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INDEPENDENT REGULATORY
REVIEW COMMISSION

June 15, 2010

SENT VIA EMAIL and HAND DELIVERED
RegComments@state.pa.us

Environmental Quality Board
Pennsylvania Environmental Quality Board
P.O. Box 8477
Harrisburg, PA 17105-8477

RE: 25 *Pa. Code* Chapter 93
Ambient Water Quality Criterion Chloride (Ch)
40 *Pa. Bulletin* 2264 (May 1, 2010)

Dear Members of the Board:

The Pennsylvania Coal Association (PCA) submits the following comments in response to the above referenced proposed rulemaking.

PCA is the principal trade organization representing bituminous coal operators - underground and surface, large and small - as well as other associated companies whose businesses rely on a thriving coal economy. PCA member companies produce over 80 percent of the bituminous coal annually mined in Pennsylvania, which totaled 68 million tons in 2008.

Pennsylvania is the 4th leading coal producing state and its mining industry is a major source of employment and tax revenue. Latest data indicates it created 41,500 direct and indirect jobs with more than $7 billion in economic input stimulated by the activity of the industry.

General Comments

The proposed limit for chloride is premature because the PA Department of Environmental Protection (PADEP) has failed to provide a strong scientific basis for the limit, has failed to fully consider the immediate and long-range economic impact of the proposed limits on the Commonwealth and its citizens and industries, and has failed to consider less burdensome alternatives. For these reasons and the additional reasons below, PCA requests the EQB to disapprove PADEP's proposed chloride rulemaking.

The preamble to the above proposed rulemaking states:

> "The Department recommends adopting these national chloride criteria for protection of aquatic life due to increasing concerns about the statewide impact of natural gas extraction from the Marcellus Shale formation."[1]

This statement is misleading. First, it implies that the proposed in-stream criteria for chloride are actually national criteria imposed by the Environmental Protection Agency (EPA) which must be adopted by the various states. This is not the case. The chloride criteria proposed for adoption by PADEP are derived from a document prepared over 22 years ago, entitled *Ambient Water Quality Criteria for Chloride* (EPA, 1988) (hereafter referred to as *1988 EPA Recommended Criteria for Chloride*). This document does not establish national criteria, but instead sets out recommended guidelines which are not binding on Pennsylvania or any other state. Further, as discussed in more detail below, EPA no long even endorses the chloride criteria it recommended 22 years ago. Instead, as recently as 2008, EPA staff in discussions regarding the Iowa chloride and TDS water quality standards, concluded that its 1988 criteria were too stringent and based on flawed data and were developed using an inappropriate testing methodology.[2]

Second, the above statement is a misleading because it indicates that Marcellus Shale drilling activities are the reason why this new proposal is needed and, by implication, suggests it will have no impact on other industries in Pennsylvania. At the current time, Marcellus drillers are not generally authorized by PADEP to discharge any drilling (or other associated) waste waters containing chloride or other dissolved solids into any stream in the Commonwealth. Therefore, the proposed rulemaking should have little to no new impact on that industry. However, the proposed regulation does have the potential to again sweep in a wide range of many other Pennsylvania industries, including the mining industry, who to date have not been generally required to sample for, or treat chloride, in their wastewater discharges.

In addition, the Preamble to the proposed rule discusses the relationship between chlorides and osmotic pressure. PADEP states that the current osmotic pressure standard of 50 mOsm/kg is intended to protect aquatic life from the adverse impacts of parameters such as chlorides. They indicate the proposed new water quality standards for chloride are needed due to administrative challenges and are developing the proposed water quality standard for chlorides because it is better suited to the mass-balance approach in order to maintain the existing osmotic pressure standard, while still retaining the current osmotic pressure standard. Consequently, PADEP is developing a water quality standard that achieves the same objective as a current water standard. It is unclear why, aside from convenience, a second set of water quality standards for chloride is necessary to protect aquatic life when such protection is already provided by the water quality standard for osmotic pressure.

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[1] 40 *Pa. Bulletin* 2265.

[2] Gregory L. Sindt, P.E., *"Chloride and TDS Water Quality Standards,"* January 15, 2008.

