocriteria are needed to define the tiers and significant changes of ecology associated with the BCG model (Barbour et al. 1996, USEPA 2005).

If sufficient data are available, the concept of tiering along the BCG can also be applied to water quality criteria (USEPA 2005). Once a tiered use system is in place, the regulatory agency can develop water quality criteria that are specific to the requirements of the aquatic life in each tier. Tier-specific criteria are necessary because the differing quality of the aquatic communities that is represented by the BCG cannot be supported by the same water quality (USEPA 2005). For example, the dissolved oxygen concentration necessary to support a Tier 5 aquatic community would not support the more natural and sensitive species that make up a Tier 1 community. Therefore, water quality criteria that are specific to each tiered use must be developed. Enacting specific water quality criteria provides a more accurate level of protection and allows resources to be used more efficiently (USEPA 2005).

Several states have incorporated aspects of a TALU system into their water quality standards and management decisions. The States of Ohio and Maine are two of the most successful examples of TALU implementation.

## 2.1 The TALU Approach in Ohio

The State of Ohio currently implements warmwater aquatic life use classifications that are tiered according to regional biocriteria (Yoder and Rankin 1995). Ohio applies 4 tiered uses as compared to the six in the conceptual BCG. The tiered warmwater categories are Exceptional, Warmwater, and Modified Warmwater Habitat (Figure 2). Ohio also has a Limited Resource Water category that is applied to warm and cold waters.

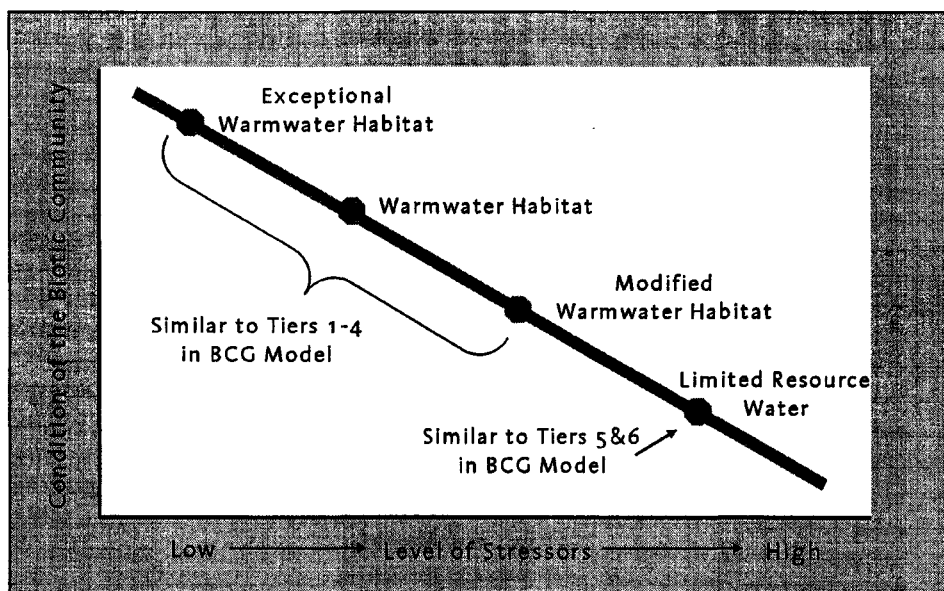


FIGURE 2. Warmwater Aquatic Life Use Designations in Ohio.

Exceptional Warmwater Habitat (EWH) is assigned to waters with unique and unusual assemblages of aquatic life. The Warmwater Habitat (WWH) designation applies to most of the state's rivers and streams. The Modified Warmwater Habitat (MWH) and Limited Resource Water (LRW) uses are applied to rivers and streams on which natural or non-remedial, human-caused conditions preclude attainment of a balanced warmwater aquatic community. The MWH and LRW uses may only be assigned following the completion of a Use Attainability Analysis (UAA) that demonstrates the WWH use cannot be met. These tiers represent the varying levels of biological condition that are attainable in the state. Actual numeric thresholds between tiers vary by physiogeographic region.

The warmwater use designations in Ohio also have several numeric water quality criteria that are specific to each TALU. Most notably, criteria for dissolved oxygen (Table 2) differ by use and in some cases, by region (OAC 3745-1-07, Table 7-1). These specific criteria reflect the varying level of water quality that is required to support the biota in each tier.



TABLE 2. Dissolved Oxygen Criteria in Ohio.

Use Tier (Name)	Dissolved Oxygen	
	(Minimum)	(Average)
Exceptional WW Habitat	5	6
WW Habitat	4	5
Modified WW Habitat	3*	4
Limited Resource Water	2	3

\*Minimum dissolved oxygen in Huron/Erie Lake Plain (HELP) ecoregion is 2.5 mg/L.

The Center for Applied Bioassessment and Biocriteria (CABB) assessed use attainment in Ohio’s EWH and MWH waters under the current tiered use system and compared it to use attainment under a single warmwater aquatic life use designation. Researchers from CABB concluded that the tiered system more accurately reflected use attainment across habitats compared to a single use designation (CABB 2003). Specifically, CABB (2003) determined that:

- Waters evaluated presuming a single aquatic life use exhibited fewer impairments than the same waters evaluated under the presumption of a tiered system (Figure 3);
- A single use approach would generally be underprotective of EWH waters; and
- A single use approach mischaracterized attainment status of MWH waters and was likely over-protective.

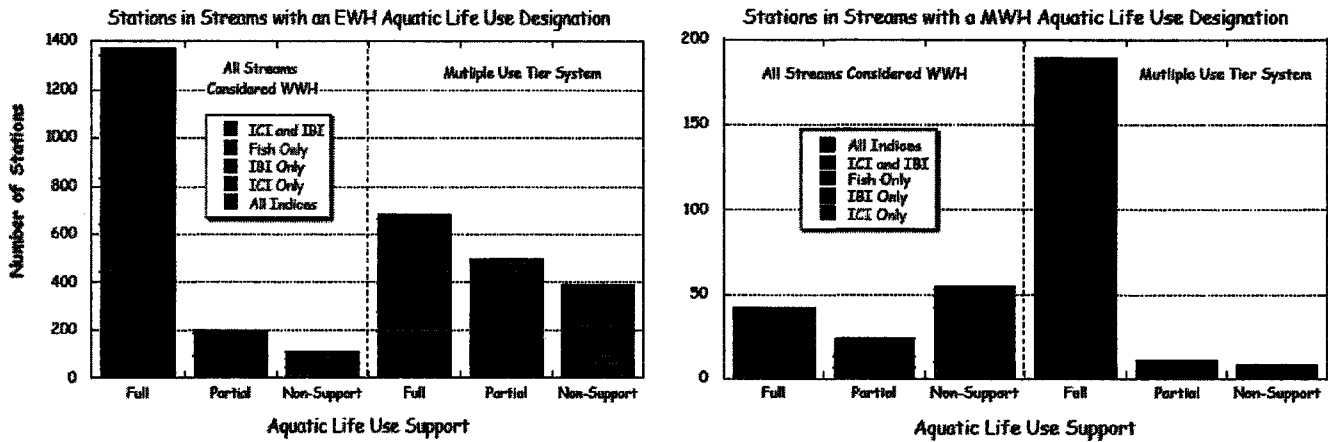


FIGURE 3. Results from TALU Designation Evaluation Performed by CABB. (Adapted from CABB 2003).

## 2.2 The TALU Approach in Maine

The current TALU system in Maine began with the development of narrative biological standards for 4 aquatic life use classes. These use classifications are based on the BCG concept (Figure 4). Class AA waters are those in which the habitat is natural and free-flowing with naturally occurring aquatic life communities. The narrative biological standard for Class A waters is identical to Class AA except that Class A waters do not have to be free-flowing. The Class B use is assigned to those waters which have unimpaired habitat and water quality sufficient to support indigenous aquatic species. The lowest use, Class C, is applied to those waters whose habitat may be impaired but still maintains water quality sufficient to support indigenous aquatic species (USEPA 2005).

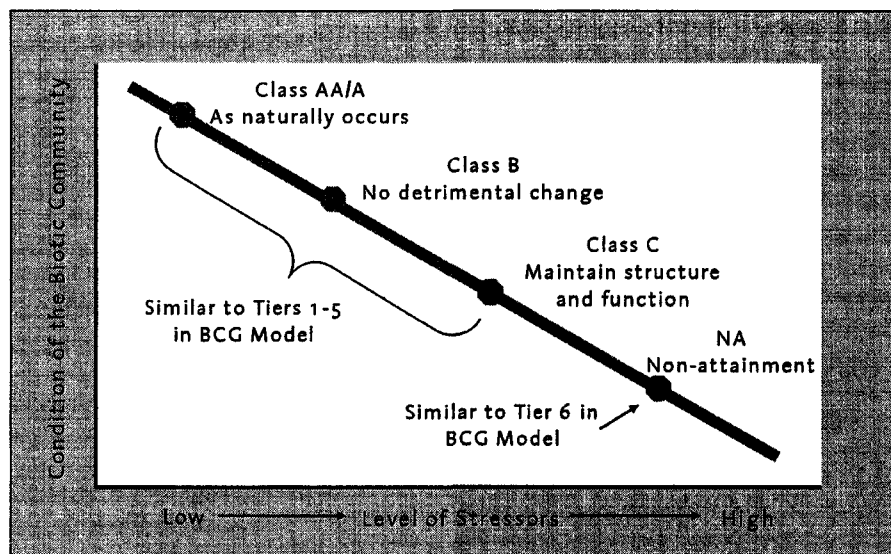


FIGURE 4. Tiered Aquatic Life Use Designations in Maine.

Maine's narrative descriptions were later quantified with a probability-based statistical model developed from a set of baseline data collected by the staff at the Maine Department of Environmental Protection (MDEP) (Courtemanch 1995). The baseline data set consisted of 144 macroinvertebrate samples collected from streams across the state (USEPA 2005). Biologists at MDEP evaluated the samples according to 31 variables and assigned each sample to one of the 4 narrative use classes. From this evaluation, they were able to develop a linear discriminant model that is used to assign a TALU classification to the targeted waterbody based on biological data collected from the stream.

Maine's TALU classifications are associated with specific dissolved oxygen and bacteria water quality criteria (MRSA Title 38 Section 465) (Table 3). Interestingly, the tiered use classifications were developed to be consistent with the tiered water quality criteria instead of the reverse (USEPA 2005).

MDEP designed the classifications around the tiered criteria because they reasoned that different levels of water quality would support different aquatic communities.

TABLE 3. Tier-Specific Aquatic Life Use Criteria in Maine.

Use Classification (name)	Dissolved Oxygen (mg/L) (Saturation)		<i>E. Coli</i> * (col/100mL)
Class AA	Natural	Natural	Natural
Class A	7	75%	Natural
Class B	7	75%	64/427
Class C	5	60%	142/949

\*Geometric Mean/Instantaneous Maximum.

The TALU systems in Ohio and Maine are two examples of successful BCG implementation to protect biologic integrity. The TALUs in each of these programs are similar in that (USEPA 2005):

- The uses are ecologically based;
- The uses consider both structure and function of the aquatic community;
- Use attainment is judged according to numeric biocriteria developed from reference waterbodies; and
- The implementation of the TALUs integrates monitoring, assessment, and the state water quality standards.

It is clear that incorporation of the TALU approach within a Water Quality Standards framework meets biological integrity provisions of the Clean Water Act. In the following Sections, we provide a snapshot and discussion of how selected states are designating aquatic life uses.

### 3.0 REVIEW DISCUSSION

As part of the EWRAP task, MEC staff evaluated aquatic life use designations of thirteen states listed in Table 4 (excluding Missouri). States were chosen based on one or more of the following three attributes:

- 1) The state is in close proximity to Missouri;
- 2) The state has an established biological assessment program;
- 3) The state has diverse aquatic resources.

TABLE 4. States Evaluated for Aquatic Life Use Designations.

State	Criterion	State	Criterion
Kansas	1,2	Oklahoma	2
Iowa	1,2	Idaho	2
Nebraska	1,2	Wisconsin	2,3
Ohio	2	Kentucky	1,2
Maine	2	Washington	2
Arkansas	2,3	Oregon	2,3
Arizona	2		

### 3.1 Missouri Aquatic Life Use Designations

The state of Missouri does not implement a biologically tiered system. Currently, Missouri designates a waterbody as having one of the following aquatic life uses:

- Coldwater Fishery
- Coolwater Fishery
- General Warmwater Fishery
- Limited Warmwater Fishery

Missouri's aquatic life uses are currently differentiated based on the presence of recreational fish communities and do not reflect the BCG. However, the MDNR bioassessment program has utilized draft numeric biocriteria to evaluate use attainment since the 1990s. Missouri has not formally adopted the numeric biocriteria into rule. Rather, MDNR protects aquatic life by applying general criteria such as 10 CSR 20.7-31(3)(G) which states that "Waters shall be free from physical, chemical, or hydrologic changes that would impair the biological community (Carnahan 2005)."

### 3.2 Use Designation Approaches in Other States

Three common approaches to aquatic life use designation identified across selected states that were:

- Habitat;
- Important fishery or fishery type; and
- Regional or Physiogeographic differences

Eleven of thirteen selected states are similar to Missouri in that aquatic life uses are based on habitat or fishery types (Table 5). Habitat based use classifications are generally those that are grouped according to water temperature and commonly consist of warm, cool, or cold water matrices. Fishery use classifications are those that protect a particular species or taxa, such as the Bull Trout designation in Idaho or the Warm Water Sport Fishery designation in Wisconsin. Several reviewed states assign a salmonid or trout use designation to protect cold water species. Regional or physiogeographic classifications are often used in combination other designation methods. For example, the state of Arkansas' use designations are based on fishes expected to occur in a particular region. Although fishery or habitat classifications are a common designation approach, they do not represent a biologically tiered approach.

### 3.3 Review Summary

TALUs based on the BCG model are not widely implemented in the states that MEC evaluated. Of the 13 states reviewed, only Maine and Ohio utilize biologically tiered use designations (Table 5). At the time of this review, Iowa was in the process of refining their uses from a habitat based approach to more accurately reflect the BCG. More commonly, states implement alternate systems or combination of systems in designating aquatic life uses (Table 5).

TABLE 5. Predominant Aquatic Life Use Types for Selected States.

State	Basis for Use Designation				Other Uses		
	Habitat	Fishery	Regional	BCG	Lower Use	Higher Use	Effluent Dependent
Missouri	X	X			X		
Kansas	X				X		
Iowa	X	X			X		
Nebraska	X						
Ohio				X	X	X	
Maine				X		X	
Arkansas			X				
Arizona	X						X
Oklahoma	X	X			X		
Idaho	X	X			X		
Wisconsin	X	X			X		
Kentucky	X						
Washington		X*					
Oregon	X	X	X				

\*Use classifications not yet approved by EPA.

### 4.0 CONCLUSIONS

Data requirements for tiered designation approaches are relatively intensive and may explain why so few states have adopted the TALU approach. Long-term biological data are necessary to develop the numeric thresholds needed to position waters within appropriate tiers. All states evaluated as part of this project have established bioassessment programs, yet only two (Ohio and Maine) have established TALU designations in their WQS. Individual state information regarding aquatic life uses and the associated numeric criteria are available in Appendix A.

Based on data and information supplied to MEC by MDNR, Missouri likely has sufficient biomonitoring data to develop tiered biological uses for Wadeable perennial streams within warm and coldwater habitats. Data collection for large rivers, lakes, and smaller ephemeral or intermittent waters lag behind Wadeable streams.

## 5.0 REFERENCES

- Barbour, M.T., Stribling, J.B, and J. Gerritsen. 1996. Biological Criteria Technical Guidance for Streams and Small Rivers. Office of Science and Technology. EPA/822/B-96/001.
- Center for Applied Bioassessment and Biocriteria. 2003. Tiered Aquatic Life Uses and Comparison of Biological-Based Attainment/Impairment Measures: Single vs. Multiple Tiers. Fact Sheet Columbus, Ohio. Fact Sheet 1-CABB-03.
- Courtemanch, D.L, 1995. Merging the science of biological monitoring with water resource management policy: criteria development, pp. 315-325 (Chapter 20). In W.S. Davis and T. Simon (eds.). Biological Assessment and Criteria: Tools for Water Resource Planning and Decision Making. Lewis Publishers, Boca Raton, FL.
- Davies S.P., and S.K. Jackson. 2006. The biological condition gradient: a descriptive model for interpreting change in aquatic ecosystems. Ecological Applications. 16(4) 1251-1266.
- Jackson, Susan. 2003. Using Biological Assessments to Refine Designated Aquatic Life Uses: EPA/State Workgroup. National Biological Assessment Workshop.
- Missouri Department of Natural Resources. 2002. Biological Criteria for Wadeable/Perennial Streams of Missouri. Air and Land Protection Division Environmental Services Program. Jefferson City, MO. 47 pages.
- Sowa, S., D. Diamond, R. Abbitt, G. Annis, T. Gordon, M. Morey, G. Sorensen, and D. True. 2004. The Aquatic Component of Gap Analysis: A Missouri Prototype. Final Report Issued to The United States Department of Defense Legacy Program. Missouri Resource Assessment Partnership, University of Missouri-Columbia.
- USEPA (U.S. Environmental Protection Agency). 1994. *Water Quality Standards Handbook: Second Edition*. Office of Water, Washington, DC. EPA 823-B-94-005b
- USEPA (U.S. Environmental Protection Agency) 2005. Use of Biological Information to Better Define Designated Aquatic Life Uses in State and Tribal Water Quality Standards: Tiered Aquatic Life Uses. Office of Science and Technology, Washington, DC. EPA 822-R-05-001.
- Yoder, C. and E. Rankin. 1995. Biological Criteria Program Development and Implementation in Ohio, pp. 109-144 (Chapter 9). In W.S. Davis and T. Simon (eds.). Biological Assessment and Criteria: Tools for Water Resource Planning and Decision Making. Lewis Publishers, Boca Raton, FL.
- Yoder, Chris, Rankin, Edward, and DeShon, Jeffrey. 2003. Implementation of Tiered Aquatic Life Uses: Ohio Rivers and Streams, 1978-Present. National Biological Assessment Workshop.

**APPENDIX A**

**STATE AQUATIC LIFE USE DESIGNATION SUMMARIES**

**Appendix A.1**  
**Kansas Aquatic Life Use Information**  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The aquatic life use designations are somewhat tiered along a gradient of biological conditions although there are no thresholds included in the Kansas Water Quality Standards by which to differentiate them.

Kansas only has the term aquatic life support use as a use designation. This designation is further broken down into special, expected, and restricted aquatic life uses. The language from the water quality standards is as follows:

*Aquatic Life Support Use*

The use of a classified surface waters for the maintenance of the ecological integrity of streams, lakes, wetlands, and ponds, including the sustained growth and propagation of native aquatic life; naturalized, important, recreational aquatic life; and indigenous or migratory semiaquatic or terrestrial wildlife directly or indirectly dependent on surface waters other than stream segments for survival.

*Special Aquatic Life Use Waters*

Classified surface waters containing combinations of habitat types and indigenous biota not found commonly in the state or surface waters other than stream segments that contain representative populations of threatened or endangered species.

*Expected Aquatic Life Use Waters*

Classified surface waters containing habitat types and indigenous biota commonly found or expected in the state.

*Restricted Aquatic Life Use Waters*

Classified surface waters containing indigenous biota limited in abundance or diversity by the physical quality or availability of habitat, due to natural deficiencies or artificial modifications, compared to more suitable habitats in adjacent waters.



**Biological Criteria**

Narrative:       Numeric:       None:

The State of Kansas does not have any biological criteria listed in their water quality standards.

**Use-Specific Criteria**

Dissolved Oxygen:       Ammonia:       Other:       None:

The State of Kansas does not have any use-specific criteria.

**Information Sources**

Kansas Water Quality Standards, KAR 28-16

Kansas Department of Health and Environment, Link to Supporting Documents  
<http://www.kdheks.gov/water/index.html#Adopted%20Regulations>

Appendix A.2  
Iowa Aquatic Life Use Information  
(As of 3/31/08)

Aquatic Life Use Designations

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

Iowa recently revised their aquatic life use designations from habitat/fishery based uses to uses that more closely reflect a biological condition gradient although there is minimal discussion of the biologically relevant distinctions between each of the use categories. EPA has approved the new uses (February 2008) and they are now being implemented in the state.

*Cold Water Aquatic Life— Type 1 (Class B(CW1))*

Waters in which the temperature and flow are suitable for the maintenance of a variety of cold water species, including reproducing and nonreproducing populations of trout (*Salmonidae* family) and associated aquatic communities.

*Cold Water Aquatic Life— Type 2 (Class B(CW2))*

Waters that include small, channeled streams, headwaters, and spring runs that possess natural cold water attributes of temperature and flow. These waters usually do not support consistent populations of trout (*Salmonidae* family), but may support associated vertebrate and invertebrate organisms.

*Warm Water— Type 1 (Class B(WW-1))*

Waters in which temperature, flow and other habitat characteristics are suitable to maintain warm water game fish populations along with a resident aquatic community that includes a variety of native nongame fish and invertebrate species. These waters generally include border rivers, large interior rivers, and the lower segments of medium-size tributary streams.

*Warm Water— Type 2 (Class B(WW-2))*

Waters in which flow or other physical characteristics are capable of supporting a resident aquatic community that includes a variety of native nongame fish and invertebrate species. The flow and other physical characteristics limit the maintenance of warm water game fish populations. These waters generally consist of small perennially flowing streams.

*Warm Water— Type 3 (Class B(WW-3))*

Waters in which flow persists during periods when antecedent soil moisture and groundwater discharge levels are adequate; however, aquatic habitat typically consists of nonflowing pools during dry periods of the year. These waters generally include small streams of marginally perennial aquatic habitat status.

Such waters support a limited variety of native fish and invertebrate species that are adapted to survive in relatively harsh aquatic conditions.

*Lakes and Wetlands - (Class B(LW))*

These are artificial and natural impoundments with hydraulic retention times and other physical and chemical characteristics suitable to maintain a balanced community normally associated with lake-like conditions.

Iowa also has two use designations for "High Quality Waters" that are of biological or recreational significance.

**Biological Criteria**

Narrative:       Numeric:       None:

The State of Iowa does not include biological criteria in the state water quality standards however they do have substantial warm water and cold water aquatic life use attainability analysis guidance that include a biological assessment.

**Use-Specific Criteria**

Dissolved Oxygen:       Ammonia:       Other:       None:

The State of Iowa has use-specific dissolved oxygen, ammonia, temperature, and other toxics criteria. Below is a table of the dissolved oxygen criteria only. Other use specific criteria may be found in the state water quality standards.

	B(CW1)	B(CW2)	B(WW-1)	B(WW-2)	B(WW-3)	B(LW)
Minimum value for at least 16 hours of every 24-hour period	7.0	7.0	5.0	5.0	5.0	5*
Minimum value at any time during every 24-hour period	5.0	5.0	5.0	4.0	4.0	5*

*\* Applies only to the upper layer of stratification in lakes*

**Information Sources**

Iowa DNR News Release Regarding EPA Approval  
[http://www.iowadnr.com/news/08feb/epa\\_wq.html](http://www.iowadnr.com/news/08feb/epa_wq.html)

Iowa Water Quality Standards Webpage  
<http://www.iowadnr.com/water/standards/index.html>

Iowa Water Quality Standards, Iowa Administrative Code, Chapter 61  
<http://www.iowadnr.com/water/standards/files/chapter61.pdf>

Iowa Use Attainability Assessment Procedures  
<http://www.iowadnr.com/water/standards/files/warmwater.pdf>  
<http://www.iowadnr.com/water/standards/files/04cwp.pdf>

**Appendix A.3**  
**Nebraska Aquatic Life Use Information**  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The aquatic life use designations in Nebraska are based on water temperature. The State of Nebraska has four different classes of aquatic life use designations. They are: Warmwater A and B, Coldwater A and B. Nebraska uses narrative and general criteria to determine use attainments. There are biological criteria in the WQS. They are narrative and refer to a "key species" approach. A key species is an endangered, threatened, sensitive, or recreationally important aquatic species associated with a particular water body and its aquatic life use class. Key species are listed in the standards by basin.

*Warmwater*

These are waters which provide, or could provide, a habitat consisting of sufficient water volume or flow, water quality, and other characteristics such as substrate composition which are capable of maintaining year-round populations of warmwater biota. Warmwater biota are considered to be life forms in waters where temperatures frequently exceed 25°C (77°F).

*Warmwater Class A*

Waters that provide or have the potential to provide suitable habitat for maintaining one or more key species and are capable of maintaining year-round populations of a variety of other fish, organisms, and plants.

*Warmwater Class B*

These are waters in which habitat conditions limit aquatic life. These waters can only maintain tolerant warmwater fish and organisms year-round. Habitat conditions limit year-round support of key fish species.

*Coldwater*

These are waters which provide, or could provide, a habitat consisting of sufficient water volume or flow, water quality, and other characteristics such as substrate composition which are capable of maintaining year-round populations of coldwater biota. Coldwater biota are considered to be life forms in waters where temperatures seldom exceed 25°C (77°F).

*Coldwater Class A*

These waters provide habitat that support naturally reproducing salmonid populations year-round. They also support other coldwater organisms year-round.

*Coldwater Class B*

These waters provide or could provide habitat capable of maintaining year round salmonid populations. Habitat conditions in these waters limit natural reproduction of salmonids.

**Biological Criteria**

Narrative:       Numeric:       None:

The State of Nebraska has narrative biological criteria that utilize a "key species" approach. A key species is an endangered, threatened, sensitive, or recreationally important aquatic species associated with a particular water body and its aquatic life use class. Key species are listed in the state water quality standards by basin.

"Any human activity causing water pollution which would significantly degrade the biological integrity of a body of water or significantly impact or displace an identified "key species" shall not be allowed except as specified in Chapter 2."

**Use-Specific Criteria**

Dissolved Oxygen:       Ammonia:       Other:       None:

The State of Nebraska has use-specific dissolved oxygen, ammonia, and metal/inorganics water quality criteria listed in their water quality standards. Dissolved oxygen criteria are listed below; see the state Water Quality Standards for the additional use-specific criteria.

Nebraska Dissolved Oxygen Criteria	
<u>Coldwater Class A</u>	
June 1 - Sept. 30	October 1 - May 31
4 mg/L 1-Day Minimum <sup>1</sup>	8 mg/L 1-Day Minimum <sup>2</sup>
5 mg/L 7-Day Mean Minimum	9.5 mg/L 7-day Mean <sup>1</sup>
6.5 mg/L 30-day Mean	
<u>Coldwater Class B</u>	
April 1 - June 30	July 1 - March 31
5 mg/L 1-Day Minimum <sup>3</sup>	4 mg/L 1-Day Minimum <sup>4</sup>
6.5 mg/L 7-Day Mean	5 mg/L 7-Day Mean <sup>3</sup>
	6.5 mg/L 30-Day Mean
<u>Warmwater Class A/B</u>	
April 1 - Sept. 30	October 1 - March 31
5 mg/L 1-Day Minimum <sup>5</sup>	3 mg/L 1-Day Minimum <sup>6</sup>
6.0 mg/L 7 Day Mean <sup>5</sup>	4 mg/L 7-Day Mean
	5.5 mg/L 30-Day Mean

<sup>1</sup> Salmonid Early Life Stages(SELS) Present

<sup>2</sup> All Life Stages Other Than SELS

<sup>3</sup> Coldwater Early Life Stages (CELS) Present

<sup>4</sup> All Life Stages Other Than CELS

<sup>5</sup> Early Life Stages (ELS) Present

<sup>6</sup> All Life Stages Other Than ELS

**Information Sources**

Nebraska Water Quality Standards, Nebraska Administrative Code, Title 117, Chapter 4

Appendix A.4  
Ohio Aquatic Life Use Information  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The aquatic life use designations are based on regional Biological Condition Gradients.

The State of Ohio has seven different aquatic life classifications one of which (Limited Warmwater) is being phased out. Limited Resource Water and Modified Habitat Warmwater uses are designated only after a UAA shows irretrievable conditions (see page 4 of this report).

Use classifications are designated according to data gathered from biological assessments. Of the seven classifications, the warmwater uses exhibit the truest biological tiering.

*Exceptional Warmwater*

These are waters capable of supporting and maintaining an exceptional or unusual community of warmwater aquatic organisms having a species composition, diversity, and functional organization comparable to the seventy-fifth percentile of the identified reference sites on a statewide basis. The attributes of species composition, diversity and functional organization will be measured using the index of biotic integrity, the modified index of well-being and the invertebrate community index as defined in "Biological Criteria for the Protection of Aquatic Life: Volume II, Users Manual for Biological Field Assessment of Ohio Surface Waters."

*Warmwater*

These waters are capable of supporting and maintaining warm water communities comparable to the twenty-fifth percentile of the identified reference sites within an ecoregion. For all ecoregions, the attributes of species composition, diversity and functional organization will be measured using the index of biotic integrity, the modified index of well-being and the invertebrate community index as defined in "Biological Criteria for the Protection of Aquatic Life: Volume II, Users Manual for Biological Field Assessment of Ohio Surface Waters."

*Limited Warmwater*

These are waters that were temporarily designated in the 1978 water quality standards as not meeting specific warmwater habitat criteria. Criteria for the support of this use designation are the same as the criteria for the support of the use designation warmwater habitat. However, individual criteria are varied on a case-by-case basis and supersede the criteria for warmwater habitat where applicable.

Any exceptions from warmwater habitat criteria apply only to specific criteria during specified time periods and/or flow conditions. The adjusted criteria and conditions for specified stream segments are denoted as comments in rules 3745-1-08 to 3745-1-30 of the Administrative Code. Stream segments currently designated limited warmwater habitats will undergo use attainability analyses and will be redesignated other aquatic life habitats. No additional stream segments will be designated limited warmwater habitats.

*Modified Warmwater*

These are waters that have been the subject of a use attainability analysis and have been found to be incapable of supporting and maintaining a balanced, integrated, adaptive community of warmwater organisms due to irretrievable modifications of the physical habitat. Such modifications are of a long-lasting duration (i.e., twenty years or longer) and may include the following examples: extensive stream channel modification activities permitted under sections 401 and 404 of the act or Chapter 6131. of the Revised Code, extensive sedimentation resulting from abandoned mine land runoff, and extensive permanent impoundment of free-flowing water bodies. The attributes of species composition, diversity and functional organization will be measured using the index of biotic integrity, the modified index of well-being and the invertebrate community index as defined in "Biological Criteria for the Protection of Aquatic Life: Volume II, Users Manual for Biological Field Assessment of Ohio Surface Waters."

*Seasonal Salmonid*

These are rivers, streams and embayments capable of supporting the passage of salmonids from October to May and are water bodies large enough to support recreational fishing. This use will be in effect the months of October to May. Another aquatic life habitat use designation will be enforced the remainder of the year (June to September).

*Coldwater*

This classification is for waters that have characteristics associated with inland trout streams and/or native fauna.

*Limited Resource Water*

These are waters that have been the subject of a use attainability analysis and have been found to lack the potential for any resemblance of any other aquatic life habitat as determined by the biological criteria. The use attainability analysis must demonstrate that the extant fauna is substantially degraded and that the potential for recovery of the fauna to the level characteristic of any other aquatic life habitat is realistically precluded due to natural background conditions or irretrievable human-induced conditions. Furthermore, one or more "causative factors" listed in 3745-1-07(B)(1)(g) of the WQS must be assigned to these waters.



**Biological Criteria**

Narrative:       Numeric:       None:

Ohio uses both narrative and numeric criteria to protect designated aquatic life uses. Narrative criteria are contained in OAC 3745-01-07(A)(6). The State of Ohio uses a multiple biologic indices in order to develop regional biological criteria for different stream types. The full table (Table 7-15) of biological criteria may be found in the water quality standards. Below is a table showing of biological criteria from one region in Ohio.

	Huron/Erie Lake Plain		
	Modified WW	WW Habitat	Exceptional WW
<b>Index of Biotic Integrity</b>			
Wading Sites	22	32	50
Boat Sites	20-22	34	48
Headwater Sites	20	28	50
<b>Modified Index of Well-Being</b>			
Wading Sites	5.6	7.3	9.4
Boat Sites	5.7	8.6	9.6
<b>Invertebrate Community Index</b>			
Artificial Substrate Samplers	22	34	46

**Use-Specific Criteria**

Dissolved Oxygen:       Ammonia:       Other:       None:

The State of Ohio has use specific water quality criteria for dissolved oxygen, ammonia, chlorine, pH, and temperature. Dissolved oxygen criteria are listed below; see the state Water Quality Standards for the additional use-specific criteria.

**Ohio Dissolved Oxygen Criteria**

Aquatic Life Use (name)	Minimum (mg/L)	Minimum 24- hour Average (mg/L)
Warmwater	4	5
Exceptional Warmwater	5	6
Modified Warmwater	3	4
Coldwater	6	7
Limited Resource Water	2	3

**Information Sources**

Ohio Water Quality Standards, Ohio Administrative Code 3745-1  
<http://www.epa.state.oh.us/dsw/rules/3745-1.html>

**Appendix A.5**  
**Maine Aquatic Life Use Information**  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The aquatic life use designations are based on the Biological Condition Gradient model.

*Class AA Waters*

These waters are the highest classification and are outstanding natural resources. These waters are suitable for the designated uses of drinking water after disinfection, fishing, recreation in and on the water and navigation and as habitat for fish and other aquatic life. The habitat is characterized as free flowing and natural. Aquatic life, dissolved oxygen, and bacteria levels are as naturally occurs.

*Class A Waters*

These waters are of such quality that they are suitable for the designated uses of drinking water after disinfection; fishing; agriculture; recreation in and on the water; industrial process and cooling water supply; hydroelectric power generation, except as prohibited under Title 12, section 403; navigation; and as habitat for fish and other aquatic life. The habitat must be characterized as natural. Dissolved oxygen must be 7.0 mg/L or 75% saturated, whichever is higher. Aquatic life and bacteria levels are as naturally occurs.

*Class B Waters*

Class B waters must be of such quality that they are suitable for the designated uses of drinking water supply after treatment; fishing; agriculture; recreation in and on the water; industrial process and cooling water supply; hydroelectric power generation, except as prohibited under Title 12, section 403; navigation; and as habitat for fish and other aquatic life. The habitat must be characterized as unimpaired.

*Class C Waters*

Class C waters must be of such quality that they are suitable for the designated uses of drinking water supply after treatment; fishing; agriculture; recreation in and on the water; industrial process and cooling water supply; hydroelectric power generation, except as prohibited under Title 12, section 403; navigation; and as a habitat for fish and other aquatic life.

**Biological Criteria**

Narrative:       Numeric:       None:

The narrative biological criteria for the State of Maine are included in the use descriptions above. Maine does not include numeric criteria in the state water quality standards but it is the only state in this review that uses a linear discriminant model based on a reference stream bioassessment database to assess use attainment.

**Use-Specific Criteria**

Dissolved Oxygen:       Ammonia:       Other:       None:

The State of Maine has use-specific dissolved oxygen and bacteria.

	<b>Dissolved Oxygen Numeric Criteria</b>	<b>Bacteria (<i>E. coli</i>) Numeric Criteria</b>	<b>Habitat Narrative Criteria</b>	<b>Aquatic Life (Biological) Narrative Criteria</b>
<b>Class AA</b>	as naturally occurs	as naturally occurs	free flowing and natural	No direct discharge of pollutants: <i>as naturally occurs</i>
<b>Class A</b>	7 ppm; 75% saturation	as naturally occurs	natural	<i>as naturally occurs</i>
<b>Class B</b>	7 ppm; 75% saturation	64/100 ml (g.m. <sup>*</sup> ) or 427/100 ml (inst. <sup>†</sup> )	unimpaired	Discharges <i>shall not cause adverse impact</i> to aquatic life in that the receiving waters shall be of sufficient quality to <i>support all aquatic species indigenous to the receiving water without detrimental changes to the resident biological community.</i>
<b>Class C</b>	5 ppm; 60% saturation	142/100 ml (g.m. <sup>*</sup> ) or 949/100 ml (inst. <sup>†</sup> )	habitat for fish and other aquatic life	Discharges <i>may cause some changes</i> to aquatic life, provided that the receiving waters shall be of sufficient quality to <i>support all species of fish indigenous to the receiving waters and maintain the structure and function of the resident biological community.</i>

\* g.m., geometric mean; † inst., instantaneous level

**Information Sources**

Maine Water Quality Standards, Maine Revised Statutes, Title 38, Chapter 3, Subchapter 1, Article 4A <http://janus.state.me.us/legis/statutes/38/title38ch3seco.html>

Davies S.P., and S.K. Jackson. 2006. The biological condition gradient: a descriptive model for interpreting change in aquatic ecosystems. Ecological Applications. 16(4) 1251-1266.

USEPA (U.S. Environmental Protection Agency 2005. Use of Biological Information to Better Define Designated Aquatic Life Uses in State and Tribal Water Quality Standards: Tiered Aquatic Life Uses. US EPA Office of Science and Technology, Washington, DC. EPA 822-R-05-001.

**Appendix A.5**  
**Arkansas Aquatic Life Use Information**  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The State of Arkansas divides the fisheries beneficial use into three categories: trout, lakes, and streams. The streams category is further divided by region and each region has fish species listed in the standards that are typically representative of the region (key species and indicator species).

**Fisheries**

Trout

Lakes

Streams

Ozark Highlands Ecoregion

Boston Mountains Ecoregion

Arkansas River Valley

Ouachita Mountains Ecoregion

Typical Gulf Coastal Ecoregion

Springwater Influenced Gulf Coastal Ecoregion

Least Altered Delta Ecoregion

Channel Altered Delta Ecoregion – w/example of species list

**Key Species**

Blacktail shiner

Drum

Carp

Channel catfish

Green sunfish

Spotted gar

**Indicator Species**

Mosquitofish

Gizzard shad

Emerald shiner

**Biological Criteria**

Narrative:  Numeric:  None:

The State of Arkansas does include narrative criteria to protect biological integrity in their water quality standards document. Regulation 2.405 is as follows:

“For all waters with specific fisheries use designated in Appendix A, aquatic biota should not be impacted. Aquatic biota should be representative of streams that have the ability to support the designated fishery, taking into consideration the seasonal and natural variability of the aquatic biota community under naturally varying habitat and hydrological conditions; the technical and economic feasibility of the options

available to address the relevant conditions; and other factors. An aquatic biota assessment should compare biota communities that are similar in variety and abundance, based upon either an in-stream study including an upstream and downstream comparison, a comparison to a reference water body within the same ecoregion, or a comparison to community characteristics from a composite of reference waters. The reference stream should have similar habitat and hydrologic conditions. Such a comparison should consider the seasonal and natural variability of the aquatic biota community. It is the responsibility of the Department to collect and evaluate the data for an aquatic biota assessment and such data will not be used to develop or impose permit limits.”

**Use-Specific Criteria**

Dissolved Oxygen:  Ammonia:  Other:  None:

The State of Arkansas has use-specific/ecoregion-specific dissolved oxygen, turbidity, temperature, and pH water quality criteria.

The dissolved oxygen criteria were developed by the Arkansas Department of Pollution Control and Ecology following a statewide assessment of regional reference stream conditions. The statewide assessment included the collection of physical, chemical, and biological data during two, one-week long sampling efforts (one Spring, one Summer) at multiple reference sites in the various ecoregions. Dissolved oxygen was measured continuously during each of the two assessments. The dissolved oxygen criteria in the current Water Quality Standards are based on the results of that study (Bennett et al. 1987, Giese et al. 1987).

**Dissolved Oxygen Criteria in mg/L for Arkansas Ecoregions - Primary (Critical)**

Ecoregion	Watershed Area			
	< 10 mi <sup>2</sup>	10 - 100 mi <sup>2</sup>	> 100 mi <sup>2</sup>	
Ozark Highlands	6 (2)	6 (5)	6 (6)	
Delta (Least and Channel-Altered)	5 (2)	5 (3)	5 (5)	
	< 10 mi <sup>2</sup>	10 - 150 mi <sup>2</sup>	151 - 400 mi <sup>2</sup>	> 400 mi <sup>2</sup>
Arkansas River Valley	5 (2)	5 (3)	5 (4)	5 (5)
	< 10 mi <sup>2</sup>	10 - 500 mi <sup>2</sup>	> 500 mi <sup>2</sup>	
Typical Gulf Coast	5 (2)	5 (3)	5 (5)	
	< 10 mi <sup>2</sup>	> 10 mi <sup>2</sup>		
Ouachita Mountains	6 (2)	6 (6)		
Boston Mountains	6 (2)	6 (6)		
	All Watersheds			
Springwater-influenced Gulf Coastal	6 (5)			
Trout	6 (6)			

Critical season: That period of the year when water temperatures exceed 22°C. This is normally the hot, dry season and after the majority of the fish spawning activities have ceased. This season occurs during a different time frame in different parts of the state, but normally exists from about mid-May to mid-September.

Primary season: That period of the year when water temperatures are 22°C or below. This includes the major part of the year from fall through spring, including the spawning season of most fishes. It normally occurs from about mid-September to mid-May.

For purposes of determining effluent limits, a 1 mg/l diurnal depression below the applicable critical dissolved oxygen criterion is allowed when water temperatures exceed 22°C for no more than 8 hours during any 24-hour period.

Ecoregion/Basin	Turbidity	Temperature	pH <sup>1</sup>
	Primary (Stormflow)	°C	SU
Ozark Highlands	10 (17)	29	6.0 - 9.0
Boston Mountains	10 (19)	31	6.0 - 9.0
Arkansas River Valley	21 (40)	31	6.0 - 9.0
Ouachita Mountains	10 (18)	30	6.0 - 9.0
Springwater-influenced Gulf Coastal	21 (32)	30	6.0 - 9.0
Typical Gulf Coastal	21 (32)	30	6.0 - 9.0
Least-Altered Delta	45 (84)	30	6.0 - 9.0
Channel-Altered Delta	75 (250)	32	6.0 - 9.0
Arkansas River	50 (52)	32	6.0 - 9.0
Mississippi River	50 (75)	32	6.0 - 9.0
Red River	50 (150)	32	6.0 - 9.0
St. Francis River	75 (100)	32	6.0 - 9.0
Trout	10 (15)	20	6.0 - 9.0

<sup>1</sup> - As a result of waste discharges, the pH of water in streams or lakes must not fluctuate in excess of 1.0 unit over a period of 24 hours and pH values shall not be below 6.0 or above 9.0.

### Information Sources

Bennett, C., Giese, J., Keith, B., Maner, M., McDaniel, R., O'Shaughnessy, N., and B. Singleton. 1987. Physical, Chemical, and Biological Characteristics of Least-Disturbed Reference Streams in Arkansas' Ecoregions – Volume I Data Compilation. Arkansas Department of Pollution Control and Ecology.