In the recent comment and response document PADEP prepared in connection with the new chapter 95 wastewater discharge regulations for TDS, they rejected certain comments that urged more restrictive standards for TDS be adopted to protect aquatic life, stating that "the Department has reviewed the relevant data and determined that **the current osmotic pressure criterion in water quality standards regulations provides protection for aquatic life at the point of discharge"** [emphasis added].

Additionally, in spite of PADEP's basis and rationale for the chloride standard as a mechanism of achieving osmotic pressure protection, the proposed chloride water quality standard is more restrictive that the current osmotic pressure standard. Using the Morse equation, the concentration of chlorides required to exceed 50 mOsm/kg osmotic pressure is 1,642 mg/l, which is far in excess of the proposed acute and chronic chloride levels. If PADEP's intent is to issue a chlorides standard to ensure achieving the current osmotic pressure water quality standard, then the chlorides limits in the proposed Chapter 93 rule change are too restrictive and must be re-evaluated.

Specific Comments

1. The Proposed Rulemaking Is Not Based On The Best, Currently Available Data Related To The Aquatic Affects of Chloride Which Indicates That Far Higher In-stream Concentrations of Chloride Are Acceptable.

Section 304(a)(1) of the Clean Water Act requires EPA to develop criteria for water quality that accurately reflects the latest scientific knowledge. These criteria are based solely on data and scientific judgments on pollutant concentrations and environmental or human health effects. The preamble to the above rulemaking and the rationale document submitted to the Environmental Quality Board (EQB) by the Department make it abundantly clear that the **sole basis** for the proposed new chloride water quality criterion is the *1988 EPA Recommended Criteria for Chloride*.

On this issue, the preamble to this proposal states:

> "[t]he Department has reviewed the EPA ambient water quality criteria development document and agrees with the **data** ....used to develop the criteria." 40 Pa.B.2265.

A similar statement appears in the Regulatory Analysis Form submitted by PADEP to the Independent Regulatory Review Commission.

The Department's agreement with EPA's 1988 data is completely unjustified because even EPA no longer considers the data used to develop the *1988 EPA Recommended Criteria for Chloride* to be the best available data. Concerns with using this document in modern day range from a lack of standardization and quality assurance procedures to control mortality, temperature and culturing methods of test organisms, to inappropriate dilution waters and lack of other relevant information.

Subsequent work has confirmed that significant data was NOT considered by EPA when it developed the *1988 EPA Recommended Criteria for Chloride*. As result, many

EPA staff now consider that criteria to be too stringent. The following excerpt from a 2008 paper prepared by Gregory L. Sindt, P.E., EPA staff, in connection with the State of Iowa's recent development of a chloride water quality standard in that state confirms this:

> *"The US EPA 1988 national guideline for chloride toxicity are considered by IDNR [Iowa Department of Natural Resources] and many USEPA staff as too stringent."* [3]

The basis for Iowa Department of Natural Resources' (IDNR) and EPA's more recent 2008 conclusion is that the 1988 standard was significantly affected by data reviewed on a sensitive species (the fingernail clam) which was misleading because of the manner in which the tests on that species was conducted. More importantly, recent testing on this species indicates that the actual impacts only occur at a far higher concentrations of chloride (about 1,400 mg/L) and not at what was thought to be the case over 22 years ago (682 +/- mg/L) when the *1988 EPA Recommended Criteria for Chloride* was developed and published. Indeed, when the current data for chloride toxicity is considered, instead of a chronic value of 230 mg/L (the number proposed in the above rulemaking), a far higher chronic value (663 mg/L) is supportable.[4]

Furthermore, had PADEP done a reasonable search of available science it would also have reviewed the extensive testimony on this issue provided to the Iowa Environmental Protection Commission which included the following statement from Dr. Wesly Birge, a Professor at the University of Kentucky's Graduate Center for Toxicology and Department of Biology. Dr. Birge, an internationally recognized expert in aquatic toxicology, has worked extensively with the USEPA. His testimony before Iowa's Department of Natural Resources, Environmental Protection Commission in 2004[5] unequivocally undercuts PADEP's reliance on the *1988 EPA Recommended Criteria for Chloride*, Dr. Birge provided the following written statements:

> "Based on the available information, I feel that establishing a chronic aquatic life criterion for chloride of 564 mg/L is scientifically justifiable and is protective of aquatic life, and that establishing a chronic criterion of 372 mg/L based on only one chronic test with Daphnia pulex in reconstituted water is not justified."
>
> "US EPA proposed a chronic value of 230 mg chloride/L. This was based solely on laboratory toxicity tests and acute-chronic ratios. The former most always overestimates risk and the ratios are clearly invalid (emphasis added). The basic mechanisms involved in acute toxicity most always are significantly different from those involved in chronic toxicity."

Facing concerns that their initial proposed chlorides criteria were not scientifically defensible, IDNR continued to work with EPA. IDNR has also published data

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[3] Ibid.

[4] Ibid.

[5] http://www.iowadnr.gov/epc/archive/04feb16m.pdf. This document contains a wealth of other testimony and data which calls into question the use of the *1988 EPA Recommended Criteria for Chloride* and which supports far higher limits for Chlorides.

which was developed with the assistance of the EPA-Duluth, Office of Research and Development, which led Iowa, and EPA, to conclude that the *1988 EPA Recommended Criteria for Chloride* was far too stringent. This data is summarized at page 3 of an IDNR report[6], and confirms that test species (similar to those used to development the *1988 EPA Recommended Criteria for Chloride*) can tolerate far higher concentrations of chloride than was previously thought to be the case. A copy of this report is also attached to these comments.

PADEP did not conduct a thorough review of the current science on chloride aquatic toxicity before proposing this rulemaking resulting in a totally deficient review. Since several states and EPA themselves have questioned the use of the 1988 criteria, it is completely inappropriate for PADEP to adopt the 1988 criteria without evaluating the errors and limitations of the 1988 criteria and additional information generated since 1988. For this reason alone, the rule should be rejected by the EQB.

2. There Is No Rational Causal Link Between The Proposed Rulemaking And The Purported Harm.

In an attempt to disguise the lack of a solid technical basis for the proposed rulemaking, the Department references a sequence of sampling data on the Monongahela River in the fall of 2008. Page 3 of PADEP's rationale document for chlorides states:

> "Chlorides and Sulfates can be a significant source of TDS in wastewater discharges. During the fall of 2008, water quality issues related to these parameters emerged in the Monongahela River basin."[7]

A review of 22 pages of chloride data from 2008 until March 28, 2010 on PADEP's own website[8] indicates chloride values are nowhere near exceeding even the public drinking water standard.

Page 3 of PADEP's rationale document for chlorides also states:

> " Elevated Chloride levels were also observed in the Monongahela and on at least one major tributary - South Fork Tenmile Creek."

A review of the Final Report of the Comprehensive Ichthyofaunal Survey of Tenmile Creek Watershed[9] contains statements that are in conflict with PADEP's supporting data which they are using to move forward a chloride standard. These statements include:

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[6] Iowa Department of Natural Resources, *"Water Quality Standards Review: Chloride, Sulfate and Total Dissolved Solids,"* February 9, 2009. (http://www.iowadnr.gov/water/standards/files/ws_fact.pdf)

[7] See PA Department of Environmental Protection website.

[8] Data can be found at: http://files.dep.state.pa.us/RegionalResources/SWRO/SWROPortalfiles/monongahelarivertdschlorideandsulfatesamplingresults.pdf

[9] Argent, David G. and Kimmel, William G., *"A Comprehensive Ichthyofaunal Survey of Tenmile Creek Watershed Phase I"*, California University of PA, March 2008.

> "Tenmile Creek Watershed located in Washington/Greene Counties, the second largest tributary to the Monongahela River in Pennsylvania, emerges as an area that may harbor a diverse ichthyofauna, but whose aquatic biota remains largely unassessed."[10]
>
> "Our collections added nearly 30 species/hybrids to the ichthyofauna of Tenmile and its South Fork."[11]
>
> "The ichthyofauna documented in this study nearly triples the historical species richness recognized by Cooper (1983)."[12]

In addition, neither the Tenmile Creek Watershed Phase I Report nor the Phase II Report[13] indicates any actual chloride sampling results, yet PADEP is using this as justification for setting a chloride standard.