Giese, J., Keith, B., Maner, M., McDaniel, R., and B. Singleton. 1987. Physical, Chemical, and Biological Characteristics of Least-Disturbed Reference Streams in Arkansas' Ecoregions – Volume II Data Analysis. Arkansas Department of Pollution Control and Ecology.

Arkansas Surface Water Quality Standards, Arkansas Pollution Control and Ecology Regulation 2 [http://www.adeq.state.ar.us/regs/files/reg02\\_final\\_071125.pdf](http://www.adeq.state.ar.us/regs/files/reg02_final_071125.pdf)

Other Informational Documents [http://www.adeq.state.ar.us/water/reports\\_data.htm](http://www.adeq.state.ar.us/water/reports_data.htm)

**Appendix A.7**  
**Arizona Aquatic Life Use Information**  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The aquatic life use designations are based on water temperature.

The State of Arizona has 4 aquatic life use designation categories. They are:

- 1) Aquatic and Wildlife Coldwater;
- 2) Aquatic and Wildlife Warmwater;
- 3) Aquatic and Wildlife Ephemeral;
- 4) and Aquatic and Wildlife Effluent-Dependent.

For tributaries that are not listed in Appendix B of the water quality standards, the following uses apply:

- The Aquatic and Wildlife Ephemeral use applies to an unlisted tributary that is an ephemeral water;
- The Aquatic and Wildlife Cold Water use applies to an unlisted tributary that is a perennial or intermittent surface water and is above 5000 feet in elevation; and
- The Aquatic and Wildlife Warm Water use applies to an unlisted tributary that is a perennial or intermittent surface water and is below 5000 feet in elevation.

The water quality standards state that the Director must classify a surface water as an effluent-dependent water by rule and that he may adopt site-specific water quality standards for an effluent-dependent water by rule. The standards also state that the Director may allow a discharge into a stream if it creates or supports an ecologically valuable ecosystem (called a net ecological benefit in standards).

**Biological Criteria**

Narrative:  Numeric:  None:

The State of Arizona has proposed numeric biocriteria based on the 25<sup>th</sup> percentile of reference stream data for both warm and coldwater aquatic life uses. It appears as though these criteria are still in draft form and have not yet been adopted into the state water quality standards.



Use-Specific Criteria

Dissolved Oxygen:  Ammonia:  Other:  None:

The State of Arizona has use-specific pH, temperature, suspended sediment, and dissolved oxygen criteria.

	pH	Max. Temperature Increase	Max. Sus. Sediment <sup>1</sup>	Dissolved Oxygen <sup>2</sup>
AW Warm	6.5 - 9	3 C	80 mg/L	6.0 mg/L or at least 90% of saturation
AW Cold	6.5 - 9	1 C	80 mg/L	7.0 mg/L or at least 90% of saturation
AW Ephemeral <sup>4</sup>	6.5 - 9			
AW Eff. Dependent <sup>3</sup>	6.5 - 9	1 C		3.0 mg/L - Three hours after sunrise to sunset 1.0 mg/L - Sunset to three hours after sunrise or at least 90% of saturation

- 1 - Geometric mean 4 sample minimum at baseflow
- 2 - Single sample minimum
- 3 - Classified by rule, director may apply site-specific criteria
- 4 - Protected from acute toxicity

Information Sources

Arizona Administrative Code Title 18 Chapter 11  
[http://www.azsos.gov/public\\_services/Title\\_18/18-11.htm](http://www.azsos.gov/public_services/Title_18/18-11.htm)

Appendix A.8  
Oklahoma Aquatic Life Use Information  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The aquatic life use designations are based water temperature and fishery type.

Aquatic life uses are given the default designation (Warm Water Aquatic Community) unless a UAA shows that it should be designated otherwise.

The fish and wildlife propagation beneficial use is divided into 4 categories in Oklahoma. They are:

*Habitat Limited Aquatic Community*

This beneficial use is determined after a UAA demonstrates that the waterbody cannot fully support a warm water aquatic community.

*Warm Water Aquatic Community (Default Category)*

This use is assigned when habitat and water quality are adequate to support warm water climax fish communities.

*Cool Water Aquatic Community – Excluding lakes*

This is a subcategory of the beneficial use category "Fish and Wildlife Propagation" where the water quality, water temperature and habitat are adequate to support cool water climax fish communities and includes an environment suitable for the full range of cool water benthos. Typical species may include smallmouth bass, certain darters and stoneflies.

*Trout Fishery*

This is a subcategory of the beneficial use where the water quality, water temperature and habitat are adequate to support a seasonal put and take trout fishery.

**Biological Criteria**

Narrative:  Numeric:  None:

Oklahoma has narrative biocriteria that state that aquatic life should not exhibit degraded conditions as compared to regional reference conditions or to historical data from the same waterbody. Specific numeric biological criteria are not included in the state water quality standards.

**Use-Specific Criteria**

Dissolved Oxygen:  Ammonia:  Other:  None:

The State of Oklahoma has use specific water quality criteria for dissolved oxygen, temperature, and turbidity.

Use Designation	Applicable Dates	Dissolved Oxygen Minimum	Temperature
<b>Habitat Limited Aquatic Community</b>			
Early Life Stages	4/1 - 6/15	4.0	25
Other Life Stages			
Summer Conditions	6/16 - 10/15	3.0	32
Winter Conditions	10/16 - 3/31	3.0	18
<b>Warm Water Aquatic Community</b>			
Early Life Stages	4/1 - 6/15	6.0 <sup>1</sup>	25
Other Life Stages			
Summer Conditions	6/16 - 10/15	5.0 <sup>1</sup>	32
Winter Conditions	10/16 - 3/31	5.0	18
<b>Cool Water Aquatic Community/Trout</b>			
Early Life Stages	3/1 - 5/31	7.0 <sup>1</sup>	22
Other Life Stages			
Summer Conditions	6/1 - 10/15	6.0 <sup>1</sup>	29
Winter Conditions	10/16 - 2/28	6.0	18

<sup>1</sup> Due to natural diurnal dissolved oxygen fluctuations, a 1.0 mg/L dissolved oxygen concentration deficit is allowed for no more than 8 hours during any 24-hour period.

**Information Sources**

Oklahoma Water Quality Standards, Oklahoma Administrative Code, Title 785, Chapter 45. <http://www.oar.state.ok.us>

Oklahoma Water Quality Standards Implementation, Oklahoma Administrative Code, Title 252, Chapter 690. <http://www.deq.state.ok.us/rules/690.pdf>

**Appendix A.9**  
**Idaho Aquatic Life Use Information**  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The aquatic life use designations are based on fisheries type.

The following are the five aquatic life use designations listed in the state water quality standards are:

*Cold Water*

This classification is applied when the water quality is appropriate for the protection and maintenance of a viable aquatic life community for coldwater species.

*Salmonid Spawning*

This classification is used in waters that provide or could provide a habitat for active self propagating populations of salmonid fishes.

*Seasonal Cold Water*

This is used when the water quality is appropriate for the protection and maintenance of a viable aquatic life community of cool and cold water species, where cold water aquatic life may be absent during, or tolerant of, seasonally warm temperatures.

*Warm Water*

This is used when the water quality is appropriate for the protection and maintenance of a viable aquatic life community for warm water species.

*Modified*

This is applied when the water quality is appropriate for an aquatic life community that is limited due to one or more conditions that preclude attainment of reference streams or conditions.

The Idaho Department of Environmental Quality (IDEQ) also has a Bull Trout use designation that is a subcategory of the Cold Water use. The Bull Trout use applies only to specific watersheds in the state.

**Biological Criteria**

Narrative:  Numeric:  None:

The State of Idaho does not include any biological criteria in the general or numeric criteria sections of their water quality standards. However, Section 053 of the

standards state that aquatic habitat parameters, biological parameters, and natural conditions should be considered when assessing use attainment. Additionally, the department may give less weight to pH, turbidity, dissolved oxygen, and temperature criteria if aquatic habitat and biological data indicate to the assessor that aquatic life beneficial uses are otherwise supported. IDEQ provides substantial guidance for determining beneficial use support through biological monitoring.

**Use-Specific Criteria**

Dissolved Oxygen:  Ammonia:  Other:  None:

The State of Idaho has use-specific dissolved oxygen, ammonia, temperature, and turbidity water quality criteria.

Metric	Warm Water	Seasonal Cold Water	Cold Water	Salmonid Spawning	Bull Trout
MDMT	33 °C	26 °C	22 °C	13 °C	N/A
MWMT	N/A	N/A	N/A	N/A	13 °C
MDAT	29 °C	23 °C	19 °C	9 °C	N/A

MDMT - Maximum Daily Maximum Temperature

MWMT - Maximum Weekly (7-day average) Maximum Temperature

MDAT - Maximum Daily Average Temperature

	DO	Turbidity	Ammonia
Bull Trout	same as CW	same as CW	same as CW
Cold Water	> 6 mg/L at all times	No greater than 50 NTU (instantaneous) of background <sup>1</sup> No greater than 25 NTU of background for 10 consecutive days <sup>1</sup>	Specific formula in standards based on Temperature and pH
Cold Water -Sal. Spawning	1-day minimum 5 mg/L, 7-day average 6 mg/L <sup>2</sup> 1-day minimum not less than 6 mg/L or 90% of saturation		Specific formula in standards based on Temperature and pH
Seasonal Cold Water <sup>3</sup>	> 6 mg/L at all times		Specific formula in standards based on Temperature and pH
Warm Water	Exceeding 5 mg/L at all times		Specific formula in standards based on Temperature and pH
Modified	Case-by-Case	Case-by-Case	Case-by-Case

1 - Below mixing zone

2 - Intergavel O<sub>2</sub>

3 - Between summer solstice and autumn equinox

**Information Sources**

Idaho Administrative Code, Department of Environmental Quality, Water Quality Standards, IDAPA 58.01.02

[http://www.deq.state.id.us/water/data\\_reports/surface\\_water/monitoring/standards.cfm](http://www.deq.state.id.us/water/data_reports/surface_water/monitoring/standards.cfm)

Link to Surface Water Monitoring Documents

[http://www.deq.state.id.us/water/data\\_reports/surface\\_water/monitoring/overview.cfm](http://www.deq.state.id.us/water/data_reports/surface_water/monitoring/overview.cfm)

Appendix A.10  
Wisconsin Aquatic Life Use Information  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The State of Wisconsin has 5 aquatic life categories however, only the Cold Water, Warm Water Sport Fish, and Warm Water Forage Fish uses are considered suitable for the protection and propagation of fish and wildlife communities.

*Cold Water Communities*

This subcategory includes surface waters capable of supporting a community of cold water fish and other aquatic life, or serving as a spawning area for cold water fish species. This subcategory includes, but is not restricted to, surface waters identified as trout water by the department of natural resources (Wisconsin Trout Streams, publication 6-3600 (80)).

*Warm Water Sport Fish Communities*

This subcategory includes surface waters capable of supporting a community of warm water sport fish or serving as a spawning area for warm water sport fish.

*Warm Water Forage Fish Communities*

This subcategory includes surface waters capable of supporting an abundant diverse community of forage fish and other aquatic life.

*Limited Forage Fish Communities (Intermediate surface waters)*

This subcategory includes surface waters of limited capacity and naturally poor water quality or habitat. These surface waters are capable of supporting only a limited community of forage fish and other aquatic life.

*Limited Aquatic Life Communities (Marginal surface waters)*

This subcategory includes surface waters of severely limited capacity and naturally poor water quality or habitat. These surface waters are capable of supporting only a limited community of aquatic life.

According to the document entitled "Guidelines for Designating Fish and Aquatic Life Uses for Wisconsin Surface Waters," the State of Wisconsin is pursuing the development of 17 sub-categories of the aquatic life uses listed above. Until those sub-categories are officially included in the Wisconsin Administrative Code, the 5 uses above will apply.

**Biological Criteria**

Narrative:       Numeric:       None:

The State of Wisconsin does not include biological criteria in the state water quality standards.

**Use-Specific Criteria**

Dissolved Oxygen:       Ammonia:       Other:       None:

In Cold Water Communities, no significant artificial increases in water temperature are allowed where trout reproduction is protected. Temperature may not exceed 89°F for warm water fishes.

Use	Dissolved Oxygen Minimum
Cold Water Communities	6.0 <sup>1</sup>
Warm Water Forage Fish Communities	5.0
Warm Water Sport Fish Communities	5.0
Limited Forage Fish Communities	3.0
Limited Aquatic Life Communities	1.0

<sup>1</sup> 7.0 mg/l during spawning season.

**Information Sources**

Ball, J. and P. LaLiberte. 2004. Guidelines for Designating Fish and Aquatic Life Uses for Wisconsin Surface Waters. Wisconsin Department of Natural Resource, Bureau of Watershed Management. Madison, Wisconsin. PUBL-WT-807-04.

Wisconsin Water Quality Standards, Wisconsin Administrative Code, Chapters NR 102, 104, and 105.

**Appendix A.11**  
**Kentucky Aquatic Life Use Information**  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The aquatic life use designations are based on water temperature. The two uses are:

*Warm Water Aquatic Life*  
*Cold Water Aquatic Life*

**Biological Criteria**

Narrative:  Numeric:  None:

The State of Kentucky does not have true biological criteria in their water quality standards.

**Use-Specific Criteria**

Dissolved Oxygen:  Ammonia:  Other:  None:

The State of Kentucky has use-specific temperature, dissolved oxygen, alkalinity, and flow criteria.

	Temperature	Dissolved Oxygen	Alkalinity	Flow
Warm Water	Shall not exceed 31.7 C, Site specific temp. allowed	Minimum 5.0 mg/L daily average, Instantaneous minimum 4.0 mg/L	Natural alk. may not be reduced by more than 25%, If natural alk. < 20 mg/L CaCO <sub>3</sub> then no reduction allowed	May not be altered to the degree that aquatic life are adversely affected
Cold Water	Shall not be increased above natural levels	Minimum 6.0 mg/L daily average, Instantaneous minimum 5.0 mg/L	-----	-----

**Information Sources**

<http://www.lrc.ky.gov/kar/title401.htm>



---

Appendix A.12  
Washington Aquatic Life Use Information  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The aquatic life use designations are primarily based on fishery type.

*Char Spawning and Rearing*

The key identifying characteristics of this use are spawning or early juvenile rearing by native char (bull trout and Dolly Varden), or use by other aquatic species similarly dependent on such cold water. Other common characteristic aquatic life uses for waters in this category include summer foraging and migration of native char; and spawning, rearing, and migration by other salmonid species.

*Core Summer Salmonid Habitat*

The key identifying characteristics of this use are summer (June 15 - September 15) salmonid spawning or emergence, or adult holding; use as important summer rearing habitat by one or more salmonids; or foraging by adult and subadult native char. Other common characteristic aquatic life uses for waters in this category include spawning outside of the summer season, rearing, and migration by salmonids.

*Salmonid Spawning, Rearing, and Migration*

The key identifying characteristic of this use is salmon or trout spawning and emergence that only occurs outside of the summer season (September 16 - June 14). Other common characteristic aquatic life uses for waters in this category include rearing and migration by salmonids.

*Salmonid Rearing and Migration Only*

The key identifying characteristic of this use is use only for rearing or migration by salmonids (not used for spawning).

*Non-Anadromous Interior Redband Trout*

For the protection of waters where the only trout species is a non-anadromous form of self-reproducing interior redband trout (*O. mykiss*), and other associated aquatic life.

*Indigenous Warm Water Species*

For the protection of waters where the dominant species under natural conditions would be temperature tolerant indigenous nonsalmonid species. Examples include dace, redband shiner, chiselmouth, sucker, and northern pikeminnow.

**Biological Criteria**

Narrative:       Numeric:       None:

The State of Washington does not include biological criteria in their water quality standards.

**Use-Specific Criteria**

Dissolved Oxygen:       Ammonia:       Other:       None:

The State of Washington has use-specific criteria for dissolved oxygen, temperature, and turbidity. Use specific turbidity criteria may be found in the state water quality standards.

Use Designation	Char Spawning and Rearing	Core Summer Salmonid Habitat	Salmonid Spawning, Rearing, and Migration	Salmonid Rearing and Migration Only	Non-Anadromous Interior Redband Trout	Indigenous Warm Water Species
Dissolved Oxygen (Daily Minimum)	9.5	9.5	8	6.5	8	6.5
Temperature <sup>1</sup> (Celsius)	12.0 <sup>2</sup>	16.0	17.5	17.5	18.0	20.0

<sup>1</sup> 7-day average of maximum daily temperatures.

<sup>2</sup> Criteria is 9 for Char Spawning only.

**Information Sources**

Washington Water Quality Standards, Washington Administrative Code, Title 173, Chapter 173-201A  
<http://apps.leg.wa.gov/WAC/default.aspx?cite=173-201A>

Washington Department of Ecology,  
<http://www.ecy.wa.gov/programs/wq/swqs/index.html>

**Appendix A.13**  
**Oregon Aquatic Life Use Information**  
(As of 3/31/08)

**Aquatic Life Use Designations**

Basis for Use Development:

Biological:  Fishery:  Habitat:  Physiogeographic:  Other:

The aquatic life use designations are divided by river basin and are based on water temperature and fishery type. For example, in the North Coast -Lower Columbia Basin, the aquatic uses are: anadromous fish passage, salmonid fish rearing, salmonid fish spawning, and resident fish and aquatic life.

*Bull Trout Juvenile Rearing and Spawning*

The Bull trout juvenile rearing and spawning use was designated based on the Idaho Department of Environmental Quality's (IDEQ) "Bull Trout Habitat Designation Report: Technical Work Group Recommendations" (2003). IDEQ believes it is necessary and appropriate to designate areas identified as potential bull trout rearing and spawning habitat (identified in both of the above reports) in addition to where current use occurs because bull trout habitat in the State has been greatly reduced and fragmented, and because bull trout are listed under the federal Endangered Species Act (ESA). The additional habitat will allow local populations to grow to the point they: (1) are reconnected with other local populations and with foraging habitats, (2) are large enough to withstand losses due to natural stresses and events (e.g., drought); and (3) maintain the genetic diversity to support a viable population.

*Core Cold Water Habitat*

Core cold-water habitat designations identify and ensure the protection of colder water habitats that provide more optimal conditions for salmon and steelhead juvenile rearing and that protect summer bull trout sub-adult and adult foraging and migration. In addition, these areas would provide colder holding waters for pre-spawning adults.

*Salmon and Trout Juvenile Rearing and Migration*

DEQ proposes to designate "Salmon and Trout Rearing and Migration Use" for waters where:

1. salmon or steelhead rearing occurs in July or August;
2. rainbow or coastal cutthroat trout rearing occurs; and
3. all waters upstream of the waters identified above.

*Salmon and Steelhead Migration Corridors*

DEQ proposes to designate waters as "salmon and trout migration corridors" where ODFW distribution and timing information indicates there is migration use but no rearing use in July or August or information suggests a lower mainstem river is primarily a migration corridor during the period of summer maximum temperatures,

and there is some evidence to suggest that temperatures would naturally reach 20°C/68°F.

*Lahontan Cutthroat and Redband Trout Use*

These two trout species are found in Eastern Oregon. ODFW has not updated their distribution database in this part of the State or collected life stage timing data for interior basins that do not have anadromous fish, so DEQ had to rely on other sources of information. Lahontan Cutthroat trout are limited to the Upper Quinn and Alvord Lakes basins in southeastern Oregon (USFWS 1995, Dunham 1999).

*Cool Water Species*

There are a limited number of streams or stream reaches within the anadromous basins of the State that either have no salmonid fish use during the warmest part of the summer (July or August). If ODFW information is available that shows a stream reach has no salmonid fish use (rearing or migration) during July or August, it may be designated for cool water species.

*Borax Lake Chub*

The Borax Lake Chub are located in a very limited area in the Alvord Lake Subbasin in the waters associated with Borax Lake and Lower Borax Lake in Harney County.

**Biological Criteria**

Narrative:       Numeric:       None:

The water quality standards state that waters of the State must be of sufficient quality to support aquatic species without detrimental changes in the resident biological communities.

**Use-Specific Criteria**

Dissolved Oxygen:       Ammonia:       Other:       None:

The State of Oregon has use-specific dissolved oxygen and water temperature criteria.

Use Designation	Temperature <sup>1</sup> (Celsius)
Salmon and Trout Rearing and Migration Use	20
Salmon and Steelhead Spawning Use	13
Cold Water	16
Lahontan Cutthroat Trout or Redband Trout	20
Bull Trout	12
Cool Water	----
Warm Water	----

<sup>1</sup> 7-day average maximum criteria.

Class	Concentration and Period <sup>1</sup> (All Units are mg/L)				Use/Level of Protection
	30-D	7-D	7-Mi	Min	
Salmonid Spawning		8.0 <sup>2</sup>		9.0 <sup>3</sup>	Principal use of salmonid spawning and incubation of embryos until emergence from the gravels. Low risk of impairment to cold-water aquatic life, other native fish and invertebrates.
Cold Water	8.0		8.5	6.0	Principally cold-water aquatic life. Salmon, trout, cold-water invertebrates, and other native cold-water species exist throughout all or most of the year. Juvenile anadromous salmonids may rear throughout the year. No measurable risk level for these communities.
Cool Water	6.5		5.0	4.0	Mixed native cool-water aquatic life, such as sculpins, smelt, and lampreys. Waterbodies includes estuaries. Salmonids and other cold-water biota may be present during part or all of the year but do not form a dominant component of the community structure. No measurable risk to cool-water species, slight risk to cold-water species present.
Warm Water	5.0			4.0	Waterbodies whose aquatic life beneficial uses are characterized by introduced, or native, warm-water species.
No Risk	No Change from Background				The only DO criterion that provides no additional risks is "no change from background". Waterbodies accorded this level of protection include marine waters and waters in Wilderness areas.

**Note:**  
**Shaded values present the absolute minimum criteria, unless the Department believes adequate data exists to apply the multiple criteria and associated periods.**

<sup>1</sup> 30-D = 30-day mean minimum as defined in OAR 340-41-006.  
<sup>2</sup> 7-D = 7-day mean minimum as defined in OAR 340-41-006.  
<sup>3</sup> 7-Mi = 7-day minimum mean as defined in OAR 340-41-006.  
 Min = Absolute minimums for surface samples when applying the averaging period, spatial median of IGDO.

<sup>2</sup> When Intergavel DO levels are 8.0 mg/L or greater, DO levels may be as low as 9.0 mg/L, without triggering a violation.

<sup>3</sup> If conditions of barometric pressure, altitude and temperature preclude achievement of the footnoted criteria, then 95 percent saturation applies.

<sup>4</sup> Intergavel DO criterion, spatial median minimum.

<sup>5</sup> If conditions of barometric pressure, altitude, and temperature preclude achievement of 8.0 mg/L, then 90 percent saturation applies.

Information Sources

Oregon Water Quality Standards, Oregon Administrative Rules, OAR 340-041  
[http://arcweb.sos.state.or.us/rules/OARs\\_300/OAR\\_340/340\\_041.html](http://arcweb.sos.state.or.us/rules/OARs_300/OAR_340/340_041.html)

Oregon Department of Environmental Quality, Water Quality Standards Webpage  
<http://www.deq.state.or.us/wq/standards/standards.htm>

**Water Quality Standards Review:  
Chloride, Sulfate and Total Dissolved Solids**

Iowa Department of Natural Resources  
Consultation Package  
February 9, 2009

## Table of Contents

<b>Iowa's Water Quality Standard Review: Chloride</b>	3
1. Background	3
2. Current EPA National Criteria	3
3. New Toxicity Testing Data	3
4. Summary of Proposed Criteria Options	5
5. Final Proposed Chloride Criteria	6
References	8
<b>Iowa's Water Quality Standard Review: Sulfate</b>	9
1. Sulfate and TDS	9
2. Existing Water Quality Standards	9
3. The Illinois Approach	10
4. Similarities between Iowa and Illinois Surface Water Quality	12
5. Conclusions and Recommended Sulfate Standard	12
6. Proposed Sulfate Standard Implementation	13
Appendix A: Statewide Hardness, Chloride and Sulfate Distribution in Iowa Surface Waters	14
Appendix B: Illinois Environment Protection Agency Draft Justification for Changing Water Quality Standards for Sulfate, Total Dissolved Solids and Mixing Zones	16
<b>Iowa's Water Quality Standard Review: Total Dissolved Solids</b>	62
1. Background	62
2. The Current Interim TDS Site-Specific Approach	62
3. Literature Review on TDS Toxicity Data	63
4. Justification for Replacing TDS Standard with Specific Ion Criteria	67
4A. Implementation Issues with the Interim TDS Site-Specific Approach	67
4B. Lack of Scientific Support	68
4C. Protection of Designated Uses by Individual Ion Criteria	69
4D. TDS/Chloride Monitoring Study	70
4E. Measures to Reduce TDS Concentrations	72
5. Recommendations for Specific Ion Criteria	73
Appendix A: TDS Site Specific Approach Standard Implementation	75
Appendix B: Definitions	77
References	78

## Iowa's Water Quality Standard Review: Chloride

### 1. Background

Chloride is one of the major anions commonly found in ambient and wastewater. Chloride may get into surface water from several sources including:

- wastewater from industries and municipalities;
- effluent wastewater from water softening;
- road salting;
- agricultural runoff; and
- produced water from oil and gas wells.

The current Iowa water quality standard for chloride is 250 mg/L for drinking water use only. There are no numeric chloride standards for aquatic life protection in Iowa. However, as part of the current interim site-specific TDS approach, if in-stream chloride concentrations reach a threshold level (in-stream threshold values: acute threshold is 860 mg/l, chronic threshold is 230 mg/L), Whole Effluent Toxicity tests are required. These threshold values are equivalent to EPA's 1988 304(a) national criteria.

### 2. Current EPA National Criteria

The most recent 304(a) national criteria for chloride were published in 1988. The national criterion for chloride was derived based on the toxicity test data of sodium chloride in laboratory reconstituted water given that it is the only chloride composition with enough data available to allow derivation of a water quality criterion. Also, it is likely that most anthropogenic chloride in ambient water is associated with sodium, rather than potassium, calcium, or magnesium (EPA, 1988). In the EPA 304(a) criteria document, the acute toxicity data of chloride are available for 12 different species (genus). Table 1 lists the current EPA national criteria for chloride for aquatic life protection (EPA, 1988).

Table 1. National Aquatic Life Criteria for Chloride

Parameter	National Criteria (mg/l)	
	Acute	Chronic
Chloride	860	230

### 3. New Toxicity Testing Data

Since the EPA national criteria were published in 1988, the derivation of the criteria was based on toxicity data available before 1987. The Iowa Department of Natural Resources started a review of the chloride criteria by looking at the most up-to-date toxicity information available in 2007. As part of the effort, IDNR working together with Charles Stephan, of the EPA-Duluth, Office of Research and Development (ORD), performed a literature search to update and recalculate the 1988 acute and chronic chloride criteria based upon new toxicity data deemed acceptable following the 1985 EPA Guidelines (U.S. EPA, 1985). The literature review revealed acceptable data for several new species, which were not part of the 1988 chloride criteria document. One particular study, conducted by Wurtz and Bridges (1961), included data for several species, including two of the four species suspected of being most sensitive to chloride (a



---

planorbid snail, *Gyraulus circumstriatus*, and the fingernail clam, *Sphaerium tenue*). A second study (Khangarot 1991) included acute chloride toxicity data for the tubificid worm (*Tubifex tubifex*), which indicated that this species might also be highly sensitive to chloride, but the data were determined unacceptable for inclusion in the recalculation based on several factors. Given the importance of the Wurtz and Bridges (1961) data, the Khangarot (1991) data, and the lack of verification by other laboratories, it was determined that more toxicity data would be warranted to independently determine if those species are indeed sensitive to chloride.

EPA contracted with the Great Lakes Environmental Center (GLEC) in Columbus, OH and the Illinois Natural History Survey (INHS) at Champaign, IL to perform the additional toxicity testing. The acute toxicity of chloride to four freshwater invertebrate species: water flea (*Ceriodaphnia dubia*), fingernail clam (*Sphaerium simile*), planorbid snail (*Gyraulus parvus*), and tubificid worm (*Tubifex tubifex*), was determined under different levels of water hardness (all four species) and sulfate concentrations (*C. dubia* only). Tests with *C. dubia* acclimated and tested under different levels of total water hardness and sulfate were performed simultaneously by two different laboratories. Results were comparable. The final toxicity testing results for the four freshwater invertebrate species are published in the report "Acute Toxicity of Chloride To Select Freshwater Invertebrates, September 26, 2008".

The toxicity testing results indicate that the 48-h LC50 for *C. dubia* at 25 to 50 mg/L hardness is approximately half that of *C. dubia* exposed at 600 to 800 mg/L hardness. Conversely, sulfate over the range of 25-600 mg/L exerted only a small (inverse) effect on chloride toxicity to *C. dubia*. The mean 48-h LC50 at 25 mg/L sulfate was approximately 1,356 mg Cl/L, while at 600 mg/L sulfate, it was 1,192 mg Cl/L (reduction of 12%). Again, LC50 values between labs were consistent. Ninety-six hour LC50 values for three other freshwater invertebrate species ranged from a low of 740 mg Cl/L for *S. simile* exposed to chloride at 50 mg/L hardness, to a high of 6,008 for *T. tubifex* exposed to chloride at 200 mg/L hardness. For both species, increasing the acclimation and dilution of water hardness reduced the acute toxicity of chloride by approximately 1.4 to 1.5 times. Water hardness did not appear to influence the acute toxicity of chloride to the planorbid snail, *G. parvus*. Rank order of sensitivity to acutely lethal chloride at a given water hardness is in the order (most to least): *S. simile*>*C. dubia*>*G. parvus*>*T. tubifex*. The new toxicity testing results are shown in Table 2 and 3.

Table 2. Chloride acute toxicity to *C. dubia* at different water harnesses and single sulfate concentration

Chloride Toxicity Test	<i>C. dubia</i> 48 h LC50 (95%CI) GLEC (mg Cl/L)	<i>C. dubia</i> 48 h LC50 (95%CI) INHS (mg Cl/L)	Mean LC50 value (mg Cl/L)
<b>Acclimated to and Tested at Various Total Hardness Levels (and 65 mg/L Sulfate)</b>			
25 mg/L Hardness	947 (868-1034)	1007 (964-1052)	977
50 mg/L Hardness	955 (885-1031)	767 (684-861)	861
100 mg/L Hardness	1130 (1029-1231)	1369 (1246-1505)	1250
200 mg/L Hardness	1609 (1516-1707)	1195 (1148-1245)	1402
400 mg/L Hardness	1491 (1385-1606)	1687 (1587-1794)	1589
600 mg/L Hardness	1907 (Estimates not Reliable)	1652 (1536-1776)	1779
800 mg/L Hardness	1764 (1661-1874)	1909 (1791-2034)	1836
<b>Acclimated to and Tested at Various Sulfate Levels (and 300 mg/L Hardness)</b>			
25 mg/L Sulfate	1400 (1287-1523)	1311 (1210-1421)	1356
50 mg/L Sulfate	1720 (1634-1811)	1258 (1211-1306)	1489
100 mg/L Sulfate	1394 (1281-1516)	1240 (1203-1278)	1317
200 mg/L Sulfate	1500 (1370-1641)	1214 (1153-1278)	1357
400 mg/L Sulfate	1109 (1004-1225)	1199 (1120-1284)	1154
600 mg/L Sulfate	1206 (1161-1253)	1179 (1125-1235)	1192

Table 3. Chloride acute toxicity for fingernail clam, snail and tubificid worm

Test species	96 h LC50 (95%CI) at 50 mg/L total hardness (mg Cl/L)	96 h LC50 (95%CI) at 200 mg/L total hardness (mg Cl/L)
Fingernail clam (juveniles), <i>Sphaerium simile</i>	740 (678-807)	1100 <sup>a</sup> (1040-1164)
Planorbid snail (mixed ages), <i>Gyraulus parvus</i>	3,078 (2,771-3,418)	3,009 (2,728-3,318)
Tubificid worm (mixed ages), <i>Tubifex tubifex</i>	4,278 (3,848-4,717)	6,008 (5,563-6,489)

<sup>a</sup> Result is from a repeat test because control mortality in the first test slightly exceeded maximum acceptable mortality of 10% (15% mortality recorded). LC50 was similar to the LC50 of the failed test (1098 mg Cl/L) which was based on nominal concentrations.

#### 4. Summary of Proposed Criteria Options

Four different procedures were used to derive potential freshwater aquatic life acute criteria for chloride, and three different Acute-Chronic Ratios (ACRs = Acute LC50/Chronic End Point)

were used to derive the chronic criteria. As a result, there are a total of 4 options proposed for the **acute** criteria values and a total of 12 proposed options for the **chronic** criteria values.

Table 4 presents a summary of different proposed chloride criteria.

Proposed Cl Criteria	Different Options			
	A (N <sup>a</sup> = 35)	B (N = 35)	C (N = 23)	D (N = 29)
Acute Value (CMC)	574	$283.17(\text{hardness})^{0.203797}(\text{sulfate})^{0.07452}$	$254.3(\text{hardness})^{0.203797}(\text{sulfate})^{0.07452}$	$195.7(\text{hardness})^{0.217736}$
Chronic Value -1 (CCC1)	238	$117.36(\text{hardness})^{0.203797}(\text{sulfate})^{0.07452}$	$105.4(\text{hardness})^{0.203797}(\text{sulfate})^{0.07452}$	$81.1(\text{hardness})^{0.217736}$
Chronic Value -2 (CCC2)	360	$177.70(\text{hardness})^{0.203797}(\text{sulfate})^{0.07452}$	$159.6(\text{hardness})^{0.203797}(\text{sulfate})^{0.07452}$	$122.8(\text{hardness})^{0.217736}$
Chronic Value -3 (CCC3)	342	$168.77(\text{hardness})^{0.203797}(\text{sulfate})^{0.07452}$	$161.5(\text{hardness})^{0.203797}(\text{sulfate})^{0.07452}$	$120.7(\text{hardness})^{0.217736}$

<sup>a</sup> N = number of genera used in the calculation

The following explains the different Options of A, B, C and D.

**Option A.** Acute values were not normalized for either hardness or sulfate and the criterion is **not** dependent on either hardness or sulfate;

**Option B.** Acute values were not normalized for either hardness or sulfate, but the criterion is dependent on both hardness and sulfate;

**Option C.** Acute values were normalized for both hardness and sulfate and the criterion is dependent on both hardness and sulfate;

**Option D.** Acute values were normalized for hardness (but not sulfate) and the criterion is dependent on hardness (but not sulfate).

For all procedures:

**CCC1** was derived using ACR = 4.826, which is the geometric mean of the ACRs for Rainbow Trout and Daphnia. CCC1 is too high for species at the 5th percentile.

**CCC2** was derived using ACR = 3.187, which is the ACR for Daphnia. CCC2 is appropriate for species at the 5th percentile.

**CCC3** was derived from predicted Genus Mean **Chronic** Values that were calculated using ACR = 7.308 of Rainbow Trout for vertebrates and ACR = 3.187 of Daphnia for invertebrates. Then the similar procedure for deriving acute criterion was used to derive the chronic criterion.

The above CMCs and CCCs are expressed as “mg chloride/L”.

## 5. Final Proposed Chloride Criteria

IDNR conducted the Technical Advisory Committee (TAC) meeting on December 8<sup>th</sup>, 2008 to discuss the proposed chloride criteria. After considering input from both EPA and the TAC as well as IDNR internal discussions, Option C is selected for the acute criterion, and CCC3 under Option C is selected as the chronic criterion based on the scientific justification. The final proposed chloride criteria are listed below.

Acute chloride criterion:

$$254.3(\text{hardness})^{0.205797}(\text{sulfate})^{-0.07452}$$

Chronic chloride criterion:

$$161.5(\text{hardness})^{0.205797}(\text{sulfate})^{-0.0745}$$

Statewide default values for hardness and sulfate will be used unless site specific data is available.

---

## REFERENCES

1. Khangarot, B.S. 1991. Toxicity of metals to a freshwater tubificid worm, *Tubifex tubifex* (Muller). *Bull. Environ. Contam. Toxicol.* 46(6):906-912.
2. U.S. EPA. 1985. *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses*. PB85-227049. Washington, D.C.
3. U.S. EPA, 1988. *Ambient Water Quality Criteria for Chloride – 1988*. Office of Water, Regulations and Standards Criteria and Standards Division, Washington, DC 20460.
4. U.S. EPA. September 26, 2008. *Acute Toxicity of Chloride To Select Freshwater Invertebrates*. EPA Contract Number: 68-C-04-006, Work Assignment 4-34 Sub-task 1-15.
5. Wurtz, C.B., and C.H. Bridges. 1961. Preliminary results from macroinvertebrate bioassays. *Proc PA Acad Sci* 35:51-56.
6. Chloride Recalculation Documents
  - 08ChlorideReview.pdf
  - 08ChlorideCompare.pdf
  - 08ChloridePrA-T1.pdf
  - 08ChloridePrA-T3.pdf
  - 08ChloridePrB.pdf
  - 08ChloridePrC-T1.pdf
  - 08ChloridePrC-T3.pdf
  - 08ChloridePrD-T1.pdf
  - 08ChloridePrD-T3.pdf
  - 08ChlorideChronic.pdf
  - 08ChlorideRefs.pdf
  - 08ChlorideSulfate.pdf

## Iowa's Water Quality Standard Review: Sulfate

### 1. Sulfate and TDS

Total Dissolved Solids (TDS) is a measure of all constituents dissolved in water. The inorganic anions dissolved in water include carbonates, chlorides, sulfates and nitrates. The inorganic cations include sodium, potassium, calcium and magnesium. Thus, sulfate is a constituent of TDS and may form salts with sodium, potassium, magnesium and other cations. Sulfate ( $\text{SO}_4^{2-}$ ) is widely distributed in nature and may be present in natural waters at concentrations ranging from a few to several hundred milligrams per liter.

The IDNR ambient monitoring program routinely monitors TDS, chloride and sulfate. Table 1 shows a summary of monitoring data on TDS and its constituents from 2000 to 2007.

Table 1. TDS and Ion Concentrations in Iowa Streams

Chemicals	Iowa Ambient Monitoring Data from 2000-2006, units in mg/L		
	50 <sup>th</sup> percentile	90 <sup>th</sup> percentile	Maximum value
TDS	360	510	1,640
Chloride	23	40	170
<b>Sulfate</b>	<b>37</b>	<b>97</b>	<b>400</b>
Hardness (as $\text{CaCO}_3$ )	300	410	820

Appendix I shows the statewide sulfate, chloride and hardness levels of surface waters in Iowa based on median values. The ambient monitoring data show that the NW region has the highest ambient sulfate concentrations.

Anthropogenic sources of sulfate may come from mine drainage wastes through pyrite oxidation, reverse osmosis reject water, cooling tower blow down, etc. Coal preparation facilities wash coal to reduce sulfur emissions prior to burning in coal-fired power plants and treat wastewaters for acid-soluble metals. This practice often produces a waste containing sulfuric acid that is usually neutralized by the addition of sodium hydroxide or sometimes quicklime ( $\text{CaO}$ ) prior to release to a receiving stream, which could contain high sulfate and other ions.

### 2. Existing Water Quality Standards

Currently no federal water quality criteria exist for the protection of freshwater aquatic life for either sulfate or TDS. Iowa has never adopted numerical criteria for aquatic life protection. However, the state water quality standard includes a recommended livestock watering guideline value of 1,000 mg/L for sulfate as part of the TDS narrative criteria, which was adopted on June 16, 2004. The 1,000 mg/L sulfate guideline value is applied at the end of mixing zone for livestock watering protection.

The literature review conducted by IDNR indicates that individual ions rather than TDS criteria/limits are more appropriate to characterize toxicity related to TDS. Recent studies conducted by Illinois EPA reached the same conclusion. IDNR studied the Illinois proposed sulfate rule and recommends replacing the current site-specific TDS approach with numerical sulfate and chloride criteria.

### 3. The Illinois Approach

The Illinois EPA is proposing the final rule that deletes the TDS general use water quality standard of 1000 mg/L, and replaces the sulfate general use water quality standard of 500 mg/L with an equation that depends on chloride and hardness to be protective of aquatic life and livestock watering uses. Because sulfate toxicity is dependent on chloride and hardness concentrations, water quality chemistry and characteristics are taken into consideration when setting the sulfate standard throughout the State.

The agency asserts that in Illinois waters the toxicity associated with substances comprising a major portion of TDS is predominantly due to either chloride or sulfate. The toxicity of other ions that make up TDS, such as sodium, calcium, magnesium and carbonates is insignificant when compared to chloride and sulfate toxicity. The Illinois EPA believes that with the adoption of a sulfate standard and the existing chloride standard, the water quality standards adequately address toxicity of dissolved salts and the TDS standard is not necessary as TDS cannot predict the threshold of adverse effects to aquatic life. For example, a sample with a high chloride and TDS concentration of 2,000 mg/L is highly toxic to some species of aquatic life such as invertebrates but a sample with high sulfate at the same TDS concentration is nontoxic.

The State of Illinois worked with the USEPA Duluth Toxicity laboratory to search available toxicity test data on sulfate. Data for over 30 kinds of organisms from about 30 papers/sources were found. The literature research showed that essentially only two groups, fish and zooplankton crustaceans, were adequately represented in the database. Fish were found to be tolerant of sulfate therefore no further discussion or additional testing is necessary. Strong representation of the daphnids was expected since these are common, easily tested organisms. However, *Hyalella azteca* data was relatively scarce, and available data suggested this native species is most sensitive to sulfate. For credence to be given to the dataset of toxicity values, more data on a variety of invertebrate species was necessary to obtain, especially, since invertebrates show the highest sensitivity to sulfate.

Dr. David Soucek of the Illinois Natural History Survey was contracted to conduct the laboratory toxicity testing. Briefly summarized, his work entailed determining the acute toxicity of sulfate to four invertebrate species commonly found in Illinois and thought to fill the gaps in the existing valid database. These organisms were the water flea *Ceriodaphnia dubia*, a previously tested organism used as a gauge for comparison purposes, *Hyalella azteca*, an amphipod, *Chironomus tentans*, a midge fly, *Sphaerium simile*, a fingernail clam, and *Lampsilis siliquoidea*, a freshwater mussel. These organisms were selected based on presumed sensitivity to sulfate from literature values (*Hyalella*), the need to have data from an insect (*Chironomus*) and the perceived sensitivity of bivalve mollusks to toxicants in general (*Sphaerium* and *Lampsilis*).

Because sulfate toxicity is dependent on chloride and hardness concentrations, these water quality characteristics were taken into consideration when setting the sulfate standard throughout the State.

The State of Illinois also conducted a literature review of the adverse effects of sulfate on livestock. Based on the research, the Agency concluded that the protection of livestock watering will be achieved through the proposed standard of 2,000 mg/L sulfate over a 30-day average at locations where livestock watering occurs.