Furthermore, and most importantly, these two Tenmile Creek studies were fish surveys to document the fishery that exists in the stream as a baseline, not to determine the need for a chloride limit.

In the Preamble, the Department "recommends adopting these national chloride criteria for protection of aquatic life." However, in the very next sentence the Department states, "Scientists at the US EPA are currently conducting research to determine if the national criterion for chloride should be updated." Given PADEP's desire to use EPA reports and research with respect to chloride standards, the lack of a robust dataset indicating a chloride problem, and the billions of dollars industry will spend in control technology, we suggest the more prudent course of action would be to wait for EPA to complete their research before setting a standard. This would give PADEP sufficient time to collect the appropriate samples and complete a series of statistically significant aquatic and benthic testing in the Commonwealth. We believe the small amount of data being used by PADEP lack scientific integrity and statistical appropriateness, and are insufficient and indefensible to support PADEP's decision to propose this rulemaking.

3. The Proposed Rulemaking Is Based On A Report Which Utilizes Outdated Methodology To Assess Chloride Toxicity.

§ 304(a)(1) of the Clean Water Act requires EPA to develop criteria for water quality that accurately reflects the latest scientific knowledge. These criteria are based solely on data and scientific judgments on pollutant concentrations and environmental or human health effects.

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[10] Ibid, page 1.

[11] Ibid, page 3.

[12] Ibid, page 10.

[13] Argent, David G. and Kimmel, William G., *"A Comprehensive Ichthyofaunal Survey of Tenmile Creek Watershed Phase I"*, California University of PA, March 2008.

PADEP's Preamble further states:

> "[t]he Department has reviewed the EPA ambient water quality criteria development document and agrees with the....**methods** used to develop the criteria." 40 Pa.B.2265.

PADEP's reliance on the methodology used by EPA to develop the *1988 EPA Recommended Criteria for Chloride* is also completely unjustified because the method used to development its 1988 recommendation did not factor in the effect of water hardness on the potential toxicity of chloride.

To develop the *1988 EPA Recommended Criteria for Chloride*, EPA relied upon standard laboratory toxicity testing which used sodium chloride in laboratory reconstituted water at set concentrations.[14] However, the most recent testing methods, recommended by EPA, and used by Iowa, to develop a chloride criteria for water quality protection in that State, focuses on water hardness and states:

"Results of the research and toxicity testing completed for chloride showed that **chloride toxicity is heavily dependent on water hardness...**"[15](emphasis added). This data indicates that as water hardness increases larger amounts of chloride can be present without causing toxicity to aquatic species.[16]

Given the documented importance of water hardness on chloride toxicity, for the EQB to accept as appropriate for Pennsylvania (a state where surface water is often naturally hard) a standard which was developed without factoring in water hardness is completely unjustified and will lead to the imposition of needlessly stringent chloride effluent limits in NPDES Permits. Any chloride standard for Pennsylvania should factor in the hardness of the water to be protected.

4. The EQB Should Reject This Proposal And Insist That PADEP Consider Alternative Approaches To Regulating Chloride.

In response to the question on the Regulatory Analysis Form asking whether "any alternative regulatory provisions...have been considered and rejected" by the Department, it states: "**there are no alternative regulatory schemes to consider** in achieving the correct level protection for the aquatic life uses of water of this Commonwealth...."

First, there has been no generally documented decline in the overall health of aquatic life in this Commonwealth over the past 22 years, during which time the *1988 EPA Recommended Criteria for Chloride* were not in use, and the Department used osmotic pressure as the means for regulating chloride and other solids present in industrial discharges. This fact alone supports the conclusion that this is at least one alternative that should have been considered, namely the *status quo*.

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[14] Ibid.
[15] Ibid.
[16] Ibid.