Based on new toxicity test data and available toxicity data from the literature search (a total of 11 species), to achieve aquatic life protection and livestock watering uses, the following concentrations for sulfate must not be exceeded except in receiving waters for which mixing is allowed.

- 1) At any point where water is withdrawn or accessed for purposes of livestock watering, the average of sulfate concentrations must not exceed 2,000 mg/L when measured at a required frequency over a 30 day period.
- 2) The results of the following equations provide sulfate water quality standards in mg/L for the specified ranges of hardness (in mg/L as CaCO<sub>3</sub>) and chloride (in mg/L) and must be met at all times:
  - A) If the hardness concentration of waters is greater than or equal to 100 mg/L but less than or equal to 500 mg/L and if the chloride concentration of waters is greater than or equal to 25 mg/L but less than or equal to 500 mg/L, then:  
$$\text{Sulfate Criterion} = [ 1276.7 + 5.508 (\text{hardness}) - 1.457 (\text{chloride}) ] * 0.65$$
  - B) If the hardness concentration of waters is greater than or equal to 100 mg/L but less than or equal to 500 mg/L, and if the chloride concentration of waters is greater than or equal to 5 mg/L but less than 25 mg/L, then:  
$$\text{Sulfate Criterion} = [ -57.478 + 5.79 (\text{hardness}) + 54.163 (\text{chloride}) ] * 0.65$$
- 3) The following sulfate standards must be met at all times when hardness (in mg/L as CaCO<sub>3</sub>) and chloride (in mg/L) concentrations other than specified above are present:
  - A) If the hardness concentration of waters is less than 100 mg/L or chloride concentration of waters is less than 5 mg/L, the sulfate standard is 500 mg/L.
  - B) If hardness concentration of waters is greater than 500 mg/L and the chloride concentration of waters greater than or equal to 5 mg/L, the sulfate standard is 2,000 mg/L.



- C) If the combination of hardness and chloride concentrations of existing waters are not reflected above, the sulfate standard will be determined on a case-by-case basis in conjunction with an applicable NPDES permitting process.

The following summarizes the proposed sulfate criteria stated above.

Table 2. Proposed Sulfate Criteria for Iowa Waters

Chloride \ Hardness mg/L as CaCO <sub>3</sub>	Cl <sup>-</sup> < 5 mg/L	5 ≤ Cl <sup>-</sup> < 25	25 ≤ Cl <sup>-</sup> ≤ 500
H < 100 mg/L	500	500	500
100 ≤ H ≤ 500	500	$[-57.478 + 5.79$ (hardness) + 54.163 (chloride)] * 0.65	$[1276.7 + 5.508$ (hardness) - 1.457 (chloride)] * 0.65
H > 500	500	2,000	2,000

The justification for the Illinois proposed sulfate standard is included in Appendix II.

#### 4. Similarities between Iowa and Illinois Surface Water Quality

Similar to Illinois, TDS is dominated by the common ions of sulfate, chloride, sodium, calcium, carbonate, and magnesium. The Illinois EPA monitoring program shows average TDS of 452 mg/L. In Northern and Central Illinois streams, sulfate levels range from 30 to 150 mg/L in streams without significant human-induced sulfate sources, and mine areas typically do not exceed 500 mg/L. The average level of chloride in Illinois streams is in the 20 – 40 mg/L range. Streams impacted by road salting can seasonally be much higher. Most Illinois waters are generally classified as hard or very hard waters. These ion concentrations are comparable to that in Iowa surface waters shown in Table 1. As Illinois EPA research indicated, hardness mitigates the toxicity of sulfate to aquatic life.

As in Iowa, the sources contributing TDS and ions include discharges from ethanol plants, water treatment plants and cooling tower blow down. Another main source of sulfate and TDS in Illinois waters come from coal mining industries which no longer exist in Iowa. In addition, the aquatic life species occurrence in Iowa is similar to that in Illinois. Thus, the species included in the sulfate criteria derivation and the methodology should be applicable to Iowa waters.

#### 5. Conclusions and Recommended Sulfate Standard

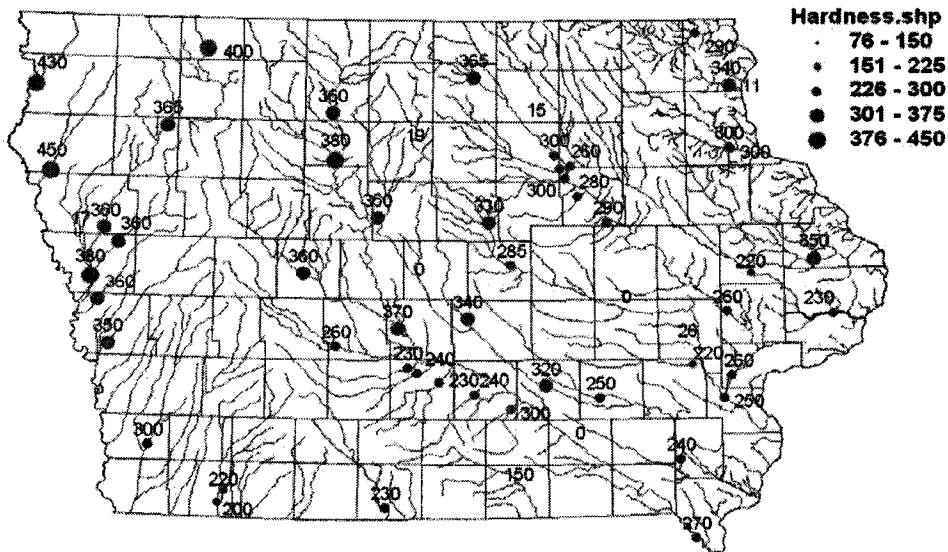
Based on the similarities in surface water quality and aquatic life species distributions between Iowa and Illinois, the same approach for TDS, sulfate and chloride criteria can be applied, that is replacing the current site-specific TDS approach with numerical sulfate and chloride criteria for aquatic life protection. Thus, between the chloride and sulfate water quality standards and the general narrative standard that regulates any discharged substance that could cause toxicity, there is no need for a TDS standard. In addition, the sulfate criteria for livestock watering will be changed from the current 1,000 mg/L to 2,000 mg/L. The guideline values of livestock watering for other ions will remain the same.

## **6. Proposed Sulfate Standard Implementation**

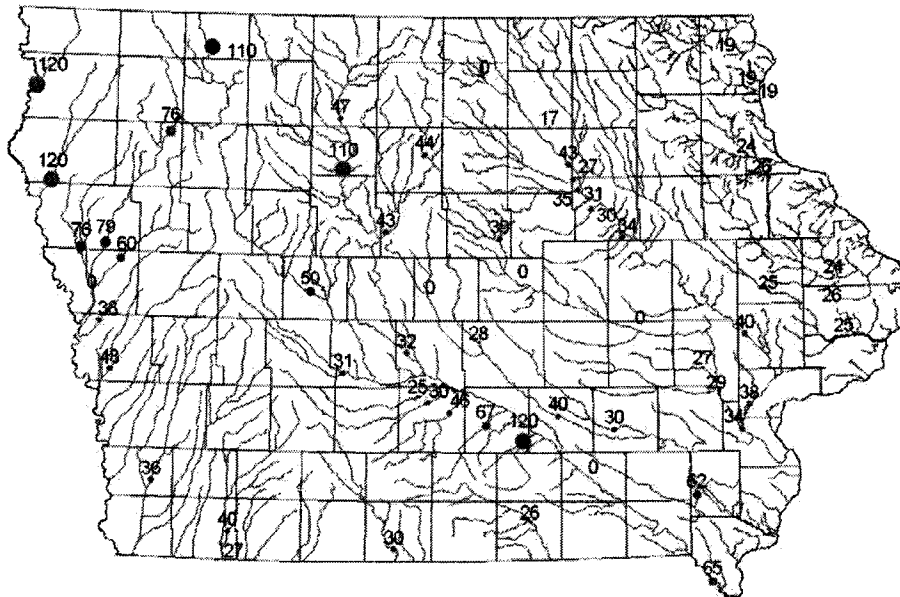
Sulfate is not a toxicant in the category of heavy metals, pesticides or other toxic natural or man-made substances, but rather is a common salt necessary for life at some concentrations. It is usually diluted in the waterbody rather quickly and is non-bioaccumulative. Also, since the sulfate standard was derived based on new toxicity data for targeted species thought to be most sensitive to sulfate, additional uncertainty was alleviated. Since the sulfate standard is derived based on acute toxicity testing data, it should be met after the allowed Zone of Initial Dilution.

Appendix A: Statewide hardness, chloride and sulfate distribution in IA surface waters

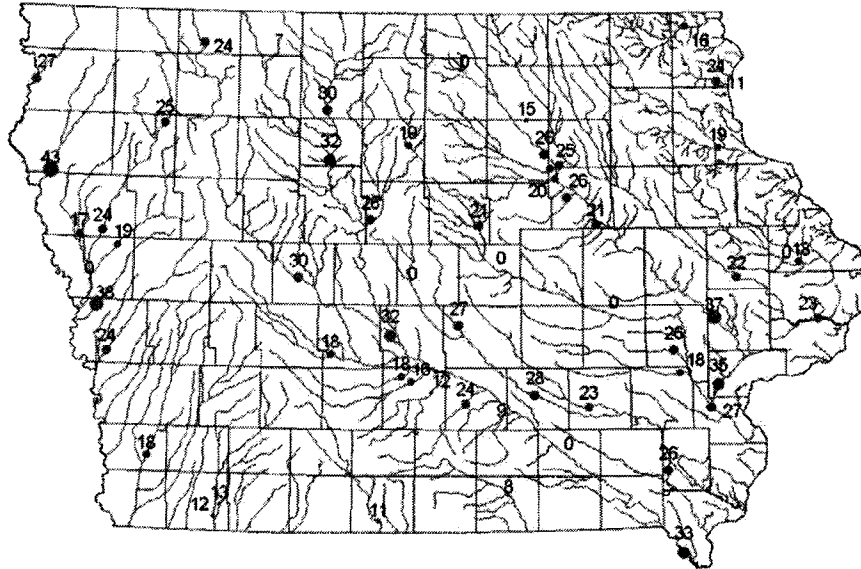
### Statewide Hardness as CaCO<sub>3</sub>



### Statewide Sulfate Monitoring Data



## Statewide Chloride Monitoring Data



**Appendix B:**

**Draft Justification for Changing Water Quality Standards for Sulfate, Total  
Dissolved Solids and Mixing Zones**

Illinois Environmental Protection Agency

September 28, 2006

**I. Introduction/Executive Summary**

Water quality standards for sulfate (500 mg/L) and total dissolved solids (TDS) (1,000 mg/L) have existed in Illinois regulations since 1972. These standards were adopted to protect aquatic life and agricultural uses but without the benefit of modern scientific studies to determine appropriate values. Coal mine effluents in particular are often high in sulfate. The Illinois Pollution Control Board (IPCB or Board) developed standards for sulfate and chloride that are unique to mine discharges, 35 Ill. Adm. Code, Subtitle D, Mine Related Water Pollution. Use of the Subtitles C and D standards for sulfates to establish National Pollutant Discharge Elimination System (NPDES) permit limits has resulted in many conflicts. Permitting many mine discharges without the Subtitle D rules would be problematic because many mines cannot meet the General Use sulfate and TDS standards. Other industries also have difficulty meeting the general standards and many have received adjusted standards or site-specific water quality standards relief from the IPCB.

In order to resolve this conflict, the Illinois Environmental Protection Agency (Illinois EPA or Agency) proposes changes to several components of the Board regulations. First, the sulfate General Use water quality standard was extensively researched and new standards are proposed to protect aquatic life and livestock watering uses. Second, the total dissolved solids (TDS) General Use standard has been evaluated and found to be both ill-suited and unnecessary for the protection of aquatic life. Therefore, the Illinois EPA proposes to delete the TDS standard from the Board regulations. Third, changes to the Board's mixing zone regulations are proposed that will better allow the Illinois EPA to administer dilution allowances to dischargers that can demonstrate attainment of water quality standards whenever discharge occurs. Finally, our proposal ensures that the sulfate limits in NPDES permits for mine discharges are based on the Subtitle C General Use water quality standard; thus eliminating the conflict that existed in the past.

As Illinois was confronted with challenges to existing permitting practices for sulfate, the need for a thorough look at the basis of the water quality standard was in order. Agency biologists have long reported that aquatic life communities appear to tolerate concentrations of these pollutants higher than the existing water quality standards. Since no national criteria exist for these pollutants and few other states even have sulfate and TDS standards, an extensive process was undertaken to gather existing information on sulfate aquatic life toxicity. When available data proved inadequate to derive a standard, new studies were commissioned with sponsorship from the USEPA, the Illinois Coal Association and the Illinois EPA. At the same time, investigations on the tolerance of livestock to sulfate in drinking water were begun.

As suspected, this new research into sulfate toxicity found that high sulfate concentrations pose a problem of osmotic (salt) balance for some aquatic organisms. Many organisms, including all fish tested and some invertebrates, are very tolerant of sulfate, so much so that no known existing concentrations in Illinois would cause harm. Other species including the invertebrate water fleas (*Daphnia* and *Ceriodaphnia*) and scud (*Hyalella*) apparently have a harder time maintaining salt balance under high sulfate conditions, which leads to toxicity. Unlike many toxicants that exert toxic effects over both short term and long term periods (acute and chronic toxicity), sulfate has been demonstrated to affect only short term survival of organisms. In other words, organisms that survive the initial osmotic shock of exposure will survive indefinitely at that concentration. The new research also found that two common constituents of natural waters, chloride and hardness, are key to an understanding of the osmotic imbalance that leads to sulfate toxicity.

Upon the evaluation of dozens of tests on a total of 11 species, equations that determine the protective amount of sulfate to aquatic life were developed for the range of chloride and hardness concentrations in Illinois waters. If the hardness and chloride concentrations of a water body are known, the protective sulfate concentration may be determined. Sulfate permit limits based on local conditions of chloride and hardness may similarly be calculated. Under these proposed standards, allowable sulfate concentrations will vary from 500 mg/L for soft or low chloride waters, to over 2,500 mg/L in hard waters of average chloride concentration (See Exhibit A). Under the Illinois EPA proposal, most of the State's waters would have allowable concentrations of at least 1,500 mg/L, considerably higher than the existing standard allows. Aquatic life-based sulfate standards are proposed as concentration not to be exceeded at any time.

Livestock watering was another use requiring an updated sulfate standard, as the existing standard was loosely based on cathartic effects to humans and livestock. A review of literature found acute exposures to be irrelevant, as livestock are capable of withstanding sulfate concentrations much higher than the proposed aquatic life standards. However, recent studies suggested that extended exposures to drinking waters high in sulfate may lead to weight loss, disease, and death of livestock, thereby warranting a chronic standard. A chronic standard of 2,000 mg/L is considered protective of livestock watering, as surface waters supporting this concentration will not lead to adverse effects on livestock or economic effects to livestock operations. In many waters, aquatic life standards will require that sulfate concentrations are maintained below the 2,000 mg/L livestock standard. However, for waters where the instantaneously applied aquatic life standard is calculated to be above 2,000 mg/L, a 30 day or longer average sulfate standard of 2,000 mg/L will apply for protection of livestock in water bodies where livestock watering occurs.

While sulfate was being evaluated, it became increasingly obvious that TDS is a very inappropriate parameter for use in water quality standards. TDS is the sum of all dissolved substances in water and is dominated by the common ions of sulfate, chloride, sodium, calcium, carbonate and magnesium in various proportions. Our investigations into sulfate toxicity reinforced the notion that it makes little sense to have a standard that covers all these substances together when the toxicity of each constituent is really what is important. For example, a TDS concentration of 2,000 mg/L with chloride as the primary anion constituent is acutely toxic to aquatic life, but the same TDS concentration composed primarily of sulfate is nontoxic. With

toxicity-based sulfate and chloride standards in force, there should be no need of a TDS standard that is incapable of predicting the threshold of adverse effects to aquatic life. The Illinois EPA is, therefore, proposing that the TDS water quality standard be deleted from the Board regulations.

Changes proposed to the mixing zone regulations will work in tandem with General Use standards to protect water body uses yet allow for economic growth. Most high sulfate mine discharges occur during wet weather events. Site drainage relatively high in suspended sediments is collected into treatment ponds where settling occurs. The treated water is then discharged to water bodies where General Use water quality standards apply. Water from the un-mined watershed also enters streams during these discharge events and provides dilution for sulfate and other substances in these effluents. For the past few years Illinois EPA has been granting wet weather discharges allowed mixing for sulfate and sometimes chloride, with consideration of these upstream flows. The Agency now proposes to amend the mixing regulations to make them clear in this regard. The changes to the mixing standards will allow mixing if it is verifiable that upstream dilution will exist whenever an effluent is discharged.

Considering the changes proposed for sulfate and TDS, the Agency is proposing to delete those portions of Subtitle D that address special water quality standards for sulfates and chlorides. Under the Agency's proposal, discharges from mines must be regulated in the same manner as other types of discharges. Water quality based permit limit decisions will now be required in lieu of special Subtitle D standards. As a housekeeping measure, an outdated portion of Subtitle D unrelated to water quality standards will also be deleted.

The changes to standards proposed in the Agency's petition are based on sound science and assure the protection of designated uses of waters of the State. These science-based standards will benefit mines and other dischargers of sulfate and other dissolved salts that are not amenable to treatment. Permit limits issued using the new sulfate and mixing regulations will be protective, yet not overly so, and will cause no unnecessary burden on economic activity.

## **II. Background: Sulfate and Total Dissolved Solids**

Sulfate is an inorganic anionic substance that forms salts with sodium, potassium, magnesium and other cations. Sodium is the dominant cation in Illinois streams where sulfate concentrations are elevated due to human activities. The 19th Edition of Standard Methods for the Examination of Water and Wastewater (1995) (see Exhibit B) gives the following account for sulfate:

Sulfate (SO<sub>4</sub><sup>2-</sup>) is widely distributed in nature and may be present in natural waters at concentrations ranging from a few to several thousand milligrams per liter. Mine drainage wastes may contribute large amounts of SO<sub>4</sub><sup>2-</sup> through pyrite oxidation. Sodium and magnesium sulfate exert a cathartic action.

The Illinois EPA's Ambient Water Quality Monitoring Network (AWQMN) gathers chemical and physical water quality data from over 200 established stream stations across the State. Nine collections are made per year going back in many cases over a thirty year period. This database provides a means to study patterns of sulfate occurrence in Illinois along with other water quality

information relevant to sulfate. In Northern and Central Illinois streams, sulfate levels range from 30 to 150 mg/L in streams without significant human-induced sulfate sources. In Southern Illinois, high readings occasionally exceed 5,000 mg/L in a few streams. Many other streams in this region have sulfate concentrations of up to 2,000 mg/L. These high sulfate streams receive effluents from coal mines. In many cases, these are abandoned, pre-law mines. Some Southern Illinois streams may have a natural component of sulfate that is higher than other parts of the State, but this is difficult to document given the extent of mining in this region. Coal mines in other regions of Illinois have only slightly elevated sulfate in their discharges and streams in mine areas typically do not exceed 500 mg/L sulfate. A few streams have elevated sulfate levels due to industrial discharges (see Table 1 on page 7 for the most pronounced examples). As in the coal mine effluents, the industrial discharges are dominated by sodium as the accompanying cation.

Total dissolved solids (TDS) is determined by filtering a water sample and measuring the residue upon evaporation of the filtrate. Sulfate, chloride, carbonate, calcium, magnesium and sodium are the main constituents of TDS in Illinois waters. Sulfate usually constitutes the majority of the TDS present when TDS is elevated over normal background levels. TDS is not usually measured by direct means in the Agency's AWQMN. In the approximately 1,000 samples collected at Intensive Basin Survey stations (another Illinois EPA monitoring program) throughout the State from 1999 to the present, where TDS is directly measured in the laboratory, TDS averaged 452 mg/L. A maximum value of 5,780 mg/L was recorded. The 95th percentile value was 1,075 mg/L meaning that about 5% of the samples did not meet the current standard of 1,000 mg/L.

Hardness is defined by Standard Methods as "the sum of calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter." Hardness is known to mitigate the toxicity of many metals to aquatic life and the Board standards are expressed accordingly. As was learned in the research to be described in this document (Section VII), hardness also mitigates the toxicity of sulfate to aquatic life. Most Illinois waters are generally classified as hard or very hard waters. USEPA recommends a reconstituted dilution water for use in toxicity testing termed "moderately hard" that has a hardness of 90 mg/L. As can be seen in Exhibit C, only about 2.5% of Illinois waters are expected to have hardness values below 90 mg/L during low flow events based on the findings of the Ambient Water Quality Monitoring Network. To produce the "Critical" hardness values in the attachment, data from a 15-year period from all stations in the network (approximately 135 samples per each of over 200 stations) were analyzed. Samples from the 10th percentile low stream flows were segregated and, of this data, the 10th percentile hardness value was determined. Therefore, the hardness values given in the attachment represent the lowest hardness expected in streams when they are at vulnerable low flows.

There is generally a north-south pattern to hardness in Illinois. Northern Illinois streams and lakes generally have hardness values in the 200-300 mg/L range. This is largely due to the limestone bedrock that underlies most of the northern 90% of the state. In contrast, several Southern Illinois streams are in areas where bedrock is comprised of sandstone or a limestone and sandstone mix that results in low hardness. Where mining occurs and sulfate values are elevated, hardness is also elevated due to exposure of the mine overburden to rainwater. None of



the low hardness Illinois streams (<100 mg/L) have high sulfate concentrations. A water quality characteristic related to hardness is the calcium to magnesium ratio, a factor thought to be important in understanding sulfate toxicity. Illinois waters consistently have a calcium-to-magnesium ratio of between 2 and 2.5:1.

Illinois also has fairly high chloride concentrations in lakes and streams. As we will describe later in this document (Section VII), chloride, along with hardness, is a controlling factor in the degree of sulfate toxicity exerted on aquatic life. The average level in streams is in the 20 – 40 mg/L range. Streams impacted by road salting can seasonally be much higher. A few streams in far Southern Illinois have very low chloride relative to the rest of the state. Lusk Creek often has only about 1 mg/L chloride and averages about 2 mg/L but also has very low sulfate concentrations. Sugar Creek in Williamson County occasionally shows samples at 1 mg/L and averages about 6 mg/L. Sugar Creek is heavily impacted by abandoned mine discharges in the area of our sampling station and has very high sulfate concentrations during some flow conditions. However, when sulfate is elevated in Sugar Creek, chloride is also elevated. The Cache River, a stream flowing in part through cypress swamps, has occasional samples measured at less than 1 mg/L chloride and averages about 10 mg/L chloride.

### **III. Existing Water Quality Standards**

The existing General Use and Lake Michigan Basin (other than for the open waters of Lake Michigan) sulfate standard is 500 mg/L. The standard was adopted by the Board in its 1972 standards rulemaking, "Water Quality Standards Revisions", R71-14. In the Board's adopting opinion, the need for this standard was described as follows:

Sulfates. As in the case of chlorides, some limit seems desirable to protect stock watering and fish. Dr. Lackey suggested that 500 mg/L would afford adequate protection for fish; McKee and Wolf give this same figure for stock watering; and this level should avoid serious adverse effects on public water supplies as well according to McKee and Wolf.

Dr. Lackey was apparently an expert witness who testified before the Board. McKee and Wolf is an early water quality criteria document (See Exhibit D).

It is interesting to note that few other states have a water quality standard for sulfate for reasons other than to protect public water supplies. A summary of sulfate and TDS standards from neighboring states is found in Exhibit E. Illinois has two sulfate standards for the protection of water uses other than drinking water. One is set at 500 mg/L and covers all General Use Waters and Lake Michigan Basin waters other than the open waters of Lake Michigan. The other is a 24 mg/L sulfate standard based on background conditions in the lake and applies only to the open waters of Lake Michigan. Neither of the Lake Michigan standards are proposed for change in this petition.

The existing General Use and non-open water Lake Michigan Basin standard for TDS is 1,000 mg/L. The Board's adopting opinion gives this description:

Total Dissolved Solids. This level of 1,000 mg/L too is based largely on Dr. Lackey's testimony, confirmed by other witnesses and by McKee and Wolf, that aquatic life should not be harmed.

In addition to the General Use standard of 1,000 mg/L, there is an open waters of Lake Michigan standard of 180 mg/L and a Secondary Contact and Indigenous Aquatic Life standard of 1,500 mg/L. The open waters standard is based on the background condition of the lake rather than aquatic life protection. The Agency proposes to remove only the General Use standard from the Board regulations.

At this time, the Agency intends to address all standards for Secondary Contact and Indigenous Aquatic Life Use waters in a future rulemaking. Completion of the ongoing investigation into Use Attainability Analysis of the Des Plaines and Chicago waterways will lead to re-evaluation of the TDS standard for these waters as well as to consider inclusion of water quality standards for chloride and sulfate.

Both sulfate and TDS standards exist for Public and Food Processing Water Supply Intake waters. The sulfate standard is 250 mg/L and the TDS standard is 500 mg/L. These standards exist to protect the quality of human drinking water sources. The Agency is not proposing to change these standards.

**IV. Site-Specific and Adjusted Standards for sulfate and TDS**

The Board has granted special relief from the existing water quality standards for sulfate and TDS on several occasions to accommodate necessary industrial discharges. The highest stream concentration of sulfate allowed to date is 1,350 mg/L for Thorn Creek. The need for this relief was the establishment of an industrial discharge tributary to a municipal sewage treatment plant. Using the proposed sulfate standards later described in this petition, Thorn Creek would have a new standard of 1759 mg/L sulfate as a result of chloride and hardness concentration within the creek. The adjusted TDS standard at this site was 2,650 mg/L. Including this case, there are seven adjusted standards proceedings and two site specific water quality standards involving sulfate and/or TDS involving nine water bodies. A least one additional pending case before the Board involves a site specific rule for TDS. The highest TDS concentration allowed by special Board relief is 3,000 mg/L found at 35 Ill. Adm. Code 304.211. While this is an effluent standard (a permit limit rather than the standard that must apply in the water body), the receiving stream has a zero 7Q10 flow and would occasionally be expected to have a TDS concentration equal to the effluent concentration.

The following table lists the IPCB granted relief from sulfate and chloride water quality standards:

Table 1. Site-specific relief granted by the IPCB for sulfate and TDS to date.

Water Body	Docket #	Discharger	Parameter	Concentration now applied to water body or permit limit

				(mg/L)
Deer Creek	AS89-3	Aqua IL (formerly Consumers IL Water Co.) – University Park	TDS	2,100
Thorn Creek	AS01-9	Thorn Creek Sanitary District and Aqua IL – University Park	Sulfate  TDS	1,160 to 1,350  2,360 to 2,650
Little Calumet River	AS01-9	Thorn Creek S.D. and Aqua IL – University Park	Sulfate  TDS	1,000  2,020
Long Point Slough and its unnamed tributary	AS93-2  R86-14 303.431	Formosa Plastics (formerly Borden Chemical)	Sulfate  TDS	1,000  3,000
Aux Sable Creek	AS93-8	Akzo Chemical	Sulfate TDS	1,000 3,000
Middle Fork North Branch Chicago River	AS99-5	Abbott Laboratories	TDS	1,500
McCook Drainage Ditch	AS02-1	Material Service Corp.	Sulfate TDS	850 1,900
Horse Creek	AS03-1	Exelon Generation	TDS	1,900
Sugar Creek	R91-23 303.323	Marathon Oil Refinery (now Marathon Ashland Petroleum	TDS	2,000

The Board also established special standards for coal mine discharges in 35 Ill. Adm. Code Subtitle D. Under these regulations, coal mine effluents are allowed to have sulfate concentrations of up to 3,500 mg/L. This regulation is also found in the listing of proposed rule changes in this petition.

#### V. Treatment to Reduce Concentrations of Sulfate and TDS

The Board has granted adjusted standards and site-specific relief for sulfate and TDS because there are no economically reasonable technologies that remove these parameters from water. Once salts are dissolved in water it is very difficult to get them back out again. Evaporation of solutions concentrated by reverse osmosis filtration would succeed to this end but would be extremely expensive. Deep well injection of high salt content waters has been used in the past,

but this technique is increasingly difficult to implement due to groundwater protection regulations. In each and every petition for special Board relief, the Agency has concluded that there is no technically feasible or economically reasonable way to remove sulfates or TDS from water.

The best way to deal with salts is to prevent them from becoming dissolved in wastewaters. With the advent of reverse osmosis technology, many industries have abandoned the use of ion-exchange water softeners. This reduces the salt content of effluents because no regenerating solutions are needed. However, other basic industrial processes still must deal with solutions of salts that create high concentrations of sulfate and TDS. Recent advances in air pollution control technology have created, as an unfortunate byproduct, new wastestreams that are high in sulfate. Prevention of sulfate and TDS build up in coal mine waters is now part of the best management practices that must be implemented at the mines. Best management practices at mines that result in the minimization of overburden and waste pile exposure to rainwater have reduced levels in mine stormwater runoff. Dr. Chugh of Southern Illinois University at Carbondale is currently leading an effort to study coal mine refuse handling practices and find ways to better manage runoff. Mining companies are participating in the study conducted by Dr. Chugh that will serve to educate dischargers to achieve lower levels of sulfates and chlorides in effluents.

**VI. Protection of Uses Potentially Impacted by Sulfate and TDS**

Other than the public water supply uses covered by the Public and Food Processing Water Supply standards, there are two uses protected by sulfate and TDS standards, namely Agriculture (livestock) use and Aquatic Life use.

**A. Livestock Uses**

**Sulfate** - Livestock watering was envisioned as one of the uses to be protected by the existing sulfate standard, as sulfate has a cathartic (diarrheic) effect on humans and animals. The existing livestock standard was justified for its listing (McKee and Wolf, see Exhibit D) as a safe concentration for stock watering based on the following reasoning:

4. Summary. On the basis of the information gleaned from literature, it appears that the following concentrations of sulfate will not be detrimental for the indicated beneficial use:

Domestic water supply.....	500 mg/l
Irrigation.....	200 mg/l
Stock watering.....	500 mg/l

Upon review of referenced data within McKee and Wolf, it seems that 500 mg/L was chosen as a conservative value by the authors. Data within the document does not support this value, as nowhere is a justifiable reference for 500 mg/L sulfate found. Rather, it appears 500 mg/L was chosen as an arbitrary value to protect against cathartic effects to unacclimated livestock, as the same value was suggested for human consumption of drinking water.

It is evident that the existing sulfate standard is outdated and an updated livestock standard is necessary. Currently, human health is adequately protected from sulfate through public water supply intake standards, livestock protection will be provided through the incorporation of an updated General Use standard. High sulfates are of concern to those involved in animal husbandry where surface waters are utilized for livestock watering. Acute, short-term, exposure to elevated sulfate-waters produces temporary cathartic effects in livestock, but these effects are non-threatening and diminish as livestock are acclimated. Chronic exposure to high sulfate-waters is much more problematic, as extended exposure may lead to weight loss, disease, and death of livestock. Extended exposure of livestock to high sulfate-waters may be detrimental to livestock operations, therefore, a chronic standard must be implemented in surface waters utilized for livestock watering.

A literary review of the adverse effects of sulfates on livestock is summarized in Exhibit F. Much of the referenced literature is quite dated, but is nonetheless included due to the limited amount of available data. Earlier studies have widely contrasting results, with adverse effects being noted as low as 1,462 mg/L sulfate, and 'no adverse effects' measured as high as 7,000 mg/L sulfate. The contrasting toxicity results of early sulfate studies are confounding, as methods and results were often incomplete and lacked critical information such as study length, food and water consumption, and cation abundances. This information is necessary when considering a study's validity. Exposure duration is an especially important parameter when considering the results of a sulfate study. For example, Weeth and Capps (See Exhibit G) discovered reduced weight gains in cattle that consumed 1,462 mg/L sulfate-water over a 30-day period. However, the results are misleading due to the abbreviated study period. The study found that food consumption was unaffected at this concentration; therefore, decreased weight gain was likely attributed to the significant increase in water excretion throughout the study, as the short exposure period did not allow sufficient time for livestock to acclimate to elevated sulfates. Increased water excretion (diarrhea) is an initial response to elevated sulfate-water. However, continued exposure to elevated sulfates will lead to acclimation and will not adversely affect livestock unless concentrations are at severe levels.

The threshold concentration at which sulfate-water will adversely affect livestock is difficult to quantify due to the complexity of sulfate and the limited amount of reputable research. However, recent studies suggest that surface water concentrations in excess of 2,000 mg/L sulfate may be detrimental to livestock operations. Loneragan et al. (See Exhibit H) found that chronic exposure to 2,360 mg/L sulfate-water decreased carcass characteristics of cattle, signifying that chronic exposure to these concentrations may result in economic losses to livestock operations. Braul and Kirychuk (See Exhibit I) found that exposure to water with 2,500 mg/L sulfate results in poor conception of cattle. Patterson et al. (2004, See Exhibit J) found that concentrations near 2,600 mg/L sulfate result in weight loss and decreased body condition of cattle. As sulfate concentrations approach 3,000 mg/L cattle drink less water and become more prone to polioencephalomalacia (PEM), a neurological disorder which leads to anorexia, blindness, seizures, and eventually death (Patterson et al. 2002, See Exhibit K). It is apparent that the severity of adverse effects on cattle quickly accelerates at concentrations between ~2,300-3,000 mg/L sulfate, therefore, warranting a more conservative standard.

Due to a limited number of studies, assorted endpoints, and questionable validity of outdated studies, a mathematical derivation for sulfate toxicity to livestock is not practical. However, by observing recent studies, it is evident that a standard of 2,000 mg/L sulfate would adequately protect livestock from reductions in food consumption, water consumption, and growth. To verify the suitability of this proposed standard, Dr. Gavin Meerdink from the Department of Veterinary Medicine at University of Illinois Champaign-Urbana was contacted. Dr. Meerdink was supplied with the data from Attachment C and was informed of our plans of implementing 2,000 mg/L sulfate as a chronic, 30-day average standard. Dr. Meerdink questioned the validity of older studies within Attachment C. He stated that much more has been learned regarding the complexity of sulfur compounds and ruminants over the last 30 years, and that the recent studies likely had better detail in experimental design. He stated that sulfur compounds within the ruminant are a complicated issue, as much variability can be attributed the sulfur content of feed as well as the ability of rumen microbes to convert sulfur compounds into sulfides. Although limited animal taxa are represented in the literature, Dr. Meerdink acknowledged that cattle are a suitable study organism, as sulfur compounds in monogastric animals (pigs, rats, etc.) are much less of an issue. In summary, Dr. Meerdink stated that a 2,000 mg/L sulfate standard would adequately protect livestock. He related that unacclimated animals may exhibit diarrhea for several days immediately after initial exposure but will suffer no economically significant weight loss or other adverse condition. In his experience, livestock will soon adapt to the higher sulfate water and the temporary symptoms will disappear. Dr. Meerdink also stated that he would feel uncomfortable setting a standard at concentrations significantly higher than 2,000 mg/L sulfate.

Based on consideration of recent literature as well as Dr. Meerdink's professional experiences, the Agency concludes that 2,000 mg/L sulfate is a protective standard for livestock in Illinois. Although cathartic effects may occur to unacclimated animals consuming 2,000 mg sulfate/L water, referenced data suggests that chronic exposure to this concentration will not result in economic impacts such as reduced growth. Further, cathartic effects are likely to diminish or disappear over time. Given that sulfate ingested by animals would produce adverse impacts over a long period of time, the 2,000 mg/L standard for sulfate is proposed as an average concentration over at least a 30-day period. The standard is applicable only in areas where water is withdrawn or accessed for purposes of livestock watering. Daily sulfate concentrations greater than 2,000 mg/L are allowable for livestock provided a 30 day average of sulfate concentrations does not exceed 2,000 mg/L. Aquatic life sulfate standards will often supersede the livestock-based standard as explained in the following section.

Total Dissolved Solids - TDS is also of concern for livestock. Montana State University Extension Service produces a newsletter called "Beef Briefs". In it, Dr. Dave Hutcheson, PhD discusses water quality for cattle. The following table from this source contains:

Table 2. Montana State University recommendations for TDS in drinking water for cattle.

Total Dissolved Solids in mg/L	Effect on Cattle
1,000 – 2,999 (slightly saline)	Should not effect health or performance but may cause temporary mild diarrhea
3,000 – 4,999 (moderately saline)	Generally satisfactory, but may cause diarrhea, especially on initial consumption

Data within Table 2 concludes that TDS concentrations as high as ~5,000 mg/L will not adversely affect livestock. It is apparent that the existing TDS standard of 1,000 mg/L is over-protective, but the implementation of a higher TDS standard is equally inappropriate, provided that individual constituents of TDS are regulated. In Illinois waters, TDS is typically composed of sulfate as the predominant anion and sodium as the predominant cation. With enforcement of the existing chloride standard (500 mg/L) and the proposed sulfate standard (2,000 mg/L), a TDS concentration of ~5,000 mg/L cannot be achieved without violating these existing standards, as other anions such as magnesium and potassium are not found at concentrations high enough to contribute to an exceedance. Any TDS concentration found in Illinois waters would be suitable for livestock use provided that sulfate and chloride standards are met. Therefore, the Agency is proposing to delete the existing TDS standard from the Board regulations.

## **B. Aquatic Life Uses**

Concern for protection of aquatic life is central to establishing water quality standards for sulfate or TDS. The Agency spent several years searching the literature and designing studies to definitively establish the maximum sulfate concentration that will be tolerated by sensitive species of aquatic life. A summary of the Agency's findings is presented in the sections that follow.

**Water Quality Standard Derivation Methodology and Literature Search for Studies on Sulfate Toxicity to Aquatic Life.** Salts containing sulfate are natural substances in the environment. It is not expected that sulfate would be highly toxic or to express toxicity in the way many synthetic industrial compounds (or natural toxic substances) do. Animals tolerate a large variation of sulfate in the aquatic environment. Sulfate is a necessary nutrient for plants, and therefore, for the stream community as a whole. However, it is not known to be limiting to the normal expression of aquatic life in aquatic ecosystems. It may also be a necessary nutrient for animals, e.g., in formation of chondroitin sulphate.

In testing the effects of variation in sulfate concentration, the sulfate is necessarily introduced in a salt form ( $\text{Na}_2\text{SO}_4$ ) to a standard medium (as defined by USEPA and ASTM). The medium contains various cations, Na, K, Mg, and Ca, and anions,  $\text{HCO}_3$ , chloride and sulfate. All of these ions are necessary for normal functioning of cells. Raising the sulfate level is not just a matter of increasing the level of the specific substances, sodium and sulfate. It also involves increasing the ionic strength of the solution as a whole. Also, the balance or ratios of some of the ions are being changed as  $\text{Na}_2\text{SO}_4$  is raised. Thus, sulfate toxicity (as for other ions) is a complex phenomenon with toxicity dissimilar to most other kinds of substances.

Sulfate is a conventional pollutant, therefore, information concerning it has been in the literature for many years. This means there may be information in older, sometimes difficult-to-find, literature. Tests done decades ago would not have been standardized in ways that are routine now. The most important problem encountered in the older studies was that heavy metal contamination in the reagents might have exerted a toxic effect when a high level of the salt of interest is necessary to produce a response. Researchers prior to the 1980's were probably

unaware that the purity of the sodium sulfate reagent used in their tests could have been a factor in the results obtained. Toxicity studies now use the most pure form available. The Agency also found that the literature contained studies done on unusual species that live in habitats with very little natural sulfate. In particular, a Canadian study was rejected because the test species was unique to an unusual mountain habitat, and was apparently very intolerant of what would be a normal level of sulfate in the Midwest. See Exhibit L for a discussion on the validity of all known studies.

The above concerns became apparent over the time as the Agency gathered data to determine a water quality standard. The USEPA aquatic life-based model ("Guidelines" See Exhibit M) requires gathering all data available and assessing their suitability to determine the water quality criterion. The Agency narrowed the search to Na<sub>2</sub>SO<sub>4</sub> given that water quality data show that sodium is the predominant cation in Illinois waters. Mainly, the Agency searched the AQUIRE database, but also found other sources. After the Agency had assembled what seemed like a complete database, it went through a preliminary examination. The Agency determined that a number of values for various taxa appeared to be unrealistically low, knowing that there seems to be a fairly balanced aquatic community in many Illinois streams with sulfate concentrations higher than these supposedly toxic test solutions. The Agency contacted experts (Drs. David Mount and Charles Stephan) at the USEPA Duluth Toxicity Laboratory to see if any efforts on deriving a sulfate criterion had been attempted at the federal level. According to Duluth Laboratory staff, no federal criterion has been completed, but some work had been done to explore the role of sulfate and total dissolved solids in aquatic life toxicity. They related that they believed there was a metals contamination problem with some of the older studies, as described above. Recent papers describing the role of sulfate, chloride and different cations were brought to the Agency's attention. Duluth Laboratory personnel also indicated which of the older papers they consider to be suspect. Eventually, data for over 30 kinds of organisms from about 30 papers/sources were found. USEPA Region 5 and The Advent Group, Inc. (employed by the Illinois Coal Association) were also involved in the assessment. By the end of this consultation process, Dr. Stephan compiled a list of toxicity test results that were considered valid for standard derivation. Toxicity values and references for these studies are given in Attachment N. A complete list of all literature sources considered, along with a brief comment regarding the acceptability of each study, is provided in Exhibit O.

The literature research showed that essentially only two groups, fish and zooplankton crustaceans, were adequately represented in the database. Fish are so tolerant of sulfate that no further discussion or additional testing is necessary. Strong representation of the daphnids is expected since these are common, easily tested organisms. However, *Hyallela azteca* data was relatively scarce, and available data suggested this native species is most sensitive to sulfate. For credence to be given to the dataset of toxicity values, more variety of invertebrate species was necessary, especially, since invertebrates show the highest sensitivity to sulfate.

Based on the review of the available data, the Agency came to the following conclusions:

- Reliable toxicity data for additional invertebrate species were needed



- Few freshwater chronic tests exist. The method of toxicity exerted by sulfates is probably the sudden change of ionic concentration, i.e., the relative saltiness of the water, rather than other types of interference with organism metabolism. If an organism can withstand the osmotic shock initially, it will probably continue to survive and function at a given sulfate level indefinitely.
- Sulfate is not a toxicant in the category of heavy metals, pesticides or other toxic natural or man-made substances, but rather is a common salt necessary for life at some concentration (Goodfellow, See Exhibit P). It does not fit the model for derivation of water quality criteria using the standard federal "Guidelines" document, and may therefore, require a sulfate-specific derivation procedure.
- An examination of data from the Ambient Water Quality Monitoring Network found that when sulfate is elevated, sodium is the major cation. When sulfate is not elevated, either sodium or calcium is the major cation. Relative cation toxicity from highest to lowest is potassium, magnesium, calcium and sodium (Mount, et. al. See Exhibit Q). Therefore, the Agency concluded that tests using sodium sulfate are appropriate for Illinois conditions.

**Newly Generated Sulfate Toxicity Data.** The Agency met with USEPA Region 5 Standards Unit staff and a representative of the Illinois Coal Association to determine the direction to be taken concerning two very important aspects of developing a new sulfate standard for Illinois. Two specific issues were considered. The first was to decide who would conduct aquatic life toxicity tests on key invertebrate species, and what those species would be. The second was to agree on a method for determining the value of the new standard from the existing acceptable toxicity data and that data which would become available from the contracted research.

Dr. David Soucek of the Illinois Natural History Survey was contracted to conduct the laboratory toxicity testing. Dr. Soucek has worked extensively on mine discharge impacts to streams. His laboratory at the University of Illinois Urbana-Champaign was determined to be fully capable of conducting the necessary tests.

On the second matter, it was agreed that because sulfate does not behave as a conventional toxicant, the USEPA's "Guidelines" approach would be replaced by a more straightforward method. It was concluded that sulfate, being a natural salt component, does not carry the risk that a true toxic substance would have. With truly toxic substances, there is a risk that untested species may exhibit much more sensitivity than did the small group of species tested, thereby meriting a safety factor. Since our efforts in generating new data targeted species thought to be most sensitive to sulfate, additional uncertainty was alleviated. It was initially proposed that the LC<sub>10</sub> (lethal concentration to 10% of exposed organisms) for the most sensitive organisms would be used in derivation of the sulfate standard. However, this approach was met with opposition from USEPA, therefore, a modified approach of the Guidelines was utilized in its place. Details and justification for use of this sulfate-specific approach is summarized below in the equation formulation section.

Research conducted by Dr. Soucek was vital to the standard derivation, as the sensitivity of several organisms was thoroughly studied and greatly increased the amount of acceptable sulfate data. Possibly of greater significance was the finding that sulfate toxicity is dependent on water chemistry, thereby emphasizing the need for a water quality-based equation rather than a statewide numerical standard derived from typical procedures. Data obtained from research conducted by Dr. Soucek is summarized in Exhibit R, final and quarterly reports summarizing this research are found in Exhibits S, T, U, V and W. Briefly summarized, his work entailed determining the acute toxicity of sulfate to four invertebrate species commonly found in Illinois and thought to fill the gaps in the existing valid database. These organisms were the water flea *Ceriodaphnia dubia*, a previously tested organism used as a gauge for comparison purposes, *Hyalella azteca*, an amphipod, *Chironomus tentans*, a midge fly, *Sphaerium simile*, a fingernail clam, and *Lampsilis siliquoidea*, a freshwater mussel. These organisms were selected based on presumed sensitivity to sulfate from literature values (*Hyalella*), the need to have data from an insect (*Chironomus*) and the perceived sensitivity of bivalve mollusks to toxicants in general (*Sphaerium* and *Lampsilis*). The first phase of Dr. Soucek's testing was to conduct standard (methodology and test waters according to nationally accepted methods) acute tests on these organisms and establish the LC<sub>50</sub> (the concentration lethal to 50 percent of the test organisms exposed) values for each species.

In the course of this first phase of testing, Dr. Soucek noted that the standardized Moderately Hard Reconstituted Water (MHRW) may be inadequate for the culture and testing of *Hyalella azteca*. (The version of MHRW used by Dr. Soucek in his studies was slightly higher in calcium sulfate than the nationally published formula resulting in a hardness of about 104 mg/L rather than the standard 90 mg/L.) He designed experiments to show that a slight increase in chloride and a different ratio of magnesium to calcium content increased the tolerance of this species to sulfate five fold. To a lesser degree, this improved balance of salts also increased the tolerance of *Ceriodaphnia* to sulfate. Further experiments showed that increasing hardness of the test water decreased toxicity of sulfate to these species. Additionally, acclimation experiments showed that *Ceriodaphnia* could be cultured at much higher sulfate concentrations than the standardized culture method would prescribe, and that this species thus acclimated had higher, though not significantly higher, tolerance to sulfate. Further tests would be needed to show statistically significant differences, however. Dr. Soucek also did limited chronic toxicity testing on *Ceriodaphnia dubia* (Second Quarterly report See Exhibit U), though not enough data has been compiled through literature review and Dr. Soucek's tests to propose a chronic standard at this time. However, results from Dr. Soucek's tests have shown that a chronic exposure period will not result in reduced survival compared to acute exposures. Additionally, Dr. Soucek has noted that he has a self-sustaining reserve culture of *Ceriodaphnia dubia* in MHRW spiked with 1,000 mg/L sulfate, therefore reproduction is not believed to be significantly impaired at this concentration.

Dr. Soucek's research clearly shows a relationship between sulfate toxicity and water chemistry parameters, namely chloride and hardness. It is believed that chloride and hardness influence the toxicity of sulfate to aquatic invertebrates due to alterations in osmoregulation. Invertebrates achieve ionic balance with surrounding water through active transport, an energy requiring activity. At intermediate chloride and higher hardness concentrations, ionic balance in the presence of elevated sulfate concentrations is achieved rather easily. At low chloride and higher

hardness concentrations, osmoregulation is increasingly difficult, resulting in utilization of energy stores in an attempt by the organism to achieve ionic balance. High levels of chloride increase sulfate toxicity as well, primarily through increasingly unbalanced osmotic conditions.

Because sulfate toxicity is dependent on chloride and hardness concentrations, these water quality characteristics must be taken into consideration when setting a standard throughout the State. For example, a single statewide numeric standard for sulfate may be sufficiently protective in one stream, but under-protective in another depending on water chemistry. To adequately protect aquatic organisms from sulfate throughout the State, it is important that chloride and hardness be considered on a site by site basis. By creating an equation that relates sulfate toxicity to chloride and hardness, these two values can be measured in a water body and entered into the equation to determine the maximum amount of sulfate allowable for that water body.

**Equation Formulation.** Using acceptable data only, chloride and hardness specific LC50 equations for sulfate toxicity to *Hyalella azteca* and *Ceriodaphnia dubia* were calculated through multiple regression with analysis of covariance. These species exhibited the highest sensitivity to sulfate and had the most studies conducted under various hardness and chloride values. LC50 values for the two species were measured or estimated with the EPA Spearman-Kärber program at various concentrations of sulfate, chloride, and hardness. The LC50 values were used to calculate equations for hardness in the range of 87 to 500 mg/L and chloride in the range of 25 to 526 mg/L, with a Ca-Mg ratio of 2.33. The equations are as follows:

C. dubia:  $LC50 = 1828 + 5.508(\text{hardness}) - 1.457(\text{chloride})$

H. azteca:  $LC50 = 1464 + 5.508(\text{hardness}) - 1.457(\text{chloride})$

Because toxicity data was acquired from tests with various concentrations of hardness and chloride, all acute values were normalized to the same water chemistry so that final acute values could be calculated. The slopes for hardness (+5.508) and chloride (-1.457) attained from the equations above were used to normalize acute values to hardness of 300 mg/L and chloride of 75 mg/L, which are typical concentrations found in Illinois waters. Normalization was performed by plugging the LC50, hardness, and chloride values for each test into the following equation:

Normalized LC50 = Test LC50 + (300 – hardness)(5.508) + (75 – chloride)(-1.457)

Only tests with hardness between 87 and 500 mg/L and chloride between 25 and 526 mg/L were capable of being normalized, as little data existed outside of these values. After normalization, genus mean acute values (GMAV) were obtained by calculating the geometric mean of all normalized values for each genera. Using the GMAVs for sulfate at hardness of 300 mg/L and chloride of 75 mg/L, the final acute value (FAV) for sulfate was calculated to be 2819.8 mg/L through procedures stated in 35 Ill. Adm. Code 302.615(c-g). With an FAV of 2819.8 mg sulfate/L, and by utilizing the slopes for hardness and chloride, the following equation was developed to estimate the acute aquatic toxicity criterion (AATC) of sulfate at ranges of hardness between 87 and 500 mg/L, and chloride between 25 and 526 mg/L. This is the final equation that will be used to predict site-specific sulfate standards within the aforementioned hardness and chloride range. After entering hardness and chloride values from a specific site, the resulting

value will be the protective concentration of sulfate at that specific site under those water quality characteristics.

$$\text{AATC} = [1276.7 + 5.508 (\text{hardness}) - 1.457 (\text{chloride})] * 0.65$$

It is important to note that a sulfate specific factor of 0.65 was added to the equation for proper protection, which deviates from the 0.5 factor specified in 302.618.i, as well as the Guidelines. Whereas, the Guidelines and Illinois Subpart F procedures use a factor derived from 219 acute toxicity tests on various toxics, a sulfate-specific factor is needed because sulfate is dissimilar from heavy metals, pesticides or other toxic natural or man-made substances used in factor derivation. The 0.65 value was derived by taking the highest tested sulfate concentrations with percent survival equal to or higher than the control treatments and dividing these values by the corresponding LC50s. The value is equivalent to the geometric mean of the quotients from 20 tests using two of the most sensitive species, *H. azteca* and *C. dubia* (See Exhibit R). In general, this value is a reflection of the average ratios between no observable adverse effect levels (NOAEL, 35 Ill. Adm. Code 302.603) and corresponding LC50s of acceptable sulfate data. Jim Keating of the USEPA has provided a justification for use of this sulfate specific factor, which is as follows:

*Why is it acceptable to multiply the FAV for sulfate by 0.65 instead of dividing the FAV by 2 as specified in the USEPA 1985 Aquatic Life Guidelines?*

The term “Final Acute Value”, or FAV, is the value protective of at least 95% of the species at the LC50 level of effect (concentration which is lethal to 50 percent of the tested organisms). To obtain a protective “Criterion Maximum Concentration”, or CMC (commonly referred to as an “acute criterion”), there must be an adjustment from an LC50 level of effect to a protective level of effect. EPA uses a factor of 0.5 as a multiplier to achieve this protective level of effect, based on an evaluation of data from numerous toxicity tests for a variety of pollutants and species where lethality data were used to determine the highest tested concentration that did not cause mortality greater than that observed in the control, which would be between 0 and 10% of the tested organisms. The steps of this evaluation may be duplicated for a separate set of toxicity data to derive a pollutant-specific adjustment factor where the data set is of sufficient quantity (multiple species represented) and quality and includes results from sensitive test species. Twenty data points from two of the most sensitive species were used in the pollutant-specific analysis for sulfate data and produced a multiplier of 0.65 to adjust from an LC50 level of effect to a protective level of effect. This value represents greater specificity and precision for sulfate than the general multiplier of 0.5. Its use with the FAV yields a criterion that is scientifically defensible and protective of aquatic life uses from the short-term lethal effects of sulfate.

**Low chloride equation.** Sulfate toxicity greatly increases at chloride levels below 25 mg/L, therefore, a separate equation was calculated for the range of 87 to 500 mg/L hardness and 5 to 25 mg/L chloride following similar procedures. All *H. azteca* data ( $n = 28$ ) within these ranges were used to calculate an LC50 equation through multiple regression with analysis of covariance.

Although fewer data were available at these ranges, it should be noted that *H. azteca* was the most sensitive species tested. The equation is as follows:

$$\text{AATC} = [-57.478 + 5.79 (\text{hardness}) + 54.163(\text{chloride})] * 0.65$$

**Extreme concentrations.** The two aforementioned equations will be acceptable for standard calculation in nearly all streams, except for rare instances where chloride and hardness values are extremely high or low and are therefore outside the acceptable range for standard calculation. Very little sulfate toxicity data is available at these water chemistry extremes, therefore, typical derivation procedures are impractical and numerical standards must be implemented. Through review of available data at these extremes, the following standards will offer adequate protection under the specified water chemistry conditions:

If the hardness concentration of waters is less than 100 mg/L or chloride concentration of waters is less than 5 mg/L the sulfate standard is 500 mg/L.

If hardness concentration of waters is greater than 500 mg/L the sulfate standard is 2,000 mg/L.

## VII. Deletion of the TDS Standard

The Agency's research into existing ion concentrations in Illinois waters found that of the common substances comprising the major portion of total dissolved solids, toxicity is always associated with either sulfate or chloride. Sodium, calcium, magnesium and carbonates make up the other ions in the majority, but these are not sufficiently toxic to create the need for individual water quality standards. Simply put, if sulfate and chloride, alone or in combination, meet the proposed standards, toxicity from the other major ions comprising "total dissolved solids" is insignificant. Therefore, TDS concentration provides no additional useful information. The existing standard is cumbersome and results in restrictions where none should exist. For example, if the sulfate water quality standard for a water body was calculated to be 2,000 mg/L under a certain level of hardness and chloride (340 mg/L and 50 mg/L, respectively), the total dissolved solids concentration of that solution would be 2,390 mg/L without adding the sodium that is associated with the sulfate and chloride. Obviously, a TDS standard of 1,000 mg/L is incapable of indicating the concentrations of dissolved substances that are harmful to aquatic life in this example. In another example, where chloride is 5 mg/L and hardness is 90 mg/L, the sulfate standard is 500 mg/L. Here, a 1,000 mg/L TDS standard may be under protective. Because of the better understanding of major ion toxicity, the Agency is proposing to delete the existing TDS standard from the Board regulations.

## VIII. Conclusions and Recommended Standards

By reviewing sulfate toxicity data, it is evident that sulfate is far less toxic than current standards indicate under most conditions found in Illinois. The current standard does not account for water chemistry conditions, which may significantly alter sulfate toxicity. Protection of aquatic life will be fully achieved through implementation of the water chemistry dependent equations as well as numerical standards. For illustrative purposes only, calculated sulfate standards at

various increments of hardness and chloride are shown in Attachment L. Numeric standards are included as well, where applicable. Exact chloride and hardness concentrations must be entered into the appropriate equation to calculate the exact sulfate standard at a specific site. Also, it is to be noted that water chemistry at specific sites may allow for sulfate standards in excess of 2,000 mg/L. Protection of livestock watering will be achieved through the proposed standard of 2,000 mg/L sulfate over a 30-day average at locations where livestock watering occurs.

In light of recent sulfate findings, the TDS standard currently in place is inappropriate. By definition TDS is a measure of all dissolved solids, yet we know that the toxicity of TDS is exerted by its individual constituents. With the advent of a protective sulfate standard expressed by the aquatic life equations and numerical standards, total dissolved solids concentrations of 3,000 mg/L or more will not be toxic if sulfate is the predominant anion and sodium the predominant cation. This is the existing case in Illinois under most high TDS concentrations. The exception to this rule is when chlorides are high. The chloride standard of 500 mg/L is thought to be protective of aquatic life toxicity. Therefore, between the chloride and sulfate water quality standards and the narrative toxics control standard (35 Ill. Adm. Code 302.210) that regulates any discharged substance that could cause toxicity, there is no need for a TDS standard. While potassium or some other more toxic cation could occur in industrial discharges, this condition has not been identified in any ambient stream or effluent setting thus far. The existing TDS standard has always been ungainly since it is really based on a worst-case combination of minerals being present. The specific constituents of the mineral content of water are better regulated individually. Thus, the Agency recommends that the TDS standard be deleted from the Board's regulations.

Changes are also proposed to the Subtitle D Mine Related Water Pollution regulations. References to relief from water quality standards are proposed to be stricken. Mine discharges will now meet water quality standards as must other categories of discharges, except where site-specific relief is given by the Board or a mixing zone is granted. Part 407 of Subtitle D is being stricken for housekeeping purposes as these regulations are no longer pertinent.

#### **IX. Changes to the Mixing Zone Standard**

The Agency has proposed updates to the mixing regulations based on the increasing need to appropriately regulate storm water runoff related discharges and other discharges that may occur when streams are not at drought flow. These changes must be evaluated within the context of existing provisions of the mixing regulations at 35 Ill. Adm. Code 302.102. Most notably, the existing mixing regulations require that the best degree of treatment as specified in Section 304.102 has been applied by the discharger. The proposed changes are not in any way designed to interfere with this basic concept embedded in the regulations since their inception. The Agency's proposal would allow mixing for substances such as sulfate, boron, chloride, and fluoride, for which no practical and reasonable treatment exist, to occur whenever adequate flow exists to dilute such effluents. Under this proposal, other substances such as metals, however, would be subjected to the treatment requirements of Section 304.102 before a possibility of mixing could be considered.

Section 302.102(b)(8):

Section 302.102(b)(8) prohibits mixing in streams that have a zero flow for a minimum of seven consecutive days at a recurrence frequency of once in ten years ("zero 7Q10 flow"). The regulation exists to protect aquatic life from discharges occurring at drought flows that could cause water quality standards to be exceeded. However, during rainfall or snowmelt events, these smaller receiving streams receive significant storm water runoff from the watershed. During these events receiving streams temporarily contain flows that may be totally nonexistent during dry periods. Additionally, flows may exist in these streams seasonally, coinciding with periodic effluent discharges. A discharge of pollutants that occurs only under these conditions will have no adverse impact to aquatic life if flows in receiving streams consistently and demonstrably ensure attainment of water quality standards.

The Agency's proposal is based on the principle found in an existing Board definition.

**Section 301.270 Dilution Ratio**

"Dilution Ratio" means the ratio of the seven-day once in ten year low flow of the receiving stream or the lowest flow of the receiving stream when effluent discharge is expected to occur, whichever is greater, to the average flow of the treatment works for the design year.

(Source: Amended at 3 Ill. Reg. no. 25, page 190, effective June 21, 1979.)

The definition of dilution ratio implies that stream flow values other than 7Q10 may be used to determine mixing and dilution allowances provided that the lowest flow of the stream when the discharge is expected to occur is used. To allow mixing for discharges to zero 7Q10 flow streams, the Agency proposes the deletion of the last sentence of Section 302.102(b)(8). The basic intent of the proposal is that mixing is permissible in zero 7Q10 flow streams if the flow in the stream is sufficient to ensure attainment of water quality standards. The other concept contained in 302.102(b)(8) dictates the percentage of stream flow that may be allowed for dilution. The definition of dilution ratio and the corresponding instruction in 302.102(b)(8) will apply to all streams, 7Q10 zero flow or not, except for certain very small receiving streams described as follows.

**Section 302.102(b)(6):**

The Agency is proposing changes to Section 302.102(b)(6) to allow mixing in very small streams without imposing the zone of passage requirement. These small streams are zero flow streams in dry weather and they are also, by nature, narrow streams. The mixture of effluent and stream water will quickly encompass the entire width of the stream bed since the stream flows present when effluents are discharged are often high velocity, typical of runoff events. Due to the high velocity effluent coming in contact with the runoff from the watershed, mixing of an effluent with the receiving stream is instantaneous during these wet weather events. One way to identify these types of streams is to compare them to 7Q10 zero flow streams using an analogous method of identification. A 7Q1.1 zero flow stream means a stream that has at least a one week period of no flow that recurs at least once annually in nine out of ten years. 7Q1.1 zero streams have very limited aquatic life habitats for the simple reason that their flow is too ephemeral to

support balanced aquatic life communities. 7Q1.1 zero flow streams may support some fish species on a seasonal basis as long as some water remains. These species are adapted to the “flashiness” of these habitats, with very low flow or zero flow conditions present one day and relatively high flow, turbulent conditions the next. Fish species that may want to migrate past an effluent outfall usually will not exist in 7Q1.1 zero flow streams. Even if migrating fish do exist, instantaneous mixing that would occur in these streams may not pose a barrier. For these reasons, the Agency’s proposal specifies that no zone of passage is required in 7Q1.1 zero flow streams. Therefore, mixing in 7Q1.1 zero flow streams would not be required to conform to containment in 25% of the area or volume of stream flow, if the dilution is greater than 3:1 or greater. Streams with greater than 7Q1.1 zero flow conditions would be subject to the provisions of Section 302.102(b)(8) that determine how much stream flow is available for mixing with an effluent.

302.102(b)(10):

The Agency is proposing changes to 302.102(b)(10) to ensure consistency with the changes made to Sections 302.102(b)(6) and (b)(8). The Agency’s proposal provides that no body of water may be used in its entirety for mixing purposes unless it is a 7Q1.1 zero flow stream.

#### **X. Economic Impact of the Proposed Changes to the Standards**

Water quality standards are developed to protect designated uses, in this case, agricultural uses and aquatic life uses. Once these values are determined, impact on economic activities can be evaluated. In the case of the proposals in this petition, there is an economic relief to be gained. The existing standards were recognized to have an impact on discharges from coal mines shortly after adoption. The IPCB responded to what would have been severe economic hardship to most mines by adopting exceptions to the standards in the Subtitle D Mine Related Water Pollution Regulations. This gave needed relief to coal mines; industrial discharges did not receive this relief and had to pursue adjusted standards/site-specific standards relief. Challenges have been entered against the relief provided by Subtitle D, hence the proposed revocation of that regulation in this petition. In light of these challenges and in the absence of this revision to update sulfate standards to scientifically justifiable levels and to delete the unnecessary TDS standards, extreme economic impact to the coal industry would ensue. Requiring coal mines to meet the existing water quality standards would result in a majority of the active mines and almost all reclamation projects to be shut down.

There is also a cost associated with the repeated granting by the Board of adjusted standards and site-specific relief to industrial dischargers, overriding water quality standards that are not scientifically justified. With new air quality regulations for sulfur emissions, these petitions may become more common.



**Exhibit D:** Sulfate and TDS water quality standards of neighboring states.

Inquiries were made to other states as to their existing or proposed water quality standards for sulfate and TDS. Michigan, Wisconsin, Minnesota, Iowa, Missouri, Indiana, Ohio and Kentucky were surveyed.

Michigan, Wisconsin, Iowa and Kentucky have no numeric aquatic life or general use standards for these substances. All these states have public water supply intake standards similar to those in Illinois. Most of the states surveyed have some sort of narrative standard that prohibits impairment from total dissolved solids or conductivity in the water.

Minnesota has a standard of 250 mg/L sulfate that applies to public water supply intakes and trout waters. For other waters, MN uses a site-specific guideline value of 1,000 mg/L which is said to come from the Canadian Water Quality guidelines manual. It is to protect young livestock, specifically young cattle, from getting diarrhea. MN also has a sulfate standard of 10 mg/L to protect wild rice. In their reply to our survey, they relate however, that MN staff believes there is little scientific justification for this low value and they seek to change the standard as part of their next Triennial Review of standards. MN has no TDS standard for waters other than public water supply intakes.

Missouri has a combined water quality standard for sulfate and chloride of 1,000 mg/L to protect aquatic life in streams with a 7Q10 flow of less than one cubic foot per second (cfs). For larger streams, the sulfate plus chloride concentration must not exceed the estimated natural background concentration by more than 20% at the 60 Q10 low flow. If higher concentrations of sulfate plus chloride can be demonstrated to protect indigenous aquatic life, then the appropriate higher concentration will be allowed. Missouri has no TDS standard to protect aquatic life or general uses.

Until recently, Indiana had standards that applied to all waters; 250 mg/L for sulfate and 750 mg/L for TDS. A rulemaking to change these standards that were described as "unworkable" by the Indiana Department of Environmental Management was proposed and adopted with USEPA approval. The TDS standard was dropped as an aquatic life protection standard and changed to 500 mg/L applicable at public water supply intakes. This creates a standard similar to those found in other states for TDS at water supply intakes. A sulfate standard of 250 mg/L is to be established at public water supply intakes and an interim standard of 1,000 mg/L was be put into effect in other waters to protect aquatic life. USEPA region 5 approved these changes under the Clean Water Act.

Ohio has a TDS standard for aquatic life of 1,500 mg/L to be met on an average basis outside of a mixing zone. No sulfate standard exists for aquatic life or general uses.

**Exhibit E:** Literature review of the adverse effects of sulfates on livestock.

<b>Animal</b>	<b>Treatment</b>	<b>Sulfate (mg/L)</b>	<b>Effect</b>	<b>Reference</b>
Cattle and weanling pigs	Water	7,000	No adverse effect	Embry et al. 1959
Cattle	Water	10,000	Reduced water and food consumption	Embry et al. 1959
Cattle	Water – 30 day	5,000	30% decrease in food consumption	Weeth and Hunter, 1971
Cattle	Water – 30 day	5,000	35% decrease in water consumption	Weeth and Hunter, 1971
Cattle	Water – 30 day	2,814	No affect on water consumption	Weeth and Capps, 1972
Cattle	Water – 30 day	2,814	12.4% reduction in food consumption	Weeth and Capps, 1972
Cattle	Water – 30 day	1,462	No reduction in food consumption	Weeth and Capps, 1972
Cattle	Water – 30 day	1,462	Reduction in weight gain	Weeth and Capps, 1972
Cattle	Water – 30 day	1,462	Increased excretion of water	Weeth and Capps, 1972
Cattle	Water – 30 day	1,450	Discriminated against drinking water	Weeth and Capps, 1972
Cattle	Water – 30 day	2,150	Rejected drinking water	Weeth and Capps, 1972
Cattle	Water – 90 day	2,500	No affect on weight gain	Digesti and Weeth, 1976
Cattle	Water – 90 day	2,500	No affect on water consumption	Digesti and Weeth, 1976

<b>Animal</b>	<b>Treatment</b>	<b>Sulfate (mg/L)</b>	<b>Effect</b>	<b>Reference</b>
Cattle	Water – 90 day	2,500	No affect on food consumption	Digesti and Weeth, 1976
Cattle	Water – 90 day	2,018	Discriminated against drinking water	Digesti and Weeth, 1976
Cattle	Water – 90 day	3,317	Rejected drinking water	Digesti and Weeth, 1976
Weanling pigs	Water	2,402	No decreased performance	Anderson and Stothers, 1978
Gilts and sows	Water	3,000	No affect on weight gain	Patterson et al. 1979
Gilts and sows	Water	3,320	No affect on reproduction	Patterson et al. 1979
Mice	Water	5,000	No reproductive effect, no effect on growth	Andres and Cline, 1988
Neonatal piglets	Liquid diet – 18 day	2,200	No affect on weight gain	Gomez et al. 1995
Cattle	Water - 113 day	2,360	Decreased carcass characteristics (dress-out)	Loneragan et al. 2001
Cattle	Water	2,500	Poor conception	Braul and Kirychuk 2001
Cattle	Water	3,000	Decreased water consumption	Zimmerman et al. 2002
Cattle	Water – 85 day	3,087	Decreased water intake and growth, 15% PEM occurrence	Patterson et al. 2002
Cattle	Water – 54 day	2,608	Weight loss and decreased body condition	Patterson et al. 2004

**Literature Cited**

- Anderson, DM and SC Stothers. 1978. Effects of saline water high in sulfates, chlorides, and nitrates on the performance of young weanling pigs. *J Anim Sci.* 49:664-667.
- Andres, DJ and TR Cline. 1988. Influence of sulfate in drinking water on mouse reproduction during two parities. *J Anim Sci.* 67:1313-1317.
- Braul, L and B Kirychuk. 2001. *Water Quality and Cattle*. Publication ENH-111-2001-10. Prairie Farm Rehabilitation Office, Agriculture and Agri-Food Canada.
- Digesti, RD and HJ Weeth. 1976. A defensible maximum for inorganic sulfate in drinking water of cattle. *J Anim Sci.* 42:1498-1502.
- Embry, LB, MA Hoelscher, RC Wahlstrom, et al. 1959. Salinity and livestock water quality. *S D Agric Ex Str Bull.* 481:5-9.
- Gomez, GG, RS Sandler, and E Seal, Jr. 1995. High levels of inorganic sulfate cause diarrhea in neonatal piglets. *J Nutr.* 125:2325-2332.
- Loneragan, GH, JJ Wagner, DH Gould, FB Garry, and MA Thoren. 2001. Effects of water sulfate concentration on performance, water intake, and carcass characteristics of feedlot steers. *J Anim Sci.* 79:2941-2948.
- Patterson, DW, RC Wahlstrom, GW Libal, et al. 1979. Effects of sulfate in water on swine reproduction and young pig performance. *J Anim Sci.* 49:664-667.
- Patterson, HH, PS Johnson, TR Patterson, DB Young, and R Haigh. 2002. Effects of water quality on performance and health of growing steers. *Proc West Sec Amer Soc Anim Sci.* 53:217-220.
- Patterson, HH, PS Johnson, EH Ward, and RN Gates. 2004. Effects of sulfates in water on performance of cow-calf pairs. *Proc West Sec Amer Soc Anim Sci.* 55:265-268.
- Weeth, HJ and DL Capps. 1972. Tolerance of growing cattle for sulfate-water. *J Anim Sci.* 34:256-260.
- Weeth, HJ and JE Hunter. 1971. Drinking of sulfate-water by cattle. *J Anim Sci.* 32:277-281.

**Exhibit M:** Literature toxicity values considered valid for standard derivation.

Common Name	Scientific Name	Acute Value (mg/L)	Chloride (mg/L)	Ca-Mg ratio (weight)	Hardness (mg/L)	Reference
Water flea <sup>1</sup>	<i>Ceriodaphnia dubia</i>	2,083	1.9	1.15	84	Mount et al. 1997
Water flea <sup>1</sup>	<i>Ceriodaphnia dubia</i>	1,038	931	1.15	84	Mount et al. 1997
Water flea	<i>Ceriodaphnia dubia</i>	2,130	NA <sup>2</sup>	NA	NA	Warne and Schifko 1999
Water flea	<i>Ceriodaphnia dubia</i>	1,827	NA	NA	NA	Warne and Schifko 1999
Water flea	<i>Daphnia magna</i>	6,173	NA	NA	NA	Arambasic et al. 1995
Water flea <sup>1</sup>	<i>Daphnia magna</i>	3,097	1.9	1.15	84	Mount et al. 1997
Water flea <sup>1</sup>	<i>Daphnia magna</i>	1,927	1729	1.15	84	Mount et al. 1997
Water flea	<i>Daphnia magna</i>	5,816	NA	NA	563	Meyer et al. 1985
Water flea	<i>Daphnia magna</i>	5,218	NA	NA	105	BC Research 1998; Pickard et al. 1999
Water flea <sup>3</sup>	<i>Daphnia magna</i>	1,262	2.4	1.15	25	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	1,307	2.4	1.15	25	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	1,513	2.4	6.26	25	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	1,628	2.4	6.26	25	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	1,893	2.4	11.6	25	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	2,111	2.4	11.6	25	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	3,045	0.4	1.15	100	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	3,247	2.4	1.15	100	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	3,835	2.4	6.26	100	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	3,842	2.4	6.26	100	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	4,295	2.4	11.6	100	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	4,541	2.4	11.6	100	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	957	2.4	NA	25	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	1,768	2.4	NA	50	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	3,155	2.4	NA	75	Davies 2002; Davies et al. 2003
Water flea <sup>3</sup>	<i>Daphnia magna</i>	537.2	0.7	1.16	27	PESC 1996; Davies 2002
Water flea <sup>3</sup>	<i>Daphnia magna</i>	6,281	108	11	100	PESC 1996; Davies 2002
Water flea <sup>3</sup>	<i>Daphnia magna</i>	7,442	112	6.27	250	PESC 1996; Davies 2002
Amphipod	<i>Hyalella azteca</i>	1,226	NA	NA	111	BC Research 1998; Pickard et al. 1999
Amphipod <sup>3</sup>	<i>Hyalella azteca</i>	491	8.9	5.45	28	Davies 2002; Davies et al. 2003
Amphipod <sup>3</sup>	<i>Hyalella azteca</i>	1,518	17.8	5.4	56	Davies 2002; Davies et al. 2003
Amphipod <sup>3</sup>	<i>Hyalella azteca</i>	1,700	27	5.4	84	Davies 2002; Davies et al. 2003
Amphipod <sup>3</sup>	<i>Hyalella azteca</i>	2,971	36	5.4	112	Davies 2002; Davies et al. 2003
Amphipod <sup>3</sup>	<i>Hyalella azteca</i>	4,864	89	5.42	281	Davies 2002; Davies et al. 2003
Amphipod <sup>3</sup>	<i>Hyalella azteca</i>	205	0.7	1.16	27	PESC 1996; Davies 2002
Amphipod <sup>3</sup>	<i>Hyalella azteca</i>	3,711	108	11	100	PESC 1996; Davies 2002
Amphipod <sup>3</sup>	<i>Hyalella azteca</i>	6,787	112	6.27	250	PESC 1996; Davies 2002
Midge <sup>3</sup>	<i>Chironomus tentans</i>	6,667	0.7	1.16	27	PESC 1996; Davies 2002
Midge <sup>3</sup>	<i>Chironomus tentans</i>	5,868	108	11	100	PESC 1996; Davies 2002
Midge <sup>3</sup>	<i>Chironomus tentans</i>	4,173	112	6.27	250	PESC 1996; Davies 2002
Fathead minnow <sup>1</sup>	<i>Pimephales promelas</i>	5,383	1.9	1.15	84	Mount et al. 1997
Fathead minnow <sup>1</sup>	<i>Pimephales promelas</i>	2,059	1,847	1.15	84	Mount et al. 1997
Fathead minnow	<i>Pimephales promelas</i>	10,280	NA	NA	563	Meyer et al. 1985
Channel catfish	<i>Ictalurus punctatus</i>	11,000	87	4.9	412	Reed and Evans 1981
Largemouth bass	<i>Micropterus salmoides</i>	13,000	87	4.9	412	Reed and Evans 1981
Bluegill	<i>Lepomis macrochirus</i>	12,000	87	4.9	412	Reed and Evans 1981
Bluegill <sup>4</sup>	<i>Lepomis macrochirus</i>	9,130	9.5	2.9	44	Trama 1954
Bluegill	<i>Lepomis macrochirus</i>	8,792	9.5	2.9	44	Cairns and Scheier 1959
Bluegill	<i>Lepomis macrochirus</i>	8,623	9.5	2.9	44	Cairns and Scheier 1959
Bluegill	<i>Lepomis macrochirus</i>	8,454	9.5	2.9	44	Cairns and Scheier 1959
Mosquitofish <sup>5</sup>	<i>Gambusia affinis</i>	11,159	NA	40	NA	Wallin et al. 1957

Notes:

1. The acute values for *C. dubia*, *D. magna*, and the fathead minnow indicate the relative sensitivities of the three species to sulfate.
2. NA = not available.
3. Although some important information concerning test conditions is not available regarding tests reported by Davies (2002), Davies et al. (2003), and PESC (1996), these tests are considered acceptable because ASTM, U.S. EPA, and/or Canadian standard procedures were followed.
4. See also: Academy of Natural Sciences (1960) and Patrick et al. (1968)
5. The test organism were undoubtedly stressed, but the test demonstrates that this species is not sensitive to sulfate.
6. This table does not contain any acute values for salmonids because such values will not be used in Illinois criteria calculations.
7. C. Stephan created this table by revising a table that was prepared by ADVENT.

### Literature Cited

- Arambasic, MB et al. 1995. Acute Toxicity of Heavy Metals (Copper, Lead, Zinc), Phenol and Sodium on *Allium cepa* L., *Lepidium sativum* L. and *Daphnia magna* ST.: Comparative Investigations and the Practical Applications. *Water Res* 29:497-503.
- BC Research Inc. 1998. Brenda mines sulphate and molybdenum toxicity testing. Prepared for Noranda Mining and Exploration Inc., Brenda Mines Division. Project No. 2-11-825/826.
- Cairns, JCJ and A Scheir. 1959. The relationship of bluegill sunfish body size to its tolerance for some common chemicals. *Proc 13th Ind Waste Conf, Purdue Univ Eng Bull* 96:243-252.
- Davies, TD. 2002. Sulphate Toxicity to Freshwater Organisms and Molybdenum Toxicity to Rainbow Trout (*Oncorhynchus mykiss*). Master's Thesis, Dept. of Resource Management and Environmental Studies, Univ. of British Columbia.
- Davies, T.D., J.S. Pickard, and K.J. Hall. Undated. Sulphate Toxicity to Freshwater Organisms and Molybdenum Toxicity to Rainbow Trout Embryos/alevins. Available at: [www.trcr.bc.ca/docs/2003-davies\\_etal.pdf](http://www.trcr.bc.ca/docs/2003-davies_etal.pdf)
- Meyer, JS et al. 1985. Chemistry and Aquatic Toxicity of Raw Oil Shale Leachates from Peceance Basin, Colorado. *Environ Toxicol Chem* 4:559-572.
- Mount, DR, DD Gulley, JR Hockett, TD Garrsion, and JM Evans. 1997. Statistical Models to Predict the Toxicity of Major Ions to *Ceriodaphnia dubia*, *Daphnia magna* and *Pimephales promelas* (Fathead Minnows). *Environ Toxicol Chem* 16(10):2009-2019.
- Pacific Environmental Science Centre (PESC). 1996. Analysis of Laboratory Bioassays. (Cited as "1996" by Singleton (2000) and Davies (2002).
- Pickard, J, P McKee, and J Stroiazzo. 1998. Site specific multi-species toxicity testing of sulphate and molybdenum spiked with mining effluent and receiving water. Aquatic Toxicity Workshop, Quebec City.

Reed, P and R Evans. 1981. Acute Toxicity of Chlorides, Sulfates and Total Dissolved Solids to Some Fishes in Illinois. State Water Survey Division, Water Quality Section, Peoria, IL, IL Dept of Energy and Natural Resources, SES Contract Report 283.

Trama, FB. 1954. The acute toxicity of some common salts of sodium, potassium and calcium to the common bluegill. Proc Acad Nat Sci Philadelphia 106:185-205.

Wallen, IE et al. 1957. Toxicity to *Gambusia affinis* of certain pure chemicals in turbid waters. Sewage Ind Wastes 29(6):695-711.

Warne, M St. J, and AD Schifko. 1999. Toxicity of Laundry Detergent Components to a Freshwater Cladoceran and Their Contribution to Detergent Toxicity. Ecotoxicol Environ Saf. 44:196-206.

**Exhibit K**

The following table is a list of references compiled by Dr. Charles Stephan that contain data regarding the toxicity of sulfate to aquatic animals. The table also contains various documents that were cited in various sources as possibly containing data regarding the toxicity of sulfate to aquatic animals. A comment for each reference is also included that explains the rationale for acceptance or rejection of these studies.

A number in parentheses at the end of the citation is the AQUIRE reference number of the document.

For the purposes of this project, the only chemicals that are considered acceptable for use in aquatic toxicity tests on sulfate are calcium sulfate, magnesium sulfate, potassium sulfate, and sodium sulfate. Interpreting results obtained with these four salts is not straightforward because potassium and magnesium apparently are sufficiently toxic to impact the results of tests in which their salts are used.

All LC50s and EC50s given below are for sulfate, not for the salt used in the test. In some cases the results do not take into account the concentration of sulfate in the dilution water.

<b><u>Reference</u></b>	<b><u>Comment</u></b>
Abraham, T.J., K.Y.M. Salih, and J. Chacko. 1986. Effects of Heavy Metals on the Filtration Rate of Bivalve <i>Villorita cyprinoides</i> (Hanley) Var. <i>Cochinensis</i> . <i>Indian J. Mar. Sci.</i> 15:195-196. (A: 12315)	No results concerning sulfate.
Academy of Natural Sciences. 1960. The Sensitivity of Aquatic Life to Certain Chemicals Commonly Found in Industrial Wastes. Final Report No. RG-3965(C2R1). Academy of Natural Sciences, Philadelphia, PA. (A: 5683)	All relevant test results are acceptable.
Anderson, B.G. 1944. The Toxicity Thresholds of Various Substances Found in Industrial Wastes As Determined by the Use of <i>Daphnia magna</i> . <i>Sewage Works J.</i> 16(6):1156-1165. (A: 2171)	No test results are acceptable because the test duration was only 16 hr.
Anderson, B.G. 1946. The Toxicity Thresholds of Various Sodium Salts Determined by the Use of <i>Daphnia magna</i> . <i>Sewage Works J.</i> 18(1):82-87. (A: 2130)	Test results with <i>D. magna</i> but they probably are not useful.



<u>Reference</u>	<u>Comment</u>
Anderson, B.G. 1948. The Apparent Thresholds of Toxicity of <i>Daphnia magna</i> for Chlorides of Various Metals When Added to Lake Erie Water. <i>Trans. Amer. Fish. Soc.</i> 78:96-113.	No results concerning sulfate.
Anderson, K.B., R.E. Sparks, and A.A. Paparo. 1978. Rapid Assessment of Water Quality, Using the Fingernail Clam, <i>Musculium transversum</i> . WRC Research Report No. 133. University of Illinois, Water Resources Center, Urbana, IL.	The results of tests on sulfate are not acceptable because the observed effect was on ciliary beating rate.
Arambasic, M.B., S. Bjelic, and G. Subakov. 1995. Acute Toxicity of Heavy Metals (Copper, Lead, Zinc), Phenol and Sodium on <i>Allium cepa</i> L., <i>Lepidium sativum</i> L. and <i>Daphnia magna</i> St.: Comparative. <i>Water Res.</i> 29(2):497-503. (A: 13712)	Test results with <i>D. magna</i> but they probably are not useful.
Battelle's Columbus Laboratories. 1971. Water Quality Criteria Data Book - Vol 3. 18050GWV05/71. Water Pollution Control Research Series, U.S. EPA.	All results are secondary information.
BC Research Inc. 1998. Brenda Mines Sulphate and Molybdenum Toxicity Testing. Prepared for Noranda Mining and Exploration Inc., Brenda Mines Division. Project No. 2-11-825/826.	Rainbow trout eggs were sensitive to sulfate in creek water. Concentration of chloride is unknown, but cations were measured.
Beauchamp, R.S.A. 1953. Sulphates in African Island Waters. <i>Nature</i> 171:769-771.	No results concerning sulfate.
Becker, A.J.J., Jr., and E.C. Keller, Jr. 1973. The Effects of Iron and Sulfate Compounds on the Growth of <i>Chlorella</i> . <i>Proc. W. Va. Acad. Sci.</i> 45(2):127-135. (A: 8598)	All tests were with algae.
Bell, T.A., C.S. Arume, and D.V. Lightner. 1987. Efficacy of Formalin in Reducing the Levels of Peritrichous Ciliates on Cultured Marine Shrimp. <i>J. Fish Dis.</i> 10(1):45-51. (A: 963)	No results concerning sulfate.
Black, H.H., G.N. McDermott, C. Henderson, W.A. Moore, and H.R. Pahren. 1957. Industrial Wastes Guide: By-Product Coke Industry. <i>Sewage Ind. Wastes</i> 29:53-75.	No results concerning sulfate.