Second, EPA's website[17] indicates "States may use the criteria that are developed by EPA to help set water quality standards that protect the uses of their waters **or they may develop their own water quality criteria."** '[emphasis added]

Third, and more importantly, if there is a true need to more aggressively regulate chloride in industrial discharges (which has yet to be proven), one clear available alternative is do what was recently done in Iowa and that is to open the subject up to a full and reasonable public debate and to consider each of the approaches which Iowa considered, including adopting an approach to regulating Chlorides which is premised upon the hardness and sulfate content of the receiving stream, an approach that is also now under consideration in the State of Missouri, where on March 3 of this year a petition was presented to that State's environmental regulatory agency to amend the chloride standard to follow the Iowa alternative approach.[18]

5. The Proposal's Economic Analysis Is Insufficient And Misleading And Doesn't Address/Understand Competition.

Nothing in the materials provided by PADEP assign any costs to the new monitoring requirements that would necessarily result if the proposed chloride standard was imposed. Currently, most dischargers regulated by PADEP are authorized to take periodic grab samples of their discharges, send these samples to outside labs, and report the test results on a monthly basis. However, to determine whether or not a discharge is in compliance with a chloride standard such as, a 1-hour average of 860 mg/L or a 4-day average of 230 mg/L, the discharger will need to install equipment that is capable of monitoring and sampling a waste water discharge 24 hours per day, seven days a week—continuous discharge monitors. Such equipment is costly to acquire and equally costly to operate. In addition, it requires a source of power to operate on a 24-hour basis which will not be present at remote locations were many discharges associated with mineral extraction activities are located. Consequently, the costs of providing power to such sites will also be a factor.

In addition, the only alternatives noted by PADEP are ones associated with oil and gas operations. PADEP has not reviewed the economic impact of this regulation on other major industrial or municipal sectors and, in particular, has not thought through all the implications of this proposed rulemaking including the adverse effects on the competitiveness of the coal industry. As PADEP knows from presentations by the various industry sectors involved with the TDS Chapter 95 Taskforce, the only type of technology that could meet the new chloride limits are ones involving evaporation, crystallization or reverse osmosis technologies. Installation and operation costs, the costs of which to install and operate are prohibitive at any currently operating mining operation in Pennsylvania.

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[17] Http://www.epa.gov/waterscience/criteria/basic/htm

[18] Missouri Agribusiness Association, Petition Requesting Revision to Chloride and Sulfate Water Quality Standards. February 5, 2010 to Missouri Clean Water Commission.

PCA presented to PADEP an impact analysis of the proposed TDS rulemaking on the bituminous mining sector.[19] The data received for this analysis accounted for 85 percent of the 68 million tons of coal produced annually in Pennsylvania and potential flows to be treated of 26,725 gallons per minute. This analysis and related costs are just as accurate for chloride removal as they were for TDS.

We would remind PADEP that the technologies available to treat chlorides are limited, depend upon the individual chemical constituents of the water to be treated, and have unique and significant technical and economic feasibility issues.

For the bituminous coal mining industry, the only technology potentially capable of achieving the chloride levels PADEP is proposing, is reverse osmosis combined with evaporation and crystallization and pretreatment. Based on the study conducted by CME Engineering for PCA[20], the cost to the bituminous coal mining industry to install technology to treat chlorides is:

- **$1.325 billion in capital costs,**
- **$133 million every year for operation and maintenance costs, and**
- **$134 million for bonding a 500 gallon per minute zero liquid discharge treatment system, as calculated with the AMD treat and bond/trust fund calculation spreadsheets.**
- These costs **do not** include dollars for land acquisition, site development, utility extensions, etc. necessary to construct a treatment plant.

PADEP indicates reverse osmosis facilities should produce satisfactory effluent at a cost of less than 1 cent per gallon.[21] PADEP has indicated publicly that this number is based on information from vendors whose sole purpose is to develop a market and sell their products. Notwithstanding the CME Report, several of our members have conducted studies based on specifics at their facilities that show the cost to be significantly higher. We would caution PADEP in giving higher value to sales representatives' pitches than to industries who have conducted studies based on their specific criteria and who answer to shareholders regarding expenditures and the operation of their facilities.