<u>Reference</u>	<u>Comment</u>
Boge, G., A. Rigal, and G. Peres. 1982a. Effects of the sulphate ions on some enzymatic activities in the gut and the gill of the eel ( <i>Anguilla anguilla</i> ) in a constant temperature culture. <i>Ann. Inst. Michel Pacha, Lab. Marit. Physiol.</i> 13:1-11.	Not obtained because data concerning enzyme activities are not relevant.
Boge, G., A. Rigal, and G. Peres. 1982b. Effects of the sulphate ions on some enzymatic activities in the gut and the gill of the eel ( <i>Anguilla anguilla</i> ) during thermal stress. <i>Ann. Inst. Michel Pacha, Lab. Marit. Physiol.</i> 13:12-19.	Not obtained because data concerning enzyme activities are not relevant.
Boge, G., A. Rigal, and G. Peres. 1982c. Effects of the calcium sulphate and potassium sulphate upon different enzyme activities in the intestine of the trout ( <i>Salmo gairdneri</i> R.) maintained at constant temperature. <i>Cah. Lab. Hydrobiol. Montereau No.</i> 14:7-11.	Not obtained because data concerning enzyme activities are not relevant.
Boge, G., A. Rigal, and G. Peres. 1982d. Effects of calcium sulphate and potassium sulphate upon different enzyme activities of trout ( <i>Salmo gairdneri</i> R.) after the production of thermal shocks. <i>Cah. Lab. Hydrobiol. Montereau No.</i> 14:13-16. (See: Nijman, R.A. 1993)	Not obtained because data concerning enzyme activities are not relevant.
Bringmann, G., and R. Kuhn. 1959. The Toxic Effects of Waste Water on Aquatic Bacteria, Algae, and Small Crustaceans. <i>Gesund. Ing.</i> 80:115-120. (English Translation: TR-TS-0002). (A: 607)	No tests on calcium, magnesium, potassium, or sodium sulfate.
Brown, E.R., L. Keith, J.J. Hazdra, and T. Arndt. 1973. Tumors in Fish Caught in Polluted Waters: Possible Explanations. IN: Y. Ito and R.M. Dutcher (eds.), <i>Comparative Leukemia Research 1973, Leukemogenesis, Bibl. Haematol. No. 40</i> , Univ. of Tokyo Press, Tokyo/Karger, Basel 47-57. (A: 2143)	The results of tests on sulfate are not acceptable because very little information is available.
Buikema, A.L. Jr., B.R. Niederlehner, and J. Cairns, Jr. 1981. The Effects of a Simulated Refinery Effluent and Its Components on the Crustacean, <i>Mysidopsis bahia</i> . <i>Arch. Environ. Contam. Toxicol.</i> 10:231-240. (A: 14256)	No results concerning sulfate.
Cairns, J.C.J., and A. Scheier. 1959. The Relationship of Bluegill Sunfish Body Size to its Tolerance for Some Common Chemicals. <i>Proc. 13th Ind. Waste Conf., Purdue Univ, Eng. Bull</i> 43:243-252. (A: 930)	All relevant test results are acceptable.

<u>Reference</u>	<u>Comment</u>
Chapman, P.M., H. Bailey, and E. Canaria. 2000. Toxicity of Total Dissolved Solids Associated with Two Mine Effluents to Chironomid larvae and early life stages of rainbow trout. <i>Environ. Toxicol. Chem.</i> 19:210-214.	All tests were on synthetic effluents.
Davies, T.D. 2002. Sulphate Toxicity to Freshwater Organisms and Molybdenum Toxicity to Rainbow Trout ( <i>Oncorhynchus mykiss</i> ). Master's Thesis, Dept. of Resource Management and Environmental Studies, Univ. of British Columbia.	All relevant tests with <i>D. magna</i> and <i>H. azteca</i> are acceptable. Test results with striped bass are very interesting.
Davies, T.D., J.S. Pickard, and K.J. Hall. Undated. Sulphate Toxicity to Freshwater Organisms and Molybdenum Toxicity to Rainbow Trout Embryos/alevins. Available at: <a href="http://www.trcr.bc.ca/docs/2003-davies_etal.pdf">www.trcr.bc.ca/docs/2003-davies_etal.pdf</a>	Same data as Davies (2002).
Den Dooren de Jong, L.E. 1965. Tolerance of <i>Chlorella vulgaris</i> for Metallic and Non-Metallic Ions. <i>Antonie Leeuwenhoek J. Microbiol. Serol.</i> 31:301-313. (A: 2849)	All results are for an algal species.
Deniseger, J. 1997 Draft. In-situ Coho Egg Bioassays and Chronic Daphnia Bioassays Done in the Vicinity of Quinsam Coal in Response to an Increasing Trend in Sulphate Levels. Ministry of Environment, Lands and Parks. Nanaimo. BC.	All toxicity tests were on river waters, most of which contained one or more effluents.
Department of Scientific and Industrial Research. 1953. Water Pollution Research 1952. Report of the Water Pollution Research Board, Water Pollution Research Laboratory, H.M. Stationary Office, London. (A: 20590)	Rainbow trout were exposed for only 24 hr. In addition, little additional information is available regarding the test method used.
Dickerson, K.K., W.A. Hubert, and H.L. Bergman. 1996. Toxicity Assessment of Water from Lakes and Wetlands Receiving Irrigation Drain Water. <i>Environ. Toxicol. Chem.</i> 15:1097-1101.	Additional validation of the models developed by Mount et al. (1996).
Dietz, T.H., and R.A. Byrne. 1999. Measurement of Sulfate Uptake and Loss in the Freshwater Bivalve <i>Dreissena polymorpha</i> Using a Simi-microassay. <i>Can. J. Zool.</i> 77:331-336. (A: 48713)	No toxicity test results
Doudoroff, P., and M. Katz. 1950. Critical Review of Literature on the Toxicity of Industrial Wastes and Their	All results are secondary information.

Components to Fish. Sewage Ind. Wastes 22:1432-1458.

Reference

Comment

Doudoroff, P., and M. Katz. 1953. Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals, as Salts. Sewage Ind. Wastes 25:802-839.

All results are secondary information.

Dowden, B.F. 1960. Cumulative Toxicities of Some Inorganic Salts to *Daphnia magna* as Determined by Median Tolerance Limits. Proc. La. Acad. Sci. 23:77-85. (A: 2465)

The dilution water was from a drainpipe-fed lake on the LSU campus.

Dowden, B.F., and H.J. Bennett. 1965. Toxicity of Selected Chemicals to Certain Animals. J. Water Pollut. Control Fed. 37(9):1308-1316. (A: 915)

Results are not acceptable if the duration was too long or too short or if the dilution water was from a drainpipe-fed lake on the LSU campus. Test results with *D. magna* but they probably are not useful.

EG&G Bionomics. 1978. The effects of sulfate on eggs and fry of rainbow trout (*Salmo gairdneri*) during continuous aqueous exposure. Report #BW-78-1-006.

Chronic test on calcium sulfate using eggs and fry (through 60 days post-hatch) of rainbow trout in poorly characterized well water. No toxicity at highest tested concentration of 732 mg/L.

EG&G Bionomics. 1979. The chronic toxicity of sulfate to the water flea (*Daphnia magna*). Report #BW-79-10-546.

Chronic test on calcium sulfate using *D. magna* in poorly characterized reconstituted water. No toxicity at highest tested concentration of 1600 mg/L.

Fisher, S.W., P. Stromberg, K.A. Bruner, and L.D. Boulet. 1991. Molluscicidal Activity of Potassium to the Zebra Mussel, *Dreissena polymorpha*: Toxicity and Mode of Action. Aquat. Toxicol. 20:219-234. (A: 11011)

For zebra mussels and potassium sulfate, 24-hr LC50 = 112 mg/L, but the potassium is said to be the cause of the toxicity.

Frahm, J.P. 1975. Toxicity Tolerance Studies Utilizing Periphyton. (Toxitoleranzversuche an Wassermoosen). Gewasser Und Abwasser 57/58:59-66. (A: 7922)

Results for ammonium sulfate, but not for calcium, magnesium, potassium, or sodium sulfate.

Freeman, L. 1951. The Toxicity Thresholds of Certain

CS requested this.

Sodium Sulfonates for *Daphnia magna* Straus. Thesis, Louisiana State University, Baton Rouge, LA.

**Reference**

**Comment**

Freeman, L., and I. Fowler. 1953. Toxicity of Combinations of Certain Inorganic Compounds to *Daphnia magna* (Straus). *Sewage Ind. Wastes* 25(10):1191-1195. (A: 2462)

Test results with *D. magna* but they probably are not useful.

Gannon, J.E., and S.A. Gannon. 1975. Observations on the Narcotization of Crustacean Zooplankton. *Crustaceana* (Leiden) 28(2):220-224. (A: 2585)

Magnesium sulfate was an ineffective narcotizing agent.

Goetsch, P.A., and C.G. Palmer. 1997. Salinity Tolerances of Selected Macroinvertebrates of the Sabie River, Kruger National Park, South Africa. *Arch. Environ. Contam. Toxicol.* 32(1):32-41. (A: 17845)

96-hr LC50 = 446 mg/L but river water and industrial-grade Na<sub>2</sub>SO<sub>4</sub> were used, organisms were not identified to species and not obtained in North America, some control mortalities were >10%, temperature varied by 3 to 6 C, and the field-collected organisms were not adequately acclimated.

Gohar, H.A.F., and H. El-Gindy. 1961. Tolerance of Vector Snails of Bilharziasis and Fascioliasis to Some Chemicals. *Proc. Egyptian Acad. Sci.* 16:37-48.

The results of tests on sulfate are not acceptable because the tests were 24-hr exposures to high concentrations.

Goodfellow, W.L. et al. 2000. Major Ion Toxicity in Effluents: A Review with Permitting Recommendations. *Environ. Toxicol. Chem.* 19:175-182.

No toxicity test results.

Hancher, C.W., P.A. Taylor, A. Stewart, K.R. Zabelsky, and J.M. Napier. 1987. Development and Operational Performance of the Central Pollution Control Facility II/S-3 Liquid Treatment Facility. Oak Ridge Y-12 Plant. ORNL/M-609.

No test result is acceptable because too little information is available

Hart, W.B., P. Doudoroff, and J. Greenbank. 1945. The Evaluation of the Toxicity of Industrial Wastes, Chemicals and Other Substances to Fresh-Water Fishes. Waste Control Lab, Atlantic Refining Co., Philadelphia, PA.

No toxicity test results.

Harukawa, C. 1922. Preliminary report on the toxicity of colloidal sulphur to fish. *Trans. Amer. Fish. Soc.* 52:219-224.

No test results are acceptable because only two fish were exposed to one concentration for 24 hr and very little information is available.

**Reference**

**Comment**

Haydu, E.P., H.R. Amberg, and R.E. Dimick. 1952. The Effect of Kraft Mill Waste Components on Certain Salmonid Fishes of the Pacific Northwest. *TAPPI* 35:545-549.

Even if it cannot be used in the calculation of an SMAV, the 120-hr LC50 of about 8687 for silver salmon implies that this species is not sensitive to sulfate. Test results for cutthroat trout are probably not useful.

Henderson, C., Q.H. Pickering, and J.M. Cohen. 1959. The toxicity of synthetic detergents and soaps to fish. *Sewage Ind. Wastes* 31:295-306.

Even if they cannot be used to calculate a SMAV, the 96-hr LC50s of 6087 and 9130 mg/L imply that the fathead minnow is not sensitive to sulfate.

Henderson, C., Q.H. Pickering, and C.M. Tarzwell. 1960. The toxicity of organic phosphorus and chlorinated hydrocarbon insecticides to fish. IN: *Biological Problems in Water Pollution*, C.M. Tarzwell (ed), Robt. A. Taft San. Eng. Center, Cincinnati, OH., Tech. Rept. W60-3:76-88. (A: 936)

No results concerning sulfate. Probably an incorrect citation in "Battelle's Columbus Laboratories (1971)".

Herbert, D.W.M., and A.C. Wakeford. 1962. The Effect of Calcium Sulfate on the Survival of Rainbow Trout. *Water Waste Treat. J.* 8:608-609.

No rainbow trout died during a 28-day exposure to 1456 mg/L.

Hirsch, E. 1914. Untersuchungen uber die biologische Wirkung einiger Salze. *Zool. Jahrbucher, Abt. f. allgem. Zool. u. Physiol.* 34:559-682.

Not obtained because it probably does not contain useful information. See Doudoroff and Katz (1953).

Hodgson, E.S. 1951. Reaction Thresholds of an Aquatic Beetle, *Laccophilus maculosus* Germ., to Salts and Alcohols. *Physiol. Zool.* 24:131-140.

No useful results.

Hughes, J.S. 1969. Toxicity of Some Chemicals to Striped Bass (*Roccus saxatilis*). Proceedings of the Twenty-second Annual Conference of the Southeastern Association. (A: 5990)

The methodology is also described in Hughes (1971).

For striped bass the 96-hr LC50 is 250 mg/L for larvae and 3500 mg/L for fingerlings, but the sodium sulfate was technical grade and the fish were not adequately acclimated.

### Reference

### Comment

Hughes, J.S. 1973. Acute Toxicity of Thirty Chemicals to Striped Bass (*Morone saxatilis*). Louisiana Wild Life and Fisheries Commission. (A: 2012)

Same data as above.

Ingersoll, C.G. et al. 1992. The Use of Freshwater and Saltwater Animals to Distinguish between the Toxic Effects of Salinity and Contaminants in Irrigation Drain Water. *Environ. Toxicol. Chem.* 11:503-511.

No test results are specifically relevant to sulfate.

Jaffe, R.L. 1995. Rapid Assay of Cytotoxicity Using *Tetramitus flagellates*. *Toxicol. Ind. Health* 11(5):543-558. (A: 5895)

All results are for an unicellular species.

Jaworska, M., J. Sepiol, and P. Tomasik. 1996. Effect of Metal Ions Under Laboratory Conditions on the Entomopathogenic *Steinernema carpocapsae* (Rhabditida: Steinernematidae). *Water Air Soil Pollut.* 88(3/4):331-341. (A: 17002)

The dilution water was distilled water.

Jaworska, M., A. Gorczyca, J. Sepiol, and P. Tomasik. 1997. Effect of Metal Ions on the Entomopathogenic Nematode *Heterorhabditis bacteriophora* Poinar (Nematoda: Heterorhabditidae) Under Laboratory Conditions. *Water Air Soil Pollut.* 93:157-166. (A: 40155)

The dilution water was distilled water.

Jayaraj, Y.M., B. Aparanji, and P.M. Nimbargi. 1992. Amelioration of Heavy Metal Toxicity on Primary Productivity of Aquatic Ecosystems by Calcium, Magnesium and Iron. *Environ. Ecol.* 10(3):667-674. (A: 8019)

These were studies of antagonism. The observed effect was reduction in primary productivity.

Jones, J.R.E. 1941. A Study of the Relative Toxicity of Anions, with *Polycelis nigra* As Test Animal. *J. Exp. Biol.* 18:170-181. (A: 10013)

The dilution water was distilled water.

Jones, J.R.E. 1947. The Oxygen Consumption of *Gasterosteus aculeatus* L. in Toxic Solutions. *J. Exp. Biol.* 23:298. (Water Pollut. Abs. 20, June 1947). No test results concerning sulfate.

Jones, J.R.E. 1948. A Further Study of the Reactions of Fish to Toxic Solutions. *J. Exp. Biol.* 25:22. No test results concerning sulfate.

### Reference

### Comment

Kanta, S., and T.A. Sarma. 1980. Biochemical Studies on Sporulation in Blue-Green Algae II. Factors Affecting Glycogen Accumulation. *Z. Allg. Mikrobiol.* 20(7):459-463. (A: 5052) All results are for an algal species.

Kemp, H.T., R.L. Little, V.L. Holoman, and R.L. Darby. 1973. Water Quality Criteria Data Book - Vol. 5. 18050HLA09/73. Water Pollution Control Research Series, U.S.EPA. All results are secondary information.

Kennedy, A.J., D.S. Cherry, and R.J. Currie. 2003. Field and Laboratory Assessment of a Coal Processing Effluent in the Leading Creek Watershed, Meigs County, Ohio. *Arch. Environ. Contam. Toxicol.* 44:324-331. No test results are specifically relevant to sulfate.

Kennedy, A.J., D.S. Cherry, and R.J. Currie. 2004. Evaluation of Ecologically Relevant Bioassays for a Lotic System Impacted by a Coal-mine Effluent, using *Isonychia*. *Environ. Monitor. Assess.* 95:37-55. In 7-day exposures to a simulated effluent high in sulfate, a mayfly was more sensitive than *C. dubia*.

Kennedy, A.J., D.S. Cherry, and C.E. Zipper. 2005. Evaluation of Ionic Contribution to the Toxicity of a Coal-Mine Effluent Using *Ceriodaphnia dubia*. *Arch. Environ. Contam. Toxicol.* 48:155-162. Increased hardness reduced the acute and chronic toxicity of sodium sulfate in waters that simulated the effluent from a specific mine. A model, which is probably the Mount et al. (1996) model, did not fit the data.

Khangerot, B.S. 1991. Toxicity of Metals to a Freshwater Tubificid Worm, *Tubifex tubifex* (Muller). *Bull. Environ. Contam. Toxicol.* 46:906-912. (A: 2918) LC50 = 626 mg/L; concentration of sulfate in dilution water is unknown; magnesium sulfate was used; chloride = 10 mg/L; hardness = 900 mg/L.



Khangarot, B.S., and P.K. Ray. 1989. Investigation of Correlation Between Physicochemical Properties of Metals and Their Toxicity to the Water Flea <i>Daphnia magna</i> Straus. <i>Ecotoxicol. Environ. Saf.</i> 18(2):109-120. (A: 6631)	LC50 = 1359 mg/L, concentration of sulfate in dilution water is unknown; magnesium sulfate was used; chloride = 7 mg/L; hardness = 1660 mg/L.
Koel, T.M., and J.J. Peterka. 1995. Survival to Hatching of Fishes in Sulfate-saline Waters, Devils Lake, North Dakota. <i>Can. J. Fish. Aquat. Sci.</i> 52:464-469.	Sodium-sulfate waters limit the hatching success of several species of fish.
<b><u>Reference</u></b>	<b><u>Comment</u></b>
LeBlanc, G.A., and D.C. Surprenant. 1984. The influence of mineral salts on fecundity of the water flea ( <i>Daphnia magna</i> ) and the implications on toxicity testing on industrial wastewater. <i>Hydrobiologia</i> 108:25-31.	All relevant test results are acceptable.
Linden, E., B.E. Bengtsson, O. Svanberg, and G. Sundstrom. 1979. The Acute Toxicity of 78 Chemicals and Pesticide Formulations Against Two Brackish Water Organisms, the Bleak ( <i>Alburnus alburnus</i> ) and the Harpacticoid. <i>Chemosphere</i> 8(11/12):843-851. (A: 5185)	All toxicity tests were performed in brackish water.
Luther, M., and C.J. Soeder. 1991. 1-Naphthalenesulfonic Acid and Sulfate as Sulfur Sources for the Green Alga <i>Scenedesmus obliquus</i> . <i>Water Res.</i> 25(3):299-307. (A: 91)	All results are for an algal species.
Masnado, R.G., S.W. Geis, and W.C. Sonzogogni. 1995. Comparative Acute Toxicity of a Synthetic Mine Effluent to <i>Ceriodaphnia dubia</i> , larval Fathead Minnow, and the Freshwater Mussel <i>Anodonta imbecilis</i> . <i>Environ. Toxicol. Chem.</i> 14:1913-1920.	All toxicity tests were on a synthetic mine effluent.
McKee, J.E., and H.W. Wolf. 1963. <i>Water Quality Criteria</i> , 2nd ed. California State Water Quality Control Board. Publication No. 3-A.	All results are secondary information.
Meyer, J.S., et al. 1985. Chemistry and Aquatic Toxicity of Raw Oil Shale Leachates from Peceanne Basis, Colorado. <i>Environ. Toxicol. Chem.</i> 4:559-572.	All relevant test results are acceptable.
Mount, D.R., D.D. Gulley, J.R. Hockett, T.D. Garrison, and J.M. Evans. 1997. Statistical Models to Predict the Toxicity of Major Ions to <i>Ceriodaphnia dubia</i> , <i>Daphnia magna</i> and <i>Pimephales promelas</i> (Fathead Minnows).	All relevant test results are acceptable.

Environ. Toxicol. Chem. 16(10):2009-2019. (A: 18272)

Muegge, O.J. 1956. Physiological Effects of Heavily Chlorinated Drinking Water. Jour. Amer. Water Works Assoc. 48:1507-1509.

No results concerning sulfate. Probably an incorrect citation in McKee and Wolf (1963).

### Reference

### Comment

Mukai, H. 1977. Effects of Chemical Pretreatment on the Germination of Statoblasts of the Freshwater Bryozoan, *Pectinatella gelatinosa*. Biol. Zentralbl. 96:19-31. (A: 705)

This species is not known to exist in North America and the organisms were not obtained in North America. The dilution water was distilled water; exposure duration was 2 hr.

National Council for Stream Improvement. 1947. The Toxicity of Kraft Pulping Wastes to Typical Fish Food Organisms. Tech. Bull. 10.

Not obtained because it probably does not contain any primary data concerning the sulfate salts of calcium, magnesium, potassium, or sodium.

National Council for Stream Improvement. 1948. A Study of the Toxic Components of the Waste Waters of Five Typical Kraft Mills. Tech. Bull. 16.

No information concerning sulfate.

National Council for Stream Improvement. 1949. The Toxicity of Kraft Pulping Wastes to Important Fish Food Species of Insect Larvae. Tech. Bull. 25.

Not obtained because it probably does not contain any primary data concerning the sulfate salts of calcium, magnesium, potassium, or sodium.

Nijman, R.A. 1993. Ambient Water Quality Objectives for the Yakoun River and its Tributaries. Ministry of Environment, Lands and Parks, British Columbia.

No test results concerning sulfate.

Oshima, S. 1931. On the toxic action of dissolved salts and their ions upon young eels (*Anguilla japonica*). Jour. Imperial Fisheries Exp. Sta. 2:139-193.

Not obtained because it probably does not contain useful information. See Doudoroff and Katz (1953).

Pacific Environmental Science Centre (PESC). 1996. [Cited as "1996" by Singleton (2000) and Davies (2002).]

All relevant test results are acceptable.

Patrick, R., J. Cairns Jr., and A. Scheier. 1968. The Relative Sensitivity of Diatoms, Snails, and Fish to Twenty Common Constituents of Industrial Wastes. <i>Prog. Fish-Cult.</i> 30(3):137-140. (A: 949)	All relevant test results are acceptable.
Pickard, J, P McKee, and J Stroiazzo. 1998. Site specific multi-species toxicity testing of sulphate and molybdenum spiked with mining effluent and receiving water. <i>Aquatic Toxicity Workshop</i> , Quebec City.	All relevant test results are acceptable.
<b><u>Reference</u></b>	<b><u>Comment</u></b>
Pillard, D.A. et al. 2000. Predicting the Toxicity of Major Ions in Seawater to Mysid Shrimp ( <i>Mysidopsis bahia</i> ), Sheepshead Minnow ( <i>Cyprinodon variegatus</i> ), and Inland Silverside Minnow ( <i>Menidia beryllina</i> ). <i>Environ. Toxicol. Chem.</i> 19:183-191.	All data are for saltwater species.
Reed, P., and R. Evans. 1981. Acute toxicity of chlorides, sulfates, and total dissolved solids to some fishes in Illinois. Illinois Department of Energy and Natural Resources, State Water Survey Division. SWS Contract Report 283. (A: 60643)	All relevant test results are acceptable.
Reimschuessel, R., R.O. Bennett, E.B. May, and M.M. Lipsky. 1989. Renal Histopathological Changes in the Goldfish ( <i>Carassius auratus</i> ) After Sublethal Exposure to Hexachlorobutadiene. <i>Aquat. Toxicol.</i> 15(2):169-180. (A: 2046)	No results concerning sulfate. Possibly an incorrect reference because the first author has done much work with medicines that are sulfates.
Reinfelder, J.R., and N.S. Fisher. 1994. The Assimilation of Elements Ingested by Marine Planktonic Bivalve Larvae. <i>Limnol. Oceanogr.</i> 39(1):12-20. (A: 20560)	No toxicity test results.
Robinson, D.J.S., and E.J. Perkins. 1977. The Toxicity of Some Wood Pulp Effluent Constituents. <i>Cumbria Sea Fish. Comm., Sci. Rep. No.74/1</i> , The Courts, Carlisle, England:22. (A: 15285)	All toxicity tests were in sea water.
Rudolfs, W., et al. 1950. Review of Literature on Toxic Materials Affecting Sewage Treatment Processes, Streams, and B.O.D. Determinations. <i>Sewage Ind. Wastes</i> 22:1157-1187(?).	No results concerning sulfate.
Saliba, L.J., and M. Ahsanullah. 1973. Acclimation and Tolerance of <i>Artemia salina</i> and <i>Ophryotrocha labronica</i>	All toxicity tests were on copper sulfate.

to Copper Sulphate. *Mar. Biol.* 23(4):297-302. (A: 5168)

Sanders, D.F. 1993. Letter and attachments to S. LaDieu regarding chronic toxicity tests using *Ceriodaphnia dubia* and the fathead minnow in connection with Thorn Creek.

7-day life-cycle test with *C. dubia* and 7-day "chronic" test with fathead minnow on sodium sulfate in creek water. No toxicity at highest tested concentration of 1301 mg/L.

### Reference

### Comment

Scheuring, L., and H. Stetter. 1950/51. Experiments on the effect of sodium sulphate on water organisms. *Vom Wasser* 18:78-100. [*Water Pollut. Abs.* 27(8):191 (1952) says "concentrations of sodium and other sulphates such as would be found in streams have no serious damaging effect on the biology of the water."] ]

Not obtained. Doudoroff and Katz (1953) summarize the results as "Sodium sulfate also is not very toxic to fish and fish eggs."

Selitrennikova, M., and Sachurina, E. 1953. Experiences in the Organization of Sewage Fields in the Hot Climate of Uzbekistan. *Hygiene and Sanitation (Moscow)* 7:17

Not obtained because it probably does not contain any useful information.

Sheplay, A.W., and T.J. Bradley. 1982. A Comparative Study of Magnesium Sulphate Tolerance in Saline-Water Mosquito Larvae. *J. Insect Physiol.* 28(7):641-646. (A: 15695)

All tests were performed in 50% seawater.

Singleton, H. 2000. Ambient Water Quality Guidelines for Sulfate. Ministry of Environment, Lands and Parks (BC MELP), Province of British Columbia, Canada.

All test results are secondary information. There is an extensive table of test results.

Soucek, D.J. 2005. Third Quarterly Progress Report.

All test results are acceptable.

Soucek, D.J., and A.J. Kennedy. 2005. Effects of Hardness, Chloride, and Acclimation on the Acute Toxicity of Sulfate to Freshwater Invertebrates. *Environ. Toxicol. Chem.* 24:1204-1210.

All test results are acceptable.

Staub, R.S., J.W. Appling, and J. Haas. 1973. Effects of Industrial Effluents on Primary Phytoplankton Indicators. PB220741. NTIS.

All tests were with phytoplankton.

Stanley, R.A. 1974. Toxicity of Heavy Metals and Salts to Eurasian Watermilfoil (*Myriophyllum spicatum* L.). *Arch. Environ. Contam. Toxicol.* 2(4):331-341. (A: 2262)

All tests were with Eurasian watermilfoil.

Stark, J. 1999. Letter and attachments to S. LaDieu regarding chronic toxicity tests using *Ceriodaphnia dubia* and the fathead minnow in connection with Thorn Creek.

7-day life-cycle test with *C. dubia* and 7-day "chronic" test with fathead minnow on sodium sulfate in creek water. No toxicity at highest tested concentration of 1381 mg/L.

### Reference

### Comment

Stora, G. 1975. Contribution a L'Etude de la Notion de Concentration Lethale. Limite Moyenne Appliquee a Des Invertebrea Marins. II. CL50 et Determination de la Toxicite de produits Polluants. Rev. Int. Oceanogr. Med. 37-38:97-123. (A: 5928)

No results for calcium, magnesium, potassium, or sodium sulfate.

Stora, G. 1978. Evolution Compree de la Sensibilite de Deux Polychetes Soumises a L'Action de Detergents En Fonction D'Une Augmentation de la Temperature Notion D'Indice de Sensibilite. Rev. Int. Oceanogr. Med. 51/52:101-133. (A: 5852)

No results for calcium, magnesium, potassium, or sodium sulfate.

Stribling, J.M. 1997. The Relative Importance of Sulfate Availability in the Growth of *Spartina alterniflora* and *Spartina cynosuroides*. Aquat. Bot. 56(2):131-143. (A: 19969)

All tests were with marsh cordgrass.

Sunila, I. 1988. Acute Histological Responses of the Gill of the Mussel, *Mytilus edulis*, to Exposure by Environmental Pollutants. J. Invertebr. Pathol. 52(1):137-141. (A: 13066)

All tests studied histological effects on a saltwater mussel.

Surber, E.W., and T.O. Thatcher. 1963. Laboratory Studies of the Effects of Alkyl Benzene Sulfonate (ABS) on Aquatic Invertebrates. Trans. Amer. Fish. Soc. 92(2):152-160. (A: 62090)

The highest concentration tested was 216 mg/L, and it was not toxic to three invertebrate species in 96 hr.

Taylor, P.A., A.J. Stewart, and L. Holt. 1988. Toxicity of Common Salts to Three Biototoxicity Test Organisms. Oak Ridge Y-12 Plant, Oak Ridge, TN. Y/DZ-420.

No test results are acceptable because too little information is available.

Tietge, et al. 1997. Major ion toxicity of six produced waters to three freshwater species: application of ion toxicity models and TIE procedures. Environ. Toxicol. Chem. 16(10):2002-2008.

Additional validation of the models developed by Mount et al. (1996).

Tomiyaama, T., and Yamagawa, A. 1950. The Effect of pH on Toxic Effects of Sulphide and of Sulphite on Young Carp. Bull. Jap. Soc. Sci. Fish. 15:9, 491. (Water Pollut. Abs. 26:5, 140, 1953).

Not obtained because it probably does not contain any primary data concerning the sulfate salts of calcium, magnesium, potassium, or sodium.

**Reference**

**Comment**

Tsuji, S., Y. Tonogai, Y. Ito, and S. Kanoh. 1986. The Influence of Rearing Temperatures on the Toxicity of Various Environmental Pollutants for Killifish (*Oryzias latipes*). J. Hyg. Chem./Eisei Kagaku 32(1):46-53. (A: 12497)

All tests used a species that is not resident in North America.

Turnbull, H., J.G. DeMann, and R.F. Weston. 1954. Toxicity of Various Refinery Materials to Fresh Water Fish. Ind. Eng. Chem. 46:324-333.

No results for calcium, magnesium, potassium, or sodium sulfate.

Turoboyski, L. 1960. Attempt to Determine the Influence of High Doses of some Chemical Compounds upon Carp Fry. Roczn. Nauk Roln. 75B(3):401-445. (A: 2540)

No test results are acceptable because all tests were for six hours at high concentrations.

Umezu, T. 1991. Saponins and Surfactants Increase Water Flux in Fish Gills. Bull. Jpn. Soc. Sci. Fish. (Nippon Suisan Gakkaishi). 57(10):1891-1896. (A: 7136)

No results for calcium, magnesium, potassium, or sodium sulfate.

Van Horn, W.M., J.B. Anderson, and M. Katz. 1949. The Effect of Kraft Pulp Mill Wastes on Some Aquatic Organisms. Trans. Amer. Fish. Soc. 79:55-63. (A: 663)

67 mg/L killed some emerald and/or spotfin shiners in 120 hr in stabilized Fox River water, but the quality of the test material and the dilution water is unknown.

Van Horn, W.M., J.B. Anderson, and M. Katz. 1950. TAPPI 33:209-212.

CS requested this.

Wallen, I.E., W.C. Greer, and R. Lasater. 1957. Toxicity to *Gambusia affinis* of Certain Pure Chemicals in Turbid Waters. Sewage Ind. Wastes 29(6):695-711. (A: 508)

Even if they cannot be used in the calculation of a SMAV, the 96-hr LC50s of >11,000 and >30000 mg/L imply that the mosquitofish is not sensitive to sulfate.

Wang, W.X., and N.S. Fisher. 1996. Assimilation of Trace Elements by the Mussel <i>Mytilus edulis</i> : Effects of Diatom Chemical Composition. <i>Mar. Biol.</i> 125:715-724. (A: 7332)	No toxicity test results.
Wang, W. 1986. Toxicity Tests of Aquatic Pollutants by Using Common Duckweed. <i>Environ. Pollut. (Ser. B)</i> 11(1):1-14. (A: 11789)	All tests were with duckweed.
<b><u>Reference</u></b>	<b><u>Comment</u></b>
Wells, M.M. 1915. The reactions and resistance of fishes in their natural environment to salts. <i>Jour. Exp. Zool.</i> 19:243-283.	All tests were preference-avoidance tests in tanks with gradients.
Wheeler, A.E., R.A. Zingaro, K. Irgolic, and N.R. Bottino. 1982. The Effect of Selenate, Selenite, and Sulfate on the Growth of Six Unicellular Marine Algae. <i>J. Exp. Mar. Biol. Ecol.</i> 57:181-194. (A: 58895)	All tests were with saltwater algae.
Williams, J.E. 1948. The Toxicity of Some Inorganic Salts to Game Fish. MS Thesis, Louisiana State University, Baton Rouge, LA.	CS requested this.
Wright, A. 1976. The Use of Recovery as a Criterion for Toxicity. <i>Bull. Environ. Contam Toxicol.</i> 15(6):747-749. (A: 5558)	No results for calcium, magnesium, potassium, or sodium sulfate.
Yamane, A.N., M. Okada, and R. Sudo. 1984. Inhibitory Effects of Laundry Detergents on the Growth of Freshwater Algae. <i>Suishitsu Odaku Kenkyu</i> 7(9):576-528. (A: 9715)	All tests were with algae.
Young, R.T. 1923. Resistance of Fish to Salts and Alkalinity. <i>Amer. Jour. Physiol.</i> 63:373-388.	No test results are acceptable because the methods used were unusual.

**Exhibit P:** Sulfate toxicity data from research conducted by Dr. Soucek.

Common Name	Scientific Name	Acute Value (mg/L)	Chloride (mg/L)	Ca-Mg ratio (weight)	Hardness (mg/L)	Reference
Water flea	<i>Ceriodaphnia dubia</i>	2,526	10	2.33	100	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,357	10	2.33	100	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,526	10	2.33	102	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,223	15	2.33	92	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,243	15	2.33	94	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,402	15	2.33	94	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,470	20	2.33	94	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,295	20	2.33	94	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,494	20	2.33	94	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,153	25	2.33	100	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,563	25	2.33	96	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	1,868	25	2.33	96	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,799	25	2.33	96	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,458	25	2.33	96	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,357	100	2.33	96	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,784	100	2.33	96	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,112	100	2.33	104	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	1,895	300	2.33	98	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	1,798	300	2.33	102	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,049	300	2.33	102	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	1,400	500	2.33	96	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	1,933	500	2.33	98	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	1,157	500	2.33	94	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,030	1.9	1.46	94	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	1,868	1.9	1.46	94	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,269	1.9	1.46	94	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,538	34	5.4	107	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,607	34	5.4	107	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,436	34	5.4	107	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	3,059	1.9	1.46	194	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,706	1.9	1.46	194	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	3,265	1.9	1.46	194	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,383	1.9	1.46	288	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	3,361	1.9	1.46	288	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	2,853	1.9	1.46	288	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	3,297	1.9	1.46	288	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	3,369	1.9	1.46	390	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	3,073	1.9	1.46	390	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	3,091	1.9	1.46	390	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	3,716	1.9	1.46	484	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	3,506	1.9	1.46	484	Soucek 2004
Water flea	<i>Ceriodaphnia dubia</i>	3,338	1.9	1.46	484	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,785	33	2.33	96	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,865	33	2.33	100	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,749	33	2.33	96	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,919	100	2.33	98	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,833	100	2.33	100	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	2,062	100	2.33	100	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,739	300	2.33	98	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,614	300	2.33	96	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,721	300	2.33	100	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,435	500	2.33	98	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,503	500	2.33	100	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,472	500	2.33	100	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	2,030	25	2.33	106	Soucek 2004
Amphipod	<i>Hyalalella azteca</i>	1,919	25	2.33	100	Soucek 2004



Common Name	Scientific Name	Acute Value (mg/L)	Chloride (mg/L)	Ca-Mg ratio (weight)	Hardness (mg/L)	Reference
Amphipod	<i>Hyalella azteca</i>	1,615	25	2.33	98	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	2,057	25	2.33	102	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	2,655	25	2.33	194	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	2,076	25	2.33	192	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	2,887	25	2.33	196	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	2,189	25	2.33	296	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	3,358	25	2.33	292	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	2,978	25	2.33	292	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	2,612	25	2.33	392	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	4,026	25	2.33	396	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	4,314	25	2.33	396	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	4,234	25	2.33	486	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	4,320	25	2.33	482	Soucek 2004
Amphipod	<i>Hyalella azteca</i>	3,825	25	2.33	482	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	1,857	1.9	1.46	89	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	2,069	1.9	1.46	81	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	2,633	1.9	1.46	83	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	2,278	33	5.4	89	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	2,122	33	5.4	96	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	2,671	1.9	2.33	274	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	2,509	1.9	2.33	285	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	3,025	33	1.46	90	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	2,582	33	1.46	87	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	2,343	33	1.46	94	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	3,139	1.9	1.46	274	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	2,712	1.9	1.46	264	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	2,297	1.9	1.46	195	Soucek 2004
Fingernail clam	<i>Spherium simile</i>	2,082	1.9	1.46	191	Soucek 2004
Fatmucket	<i>Lampsilis siliquoidea</i>	3,377	25	2.33	100	Soucek 2005
Fatmucket	<i>Lampsilis siliquoidea</i>	3,525	25	2.33	300	Soucek 2005
Fatmucket	<i>Lampsilis siliquoidea</i>	3,729	25	2.33	500	Soucek 2005
Fatmucket	<i>Lampsilis siliquoidea</i>	1,727	5	1.46	100	Soucek 2005
Fatmucket	<i>Lampsilis siliquoidea</i>	1,822	33	1.46	100	Soucek 2005

**Exhibit V:** Maximum allowable concentrations of sulfate at various concentrations of hardness and chloride calculated from equations proposed as water quality standards. Italicized values are numerical standards that apply under corresponding hardness and chloride concentrations. Values represent the concentration of sulfate not to be exceeded at any time dependent of specified water chemistry.

		Hardness (mg/L)										
		<100	100	150	200	250	300	350	400	450	500	>500
Chloride (mg/L)	0-5	500	500	500	500	500	500	500	500	500	500	500
	5	500	515	703	891	1080	1268	1456	1644	1832	2020	2000
	10	500	691	879	1067	1256	1444	1632	1820	2008	2196	2000
	15	500	867	1055	1243	1432	1620	1808	1996	2184	2372	2000
	20	500	1043	1231	1419	1608	1796	1984	2172	2360	2549	2000
	25	500	1164	1343	1522	1701	1880	2059	2238	2417	2596	2000
	50	500	1141	1320	1499	1678	1857	2036	2215	2394	2573	2000
	100	500	1093	1272	1451	1630	1809	1988	2167	2346	2525	2000
	150	500	1046	1225	1404	1583	1762	1941	2120	2299	2478	2000
	200	500	998	1177	1356	1535	1715	1894	2073	2252	2431	2000
	250	500	951	1130	1309	1488	1667	1846	2025	2204	2383	2000
	300	500	904	1083	1262	1441	1620	1799	1978	2157	2336	2000
	350	500	856	1035	1214	1393	1572	1751	1930	2109	2288	2000
400	500	809	988	1167	1346	1525	1704	1883	2062	2241	2000	
450	500	762	941	1120	1299	1478	1657	1836	2015	2194	2000	
500	500	714	893	1072	1251	1430	1609	1788	1967	2146	2000	
>500		<i>302.208g</i>	<i>302.208g</i>	<i>302.208g</i>	<i>302.208g</i>	<i>302.208g</i>	<i>302.208g</i>	<i>302.208g</i>	<i>302.208g</i>	<i>302.208g</i>	<i>302.208g</i>	<i>302.208g</i>

---

## Iowa's Water Quality Standard Review: Total Dissolved Solids

### 1. Background

Total Dissolved Solids (TDS) is a measure of all constituents dissolved in water. The inorganic anions dissolved in water include carbonates, chlorides, sulfates and nitrates. The inorganic cations include sodium, potassium, calcium and magnesium.

Prior to 2004 rule making efforts, several NPDES permittees have noted that Iowa's long standing Total Dissolved Solids (TDS) numerical criteria of 750 mg/l was inconsistent with current toxicity information. The criterion was listed as one of the General Water Quality Criteria that are applicable to all waters. Data that was provided by permittees indicated that warm water aquatic species are tolerant of a more relaxed TDS level.

During 2004, the Department conducted rule making to revise the TDS criteria and adopt chloride criteria for aquatic life protection. The rule package received considerable opposition from environmental groups and the regulated communities. As a result, the EPC adopted a site-specific approach for TDS as an interim criterion to replace the old 750 mg/L general criteria and rejected the proposed chloride criteria. The intent of the site-specific approach is to gather information based on recommendations made by the EPC, as specified in ARC 3281B, published in the April 14, 2004, Iowa Administrative Bulletin. The Department was requested to utilize the information gathered during the three-year period to propose a new standard.

The purpose of this issue paper is to recommend replacing the interim site-specific TDS general standard with numerical specific ion criteria for chloride and sulfate based on new toxicity testing information. The justification for the revision is based on the evidence that the TDS toxicity is caused by specific ions. As a result, specific ion criteria are better indicators than the integrative parameters such as TDS, conductivity and salinity for water quality protection.

### 2. The Current Interim TDS Site-Specific Approach

The interim 2004 TDS site-specific approach became effective on June 16<sup>th</sup>, 2004 and was approved by EPA on December 6<sup>th</sup>, 2004. The interim 2004 TDS site-specific approach is a general water quality criterion applies to all waters of the state and is listed in IAC 61.3(a)"g" as follows:

*g. Acceptable levels of total dissolved solids (TDS) and constituent cations and anions will be established on a site-specific basis. The implementation approach for establishing the site-specific levels may be found in the "Supporting Document for Iowa Water Quality Management Plans," Chapter IV, July 1976, as revised on June 16, 2004.*

The implementation procedure of the site-specific TDS approach is discussed on pages 40 and 41 of the *Supporting Document for Iowa Water Quality Management Plans*. Appendix A includes the implementation procedure of the site-specific TDS approach.

Based on the site-specific TDS approach for point sources that discharge directly into a general use stream (undesignated), a facility's discharge that causes the in-stream TDS concentration to be above 1000 mg/L, would require acute toxicity tests to demonstrate that the discharge will not result in toxicity to aquatic life at an in-stream concentration greater than 1,000 mg/L. This demonstration consists of collecting a sample of the discharge and having a laboratory perform a whole effluent toxicity (WET) test. The results would be used to establish an effluent limit for TDS that will be included in an NPDES permit.

For point sources that discharge directly into a designated stream, the site-specific TDS approach allows the Department to establish a site-specific TDS effluent limit following a demonstration that the discharge will not result in toxicity to aquatic life at an effluent concentration for TDS and/or its constituent chloride that could result in an in-stream level higher than threshold levels. The in-stream threshold level for TDS is 1,000 mg/L. The in-stream threshold levels for chloride are 860 mg/L and 230 mg/L (equivalent to the 1988 304(a) criteria), as the acute and chronic threshold values respectively. This demonstration consists of collecting a sample of the discharge and having a laboratory perform a whole effluent toxicity (WET) test (both acute and chronic WET tests are required if both acute and chronic thresholds are exceeded in the receiving stream). The results will be used to establish an effluent limit for TDS that will be included in an NPDES permit.

### 3. Literature Review on TDS Toxicity Data

The purpose of this review was to examine relevant published literature and other scientific reports to determine the best approach for the development of specific TDS criteria and/or ion specific criteria for the State of Iowa.

Mount *et al.* (1997) states that the toxicity of fresh waters with high dissolved solids has been shown to be dependent on the species ionic composition of the water. Integrative parameters such as conductivity, TDS, or salinity are not robust predictors of toxicity for a range of water qualities. Mount *et al.* (1997) developed regression models to predict the toxicity attributable to major ions such as  $K^+$ ,  $HCO_3^-$ ,  $Mg^{2+}$ ,  $Cl^-$ , and  $SO_4^{2-}$ . The study found that the presence of multiple cations tended to be less toxic than comparable solutions with only one cation. Also, as the hardness increases, TDS toxicity may decrease. The regression models provided highly accurate predictions for *Ceriodaphnia dubia* toxicity, but overpredict the toxicity for *Daphnia magna* and fathead minnows.

Weber-Scannell and Duffy (2007) states that TDS causes toxicity through increases in salinity, changes in the ionic composition of the water, and toxicity of individual ions. Increases in salinity have been shown to cause shifts in biotic communities, limit biodiversity, exclude less-tolerant species, and cause acute or chronic effects at specific

life stages. Changes in the ionic composition of water can exclude some species while promoting population growth of others. Concentrations of specific ions may reach toxic levels for certain species of life history stages. The research paper states that it is recommended that different limits for individual ions, rather than TDS, be used for salmonid species.

The paper also states that a water quality standard for TDS can take several approaches: 1) The standard can be set low enough to protect all species and life stages exposed to the most toxic ions or combination of ions; 2) The standard can be set to protect most species and life stages for most ions and combinations of ions; or 3) Different limits can be defined for different categories of ions or combinations of ions, with a lower limit during fish spawning, if salmonid species that have been shown to be sensitive to TDS during fertilization and egg development are present. Approach (1) may be unnecessarily restrictive, although simpler to define and implement. Approach (2), although less restrictive, may lead to adverse effects to aquatic communities. Approach (3) is more complicated to define and would require that the potential discharger determine the composition of the effluent and which species and life stages are present downstream of the effluent. Overall, Approach (3) would provide the greatest protection to aquatic species and the least unnecessary restriction to potential dischargers.

McCulloch et al. (1993) states that depending on the discharge situation, effluent toxicity due solely to TDS may be less of a regulatory problem, due to rapid dilution below toxic levels and the absence of human health or biomagnification concerns.

Chapman et al. (2000) studied TDS toxicity with two mine effluents to early life stages of rainbow trout and chironomid larvae. The toxicity tests were conducted with synthetic effluents formulated to match the ionic composition of each mine discharge. No toxicity was observed at >2000 mg/l of TDS with embryos or developing fry, but chironomids exhibited effects above 1100 mg/l of TDS (NOAECs were 1134 mg/l and 1220 mg/l for the two effluents). Chapman et al. (2000) indicated that the toxicity related to the ions in TDS is due to the specific combination and concentration of ions and is not predictable from TDS concentrations.

Hoke et al. (1992) studied the potential effects of alkalinity on cladocera. The test results indicate that the toxicity of  $\text{HCO}_3^-$  to *D. magna* might be the inhibition of the active uptake of  $\text{Cl}^-$  from water. The study also suggest that pore water alkalinity should be considered when interpreting the results of sediment pore water and effluent toxicity tests with *D. magna*, other cladocerans, and perhaps, other invertebrates and fish.

The United States Environmental Protection Agency (US EPA) currently does not have a national criterion for TDS. According to Dr. Zipper (2007), to date, 27 states have enacted a state-specific and or watershed specific criterion; however, target TDS levels and the designated uses they are intended to protect vary greatly from state to state. For example, Alaska has a criteria of 1,000 mg/L TDS to protect aquatic life throughout the state; Mississippi has a criteria of 750 mg/L monthly average for protection fish, wildlife and recreation criteria, and Illinois has a 1,500 mg/L TDS criteria supporting designated

use of secondary contact and indigenous aquatic life standards (Illinois EPA is in the process of removing TDS and replace it with sulfate standard). Water quality TDS concentrations are highly dependent on flow conditions. TDS criteria for the protection of aquatic life have only been developed in 15 of the 27 states. The lowest TDS criteria found for the protection of aquatic life was in the state of Oregon, which uses a standard of 100 mg/L for all freshwater streams and tributaries in order to protect aquatic life, public water use, agriculture, and recreation purposes. Oregon also allows the criteria in individual streams or watersheds to be increased when approved by the Oregon Division of Environmental Quality.

The impact of aberrant levels of ions differs markedly with the ion in question as well as the organism being tested. Some ions,  $\text{Ca}^{2+}$  and  $\text{K}^{+}$  for example, cause significant acute toxicity when they are deficient in the exposure media, while other ions appear to have demonstrable effects only at excess levels (API, 1999). The Colorado Department of Public Health and Environment has prepared a draft of its "Whole Effluent Toxicity Permit Implementation Guidance Document" that specifically addresses TDS as a toxicant. Permittees can follow the procedures to identify and address toxicity due to TDS ions. If the acute WET test is passed using *Daphnia magna* (which is more tolerant than *C. dubia* to TDS ions), then the permittee may request a permit amendment to change WET test species. If *D. magna* cannot tolerate the elevated TDS, or if the required test is chronic, permittees may be required to conduct an Aquatic Impairment Study (AIS) of the receiving stream. Following the AIS, WET tests may be modified to switch or remove TDS. Additional mitigation measures also may be needed.

A similar approach is used in Texas. If testing shows that the primary cause of toxicity is TDS ions, the State will evaluate, or require the permittee to evaluate, the use of an alternative test species or modified test protocol. If TDS is not coming from source water, the permittee may conduct a biological study to evaluate instream impacts. The evaluation should follow USEPA's Rapid Bioassessment Protocols. The *in situ* evaluation of aquatic communities via impairment studies can be important because laboratory WET caused by TDS ions does not necessarily reflect adverse impacts in receiving waters.

Goodfellow W.L. et al. (2000) indicate that cost-effective waste treatment control options for a facility whose effluent is toxic because of TDS or specific ions are scarce at best. However, depending on the discharge situation, TDS toxicity may not be viewed with the same level of concern as other toxicants. These discharge situations often do not require the conservative safety factors that other toxicants do. Regulatory solutions to ion imbalance toxicity when no other toxicants are present may include modifications to the site-specific exposure through discharge modification, use of alternative models (e.g., dynamic models), exposure-specific toxicity tests, or alternate mixing zones for TDS or specific ions.

The State of Illinois currently has a general use standard of 1000 mg/l for TDS, a sulfate standard of 500 mg/l, and a chloride standard of 500 mg/l for aquatic life protection. Illinois EPA is in the process of rule making to replace the TDS standard with numerical

sulfate standard (Illinois EPA, 2006). Illinois EPA states that the chloride standard of 500 mg/l is thought to be protective of aquatic life toxicity. No change is proposed for the chloride standard at this time. The Illinois EPA states that the existing TDS standard has always been ungainly since it is really based on a worst-case combination of minerals being present. The specific constituents of the mineral contents of water are better regulated individually. The Illinois EPA has recommended that the TDS standard be deleted from the Board regulations.

After reviewing available sulfate toxicity data, Illinois EPA determined more reliable toxicity data for additional invertebrate species were needed. Dr. David Soucek of the Illinois Natural History Survey was contracted to conduct the laboratory toxicity testing. Acute toxicity of sulfate to five invertebrate species was conducted. These organisms were the water flea *Ceriodaphnia dubia*, a previously tested organism used as a gauge for comparison purposes, *Hyalella azteca*, an amphipod, *Chironomus tentans*, a midge fly, *Sphaerium simile*, a fingernail clam, and *Lampsilis siliquoidea*, a freshwater mussel. The new toxicity data on sulfate clearly shows a relationship between sulfate toxicity and water chemistry parameters, namely chloride and hardness. It is believed that chloride and hardness influence the toxicity of sulfate to aquatic invertebrates due to alterations in osmoregulation. Invertebrates achieve ionic balance with surrounding water through active transport, an energy requiring activity. At intermediate chloride and higher hardness concentrations, ionic balance in the presence of elevated sulfate concentrations is achieved rather easily. At low chloride and higher hardness concentrations, osmoregulation is increasingly difficult, resulting in utilization of energy stores in an attempt by the organism to achieve ionic balance. High levels of chloride increase sulfate toxicity as well, primarily through increasingly unbalanced osmotic conditions.

Because sulfate toxicity is dependent on chloride and hardness concentrations, these water quality characteristics must be taken into consideration when setting a standard throughout the state. For example, a statewide numeric standard for sulfate may be sufficiently protective in one stream, but underprotective in another depending on water chemistry. To adequately protect aquatic organisms from sulfate throughout the state, it is important that chloride and hardness be considered on a site by site basis. By creating an equation that relates sulfate toxicity to chloride and hardness, these two values can be measured in a water body and entered into the equation to determine the maximum amount of sulfate allowable for that water body.

#### **Summary of Literature Review:**

The TDS concentration that causes adverse effects varies substantially with the ion composition. For example, the TDS lethal concentration that causes 50% mortality for an invertebrate species (*Ceriodaphnia dubia*) during 48-hour tests ranges from 390 mg/l to over 4,000 mg/l depending on the ion composition. Studies have shown that, in general, for freshwaters the relative ion toxicity was  $K^+ > HCO_3^- = Mg^{2+} > Cl^- > SO_4^{2-}$ .  $Ca^{2+}$  and  $Na^+$  did not produce significant toxicity.

One of the difficulties in developing TDS criteria is that there are no national criteria or toxicity database available.

Since TDS toxicity depends on the ion composition, it is recommended that different limits for individual ions, rather than TDS, be used. The State of Illinois is in the process of rule making that replaces the TDS criterion of 1000 mg/l with sulfate criteria (a chloride criterion of 500 mg/l is already in the rules). The challenge is what specific ion criteria should be used to replace TDS. Among the potentially most toxic ions,  $K^+$ ,  $HCO_3^-$ ,  $Mg^{2+}$ ,  $Cl^-$  and  $SO_4^{2-}$ , the effluent concentrations for the first three ions are usually relatively low. Also, the toxicity data for these ions are scarce. The only national criterion available for ions is chloride. It is possible the TDS criteria could be replaced with chloride and sulfate ion criteria. This is the approach that State of Illinois is taking with the EPA Region 5 support.

#### **4. Justification for Replacing TDS Standard by Specific Ion Criteria**

##### **A. Implementation Issues with the Interim TDS Site-Specific Approach**

The current site-specific TDS approach uses the Whole Effluent Toxicity (WET) test results to develop a numeric effluent limitation for TDS, a particular pollutant. WET testing is designed to measure the toxicity of the whole effluent including synergistic and antagonistic interactions of pollutants. It is not designed to measure the toxicity of a single pollutant in a sample.

Since the adoption of the site-specific TDS approach, there are several issues with the implementation process:

1. Chronic testing with *Ceriodaphnia* has shown inconsistent testing results for the same discharge. The chronic testing would pass at 100% effluent concentration and fail at a lower TDS concentration (higher dilution).
2. A facility does not know at the time it collects an effluent sample what the concentrations of various pollutants are in that sample as the Department requires the toxicity test to start no later than 36 hours after sample collection. However, the lab typically does not have the analytical results for that sample prior to starting the toxicity test. This has resulted in a number of cases where the toxicity test is completed only to find that the concentration of TDS in the test sample was significantly less than the highest TDS concentration measured in the discharge. In these cases, the toxicity test results cannot be used to establish a permit limit. There have been other cases where the concentration of ammonia or chlorine was high enough that the measured toxicity was likely due to one of these pollutants rather than TDS.
3. There are currently no laboratories certified by the State of Iowa to perform chronic toxicity testing. There are only 5 laboratories certified by the State of Iowa to perform acute toxicity testing and only one of these is located in Iowa.
4. The lack of laboratory capability has resulted in facilities having to schedule a test with the laboratory as much as 3-6 months before the test will actually be



performed. This is especially problematic for a controlled discharge lagoon that cannot know whether conditions will be right for discharge 3-6 months in advance. Controlled discharge lagoons only discharge every 6 months.

5. The current approach can cause difficulties for new facilities and for facilities that operate seasonally (e.g. parks, campgrounds, children's camps). If the first toxicity test does not produce valid or useful data there is a considerable delay before another test can be performed.
6. We often require facilities to change their operations such as increasing the number of cycles in order to collect the highest sample TDS concentration to be used to establish a TDS limit. The condition at which the samples are collected does not represent the normal operating conditions.
7. Variability among WET testing results is significant.

After EPA approved the interim site specific TDS approach on December 6, 2004, the Department started to implement the adopted standard. Since December 7, 2004, the Department has received TDS toxicity test data from approximately 70 facilities. All 70 facilities conducted acute toxicity tests. Chronic toxicity test data was submitted by 33 of the facilities. In general, the toxicity test data is relatively scattered. The highest TDS concentration that passed an acute toxicity test is 5,098 mg/L, and the lowest TDS concentration that passed the acute test is 325 mg/L. The highest chloride concentration that passed the acute test is 1200 mg/L and the lowest chloride concentration that passed the acute test is 14 mg/L. For chronic tests, the highest and lowest TDS concentrations that passed the chronic tests are 1980 mg/L and 29 mg/L, respectively. The highest and lowest chloride concentrations that passed the chronic tests are 930 mg/L and 5 mg/L, respectively. The summary table is shown below.

Table 1. Summary of TDS/Cl Toxicity Test Data Submitted by Facilities in Iowa

Chemicals		Concentration	
		Acute Test Passed (mg/L)	Chronic Test passed (mg/L)
TDS	Max.	5,098	1,980
	Min.	325	29
Chloride	Max.	1,200	930
	Min.	14	5.0

These testing data show significant variability in the WET results from facility to facility. It is fairly difficult to draw any meaningful conclusions from these data. It is even more challenging to derive a TDS limit from the uncertain toxicity testing results. Several TDS toxicity testing results showed pollutant sources other than TDS were the possible sources for the failure of the toxicity testing, especially those tests failed at relatively low TDS levels.

## B. Lack of Scientific Support

Total dissolved solids (TDS) is a term used to describe the combination of all dissolved inorganic or organic ions or molecules in water, and often consists of a complex mixture of cations such as sodium, calcium, magnesium, and anions including chloride and

sulfate. While these ions are present in most freshwater systems, at elevated concentrations they are potentially toxic to aquatic life. Currently, there are no federal water quality criteria for TDS for the protection of aquatic life.

The IDNR research into existing ion concentrations in Iowa waters found that of the common substances comprising the major portion of total dissolved solids, toxicity is always associated with either sulfate or chloride. Sodium, calcium, magnesium and carbonates make up the other ions in the majority, but these are not sufficiently toxic to create the need for individual water quality standards. Simply put, if sulfate and chloride, alone or in combination, meet the proposed standards, toxicity from the other major ions comprising "total dissolved solids" is insignificant. Therefore, TDS concentration provides no additional useful information. The existing standard is cumbersome and results in restrictions where none should exist. For example, if the sulfate water quality standard for a water body was calculated to be 2,000 mg/L under a certain level of hardness and chloride (340 mg/L and 50 mg/L, respectively), the total dissolved solids concentration of that solution would be greater than 2,100 mg/L without adding the sodium that is associated with the sulfate and chloride. Obviously, a TDS standard of 1,000 mg/L is incapable of indicating the concentrations of dissolved substances that are harmful to aquatic life in this example. In another example, where chloride is 5 mg/L and hardness is 90 mg/L, the sulfate standard is 500 mg/L. Here, a 1,000 mg/L TDS standard may be under protective.

Natural waters consist of numerous ionic constituents which, under the direct influence of many natural (from geologic formations) and anthropogenic (from industrial and municipal wastewater discharges, agricultural run-off, sediments, etc.) sources, may become elevated to levels toxic to aquatic life (Mount et al. 1997). Because the toxicity of the collective ionic constituents in surface waters is complex and dependent upon the concentrations of individual cations and anions and their relative proportions in a surface water matrix, integrative measures of ionic constituents such as specific conductance, total dissolved solids (TDS) and salinity have typically been used to assess toxicity to aquatic life. Unfortunately, these integrative measures of ionic composition are typically not robust predictors of toxicity for a range of water quality characteristics despite a highly significant correlation between the integrative measure and toxicity in some waters (Mount et al. 1997). Therefore, as indirect measures of the presence of inorganic dissolved solids such as chloride, bicarbonate, nitrate, sulfate, phosphate, sodium, magnesium, calcium, potassium and iron, specific conductance, TDS, and salinity have only been used as indicators of water pollution, and not as the basis for ambient water quality criteria. As such, there are no federal water quality criteria for specific conductance, TDS or salinity for the protection of aquatic life. Among the various individual ionic constituents in surface water, potassium, bicarbonate, sodium, magnesium, chloride and sulfate are most significant in terms of toxicity (Mount et al. 1997). For example, EPA has a recommended Clean Water Act 304(a) criterion for chloride (USEPA 1988), and at least two states (Illinois and Minnesota) have developed aquatic life criteria for sulfate (Soucek and Kennedy 2005).

### **C. Protection of Designated Uses by Individual Ion Criteria**

### **Aquatic Life Uses**

According to CFR131.11, States must adopt those water quality criteria that protect the designated use. Such criteria must be based on sound scientific rationale and must contain sufficient parameters or constituents to protect the designated use. For waters with multiple use designations, the criteria shall support the most sensitive use.

Since the start of the site-specific TDS standard implementation, the TDS sample data submitted by point sourced discharge facilities have shown that elevated TDS is often caused by high chloride and/or sulfate. The adoption of the numerical standard of chloride and sulfate for aquatic life protection will ensure that the resident species in Iowa waterbodies are protected. Thus, the TDS general criteria as an integrative component, becomes unnecessary.

After March 22, 2006 WQS rule, almost all waterbodies are classified as designated uses. Only a very limited number of waterbodies will remain as general use. The general use narrative criteria will still apply to these waterbodies, including that no discharge should cause acutely toxic conditions.

### **Livestock Watering Uses**

The current site-specific TDS standard includes specific ion guideline values for the protection of livestock watering. Since the implementation of the interim site-specific standard, only sulfate concentrations are occasionally elevated to raise concern. For chloride, the numerical criteria will be more stringent than livestock watering guideline values. Other ion concentrations are usually below the guideline values and do not cause potential concerns. Thus, to protect the livestock watering, the sulfate livestock watering guideline will remain, but will be replaced with a different value based on new research data.

Therefore, between the chloride and sulfate water quality standards and the narrative general criteria (IAC 61.3(2)) that regulates any discharged substance that could cause toxicity, there is no need for a TDS standard.

### **D. TDS/Chloride Monitoring Study**

In 2005, the Iowa Water Pollution Control Association, wastewater facilities from across Iowa, the Iowa DNR – Water Quality Bureau, and the Iowa DNR – Water Monitoring and Assessment Program conducted a cooperative study to monitor point source outfalls and receiving streams mainly for total dissolved solids and chloride. The study also analyzed several other common ions such as sulfate, ammonia nitrogen and phosphorous. This study was conducted to accurately and objectively assess the ion and total dissolved solid (TDS) concentrations in the outfalls of point source facilities across Iowa, upstream of outfalls, and downstream of outfalls. Sampling for this study occurred under low-flow conditions, when the impact of point source outfalls on receiving streams is the greatest.

This data collection effort was initiated in order to satisfy a recommendation from the Iowa Environmental Protection Commission to IDNR to prepare an economic analysis as part of the development of TDS and chloride standards.

There were two phases to the data collection for the project: a pilot study and a full study. Samples for the pilot study were collected during late winter at low-flow conditions (February 21 through March 6, 2005). A total of 21 wastewater dischargers participated in this 2-week pilot study. For the full study, samples were collected from 100 facilities. The one hundred facilities in the study were selected based on the associated municipal drinking water TDS and hardness levels, nature of the wastewater treated, type of treatment process, geographic location and receiving stream characteristics. The selected facilities represent a subset of Iowa wastewater dischargers that could potentially be affected by the proposed TDS and chloride water quality standards.

The study did not show a significant difference between effluent 24-hour composite samples and effluent grab samples for TDS and chloride. The data analysis seems to show that the effluent TDS and chloride levels are quickly diluted below the threshold values (TDS < 1000 mg/L, chloride < 230 mg/L) by the stream flow beyond the mixing zone under the sampling conditions. Table 2 shows a summary of effluent ion concentrations for the point sources discharges participated in the full study. More details can be found in the TDS and Chloride Study Report (IDNR, 2007).

In addition to the special TDS/chloride study, the DNR through its Ambient Monitoring Program has monitored a network of streams statewide on a monthly basis since 2000 to assess ambient stream quality conditions, identify regional differences, and determine trends in water quality. Included in the list of parameters analyzed are several ions and TDS. The number of stream sites sampled has varied from 80 to 84 from 2000 through 2007. This data set provides an indication of what typical ion and TDS concentrations are for Iowa streams. Table 3 shows a summary of TDS, chloride, sulfate and hardness values for the Iowa ambient monitoring data from 2000-2007. These monthly monitoring data represent different stream flow conditions.

Table 2. Effluent Ion Concentrations from Full Chloride Study

Parameter	Unit	# of samples	Min Value	Percentile					Max Value	Average
				10th	25th	50th	75th	90th		
Calcium	mg/l	131	27.6	44.7	60.4	79.7	117.5	152.0	869.0	101.0
Chloride	mg/l	244	20.4	87.7	179.5	371.5	604.0	756.4	8800.0	458.0
Fluoride	mg/l	244	0.5	0.5	0.5	0.5	0.5	0.7	7.7	0.6
Magnesium	mg/l	131	6.2	16.5	23.0	33.6	44.9	56.8	388.0	38.0
Nitrate-N	mg/l	244	1.0	1.0	1.0	3.0	15.0	22.1	125.0	11.4
Nitrite-N	mg/l	244	0.5	0.5	0.5	5.0	12.5	12.5	50.0	6.5
Phosphate	mg/l	244	2.0	2.0	2.3	3.4	5.0	10.0	36.4	5.7
Potassium	mg/l	131	5.0	8.7	11.5	15.7	21.7	40.5	84.5	20.2
Sodium	mg/l	131	26.4	64.6	140.0	240.0	357.0	500.0	5280.0	307.8
TDS	mg/l	244	392.0	553.6	856.3	1285.0	1885.0	2417.0	15600.0	1488.0
Sulfate	mg/l	244	2.5	46.3	64.4	168.0	345.5	448.0	801.0	211.1

Table 3. TDS and Ion Concentrations in Iowa Streams

Chemicals	Iowa Ambient Monitoring Data from 2000-2007, units in mg/L		
	50 <sup>th</sup> percentile	90 <sup>th</sup> percentile	Maximum value
TDS	360	510	1,640
Chloride	23	40	170
Sulfate	37	97	400
Hardness (as CaCO <sub>3</sub> )	300	410	820

The effluent monitoring data show that chloride and sulfate are the anions could potentially contribute to high effluent TDS levels. The ambient monitoring data indicate that that point source contributions of TDS, chloride and sulfate could dilute quickly downstream of the discharge after mixing. There is no significant impact on overall surface water quality downstream of the discharges. However, numerical criteria for specific ions such as chloride and sulfate are necessary to prevent near-field toxicity.

#### E. Measures to Reduce TDS Concentrations

Measures to reduce TDS discharges range from source reduction (low cost) to treatment technologies (high cost). Alternative implementation approaches to assess compliance are dependent on the criteria that are proposed, but could include toxicity testing and flow-variable limits. Current treatment technologies available for TDS include the following:

- Source reduction: may not be feasible in some cases
- Reverse osmosis technology: costly, need to determine how to handle the waste stream

- Thermo method: evaporation, costly
- Chemical precipitation: usually used for metals
- Integrated membrane/recycling methods: the final solids are removed by a crystallizer and the effluent used results in zero discharge.

TDS reduction should start from control in order to prevent TDS from entering the water system in the first place. This may be difficult to achieve since Iowa has relatively hard ground water. If source reductions are not possible, technological advancements may be required to remove TDS. The most widely used TDS removal technique is reverse osmosis, including single reserve osmosis operation, and integrated membrane/recycling methods. The latter are mostly used in the pilot test phase. All other methods are either relatively new, in the research stage, or only apply in specific sites and settings. Research on measures to reduce TDS in wastewater discharge shows that cost-effective technology to treat TDS is very limited.

## 5. Recommendations for Specific Ion Criteria

As the literature review indicates, integrative parameters such as TDS, conductivity and salinity are not robust predictors of toxicity for a range of water qualities. Since individual ions contribute to the TDS toxicity, specific ion criteria are better indicators than TDS for water quality protection.

Because of the better understanding of major ion toxicity, IDNR is proposing to delete the existing TDS standard (a threshold of 1,000 mg/l) from the current regulations, and to replace it with specific ion standards.

Based on the examination of available effluent ion analysis and literature review, the TDS site-specific approach may be replaced with specific ion criteria for chloride and sulfate. There is a national criterion available for chloride that was published in 1988. Since then, new toxicity data have become available. The proposed chloride criteria will be recalculated based on the national toxicity database and new toxicity data. The proposed chloride criteria are summarized in the chloride criteria review.

Mount *et al.* (1997) developed regression models to predict the toxicity attributable to major ions such as  $K^+$ ,  $HCO_3^-$ ,  $Mg^{2+}$ ,  $Cl^-$ , and  $SO_4^{2-}$ . The toxicity of  $Na^+$  and  $Ca^{2+}$  salts was primarily attributable to the corresponding anion and they are not identified as toxic by themselves. Monitoring data for effluents and ambient waters in Iowa show that the anions of chloride and sulfate could be elevated to raise concern for designated use protection.

For chloride, the numerical criteria will be updated using additional toxicity testing data performed in September of 2008 by EPA contractors in addition to the toxicity data in the 1988 304(a) criteria as well as the new toxicity data from the most recent literature review. For sulfate, the Illinois approach will be used. The proposed chloride and sulfate criteria are summarized in the chloride and sulfate criteria work element reports, respectively.

The recommended specific ion criteria for chloride and sulfate are based on the most up-to-date toxicity data and are scientifically defensible. In addition, Mount et al. (1997) found that the presence of multiple cations ameliorate the toxicity of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{K}^+$ . The increase in hardness also reduces the toxicity of these ions. The laboratory toxicity tests are usually conducted using moderately hard water that has hardness below 100 mg/L as  $\text{CaCO}_3$ . However, the median hardness for Iowa streams is 300 mg/L as  $\text{CaCO}_3$ . Both chloride and sulfate criteria will be hardness dependent in order to take into account for site-specific Iowa water conditions.

---

**Appendix A: TDS Site-Specific Approach Standard Implementation**

Total Dissolved Solids: Total Dissolved Solids (TDS) numerical criteria will be determined by applying a site specific approach for the protection of Iowa's surface waters and their specified uses. The site specific approach would first consider a guideline value of 1000 mg/l (TDS) as a threshold in-stream level at which negative impacts may begin to occur to the uses of the receiving stream. (Note, for some unusual situations where sensitive in-stream uses occur or where uses are sensitive to the ion composition of the TDS, a more restrictive guideline value may be warranted.) Sources of TDS potentially elevating a receiving stream above 1000 mg/l (TDS) would be required, upon application for a discharge permit or permit renewal, to clearly demonstrate that their discharge will not result in toxicity to the receiving stream.

The following represents the site-specific requirements to demonstrate compliance with the narrative criteria and defined uses noted in the Water Quality Standards.

1. Passage of a Whole Effluent Toxicity Test – Each source discharging TDS that may potentially elevate a receiving stream above 1000 mg/l (TDS) will be required to complete and pass an acute or an acute and chronic Whole Effluent Toxicity (WET) test with the results submitted to the Department with the application for discharge permit or permit renewal. The WET test shall be conducted using EPA approved test procedures.
  - For dischargers directly entering a Class B designated water body, acute and chronic WET tests will be conducted using a mixed combination of effluent and receiving stream water. For the acute WET test, the mixed combinations will be in the proportion of the effluent flow to 2.5 % of the natural one-day, ten-year low flow (1Q10) or protected flow or the results of a site-specific zone of initial dilution stream study. For the chronic WET test, the mixed combinations will be in the proportion of the effluent flow to 25 % of the natural seven-day, ten-year low flow (7Q10) or protected flow or the results of a site-specific mixing zone stream study.
  - For dischargers directly entering a water body classified only as a General Water of the state, an acute WET test will be conducted using 100% of the effluent flow.
2. Submit a chemical analysis of the WET test water for selected cations and anions, including Calcium, Magnesium, Potassium, Sodium, Chloride, Sulfate and Iron. Also to be included is the Total Dissolved Solids contained in the test sample. The concentration for specific ions will be evaluated to determine if exceedances occur to defined uses. Potential threshold levels where impacts to uses may occur are noted in the following Table.



**Recommended Water Quality Guidelines for Protecting Defined Uses**

Ions	Recommended Guidelines Values* (mg/l)
Calcium	1000
Chloride	1500
Magnesium	800
Sodium	800
Sulfate	1000
Nitrate+Nitrite-N	100

\* Based on the guidelines for livestock watering.

3. The protection of the defined uses requires application of the ion guidelines as 'end-of-pipe' limits in general waters. In designated waters, the guideline values would be met at the boundary of the mixing zone.

## **Appendix B: Definitions**

**TDS:** Total Dissolved Solid (TDS) is a measurement of inorganic salts, organic matter and other dissolved materials in water. The amount of TDS in a water sample is measured by filtering the sample through a 2.0 µm pore size filter, evaporating the remaining filtrate and then drying what is left to a constant weight at 180°C.

**NOAEC:** is the highest tested concentration of an effluent or a toxicant at which no adverse effects are observed on the aquatic test organisms at a specific time of observation. Determined using hypothesis testing.

**LC50:** Lethal Concentration that is the point estimate of the toxicant concentration that would be lethal to 50% of the test organisms during a specific period, usually 96 hours or 48 hours.

**IC25:** The inhibition concentration that is a point estimate of the toxicant concentration that would cause a 25% reduction in a nonlethal biological measurement of the test organisms, such as reproduction or growth.

## REFERENCES

Iowa Department of Natural Resources (IDNR) – Water Monitoring and Assessment Section. March 2007. Monitoring of Point Source Outfalls and Receiving Streams for Common Ions and Total Dissolved Solids. Cooperative Study Report by IWPCA, Wastewater Facilities across Iowa and Iowa DNR.

Mount, D.R., D.D. Gulley, J.R. Hockett, T.D. Garrison, and J.M. Evans. 1997. Statistical models to predict the toxicity of major ions to CERIODAPHNIA DUBIA, DAPHNIA MAGNA AND PIMEPHALES PROMELAS (FATHEAD MINNOWS). *Environ. Toxicol. Chem.* 16(10): 2009-2019.

Weber-Scannell, P.K., and L.K. Duffy. 2007. Effects of total dissolved solids on aquatic organisms: a review of literature and recommendation for Salmonid Species. *American Journal of Environmental Sciences.* 3(1): 1-6.

McCulloch, W.L., W.L. Goodfellow and J.A. Black. 1993. Characterization, identification and Confirmation of Total Dissolved Solids as Effluents Toxicants. In J.W. Gorsuch, F.J. Dwyer, C.J. Ingersoll, and T.W. LaPoint, eds. *Environmental Toxicology and Risk Assessment: 2<sup>nd</sup> Volume*. STP 1216. American Society for Testing and Materials, Philadelphia, PA, USA. Pp. 213-227.

Chapman, P.M., H.B. Bailey, and E. Canaria. 2000. Toxicity of Total Dissolved Solids Associated With Two Mine Effluents to Chironomid Larvae and Early Life Stages of Rainbow Trout. *Environmental Toxicology and Chemistry*, Vol. 19(1), pp. 210-214.

Hoke, R.A., W.R. Gala, J.B. Drake, and J.P. Giesy. Bicarbonate as a Potential Confounding Factor in Cladoceran Toxicity Assessments of Pore Water from Contaminated Sediments. 1992. *Can. J. Fish. Aquat. Sci.* 49: 1633-1640.

Goodfellow, W. L., L. W. Ausley, D. T. Burton, D. L. Denton, P. B. Dorn, D. R. Grothe, M. A. Heber, T. J. Norberg-King, AND J. H. Rodgers Jr. The Role Of Inorganic Ion Imbalance In Aquatic Toxicity Testing. *Environmental Toxicology And Chemistry* 19(175-182), (2001).

William L. Goodfellow, Lawrence W. Ausley, Dennis T. Burton, Debra L. Denton, Philip B. Dorn, Donald R. Grothe, Margarete A. Heber, Teresa J. Norberg-King, and John H. Rodgers, Jr. 2000. Major Ion Toxicity In Effluents: A Review with Permitting Recommendations. *Environmental Toxicology and Chemistry.* 19(1), pp. 175-182.

Zipper, C.E. and R.J. Berenzweig. March 2007. Total Dissolved Solids in Virginia Freshwater Streams: A Report to Virginia Department of Environmental Quality (Draft). Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

API. April 1999. The Toxicity of Common Ions to Freshwater and Marine Organisms. Health and Environmental Sciences Department, API Publication Number 4666. Prepared by Pillard D.A., J.R. Hockett, and D.R. DiBona.

Illinois Environmental Protection Agency. April 2006. Preliminary Technical Justification for Changing Water Quality Standards for Sulfates, Total Dissolved Solids and Mixing Zones.

## **Update on Dunkard Creek November 23, 2009**

**Louis Reynolds, Fisheries Biologist**

**USEPA Region 3  
Environmental Analysis and Innovation Division  
Office of Monitoring and Assessment  
Freshwater Biology Team**

This is an interim report on the aquatic life kill in Dunkard Creek and the investigation into the cause of the kill. Our findings at this time are preliminary. We are still learning about the ecology of the alga *Prymnesium parvum* in this region and are investigating its distribution. We will continue to make more information available as we learn of it.

### **Background**

The Dunkard Creek watershed drains approximately 180 square miles in Monongalia County in West Virginia and Greene County in Pennsylvania (WVDEP 2009). Dunkard Creek has Forks in both states and forms from the confluence of the West Virginia Fork and the Pennsylvania Fork just upstream of Brave, PA. The stream flows along the Mason Dixon Line crossing back and forth between the states until it leaves West Virginia near Buckeye Church, WV, flowing northeast toward Mount Morris, PA and then further toward its confluence with the Monongahela River.

The kill on Dunkard Creek included fish, salamanders, and mussels and began on or about September 1 (Table 1). In general, the kill has been described as massive and, in terms of mussels, complete. The kill on Dunkard Creek spans approximately 43 miles of stream (different mileages have been seen in different accounts of this kill because early in the kill, the zone was restricted to Prentice, WV, but continued to work its way upstream and downstream from there throughout the kill).

On September 9, we investigated the kill on Dunkard Creek. We collected in situ measurements of pH, dissolved oxygen, conductivity, and temperature at ten sites (D1-D10) and water samples for metals, nutrients and mining constituents at 4 sites (D4, and D8-10). Our investigation was centered on the Blacksville #2 discharge in the WV Fork of Dunkard Creek.

During the rest of September the West Virginia Department of Environmental Protection (WVDEP), West Virginia Department of Natural Resources (WVDNR), Pennsylvania Department of Environmental Protection (PADEP), and Pennsylvania Fish and Boat Commission (PAFBC) continued to sample the creek. We are currently compiling this data in a central database and hope to construct a more complete timeline of the kill.

**Table 1. Rough timeline of Dunkard Creek kill.** This kill has been investigated by WVDNR, WVDEP Regional and Charleston offices, PAFBC, PADEP Southwest Regional Office, and USEPA Wheeling Freshwater Biology Team.

August 28 –WVDNR reports high conductivity in Dunkard Creek. The conductivity may or may not have been higher at an earlier point in time. Also, we don't know how long it was at 50,000 uS

Sept 4 – Preliminary investigations by WVDNR on mussel and fish kills in Pentress, WV

Sept 4 – October 1 – WVDNR investigates kill at 44 sites and 22 observation days

Sept 4 - WVDEP samples water at 4 sites and conductivity at 31 sites

Sept 8 - 11 – WVDNR and PAFBC on site evaluating fish and mussel kill

Sept 9 – USEPA samples in situ water chemistry at 10 sites and collects water samples at 4 sites

Sept 9-18 – PFBC samples fish kill at numerous sites in PA. USEPA assisted on Sept 10

Sept 10 – PADEP samples at five sites in Dunkard Creek

Sept 13 -14 – WVDEP (Brad Swiger) sampling in Dunkard Creek

Sept 15 – PADEP samples five sites in Dunkard Creek

Sept 18 – WVDEP fly over in helicopter investigating kill

Sept 20 – USEPA and WVDEP sample algae at 6 sites in watershed

Sept 23 – WVDEP samples algae at 6 sites in watershed

Sept 30 – USEPA meets with WVU, PADEP, WVDEP

Oct 19 – WVDNR electrofishing survey at selected sites in basin

Oct 26 – CONSOL Energy, Inc. (CONSOL) reports finding golden algae in a sample collected from Whitely Creek on September 29, 2009.

## **Cause of the Fish Kill**

We now know that a substantial bloom of the golden algae *Prymnesium parvum* was present in Dunkard Creek at the time of the kill. This identification has been confirmed by experts from North Carolina, South Carolina, Florida, and Oklahoma. This saltwater alga produces a potent toxin that is capable of killing fish, mussels, and salamanders. This toxin affects gill breathing organisms and is not toxic to humans, waterfowl, or livestock (Sager et al. 2008).

*P. parvum* is found worldwide and is most common in saltwater (Sager et al. 2008). It is an invasive saltwater alga now being found in brackish (both natural and anthropogenic) inland waters and has been documented in many states (Figure 1). Since its discovery in Texas in 2001, *P. parvum* blooms have killed over 30 million fish in 33 water bodies (Sager et al. 2008).

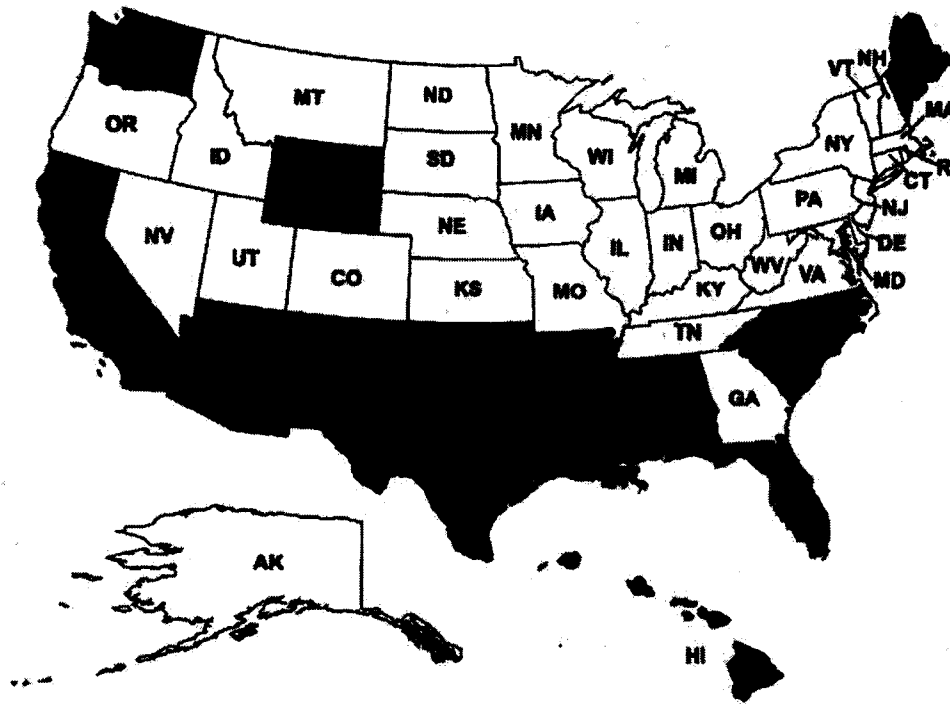


Figure 2. The states of the United States with golden alga presence reported (in dark shading).

Figure 1. Distribution of *P. parvum* in the United States (Sager et al 2008).

There are a number of factors that influence blooms of *P. parvum*:

1. *P. parvum* is a saltwater algae and blooms are associated with increased salinity (Baker et al. 2009, Sager et al. 2008, Rodgers, In Press). Blooms in Texas are limited to Central and Western Texas where natural conditions and brines associated with oil production produce saline water bodies.
2. Research has shown that the toxin produced by this algae is dependant upon the availability of cations (e.g.,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in the surrounding water. At higher pH, more cations are available for the formation of toxin. It has been noted in Texas that in waterbodies with a pH <7, fish kills do not occur despite the presence of the algae (Sager et al., 2008).
3. *P. parvum* is a mixotroph and can get its energy through photosynthesis when nutrients are sufficient. When nutrients are limited, however, it can produce toxins to kill other organisms and feed from their nutrients.
4. *P. parvum* has been found in a range of waters with TDS levels from 1000 – 100,000 mg/l TDS, and experts believe an optimum TDS range is 3000-60,000 mg/l. So, although it is a brackish water algae, it can survive in waters with relatively low TDS levels.
5. *P. parvum* competes with native algae and the saline conditions that favor *P. parvum* are stressful for its freshwater competitors.

The bloom on Dunkard Creek was noted first by a WVDEP fly-over on September 18, more than two weeks after the fish kill was discovered. Inspectors from WVDEP noticed the water was discolored and stained over the entire length of Dunkard Creek and this staining originated at a beaver dam in the headwaters of the West Virginia Fork of Dunkard Creek. This beaver pond is upstream of the Blacksville #2 mine, but downstream of another outfall from CONSOL's St. Leo Mine. WVDEP staff suspected the coloration was caused by an algal bloom. We, along with WVDEP, sampled six sites on Dunkard for algae on September 20, 2009. WVDEP subsequently sampled the week following.

Preliminary results (Table 2) show that the algae were found in sufficient numbers to produce toxin (Dr. Carmello Tomas, associate professor of biological sciences at the University of North Carolina-Wilmington). Dr. Tomas ran an Erythrocyte Lysis assay to assess the toxicity of the samples. This assay measures the percent hemolysis of erythrocytes as a measure of the toxicity of the algae (the algae produces a hemotoxin). In general he found that the areas with the highest conductivity were most impacted. Dr. Tomas reported the results to WVDEP in an email dated September 29, 2009.

**Table 2. Preliminary Results from University of North Carolina-Wilmington Laboratory.** Cells/ml is a measure of the number of algal cells in a ml. of sample. Percent hemolysis is a measure of the percent of lysed blood cells when compared to a control.

Sample	Cells/mL	% Hemolysis Cells
WANA	345,320	95.9
MDP	242,300	91.1
WTL	304,600	93.6
UMR	102,200	—
DBP	94,600	—
UBD	460	—

According to counts the densities were

1. WANA (*bridge at Wana, WV ~RM38*)
2. WTL (*beaver dam wetland ~RM20*)
3. MDP (*Mason Dixon Park ~RM44*)
4. UMR (*Upstream of Miracle Run ~RM34*)
5. DBP (*Downstream of beaver dam ~RM43*)
6. UBD (*upstream of beaver dam ~RM45*)

For hemolytic analyses the top three are in order.

Algal cell densities found by Dr. Tomas at WANA and at MDP were high enough to produce a toxic effect (as evidenced by the assay). These cell densities are high compared to other blooms that have been noted as toxic (Rodgers, In Press).



We have also been working with researchers at the University of Oklahoma Biological Station Plankton Ecology Lab. They are currently doing a genetic analysis that may determine the source of the algae and are also assessing the toxin levels.

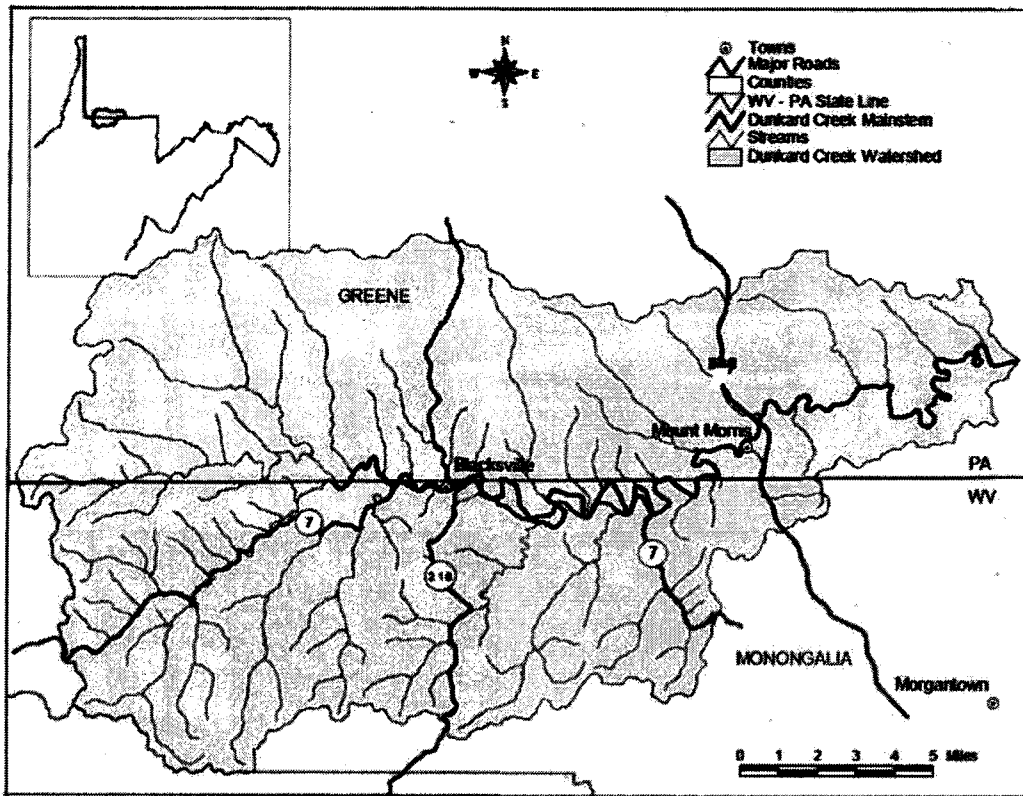
WVDEP sent fish organs to a fish pathologist with the USGS (Dr. Vicki Blazer). Her preliminary findings report organ damage consistent with a toxin.

Given what has been seen in other states and the etiology of this kill, we believe the toxin from this algae bloom led to the kill of fish, mussels, and salamanders on Dunkard Creek. At this time, we do not know where the algae originated. The elevated conductivity in the creek likely created favorable conditions for this alga to grow and produce toxin. This alga is not known to grow or produce toxin at the natural levels of TDS in Dunkard Creek (<280 mg/l).

## **Stressors in Dunkard Creek**

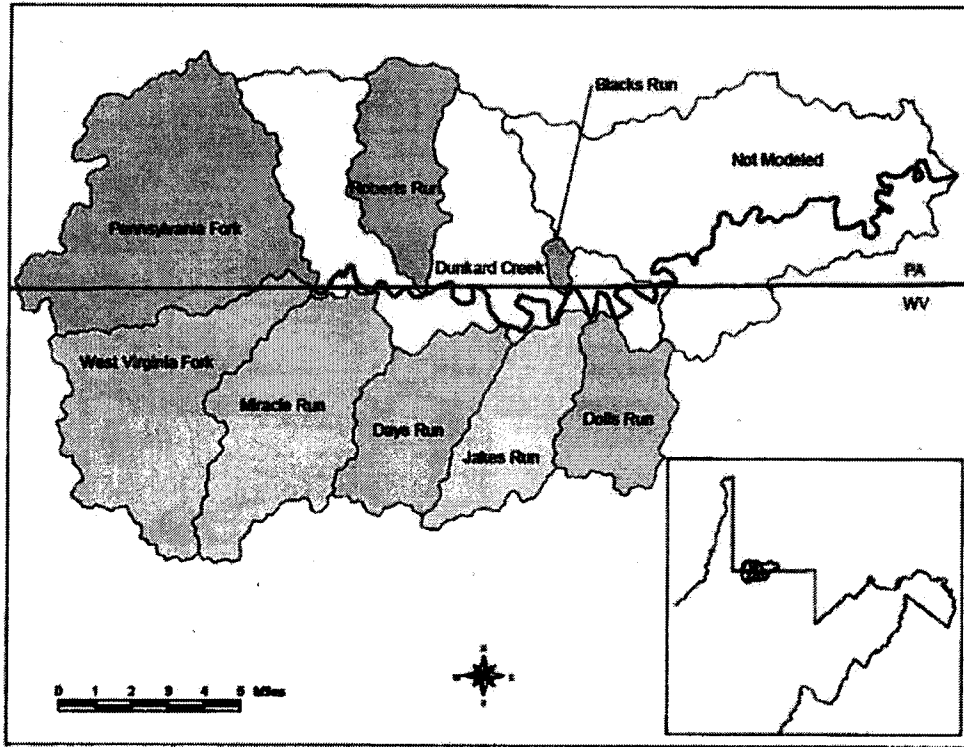
### **WVDEP's 303(d) List and TMDLs**

Elevated TDS and component ions (e.g., chloride, sulfate, magnesium, bicarbonate) are toxic to aquatic life and chronic exposure to high TDS leads to aquatic life use impairment (Pond et al. 2008). The level of TDS in Dunkard Creek during the time of the kill was many times higher than levels known to cause aquatic life use impairment. A major component of the TDS in Dunkard Creek is chloride, which is a pollutant with an EPA chronic criterion of 230 mg/L and an acute criterion of 860 mg/L (published in 1988). WVDEP adopted these criteria into its water quality standards. Many stream reaches in the Dunkard Creek watershed (Figures 2 and 3) are currently on the 303(d) list for impairments to aquatic life (Table 3), and EPA recently approved WVDEP's Total Maximum Daily Loads (TMDLs) for Dunkard Creek for some stressors (WVDEP 2009).



**Figure 3-1. Location of the Dunkard Creek watershed**

**Figure 2. General Location of Dunkard Creek Watershed (WVDEP 2009).**



**Figure 3-2. Dunkard Creek TMDL watersheds**

**Figure 3. TMDL Watersheds of Dunkard Creek (WVDEP 2009).**

Table 3. Reach impairments and stressors that have TMDLs developed for Dunkard Creek and its tributaries (WVDEP 2009).

Table 3-3. Waterbodies and impairments for which TMDLs have been developed

Subwatershed	Stream Name	NHD Code	Fe	Cl	FC	BIO
Dunkard Creek	Dunkard Creek	WV-ML-128	x		x	x
Dolls Run	Dolls Run	WV-ML-128-AC	X		x	x
Dolls Run	Pedlar Run	WV-ML-128-AC-4	X		x	x
Dolls Run	UNT/Pedlar Run RM 1.20	WV-ML-128-AC-4-B	X		x	
Dolls Run	Smoky Drain	WV-ML-128-AC-5	X		x	x
Dolls Run	Berry Hollow	WV-ML-128-AC-6	X			
Jakes Run	Jakes Run	WV-ML-128-AE	X		x	x
Jakes Run	UNT/Jakes Run RM 5.5	WV-ML-128-AE-12	X		x	
Jakes Run	UNT/Jakes Run RM 2.33	WV-ML-128-AE-4			x	
Blacks Run	Blacks Run	WV-ML-128-AF	X			x
Dunkard Creek	Hackelbender Run	WV-ML-128-AG	X			
Days Run	Days Run	WV-ML-128-AJ	X		x	x
Dunkard Creek	UNT/Days Run RM 6.2	WV-ML-128-AJ-10	X			
Dunkard Creek	UNT/Days Run RM 7.3	WV-ML-128-AJ-12	X			
Dunkard Creek	Indian Camp Run	WV-ML-128-AJ-4	X			
Days Run	Shriver Run (ML-128-AJ-8)	WV-ML-128-AJ-8	x		x	x
Days Run	Building Run (ML-128-AJ-8-C)	WV-ML-128-AJ-8-C	X		x	
Days Run	UNT/Days Run RM 5.8	WV-ML-128-AJ-9	X		x	x
Dunkard Creek	UNT/UNT RM 0.89/Days Run RM 5.8	WV-ML-128-AJ-9-C	X			
Dunkard Creek	Kings Run	WV-ML-128-AP	X			
Roberts Run	Roberts Run	WV-ML-128-AR	X		x	
Miracle Run	Miracle Run	WV-ML-128-AV	X		x	
Miracle Run	Thomas Run	WV-ML-128-AV-1			x	
Miracle Run	Scott Run	WV-ML-128-AV-11			x	
Miracle Run	UNT/Miracle Run RM 5.50	WV-ML-128-AV-16	X			
Miracle Run	UNT/Miracle Run RM 6.55	WV-ML-128-AV-18	X			
Miracle Run	Right Branch/Miracle Run	WV-ML-128-AV-3	X		x	x
PA Fork Dunkard Creek	Pennsylvania Fork/Dunkard Creek	WV-ML-128-BA	X		x	
PA Fork Dunkard Creek	Brushy Fork	WV-ML-128-BA-12	X			
PA Fork Dunkard Creek	UNT/Pennsylvania Fork RM 8.2	WV-ML-128-BA-15	X			
PA Fork Dunkard Creek	UNT/Pennsylvania Fork RM 9.55	WV-ML-128-BA-18	X			
PA Fork Dunkard Creek	Pumpkin Run	WV-ML-128-BA-4	X			
WV Fork Dunkard Creek	West Virginia Fork/Dunkard Creek	WV-ML-128-BB	x	x	x	
WV Fork Dunkard Creek	Shriver Run (ML-128-BB-10)	WV-ML-128-BB-10	X			
WV Fork Dunkard Creek	Range Run	WV-ML-128-BB-13	X		x	x

Table 3. continued. Reach impairments and stressors that have TMDLs developed for Dunkard Creek and its tributaries (WVDEP 2009).

Subwatershed	Stream Name	NHD Code	Fe	Cl	FC	BIO
WV Fork Dunkard Creek	South Fork/West Virginia Fork/Dunkard Creek	WV-ML-128-BB-14	x	x	x	
WV Fork Dunkard Creek	Middle Fork/South Fork/West Virginia Fork/Dunkard Creek	WV-ML-128-BB-14-A			x	
WV Fork Dunkard Creek	UNT/South Fork RM 3.0/West Virginia Fork/Dunkard Creek	WV-ML-128-BB-14-F	X	x		
WV Fork Dunkard Creek	North Fork/West Virginia Fork/Dunkard Creek	WV-ML-128-BB-15	X		x	x
WV Fork Dunkard Creek	Camp Run	WV-ML-128-BB-15-B	X		x	x
WV Fork Dunkard Creek	Browns Run	WV-ML-128-BB-15-B-1	X			
WV Fork Dunkard Creek	Joy Run	WV-ML-128-BB-15-B-2	X			
WV Fork Dunkard Creek	Briar Run	WV-ML-128-BB-15-B-4	X			
WV Fork Dunkard Creek	Hughes Run	WV-ML-128-BB-3	X			
WV Fork Dunkard Creek	Wise Run	WV-ML-128-BB-9	X		x	x

Note:

UNT = unnamed tributary; RM = river mile.

CL indicates chloride impairment

FC indicates fecal coliform bacteria impairment

BIO indicates a biological impairment

**Table 4. Stressors on biologically impaired reaches of Dunkard Creek. WVDEP identified ionic stress as a stressor in some reaches of Miracle Run and the WV Fork of Dunkard (WVDEP 2009).**

**Table 4-1. Significant stressors of biologically impaired streams**

WVDEP Watershed	Stream Name	WVDEP Code	Biological Stressors	WVDEP's Standard
Dunkard Creek	Dunkard Creek	WV-ML-12B	Sedimentation Organic Enrichment	Total Iron Fecal Coliform
Dolla Run	Dolla Run	WV-ML-12B-AC	Sedimentation Organic Enrichment	Total Iron Fecal Coliform
Dolla Run	Podlar Run	WV-ML-12B-AC-4	Organic Enrichment Sedimentation	Fecal Coliform Total Iron
Dolla Run	Sneaky Drain	WV-ML-12B-AC-5	Organic Enrichment Sedimentation	Fecal Coliform Total Iron
Jakes Run	Jakes Run	WV-ML-12B-AE	Organic Enrichment Sedimentation	Fecal Coliform Total Iron
Shacka Run	Shacka Run	WV-ML-12B-AF	Sedimentation	Total Iron
Days Run	Days Run	WV-ML-12B-AJ	Organic Enrichment Sedimentation	Fecal Coliform Total Iron
Days Run	Shriver Run	WV-ML-12B-AJ-8	Organic Enrichment Sedimentation	Fecal Coliform Total Iron
Days Run	UNT/Days Run RM 3.8	WV-ML-12B-AJ-9	Organic Enrichment Sedimentation	Fecal Coliform Total Iron
Miracle Run	Miracle Run	WV-ML-12B-AV	Organic Enrichment Sedimentation Ionic Stress	Fecal Coliform Total Iron Ionic Strength (To remain on the 303d List)
Miracle Run	Shilling Run	WV-ML-12B-AV-15	Ionic Stress	Ionic Strength (To remain on the 303d List)
Miracle Run	Night Branch/Miracle Run	WV-ML-12B-AV-3	Organic Enrichment Sedimentation	Fecal Coliform Total Iron
WV Fork	West Virginia Fork/Dunkard Creek	WV-ML-12B-BB	Sedimentation Organic Enrichment Ionic Stress	Total Iron Fecal Coliform Ionic Strength (To remain on the 303d List)
WV Fork	Range Run	WV-ML-12B-BB-13	Organic Enrichment Sedimentation	Fecal Coliform Total Iron
WV Fork	South Fork/West Virginia Fork/Dunkard Creek	WV-ML-12B-BB-14	Ionic Stress Organic Enrichment Sedimentation	Ionic Strength (To remain on the 303d List) Fecal Coliform Total Iron
WV Fork	North Fork/West Virginia Fork/Dunkard Creek	WV-ML-12B-BB-15	Organic Enrichment Sedimentation	Fecal Coliform Total Iron
WV Fork	Camp Run	WV-ML-12B-BB-15-B	Organic Enrichment	Fecal Coliform
WV Fork	Wine Run	WV-ML-12B-BB-9	Organic Enrichment Sedimentation	Fecal Coliform Total Iron

We also reviewed chloride toxicity information compiled by the State of Iowa for development of its chloride criterion as well as results from Canada's Ministry of the Environment. The following data are from Canada's Ministry of Environment (<http://www.env.gov.bc.ca/wat/wq/BCguidelines/chloride/chloride.html>).

Figure 4 shows the percentage of aquatic organisms affected at certain chloride concentrations. Figure 5 shows acute and chronic data for all affected species, as well as a modeled response to longer term chronic exposures. Table 5 shows the 96 hr LC 50 (concentration that kills 50% of test organisms for tested species). An LC50 represents an acute endpoint, so these levels would not be protective to longer term chronic exposures nor do they reflect effects on chronic endpoints, such as biotic growth or reproduction. Chloride LC50 levels shown in Table 4 vary widely by species and in general, fish can, in the short term, tolerate high levels. In general, invertebrates tend to be more sensitive to elevated TDS than are vertebrates.

The situation in Dunkard Creek should be considered a chronic exposure since chloride levels were elevated above the criteria for long periods of time. Tables 6 and 7 report our field and laboratory chemistry results from our field visit on September 9, 2009. The chloride levels that WVDEP, PADEP, and USEPA sampled during the kill in the area of the kill were in the range of 4000 mg/L in the West Virginia Fork of Dunkard Creek below the Blacksville #2 discharge to 400 mg/L further downstream in mainstem Dunkard, and upstream of the discharge.

Other ions (sulfate and magnesium) and metals (selenium) were also found to be elevated instream on our September 9 field visit. These other ions are also contributing to the high dissolved solids load, ionic stress, and total ion toxicity. EPA does not have aquatic life criteria for sulfate and magnesium, or for ion mixtures, but does recognize the toxicity of these ions, both alone and in combination with other ions.

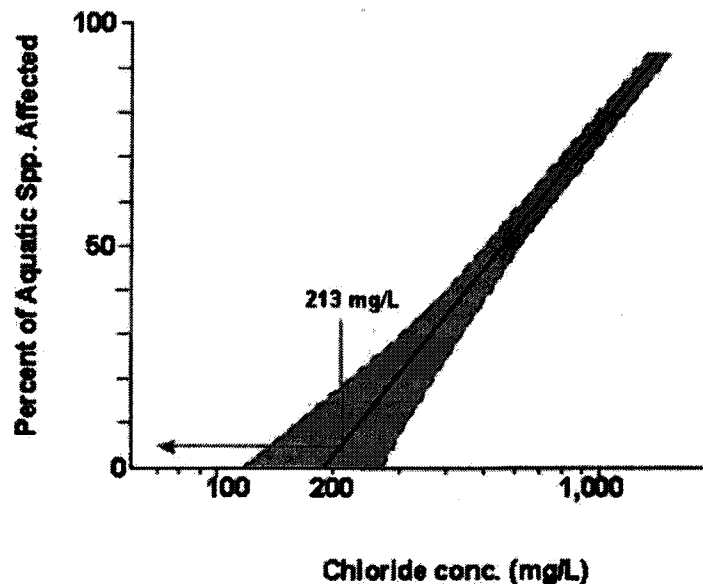


Figure 4. From (<http://www.env.gov.bc.ca/wat/wq/BCguidelines/chloride/chloride.html>) Aquatic life chronic species sensitivity distribution for chloride ion based on laboratory toxicity test data (adapted from Evans and Frick, 2000). The upper and lower 95% confidence interval are also shown. Source: Bright and Addison (2002).

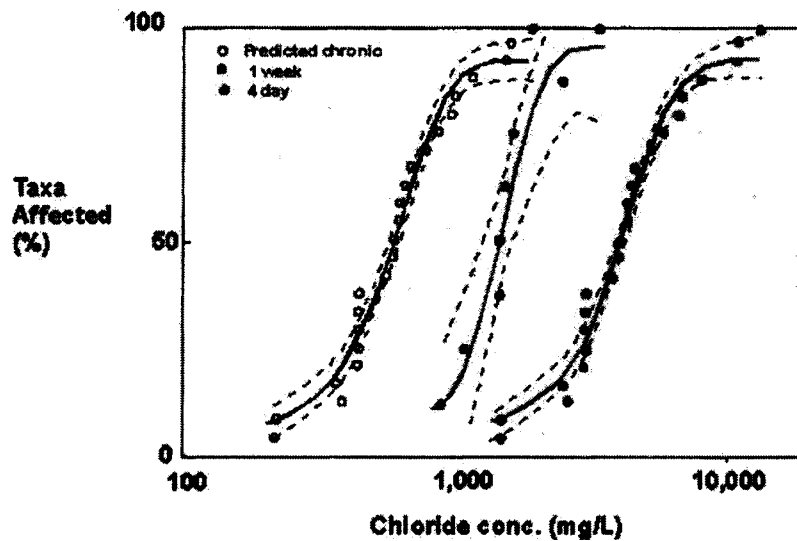


Figure 5. From <http://www.env.gov.bc.ca/wat/wq/BCguidelines/chloride/chloride.html> Predicted chronic and actual (4 day and one week) toxicity levels for aquatic life exposed to NaCl. (upper and lower 95% confidence intervals based on a log-logistic fit are shown). Source: Bright and Addison (2002).

Table 5. From <http://www.env.gov.bc.ca/wat/wq/BCguidelines/chloride/chloride.html>. Four-day LC<sub>50</sub>s of various taxa exposed to sodium chloride (adapted from Table 7-5 in Evans and Frick 2001 and Table B.6 in Bright and Addison 2002).

Species	Common Name	96 h LC <sub>50</sub> (mg Cl/L)	References
<i>Tubifex tubifex</i>	Tubificid worm	1 204	Khengarot, 1995
<i>Ceriodaphnia dubia</i>	Cladoceran	1 400	Cowgill and Milazzo, 1990
<i>Daphnia pulex</i>	Cladoceran	1 470	Birge et al., 1985
<i>Ceriodaphnia dubia</i>	Cladoceran	1 596	WI SLOH, 1995
<i>Daphnia magna</i>	Cladoceran	1 853	Anderson, 1948
<i>Daphnia magna</i>	Cladoceran	2 390	Arambasic et al., 1995
<i>Physa gyrina</i>	Snail	2 480	Birge et al., 1985
<i>Lirceus fontinalis</i>	Isopod	2 970	Birge et al., 1985
<i>Cirrhinius mrigalo</i>	Indian carp fry	3 021	Gosh and Pal, 1969
<i>Labeo rohoto</i>	Indian carp fry	3 021	Gosh and Pal, 1969
<i>Catla catla</i>	Indian carp fry	3 021	Gosh and Pal, 1969
<i>Daphnia magna</i>	Cladoceran	3 658	Cowgill and Milazzo, 1990
<i>Cricotopus trifascia</i>	Chironomid	3 795	Hamilton et al., 1975
<i>Chironomus attenatus</i>	Chironomid	4 026	Thorton and Sauer, 1972
<i>Hydroptilia angusta</i>	Caddisfly	4 039	Hamilton et al., 1975
<i>Daphnia magna</i>	Cladoceran	4 071	WI SLOH, 1995



<i>Limnephilus stigma</i>	Caddisfly	4 255	Sutcliffe, 1961
<i>Anaobolia nervosa</i>	Caddisfly	4 255	Sutcliffe, 1961
<i>Carassius auratus</i>	Goldfish	4 453	Adelman et al., 1976
<i>Pimephales promelas</i>	Fathead minnow	4 600	WI SLOH, 1995
<i>Pimephales promelas</i>	Fathead minnow	4 640	Adelman et al., 1976
<i>Lepomis macrochirus</i>	Bluegill	5 840	Birge et al., 1985
<i>Culex sp.</i>	Mosquito	6 222	Dowden and Bennett, 1965
<i>Pimephales promelas</i>	Fathead minnow	6 570	Birge et al., 1985
<i>Lepomis macrochirus</i>	Bluegill	7 864	Trama, 1954
<i>Gambusia affinis</i>	Mosquito fish	10 616	Wallen et al., 1957
<i>Anguilla rostrata</i>	American eel	10 900	Hinton and Eversole, 1978
<i>Anguilla rostrata</i>	American eel	13 085	Hinton and Eversole, 1978

Table 6. Field meter readings from USEPA sampling of Dunkard Creek on 9/9/09.

Site #	Location	Lat (WGS83)	Long (WGS83)	Temp (C)	Sp. Cond (us/cm)	DO (mg/l)	DO sat %	pH
D1	Dunkard Creek us Dolls Run	39.71386	80.11665	19.7	2257	8.67	95.3	8.28
D2	Dunkard Creek in Pentress, WV	39.71237	80.16134	20.1	2714	13.93	154.8	8.37
D3	Dunkard Creek in Blacksville, WV	39.72027	80.2084	19.5	3259	9.52	104.7	8.2
D4	Dunkard Creek ds Miracle Run	39.71949	80.24094	19.4	3911	8.85	97.3	8.13
D5	Dunkard Creek us Morris Run	39.73042	80.25139	20.67	5085	10.36	117.4	8.39
D6	Hoovers Run (trib to Dunkard)	39.72999	80.26601	18.8	770	8.64	92.8	8.45
D7	PA Fork Dunkard at T309 Bridge	39.722	80.27048	18.95	672	7.88	84.7	8.02
D8	WV Fork Dunkard ds Consol Outfall	39.72102	80.27453	21.93	18,570	13.45	165.8	8.17
D9	Consol Outfall 005 WV 0064602	39.71864	80.27777	22.64	25,250	8.34	105.3	8.55
D10	WV Fork Dunkard us Consol Outfall	39.71863	80.27785	20.62	4957	11.54	130.7	8.13

Table 7. Water chemistry parameters for 4 sites on Dunkard Creek.

Analyte	units	Upstream of	Downstream	OUTFALL	Upstream	Detection
		Miricle Run	of outfall	005	of outfall	
		D4	D8	D9	D10	
Aluminum	ug/L	47.6	45.4	57.6	135	30
Antimony	ug/L	U	U	U	U	2
Arsenic	ug/L	5	31.5	42.2	5.9	1
Barium	ug/L	80.2	47.2	U	93.3	10
Beryllium	ug/L	U	U	U	U	1
Cadmium	ug/L	U	U	U	U	1
Calcium	ug/L	111000	473000	71800	99500	5000
Chromium	ug/L	U	U	U	U	2
Cobalt	ug/L	1.2	2.2	3.4	U	1
Copper	ug/L	13.1	57.5	85.7	11.9	2
Iron	ug/L	205	451	2700	652	100
Lead	ug/L	U	U	U	U	1
Magnesium	ug/L	48500	229000	37700	32700	500
Manganese	ug/L	176	643	1290	601	15
Nickel	ug/L	9.2	24.7	32	7.3	1
Potassium	ug/L	8040	35800	55300	9550	2000
Selenium	ug/L	15.1	107	146	15.8	5
Silver	ug/L	U	U	U	U	1
Sodium	ug/L	786000	4040000	5780000	697000	10000
Thallium	ug/L	U	U	U	U	1
Hardness	ug/L	475000	2080000	3000000	383000	3300
Vanadium	ug/L	U	U	U	U	5
Zinc	ug/L	5.5	10.6	11.6	8.2	2
Chloride	mg/L	447	3740	6120	444	
Sulfate	mg/L	1360	6730	10800	1070	
Total						
Alkalinity	mg/L	162	86.2	41.6	180	20
Bicarb						
Alkalinity	mg/L	162	79.9	28.7	180	20
Carbonate						
Alkalinity	mg/L	U	U	U	U	20
Nitrite+Nitrate						
N	mg/L	1.8	1.08	1.07	U	0.01
TP Result	mg/L	0.076	<0.050	<0.050	0.092	

## Controlling the Algae Bloom

Once *P. parvum* is established in a watershed, it is difficult to eradicate and is essentially there to stay (Karen Glenn, personal comm., September 2009).

In freshwater systems, *P. parvum* toxicity is likely affected by TDS, specific cations (e.g. calcium and magnesium have been positively correlated to toxicity), temperature, nutrients, and freshwater algae, which compete with *P. parvum* for resources. Part of the problem with increasing TDS is that native algae are stressed and cannot compete with the growth of *P. parvum*.

Laboratory studies of *P. parvum* growth corroborate these correlations and interactions.

An unpublished study in Texas

(<http://www.tpwd.state.tx.us/landwater/water/environconcerns/hab/ga/workshop/media/kgugrens.pdf>) saw a decrease in growth with decreases in salinity. Baker et al. (2009) model an interaction of *Prymnesium* toxicity and phosphorous, temperature, and salinity, but conclude that these relationships may not hold at the lower salinities – the edge of the niche for *P. parvum*. The authors suggest that “(a) lower limit of salinity for population increase appears to lie between 0.5 and 1 g/L for (*P. parvum*)”.

While there has been some success in controlling blooms of *P. parvum* in aquaculture situations (Rodgers, In Press) using algaecides or nutrient additions, there has been no success in controlling them in large reservoirs or rivers and streams (Karen Glenn, personal communication, September 2009). Algaecides would be toxic to a large range of resident algae and other organisms and native algae. And under non-saline conditions, native algae can compete with *P. parvum*. Adding nutrients to ambient waters during low flows in the fall could likely result in depletion of dissolved oxygen and increase ammonia levels as well as export of nutrients to downstream waters, possibly causing or contributing to water quality standards violations downstream.

Because control of TDS is not an option in most of the affected areas in Oklahoma and Texas (as many of the affected waters are naturally brackish), controlling *P. parvum* blooms through the control of TDS has not been attempted there. We believe control of TDS on Dunkard Creek and other watersheds is the best solution to control *P. parvum* blooms. Lowering TDS and chlorides in the stream would also make it easier to restore the native fauna of Dunkard Creek and decrease the loading of TDS to the Monongahela River. A water quality criterion for TDS could be developed to protect aquatic life uses. We are currently working with USEPA HQ OST to develop an aquatic life advisory level for conductivity representative of the ion matrix in alkaline mine drainage (dominated by calcium, magnesium, sulfate, and bicarbonate). We hope these efforts can be extended to consider other ion matrices like Marcellus shale brines and coalbed methane brines that contain more chloride.

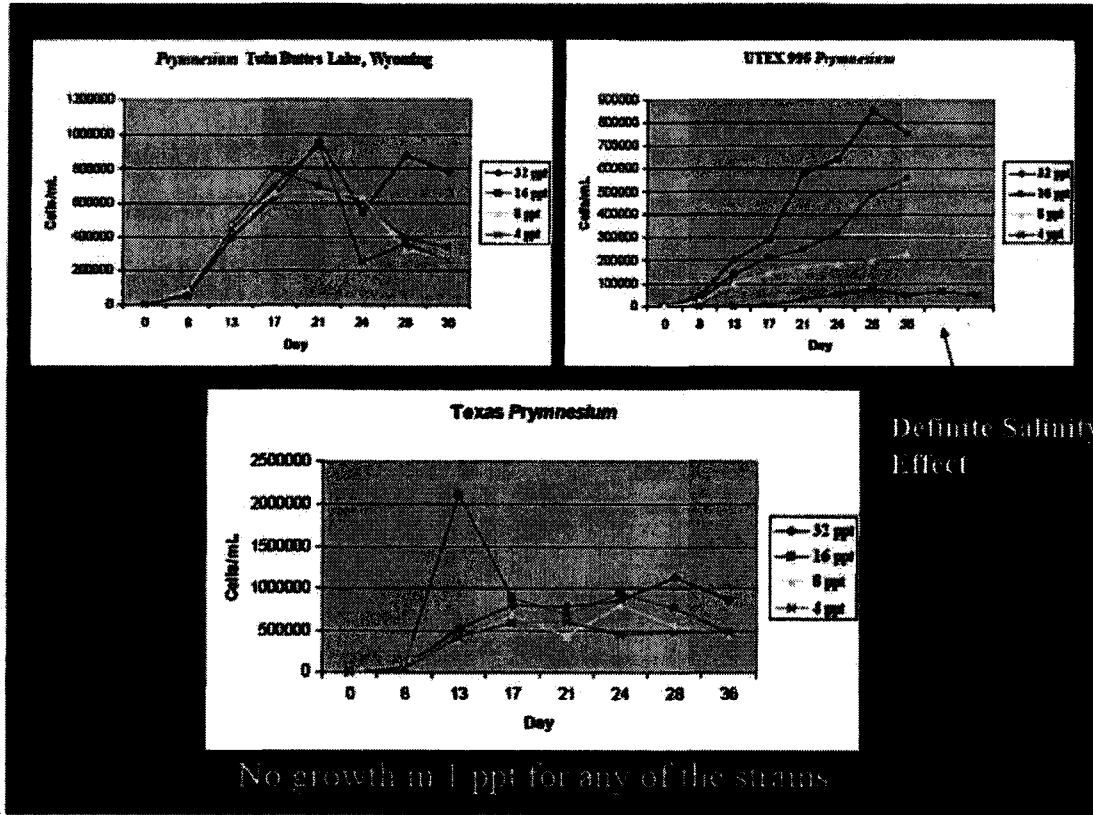


Figure 6. From <http://www.tpwd.state.tx.us/landwater/water/enviroconcerns/hab/ga/workshop/media/kugrens.pdf> showing decreased growth with decreased salinity.

## Implications for Other Waterbodies

The map presented in the beginning of this report shows that *P. parvum* has now increased its range and Dunkard Creek will serve as a source of *P. parvum* to other freshwater bodies in the region. On October 26, CONSOL reported finding golden algae in a sample collected from Whitely Creek (the adjacent watershed to the North of Dunkard Creek) on September 29, 2009. Many natural and anthropogenic vectors can spread the algae (birds, fishermen, industrial equipment, etc.) As the algae spreads, any stream with high ionic strength in excess of 750 uS could be at risk for a *P. parvum* bloom and associated fish kill.

WVDEP has since sampled *P. parvum* in 32 streams in WV with high TDS levels and we, along with the PADEP, sampled for *P. parvum* in 9 streams and 4 mainstem Monongahela River sites.

## References

Baker, Jason W, J.P. Grover, R. Ramachandranair, C. Black, T. W. Valenti, Jr., B. W. Brooks, and D. L. Roelke. Growth at the edge of the niche: An experimental study of the harmful alga *Prymnesium parvum*. *Limnology and Oceanography* 54(5), 2009, 1679–1687.

Glenn, Karen L., Research Scientist III, Laboratory Manager - Plankton Ecology Lab, University of Oklahoma Biological Station, September 2009.

Gregory J. Pond, M.E. Passmore, F.A. Borsuk, L. Reynolds, C.J. Rose. Downstream effects of mountaintop coal mining: comparing biological conditions using family- and genus-level macroinvertebrate bioassessment tools. *Journal of the North American Benthological Society* 2008, 27(3):717–737.

Rodgers, John, H. Comparison of three algaecides for controlling the density of *Prymnesium parvum*. In Press. *Journal of the American Water Resources Association*.

Sager, David, R., A Barkoh, D.L. Buzan, L.T. Fries, J.A. Glass, G.L. Kurten, J.J. Ralph, E.J. Singhurst, G.M. Southard, and E. Swanson. 2008. Toxic *Prymnesium parvum*: A potential threat to U.S. reservoirs. *American Fisheries Society Symposium* 62:261-273.

West Virginia Department of Environmental Protection. 2009. Total Maximum Daily Loads for Selected Streams in the Dunkard Creek Watershed, West Virginia Draft Report. 2009.

## Water Quality

### Ambient Water Quality Guidelines for Chloride

#### Overview Report

Prepared pursuant to Section 2(e) of the  
*Environment Management Act*, 1981

Original Signed by Margaret Eckenfelder  
Assistant Deputy Minister  
Water, Land and Air Protection  
April 24, 2003

---

Canadian Cataloguing in Publication Data  
Nagpal, N.K.

Ambient water quality guidelines for chloride

Prepared by N.K. Nagpal, D.A. Levy, and D.D. MacDonald.  
Cf. p.

ISBN

1. Water quality - Standards - British Columbia. 2. Chloride - Environmental aspects - British Columbia. I. British Columbia. Water, Air and Climate Change Branch. II. Title.

---

#### **Summary**

This document is one in a series that establishes ambient water quality guidelines for British Columbia (Table 1). This document is mainly based on a report prepared by the BC Ministry of Water, Land and Air Protection, BC Ministry of Transportation and Highways, BC Buildings Corporation and the Canadian Association of Petroleum Producers (Bright and Addison 2002), and a background report prepared for the Canadian Priority Substance List 2 Assessment of the toxicity of the application of road salt to the aquatic environment (Evans and Frick 2001). The guidelines for chloride set forth in this document are intended to protect drinking water, recreation and aesthetics, freshwater and marine aquatic life, agricultural water (irrigation and livestock watering) and wildlife uses. These guidelines are briefly described in the Section on Recommended Guidelines and are discussed in greater detail in the Appendix to the report.

[Top](#)

**Table 1. Recommended guidelines for chloride**

---

Water Use	Guideline (mg Chloride/L)
Drinking water	250
Recreation and Aesthetics	None
Freshwater Aquatic Life *	
<b>Maximum Concentration +</b>	600
<b>30-d Average Concentration ++</b>	150
Marine Life	Human activities should not cause the chloride of marine and estuarine waters to fluctuate by more than 10% of the natural chloride expected at that time and depth.
Irrigation	100
Livestock Watering	600
Wildlife	600

\* When ambient chloride concentration in the environment exceeds the guideline, then further degradation of the ambient or existing water quality should be avoided

+ Instantaneous maximums

++ Average of five weekly measurements taken over a 30-day period

The application of road salt for winter accident prevention is an important source of chloride to the environment, which is increasing over time due to the expansion of road networks and increased vehicle traffic. Road salt (most often sodium chloride) readily dissolves and enters aquatic environments in ionic forms. Although chloride can originate from natural sources, most of the chloride that enters the environment is associated with the storage and application of road salt. As such, chloride-containing compounds commonly enter surface water, soil, and ground water during snowmelt.

Chloride ions are conservative, which means that they are not degraded in the environment and tend to remain in solution, once dissolved. Chloride ions that enter ground water can ultimately be expected to reach surface water and, therefore, influence aquatic environments and humans. Among the species tested, freshwater aquatic plants and freshwater invertebrates tend to be the most sensitive to chloride. Recently, the Canadian government classified road salt as toxic under the *Canadian Environmental Protection Act* (1999).

[Top](#)

## Preface

The Ministry of Water, Land and Air Protection develops ambient water quality guidelines for British Columbia. This work has two goals:

- to provide guidance for the evaluation of data on water, sediment, and biota; and,
- to provide basis for setting site-specific ambient water quality objectives.

The guidelines represent safe conditions or safe levels of a substance in water. A water quality guideline is defined as "a maximum and/or a minimum value for a physical, chemical or biological characteristic of water, sediment or biota, which should not be exceeded to prevent detrimental effects from occurring to a water use under given environmental conditions."

The guidelines are applied province-wide, but they are use-specific, and are being developed for these water uses:

- raw drinking water, public water supply and food processing<sup>1</sup>;
- aquatic life and wildlife;
- agriculture (livestock watering and irrigation);
- recreation and aesthetics<sup>2</sup>; and
- industrial water supplies.

---

<sup>1</sup> The guidelines apply to an ambient raw water source before it is diverted or treated for domestic use. The Ministry of Health Services regulates the quality of water for domestic use after it is treated and delivered by a water purveyor.

<sup>2</sup> Guidelines relating to public health at bathing beaches will be the same as those developed by the Ministry of Health, which regulates the recreation and aesthetic water use.

The guidelines are established after considering the scientific literature, existing guidelines from other jurisdictions, and environmental conditions in British Columbia. The scientific literature provides information about the effects of toxicants on various life forms. This information is not always conclusive because it is usually based on laboratory work that, at best, only approximates field conditions. To compensate for this uncertainty and to facilitate application of the "precautionary principle", the guidelines have built-in safety factors that are conservative, but consider natural background conditions in the province.

The guidelines are used to set ambient site-specific water quality objectives for specific waterbodies. In setting the objectives, consideration is also given to present and future water uses, waste discharges, hydrology, limnology, oceanography, and existing background water quality.

In most cases, the objectives are the same as the guidelines. However, when natural background levels exceed the guidelines, the site-specific objectives could be less stringent than the guidelines. In rare instances — for example, if the resource is unusually valuable or of special provincial significance — the safety factor could be increased to support the establishment of objectives that are more stringent than the guidelines. Another approach would be to develop site-specific objectives by conducting toxicity experiments in the field or applying other procedures (MacDonald 1997).

Neither the guidelines nor the objectives derived from them have any legal standing in British Columbia. However, the objectives can be used to calculate waste discharge limits for contaminants. These limits are outlined in waste management permits, orders, and approvals, all of which have legal standing. Objectives are not usually incorporated as conditions of a permit.

Water quality guidelines are subject to review and revision as new information becomes available or as other circumstances dictate.

[Top](#)

## **Introduction**

Chloride compounds include those containing a chlorine atom as a negatively charged anion (Cl<sup>-</sup>), such as sodium chloride (NaCl). Chlorine<sup>3</sup> is a halogen (salt-forming) element with a boiling point of -33.9°C. Chlorine is never found in free form in nature, and occurs most commonly as sodium chloride. Chloride compounds are highly soluble in water<sup>4</sup>, in which they persist in dissociated form as chloride anions with their corresponding positively charged cations (e.g., sodium).

---

<sup>3</sup> The atomic weight of chlorine is 35.45, and its CAS number is 7782-50-5.



<sup>4</sup> The solubility of sodium chloride is 35.7g/100g water at 0°C.

Chloride is widely distributed in nature, generally in the form of sodium (NaCl) and potassium (KCl) salts; it constitutes about 0.05% of the earth's outer crust. By far the greatest amount of chloride found in the environment is in the oceans. Salt deposits occur frequently underground where they are mined for various industrial and domestic purposes. The Canadian salt industry produces 12.5 million metric tonnes annually from major rock salt mines in Ontario, Quebec, and New Brunswick and from vacuum pan refineries in Alberta, Saskatchewan, Ontario, New Brunswick, and Nova Scotia; nearly three-quarters of this total is rock salt used primarily for highway de-icing.

The application of road salt for winter accident prevention represents the single largest use of salt in British Columbia and serves as the primary anthropogenic source of chloride to the environment. Sodium chloride is also widely used in the production of industrial chemicals such as caustic soda (sodium hydroxide), chlorine, soda ash (sodium carbonate), sodium chlorite, sodium bicarbonate, and sodium hypochlorite. Potassium chloride is used in the production of fertilizers. In addition to the salting of highways to control ice and snow, other sources of chloride to the environment include dissolution of salt deposits, effluents from chemical industries, oil well operations, sewage, irrigation drainage, refuse leachates, sea spray, and seawater intrusion in coastal areas.

In freshwater, natural background concentrations of chloride are on the order of 1 to 100 mg/L, with maximum observed surficial concentrations in B.C. in the range of 13 to 140 mg/L (Bright and Addison 2002). High concentrations of chloride, related to the use of road salt on roads or released from storage yards or snow dumps, have been measured in ground water adjacent to storage yards, in small ponds and water courses draining large urbanized areas, and in streams, wetlands and lakes draining major roadways. While the highest concentrations of chloride are usually associated with winter and spring thaws, elevated chloride concentrations have also been measured during summer low flow periods.

As part of the CEPA Priority Substances List Assessment, Evans and Frick (2001) compiled information of the level of chlorides in the Canadian environment. The results of that review indicated that chloride concentrations in roadside snow ranged from <100 mg/L to 10,000 mg/L, with concentrations typically in the 4,000 mg/L range. By comparison, snow melt from snow storage dumps had chloride concentration ranges of 300 to 1,200 mg/L. The highest chloride concentrations are typically found in roadside ditches where melt-water is concentrated (highest reported value in Evans and Frick (2001; Table 4-5) was 19,135 mg/L for highway runoff in Ontario). The next highest concentrations (up to 4,310 mg/L) were observed in rivers and creeks in highly populated areas with significant use of road salt. Small lakes and ponds were more strongly affected by road salt than larger lakes, but are not as strongly influenced as creeks or rivers. For most of the small lakes that were sampled, chloride concentrations were below 200 mg/L (Evans and Frick 2001).

Chloride is an essential element for aquatic and terrestrial biota, representing the main extracellular anion in animals, including humans. It is a highly mobile ion that easily crosses cell membranes and is involved in maintaining proper osmotic pressure, water balance, and acid-base balance in animal tissues. Recent studies indicate that the chloride ion also plays an active role in renal function, neurophysiology, and nutrition.

Food represents the principal source of chloride that is consumed by humans. Approximately 0.6 g of chloride per day is ingested in a salt-free diet. Due to the addition of salt to food, the daily intake of chloride averages 6 g and may range as high as 12 g. If one assumes that daily water consumption is 1.5 L and that the average concentration of chloride in drinking water is 10 mg/L, the average daily intake of chloride from drinking water is approximately 15 mg per person, or only about 0.25% of the average intake from food.

Although chloride is an essential element for maintaining normal physiological functions in all aquatic organisms, elevated or fluctuating concentrations of this substance can be detrimental. More specifically, exposure to elevated levels of chloride in water can disrupt osmoregulation in aquatic organisms leading to impaired survival, growth, and/or reproduction. Because excess chloride is most frequently actively excreted from animal tissues via the kidneys or equivalent renal organs to achieve osmoregulatory balance, the bioaccumulation potential of chloride is low. Several

factors such as dissolved oxygen concentration, temperature, exposure time and the presence of other contaminants influence chloride toxicity. However, few studies have systematically evaluated the influence of confounding variables on chloride toxicity in aquatic environments.

[Top](#)

---

## **Recommended Guidelines**

### **1. Drinking Water**

It is recommended that the total concentration of chloride in drinking water should not exceed 250 mg/L.

**Rationale:** This guideline was recommended by the Canadian Council of Ministers of the Environment to protect the aesthetic qualities of drinking water (CCME 1999). More specifically, the CCME water quality guideline was established because chloride imparts an undesirable taste to water and to beverages prepared from water. In addition, it can cause corrosion in water distribution systems. The taste threshold for chloride varies depending on the associated cation that is present (e.g., sodium, potassium, etc.) and is generally in the range of 200 to 300 mg/L (Health Canada 1996). Chloride concentrations detected by taste in drinking water by panels of 18 or more people were 210, 310 and 222 mg/L for the sodium, potassium and calcium salts, respectively. The taste of coffee was affected when brewed with water containing chloride concentrations of 400, 450, and 530 mg/L from sodium chloride, potassium chloride, and calcium chloride, respectively.

### **2. Recreation and Aesthetics**

It is unlikely that chloride concentrations found in ambient waters would impair recreational activities, such as, wading or swimming. Therefore, no guideline is recommended for this water use.

### **3. Aquatic Life**

Presently, there is no Canadian water quality guideline for chloride for protection of freshwater organisms. Evans and Frick (2001) evaluated the toxicity of chloride to freshwater organisms by stratifying the existing data according to the duration of chloride exposure. For the purposes of guideline derivation below, acute toxicity tests are defined as those in which duration of exposure was less than seven days; toxicity tests of seven or more days in duration are considered to represent chronic exposures.

For exposures of 96 hours, there were 13 studies with fish, seven with cladocerans, and eight with other invertebrates (Appendix 1, Table 1). In general, fish were less sensitive to the effects of chloride than invertebrates. The 96-h LC50s ranged from 1204 to 13,085 mg chloride/L, with a geometric mean of 3940 mg chloride/L.

For chronic exposures, effective (EC50) and lethal (LC50) concentrations of chloride for nine different taxa ranged from 735 mg/L for the cladoceran, *Ceriodaphnia dubia*, to 4681 mg/L for the Eurasian watermilfoil, *Myriophyllum spicatum* (Appendix 1, Table 2).

[Top](#)

---

## **3.1 Freshwater Aquatic Life**

### **Freshwater: Chronic**

To protect freshwater aquatic life from chronic effects, the average<sup>5</sup> concentration of chloride (mg/L)

as NaCl) should not exceed 150 mg/L.

---

<sup>5</sup> Arithmetic mean is computed from five weekly samples collected over a 30-day period.

**Rationale:** The recommended water quality guideline was derived by dividing the lowest LOEC (lowest observed effect concentration) from a chronic toxicity test by a safety factor of 5. The lowest LOEC for a chronic toxicity test is 735 mg/L for *Ceriodaphnia dubia* (Appendix 1, Table 2); this chloride concentration resulted in a 50% reduction in reproduction over the 7 day test duration. Utilizing this value and following application of a safety factor of five, the chronic guideline is 150 mg/L (rounded to nearest tenth place).

The safety factor of 5 in the derivation of the chronic guideline was justified as follows: (a) Chronic data (Appendix 1, Table 2) available from the literature were scant; (b) in a recent study, Diamond et al. (1992) found a LOEC/NOEC ratio for reproduction of 3.75 in *C. dubia* exposed to NaCl for 7 days. Also, LC<sub>50</sub>/LC<sub>0</sub> of 3 and LC<sub>100</sub>/LC<sub>0</sub> of 4 were obtained by Hughes (1973), whereas the DeGreave et al. (1991) data yielded LC<sub>50</sub>/NOEC ratios that ranged from about 1.0 to 6.9; (c) additional protection may be required for those species that are more sensitive but have not yet been tested in the literature.

#### **Freshwater: Acute**

To protect freshwater aquatic life from acute and lethal effects, the maximum concentration of chloride (mg/L as NaCl) at any time should not exceed 600 mg/L.

**Rationale:** The guideline for maximum chloride concentration was derived by applying a safety factor of two to the 96-h EC<sub>50</sub> of 1204 mg/L for the tubificid worm, *Tubifex tubifex* (Appendix 1, Table 1), and rounding the number to nearest tenth. Safety factors of two is applied to the acute data because of the relative strength of the acute (Appendix 1, Table 1) data set.

[Top](#)

---

### **3.2 Marine Aquatic Life**

To protect aquatic life in marine environments, human activities should not cause the chloride concentration to fluctuate by more than 10% of the natural background expected at that time and depth.

**Rationale:** This guideline is an interim guideline that reflects the close relationship between chloride concentration and salinity in marine environments (changes in marine salinity are reflected by equivalent changes in chloride concentration<sup>6</sup>). Full strength seawater in the Pacific Ocean (Pacific deep water) has salinity about 34 parts per thousand, which is equivalent to a chloride concentration of 18,980 mg/L. Euryhaline organisms can withstand salinity fluctuations, either by tolerating changes in internal osmotic pressure or by maintaining a constant osmotic pressure through osmoregulation.

---

<sup>6</sup> Published graphs which show the relationship between total salinity and the concentration of different salt compounds can be found in U.S. Dept. of Agriculture (1954).

To protect marine aquatic life in marine environments, human activities should not cause the salinity (expressed as parts per thousand) of marine and estuarine waters to fluctuate by more than 10% of the natural salinity expected at that time and depth. This is consistent with the CCME (1999) interim salinity guideline designed to protect marine and estuarine organisms by avoiding or limiting human-induced fluctuations in the salinity regime. It is also assumed that this guideline will

protect natural circulation and mixing patterns of coastal water bodies and thereby limit effects on the physiology and distribution of marine and estuarine organisms associated with such patterns.

**Top**

---

#### **4. Irrigation**

The quality guideline for irrigation purposes is 100 mg chloride/L.

**Rationale:** The CCME (1999) water quality guidelines indicate that sensitive plants should not be irrigated with waters containing > 100 mg chloride/L. In contrast, the CCME (1999) indicates that chloride-tolerant plants can be irrigated with water up to 700 mg chloride/L. The lower of these two values, 100 mg chloride/L, is adopted as the water quality guideline for chloride in irrigation water in British Columbia. Waters with chloride concentrations below the guideline can be used for irrigation on all crops within the province.

#### **5. Livestock Watering**

The water quality guideline for livestock watering is 600 mg chloride/L.

**Rationale:** Based on the CCME (1999) water quality guidelines, the concentration of total soluble salts in water used for livestock watering should not exceed 1000 mg/L. Assuming that chloride represents 60% by weight of total soluble salts (e.g., for NaCl), then an equivalent chloride guideline is 600 mg chloride/L. Water with total soluble salt content of less than 1000 mg/L is considered excellent for all classes of livestock. Livestock health may become impaired at total soluble salt concentrations of 1000 to 3000 mg/L.

#### **6. Wildlife**

The chloride concentration in waters that are utilized by wildlife should not exceed 600 mg/L.

**Rationale:** Although numerical WQGs for the protection of wildlife were not located in the scientific literature, there is no reason to believe that wildlife species would be more sensitive to the effects of chloride than livestock species. For this reason, the WQG for livestock watering was adopted directly as the WQG for the protection of wildlife in British Columbia.

**Top**

---

### ***Application of Guidelines for Aquatic Life***

Chloride is ubiquitous in the environment. Its impact on the environment depends upon environmental conditions, including dissolved oxygen concentration, temperature, exposure time, and the presence of other contaminants. These factors should be considered when the water quality guidelines are applied to assess environmental impacts of chloride.

#### **1. Assessment of Existing Water Quality**

The environmental chemistry of chloride is relatively straightforward. Following the deposition of road salt, these compounds dissociate in the environment into chloride anion and a corresponding cation (usually sodium, since sodium chloride is the predominant form of road salt). Chloride ions enter surface water, soil, and ground water after snowmelt events and remain in solution in freshwater systems.

It is important to carefully consider background levels of chloride in the local aquatic environment and to take these data into consideration when applying the WQGs. For example, in Stuart Lake

situated in the upper part of the Fraser River watershed, chloride levels should be very low. Therefore, measured levels of chloride at, or above the WQGs, would likely indicate that anthropogenic sources are contributing to chloride levels and putting ecological receptors at risk. However, background levels of chloride in the lower (tidal) portions of the Fraser River are likely to be highly variable, and influenced by tidal cycles and salt wedge penetration. In this situation, elevated levels of chloride would not necessarily indicate a water quality problem.

**Top**

---

## **2. Setting of Water Quality Objectives**

In most cases, water quality objectives for chloride will be the same as the guidelines. When concentrations of chloride in undeveloped waterbodies are less than the recommended guidelines, then more stringent values, if justified, could apply. In some cases, socio-economic or other factors (e.g., higher background levels) may justify objectives which are less stringent than the guidelines. To adjust the guidelines recommended here to take local conditions into consideration, the BC Ministry of Environment, Lands and Parks publication, "Methods for Deriving Site-Specific Water Quality Objectives in British Columbia and Yukon" should be followed (MacDonald 1997).

Although sodium chloride is the predominant form of road salt in British Columbia, other cations in addition to sodium (e.g., calcium, magnesium and potassium) can either reduce or enhance the toxicity of chloride in natural water bodies. Complex interactions among sodium, potassium, magnesium and chloride ions may play a role in affecting the sensitivity of aquatic species to road salt runoff. Increased salt concentrations can potentially enhance the mobility of trace metals in aquatic ecosystems. Road salts can thus increase the toxicity and adverse environmental impacts of road runoff. Nutrients and organic contaminants may also be carried with road runoff, thereby contributing to stresses on aquatic organisms.

**Top**

---

## **References**

Bright, D.A. and J. Addison. 2002. Derivation of matrix soil standards for salt under the British Columbia Contaminated Sites Regulation. Royal Roads University. Prepared for BC Ministry of Water, Land and Air Protection, BC Ministry of Transportation and Highways, BC Buildings Corp., and the Canadian Association of Petroleum Producers. Victoria, BC.

Canadian Council of Ministers of the Environment (CCME). 1999. Canadian Environmental Quality Guidelines. Winnipeg, Manitoba.

Evans, M. and C. Frick. 2001. The effects of road salts on aquatic ecosystems. NWRI Contribution Series No. 01-000. National Water Resources Institute. Saskatoon, Saskatchewan.

Health Canada. 1996. Guidelines for Canadian Drinking Water Quality - Sixth Edition. Ottawa, Ontario.

MacDonald, D.D.. 1997. Methods for deriving site-specific water quality objectives in British Columbia and Yukon. British Columbia Ministry of Environment, Lands, and Parks. Victoria, B.C.

United States Department of Agriculture. 1954. Diagnosis and improvement of saline and alkali soils. Agricultural Handbook Number 60. Washington, D.C. (<http://www.usssl.ars.usda.gov/hb60/offset/hb60ntro.pdf>)

United States Environmental Protection Agency (USEPA). 1988. Ambient water quality criteria for chloride. Office of Water. Washington, D.C.

**Top**

---

---

## **Appendix 1: Supporting Documentation for the Recommended Water Quality Guidelines**

### **1. Introduction**

Road salts are applied to roadways in B.C. in order to prevent traffic accidents. During wintertime, traffic accidents can be reduced by 20 to 90% when icy and snowy roads are salted and reduced to bare pavement. The use of de-icing agents serves to keep Canadian roadways open and safe during the winter and to minimize traffic accidents, injuries, and mortality under icy and snowy conditions.

Sodium chloride is the most commonly applied road salt in North America. Road salt can be made up of different mixtures of compounds including calcium chloride, magnesium chloride, and potassium chloride. In the environment, salts dissociate into the chloride anion and a corresponding cation. Environment Canada estimated that during the 1997-98 winter, approximately 4,750,000 tonnes of sodium chloride and 110,000 tonnes of calcium chloride de-icers were applied to Canadian roads, resulting in an estimated 2,950,000 tonnes of chloride released to the environment. Of this amount, approximately 94,000 tonnes of road salt were applied in BC, with loading rates between 1 to 3 kg/m<sup>2</sup> of salted road.

Ultimately, all road salts enter the environment as a result of:

1. Storage at patrol yards (including losses from storage piles and during handling);
2. Roadway application (at the time of application as well as subsequent movement of the salts off the roadways); and,
3. Disposal of waste snow.

Releases are therefore associated with both point sources (storage and snow disposal areas) and linear sources (roadway application).

**Top**

---

### **2. Background**

The *Canadian Environmental Protection Act* (CEPA) requires that the Ministers of Environment and Health identify substances that may be harmful to the environment or constitute a danger to human health. A substance is considered to be "CEPA toxic" if it is entering the environment in a quantity or concentration or under conditions that:

1. Have or may have an immediate or long-term harmful effect on the environment or its biological diversity;
2. Constitute or may constitute a danger to the environment on which life depends; or,
3. Constitute or may constitute a danger in Canada to human life or health.

A notice to the effect that road salt is considered to be a toxic substance in Canada was filed in the Canada Gazette on Dec. 1, 2001. The notice states that based on the available data, it is considered that road salts that contain inorganic chloride salts are entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute a danger to the environment on which life depends. Therefore, it is concluded that road salts that contain inorganic chloride salts with or without ferrocyanide salts are "toxic" as defined in section 64 of the *Canadian*

• Top

---

### 3. Effects of Chloride on Aquatic Organisms

Road salt has the potential to adversely affect a wide range of aquatic organisms. Evans and Frick (2001) reviewed the literature on the biological effects of chloride and drew a number of conclusions regarding chloride salt toxicity and effects on aquatic biota. First, tolerance to elevated chloride concentrations decreases with increasing exposure time. Short-term exposures to concentrations of chloride in the hypersaline range (>50,000 mg/L salinity) may kill adult fish and other organisms rapidly (e.g., 15 minutes). As exposure time increases, tolerance to chloride decreases. Tolerance to chloride can be increased through the gradual increases in chloride concentrations, allowing the organism to develop mechanisms for dealing with the osmotic shock and other physiological stresses.

A number of studies reviewed by Evans and Frick (2001) measured the effects of physical variables on salinity tolerance. Aquatic biota are more tolerant of chloride in water in which oxygen concentrations are close to saturation. While some studies suggest that organisms are more tolerant to chloride at lower temperatures, other studies have shown that the reverse is true.

Zooplankton and benthic invertebrates appear to be relatively more sensitive to sodium chloride concentrations than fish. As well, within a given taxonomic category (e.g., benthic invertebrates or fish), there is significant inter-species variation in salinity tolerances.

Potassium chloride tends to be the most toxic salt to fish and aquatic invertebrates. Magnesium chloride is next in toxicity, followed by calcium chloride and then sodium chloride. Fish fry may be more tolerant of elevated concentrations of calcium compared to sodium chloride.

Limited studies have been conducted of the toxicity of road salts and de-icing salts to aquatic organisms. In general, toxicity is within the same general range of that observed for sodium and calcium chlorides. Road salts, by increasing the mobilization of metals, may enhance the toxicity and adverse environmental impacts from road runoff. Nutrients and organic contaminants may also be carried with this runoff, especially from heavily trafficked highways. This can also contribute to stress on aquatic organisms.

• Top

---

#### 3.1 Acute Toxicity

Data comparing the toxicity of salt to aquatic organisms were compiled by Evans and Frick (2001). Table 1 shows the measured acute values for various freshwater species exposed to sodium chloride during 96-hour acute toxicity tests. Some of the acute data represent 3-day (72-hour) exposures that were converted into 4-day estimates using a conversion factor as described in Evans and Frick (2001). In total there are 28 observations including fish (13), cladocerans (7), and other invertebrates (8). Invertebrates are more sensitive to chloride (i.e. lower 96-h LC50s) than are fish. Certain fish species (e.g., American eel) show high chloride tolerance, with corresponding high LC50 values. The 96-h LC50s range between 1204 to 13,085 mg chloride/L, with a geometric mean of 4033 mg chloride/L. Sublethal effects (immobilization response) in *Tubifex tubifex* were observed at the lowest chloride concentration of 474 mg/L. In this particular test, the immobilization response is equivalent to a lethal response, since death was confirmed following transfer of immobile worms back into control tube well water (Khangarot 1995).

#### 3.2 Chronic Toxicity

The results of chronic toxicity tests conducted on nine freshwater species indicate that chloride can

adversely affect aquatic organisms at concentrations ranging from 735 to 4681 mg/L (Table 2). Logistic modeling of chronic toxicity data (Figure 1) indicates that the 5th percentile of the sensitivity distribution for aquatic life occurs at around 213 mg/L Cl<sup>-</sup>. However, limitations in the available input data restrict the application of this relationship for deriving water quality guidelines. For this reason, Evans and Frick (2001) used the available toxicological data and published acute:chronic ratios to estimate chronic toxicity thresholds for various species of aquatic organisms. The reconstructed species sensitivity distribution was developed by first categorizing the exposure period used in the original studies into < 1 day, 1 day, 4 days, and 1 week. The extent to which these represent chronic versus acute exposure periods depends on the life history of the specific test organism used. Evans and Frick (2001) further standardized the data for exposure period, to reflect longer-term (> 1 week) chronic exposure periods. Based on an acute:chronic ratio of 7.0, the 96-h acute toxicity data were extrapolated to a predicted chronic toxicity threshold, as shown in Figure 2. The predicted community response to chloride is shown in Table 3, which presents the cumulative percentage of species affected by chronic exposures to chloride.

[Top](#)

---

### 3.3 Review of Water Quality Criteria for Chloride in Other Jurisdictions

Four jurisdictions have developed water quality criteria for chloride; these criteria are shown in Table 4 and are described below.

#### 3.3.1 State of Kentucky

Birge et al. (1985) recommended that, in order to protect aquatic life and its uses, for any consecutive 3-day period:

1. The chloride concentration should not exceed 600 mg/L;
2. The maximum concentration should not exceed 1,200 mg/L;
3. Chloride concentrations may average between 600-1,200 mg/L for up to 48 hours.

The 1,200 mg/L value was determined from an investigation of benthic community structure and fish survivorship at 7 sites downstream of a salt seepage. Survivorship and diversity was lower at the 1,000 mg/L than the 100 mg/L site and further reduced at the 3,160 mg/L site. In the laboratory, toxicity studies determined a final acute value of 760 mg/L chloride, and a final chronic value of 333 mg/L chloride.

[Top](#)

---

#### 3.3.2 United States

Water quality criteria for chloride were developed by USEPA (1988). They concluded that except possibly where a locally important species is very sensitive, freshwater organisms and their uses should not be appreciably affected unacceptably if:

1. The 4-day average concentration of chloride, when associated with sodium, does not exceed 230 mg/L more than once every three years on average;
2. The 1-hour average chloride concentration does not exceed 860 mg/L more than once every three years on average.

The criterion maximum concentration, 860 mg/L, was obtained by dividing the final acute value, 1,720 mg/L by 2. The criterion continuous concentration, 230 mg/L was obtained by dividing the final chronic value by the final acute:chronic ratio (ACR), 7.594. USEPA (1988) noted that these



criteria will not be adequately protective when the chloride is associated with potassium, calcium, or magnesium. Further, they also noted that because animals have a narrow range of acute sensitivities to chloride, excursions above this range might affect a substantial number of species.

[Top](#)

---

### 3.3.3 Canada — Freshwater

CCME (1999) has developed a number of water quality guidelines for chloride, although none are for the protection of aquatic life. These guidelines include:

1. For Canadian drinking water, chloride concentrations should not exceed 250 mg/L. This rationale is based on taste rather than human health considerations.
2. For irrigation waters, sensitive plants should not be irrigated with waters >100 mg/L while tolerant plants can be irrigated with water up to 700 mg/L. This guideline suggests that some sensitive wetland and aquatic plants would be adversely affected by growing in road salt contaminated waters at chloride concentrations as low as 100 mg/L. Quebec maintains identical guidelines.
3. Livestock can be safely watered with concentrations of total soluble salts of up to 1,000 mg/L. However, at concentrations of 1,000-3,000 mg/L livestock health may become impaired. This guideline suggests that terrestrial animals obtaining their drinking water from streams, marshes, and ponds would have their health impaired at these chloride levels. Some animals may be even more sensitive to chloride (i.e., at concentrations < 1,000 mg/L). There is no specified standard in Quebec.
4. In Quebec, aquatic life suffer acute toxicity at minimum chloride concentrations of 860 mg/L. Chronic toxicity occurs at chloride concentrations of 230 mg/L and any increases must not exceed 10 mg/L.

### 3.3.4 Canada — Marine and Estuarine Life

CCME (1999) has developed an interim water quality guideline for salinity (expressed as parts per thousand) for the protection of marine and estuarine life. Specifically:

"Human activities should not cause the salinity (expressed as parts per thousand) of marine and estuarine waters to fluctuate by more than 10% of the natural salinity expected at that time and depth."

[Top](#)

---

## References

- Adelman, I.R., L.L.J. Smith and G.D. Siesennop. 1976. Acute toxicity of sodium chloride, pentachlorophenol, guthion, and hexavalent chromium to fathead minnows (*Pimephales promelas*) and goldfish (*Carassius auratus*). J. Fish. Res. Board Can. 33: 203-208.
- Anderson, B.G. 1948. The apparent thresholds of toxicity to *Daphnia magna* for chlorides of various metals when added to Lake Erie water. Trans. Amer. Fish. Soc. 78: 96-113.
- Arambasic, M.B., S. Bjelic and G. Subakov. 1995. Acute toxicity of heavy metals (copper, lead, zinc), phenol and sodium on *Allium cepa* L., and *Daphnia magna* St.: comparative investigations and the practical applications. Water Research 29: 497-503.

- Beak International Inc. 1999. Ecotoxicology test results. Unpublished report for M.S. Evans. National Water Research Institute. Saskatoon, SK.
- Birge, W.J., J.A. Black, A.G. Westerman, T.M. Short, S.B. Taylor, D.M. Bruser, and E.D. Wallingford. 1985. Recommendations on numerical values for regulating iron and chloride concentrations for the purpose of protecting warm water species of aquatic life in the Commonwealth of Kentucky. Memorandum of Agreement No. 5429. Kentucky Natural Resources and Environmental Protection Cabinet. Lexington, KY.
- Bright, D.A. and J. Addison. 2002. Derivation of matrix soil standards for salt under the British Columbia Contaminated Sites Regulation. Royal Roads University. Prepared for BC Ministry of Water, Land and Air Protection, BC Ministry of Transportation and Highways, BC Buildings Corp., and the Canadian Association of Petroleum Producers. Victoria, BC.
- Buckley, J.A., K.P. Rustagi and J.D. Laughlin. 1996. Response of *Lemna minor* to sodium chloride and a statistical analysis of continuous measurements for EC50 and 95% confidence limits calculation. Bull. Environ. Contam. Toxicol. 57(6): 1003-1008.
- Canadian Council of the Ministers of the Environment (CCME). 1999. Canadian Environmental Quality Guidelines. Winnipeg, MB.
- Cowgill, U.M., and D.P. Milazzo. 1990. The sensitivity of two cladocerans to water quality variables: salinity and hardness. Arch. Hydrobiol. 120: 185-196.
- Degreave, G.M., J.D. Cooney, B.H. Marsh, T.L. Pollock, N.G. Reichenbach. 1992. Variability in the performance of the 7-d *Ceriodaphnia dubia* survival and reproduction test: an intra- and inter-laboratory comparison. Environ. Toxicol. Chem. 11: 851-866.
- Dowden, B.F., and H.J. Bennett. 1965. Toxicity of selected chemicals to certain animals. J. Water Pollut. Control Fed. 37: 1308-1316. (As cited in USEPA 1988).
- Evans, M. and C. Frick. 2001. The effects of road salts on aquatic ecosystems. NWRI Contribution Series No. 01-000. National Water Research Institute, Saskatoon, Saskatchewan.
- Gonzales-Moreno, S., J. Gomez-Barrera, H. Perales, and R. Moreno-Sanchez. 1997. Multiple effects of salinity on photosynthesis of the protist *Euglena garcilii*. *Physiologia Plantarum* 101: 777-786.
- Gosh, A.K., and R.N. Pal. 1969. Toxicity of four therapeutic compounds to fry of Indian major carps. Fish. Technol. 6: 120-123. (As cited in Hammer 1977).
- Hamilton, R.W., J.K. Buttner, and R.G. Brunetti. 1975. Lethal levels of sodium chloride and potassium chloride for an oligochaete, a chironomid midge, and a caddisfly of Lake Michigan. Environmental Entomology 4: 1003-1006.
- Hammer, U.T. 1977. The effects of alkali halides in the Canadian Environment National Research Council Environmental Secretariat. Ottawa, Canada.
- Hinton, M.J., and A.G. Eversole. 1978. Toxicity of ten commonly used chemicals to American eels. Agricultural Experiment Station Technical Contribution 1595. Texas A&M University. College Station, TX.
- Khargarot, B.S. 1995. Toxicity of metals to a freshwater tubificid worm, *Tubifex tubifex* (Muller). Bull. Environ. Contam. Toxicol. 46: 906-912.
- Lillius, H., T. Hastbacka, and B. Isomaa. 1995. A comparison of the toxicity of 30 reference chemicals to *Daphnia magna* and *Daphnia pulex*. Environ. Toxicol. Chem. 14: 2085-2088.
- Lowell, R.B., J.M. Culp, and F.J. Wrona. 1995. Toxicity testing with artificial streams: effects of differences in current velocities. Environ. Toxicol. Chem. 14: 1209-1217.

Stanley, R.A. 1974. Toxicity of heavy metals and salts to Eurasian milfoil (*Myriophyllum spicatum* L.). Arch. Environ. Contam. Toxicol. 2(4): 331-341.

Sutcliffe, D.W. 1961. Studies on salt and water balance in caddis larvae (*Trichoptera*): I. Osmotic and ionic regulation of body fluids in *Limnephilus affinis*. Curtis. J. Exp. Biol. 38: 501-519.

Thornton, K.W., and J.R. Sauer. 1972. Physiological effects of NaCl on *Chironomus attenuatus* (Diptera: Chironomidae). Annals of the Entomological Society of America 65: 872-875.

Trama, F.B. 1954. The acute toxicity of some common salts of sodium, potassium, and calcium to the common bluegill (*Lepomis macrochirus*). Proc. Acad. Nat. Sci. Phil. 196: 185.

USEPA (United States Environmental Protection Agency). 1988. Ambient water quality criteria for chloride. Office of Water, Washington, DC.

Wallen, I.E., W.C. Greer, and R. Lasater. 1957. Toxicity to *Gambusia affinis* of certain pure chemicals in turbid waters. The Environmental Future 29: 695.

WISLOH (Wisconsin State Laboratory of Hygiene). 1995. Unpublished data on chloride toxicity to aquatic species. From A. Letts (Technical Manager, Morton International Inc. Chicago Illinois) to M.S. Evans (National Hydrology Research Institute, Environment Canada, Saskatoon). Aug. 11, 1998.

Top

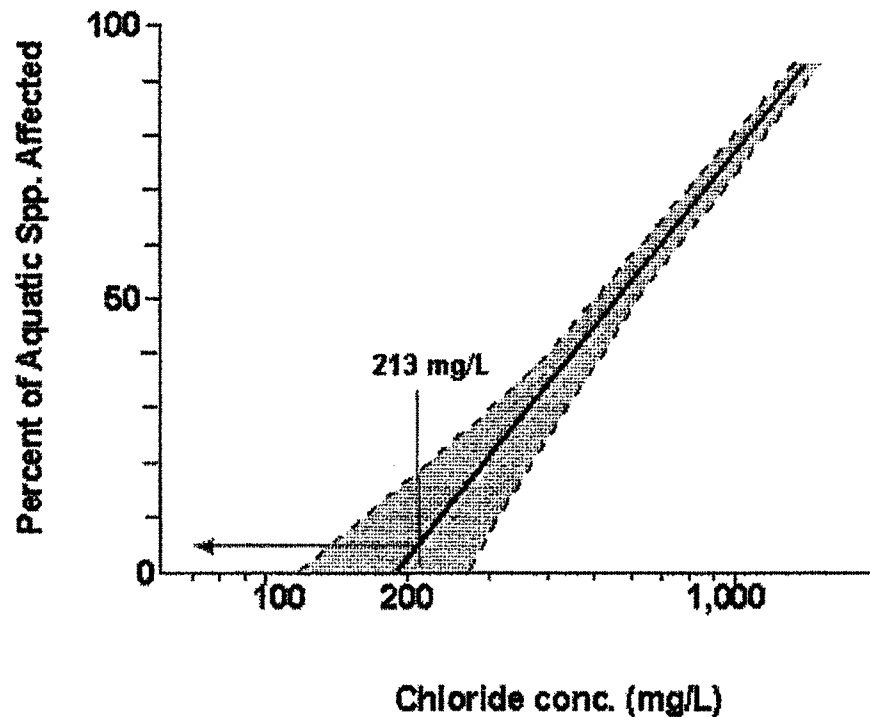


Figure 1. Aquatic life chronic species sensitivity distribution for chloride ion based on laboratory toxicity test data (adapted from Evans and Frick, 2000). The upper and lower 95% confidence interval are also shown. Source: Bright and Addison (2002).

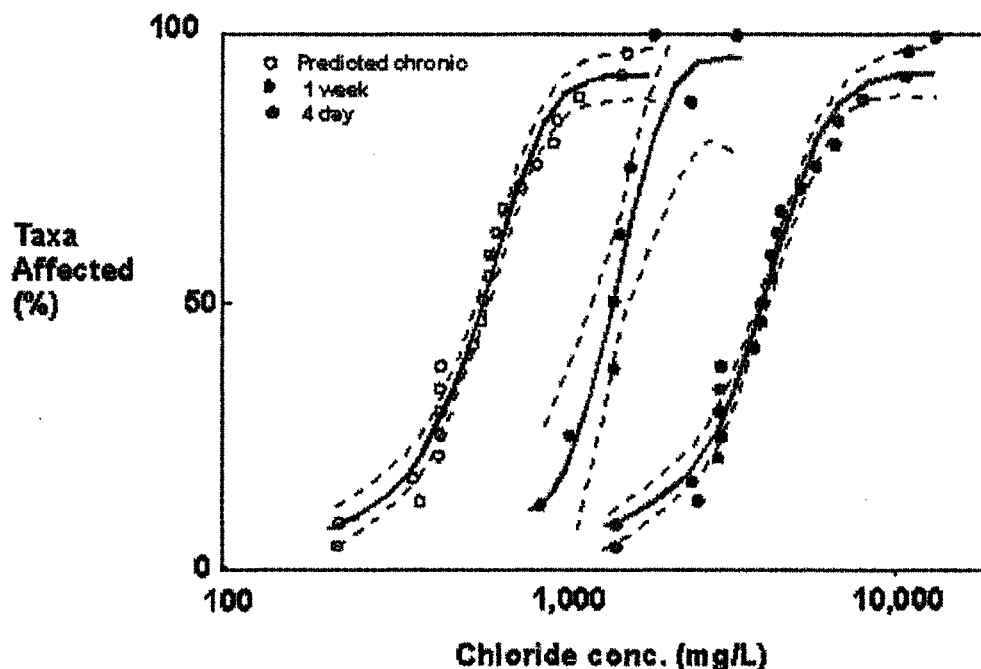


Figure 2: Predicted chronic and actual (4 day and one week) toxicity levels for aquatic life exposed to NaCl. (upper and lower 95% confidence intervals based on a log-logistic fit are shown). Source: Bright and Addison (2002).

[Top](#)

Table 1. Four-day LC<sub>50</sub>s of various taxa exposed to sodium chloride (adapted from Table 7-5 in Evans and Frick 2001 and Table B.6 In Bright and Addison 2002).

Species	Common Name	96 h LC <sub>50</sub> (mg Cl/L)	References
<i>Tubifex tubifex</i>	Tubificid worm	1 204	Khangarot, 1995
<i>Ceriodaphnia dubia</i>	Cladoceran	1 400	Cowgill and Milazzo, 1990
<i>Daphnia pulex</i>	Cladoceran	1 470	Birge et al., 1985
<i>Ceriodaphnia dubia</i>	Cladoceran	1 596	WI SLOH, 1995
<i>Daphnia magna</i>	Cladoceran	1 853	Anderson, 1948
<i>Daphnia magna</i>	Cladoceran	2 390	Arambasic et al., 1995
<i>Physa gyrina</i>	Snail	2 480	Birge et al., 1985
<i>Lirceus fontinalis</i>	Isopod	2 970	Birge et al., 1985
<i>Cirrhinius mrigalo</i>	Indian carp fry	3 021	Gosh and Pal, 1969
<i>Labeo rohoto</i>	Indian carp fry	3 021	Gosh and Pal, 1969
<i>Catla catla</i>	Indian carp fry	3 021	Gosh and Pal, 1969
<i>Daphnia magna</i>	Cladoceran	3 658	Cowgill and Milazzo, 1990
<i>Cricotopus trifascia</i>	Chironomid	3 795	Hamilton et al., 1975
<i>Chironomus attenatus</i>	Chironomid	4 026	Thorton and Sauer, 1972
<i>Hydroptila angusta</i>	Caddisfly	4 039	Hamilton et al., 1975
<i>Daphnia magna</i>	Cladoceran	4 071	WI SLOH, 1995
<i>Limnephilus stigma</i>	Caddisfly	4 255	Sutcliffe, 1961

<i>Anaobolia nervosa</i>	Caddisfly	4 255	Sutcliffe, 1961
<i>Carassius auratus</i>	Goldfish	4 453	Adelman et al., 1976
<i>Pimephales promelas</i>	Fathead minnow	4 600	WI SLOH, 1995
<i>Pimephales promelas</i>	Fathead minnow	4 640	Adelman et al., 1976
<i>Lepomis macrochirus</i>	Bluegill	5 840	Birge et al., 1985
<i>Culex sp.</i>	Mosquito	6 222	Dowden and Bennett, 1965
<i>Pimephales promelas</i>	Fathead minnow	6 570	Birge et al., 1985
<i>Lepomis macrochirus</i>	Bluegill	7 864	Trama, 1954
<i>Gambusia affinis</i>	Mosquito fish	10 616	Wallen et al., 1957
<i>Anguilla rostrata</i>	American eel	10 900	Hinton and Eversole, 1978
<i>Anguilla rostrata</i>	American eel	13 085	Hinton and Eversole, 1978

• Top

**Table 2. Results of chronic toxicity tests (> 7 day duration) conducted on freshwater organisms exposed to sodium chloride (adapted from Table 7-6 in Evans and Frick 2001 and Table B.6 in Bright and Addison 2002).**

Species	Common Name	LC <sub>50</sub> /EC <sub>50</sub> (mg Cl/L)	Measured Endpoint	References
<i>Ceriodaphnia dubia</i>	Cladoceran	735	brood size	Degreave et al., 1985
<i>Pimephales promelas</i>	Fathead minnow	874	survival	Beak 1999
<i>Ceriodaphnia dubia</i>	Cladoceran	1 068	brood size	Cowgill and Milazzo, 1990
<i>Oncorhynchus mykiss</i>	Rainbow trout	1 456	survival	Beak 1999
<i>Nitzschia linearis</i>	Diatom	1 475	cell numbers	Gonzales-Moreno et al., 1997
<i>Xenopus leavis</i>	Frog	1 524	survival	Beak, 1999
<i>Oncorhynchus mykiss</i>	Rainbow trout	1 595	survival	Beak, 1999
<i>Daphnia magna</i>	Cladoceran	2 451	brood size	Cowgill and Milazzo, 1990
<i>Pimephales promelas</i>	Larvae	3 029	growth	Beak, 1999
<i>Lemna minor</i>	Duckweed	3 150	population	Buckley et al. 1996
<i>Myriophyllum spicatum</i>	Eurasian Watermilfoil	4 291	population	Stanley, 1974
<i>Myriophyllum spicatum</i>	Eurasian Watermilfoil	4 681	growth	Stanley, 1974

• Top

**Table 3. Predicted cumulative percentage of species affected by chronic exposures to chloride (from Evans and Frick 2001).**

Cumulative % of species affected	Mean chloride concentration (mg/L)	Lower confidence limit (mg/L)	Upper confidence limit (mg/L)
----------------------------------	------------------------------------	-------------------------------	-------------------------------

5	213	136	290
10	238	162	314
25	329	260	397
50	563	505	622
75	964	882	1045
90	1341	1254	1428

**Table 4. Existing water quality criteria for chloride, as reported by Evans and Frick (2001).**

	<b>State of Kentucky: Birge et al (1985)</b>	<b>USA: USEPA (1988)</b>	<b>Canada: CCME (1999)</b>	<b>Quebec: CCME (1999)</b>
Freshwater Aquatic Life: Average chloride concentration (mg/L)	600	230		230
Maximum chloride concentration (mg/L)	1,200	860		860
Drinking water (mg/L)			250	250
Irrigation water (mg/L)			100 - 700	100 - 700
Livestock (mg/L)			1000	1000
Wildlife (mg/L)			1000	
Marine water (ppt)			+/-10	



2841

**From:** ods4@pitt.edu  
**Sent:** Tuesday, June 15, 2010 6:05 PM  
**To:** EP, RegComments  
**Cc:** eac50@pitt.edu; ods4@pitt.edu; odaysalim@gmail.com  
**Subject:** 40 Pa.B. 2264 | Pa.B. Doc. No. 10-771 | Chapter 93 Ambient Water Quality Criterion; Chloride (Ch) | Oday Salim, Staff Attorney, University of Pittsburgh Environmental Law Clinic | ods4@pitt.edu | P.O. Box 7226 Pittsburgh, PA 15213-0221  
**Attachments:** Chloride Comments.Final 6.15.2010.pdf  
**Importance:** High

Dear Environmental Quality Board members:

Please find attached a comment on the proposed revisions to Chapter 93 of the Pennsylvania Code noticed in the May 1, 2010 edition of the Pennsylvania Bulletin ("Chapter 93 Ambient Water Quality Criterion; Chloride (Ch)"; Pa.B. Doc. No. 10-771).

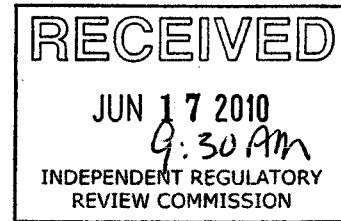
The University of Pittsburgh Environmental Law Clinic respectfully submits these comments on behalf of our client, Clean Water Action, joined by the Sierra Club, Earthjustice, the Three Rivers Waterkeeper, the Delaware Riverkeeper Network, and the Pennsylvania Council of Trout Unlimited.

Sincerely,

Oday Salim

--

Oday Salim, J.D., LL.M.  
Staff Attorney\*  
University of Pittsburgh School of Law  
Environmental Law Clinic  
\*Awaiting admission by the State Bar of California



Phone & E-Mail:  
(412) 624-4109 (my office)  
(412) 648-1300 (general clinic)  
(412) 648-1992 (fax)  
(586) 255-8857 (cell, if necessary)  
[ods4@pitt.edu](mailto:ods4@pitt.edu)

Address for U.S. Mail:  
P.O. Box 7226  
Pittsburgh, PA 15213-0221

Physical Address:  
Sennott Square, Room 5219  
210 South Bouquet Street  
Pittsburgh, PA 15213

This e-mail (and any attachments hereto) is intended only for use by the addressee(s) named herein and may contain legally privileged and/or confidential information. If you are not the intended recipient of this e-mail, you are hereby notified that any dissemination, distribution or copying of this e-mail, and any attachments hereto, is strictly prohibited. If you have received this e-mail in error, please (1) notify me by



replying to this message; (2) permanently delete the original and any electronic copies of this e-mail and any attachments; and (3) destroy any hard copies of the same. Thank you.