Furthermore, the imposition of the proposed chloride standard likely will have an immediate impact on publicly operated treatment works simply because, as noted in the Preamble, EPA itself has recognized that a major anthropogenic source of chloride is discharges from municipal wastewater plants and the use of salt on roads by municipalities. (EPA 1988) 40 Pa.B.2265. Yet, in the materials submitted by PADEP to

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[19] J. Owsiany on behalf of the Pennsylvania Coal Association. *"Mining Sector: Impact Analysis of the High TDS Strategy on the Mining Industry."* Presentation, PA DEP Water Resources Advisory Committee, Ch. 95 Taskforce, Harrisburg, PA, September 22, 2009.

[20] A full copy of the report generated by CME Engineering which contains a more detailed analysis of the treatment options and associated costs was submitted on February 11, 2010 to the Environmental Quality Board as part of PCA's comments on the proposed Chapter 95 rulemaking and is incorporated by reference. Due to size, it is attached to the hard copy only.

[21] See IRRC Regulatory Analysis Form, page 5 submitted to Mr. Kim Kaufman on April 21, 2010 and page 4 of the Preamble.

the EQB the statement is made that the proposal will have no impact on municipalities. This is simply not the case and care should be taken to fully assess the impact of the proposal on not just industry (including the agricultural industry, which according to EPA is another major source of chloride) but also on state and local government.

Moreover, other states that provide competition for the coal mining industry do not have chloride regulations, thereby making their products more price friendly as they do not have to install costly control technology. Below are some of the surrounding states' limits:

Maryland - no limit

Ohio - no limit

Tennessee - no limit

WV - Acute 860 mg/l. Note however that the limits can be changed per site based on temperature and water flow.

In their haste to develop a regulation, PADEP has failed to consider the non-water quality indirect environmental and economic impacts including residual waste generation, management and disposal challenges as well as increased power usage.

6. The Proposal is Illogical and Fails to Address Major Sources of Chlorides Such as Deicing.

On page 8 of the Regulatory Analysis Form, PADEP indicated that no other state agencies are affected by this proposal. In fact, PADEP has overlooked the impacts of other major potential sources of chloride such as road salt used for deicing. Last year, PennDOT and the PA Turnpike Commission used over 1 million tons of road salt. This number does not take into account residential usage for sidewalks, softening systems and driveways or commercial uses such as parking lots. One million tons of salt is equivalent to 650,000 tons of chlorides potentially landing up in PA waterways. In reality, some salt will remain on land and leach down into the groundwater.

In addition, the assertion that a point source discharger may be able to offset operational costs somehow by marketing its waste salt is illogical and grounded in bureaucracy. The very suggestion that industry waste valuable resources and energies removing the chlorides only to have them deposited back into the stream is absurd. No company would expose itself to the liabilities implied by disposing of wastewater on public property to make a profit. If one follows PADEP's assertion that chlorides in our waterways stress aquatic life forms and that some of the Commonwealth streams exhibit NO assimilative capacity[22], won't those same aquatic life forms be stressed by spreading sodium chloride on the roads which ultimately ends up in streams? PADEP has not shown

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[22] Page 3 of PADEP's Evaluation of Water Quality Criteria for Aquatic Life Use Protection Rationale Document date January 2010 and available on PADEP's website as noted in the Preamble.

that adding a standard for chloride will protect surface waters in view of this failure to address other chloride sources.

In light of these deficiencies, the proposed requirements need to be withdrawn and reconsidered in detail using current science. PCA appreciates the opportunity to comment.

Sincerely,

Josie Gaskey

Attachment

Cc: George Ellis

Water Quality Standards Review:

Chloride, Sulfate and Total Dissolved Solids

Iowa Department of Natural Resources
Consultation Package
February 9, 2009

Table of Contents

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	***C. dubia*** **48 h LC50 (95%CI) GLEC (mg Cl/L)**	***C. dubia*** **48 h LC50 (95%CI) INHS (mg Cl/L)**	**Mean LC50 value (mg Cl/L)**
Acclimated to and Tested at Various Total Hardness Levels (and 65 mg/L Sulfate)			
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
Acclimated to and Tested at Various Sulfate Levels (and 300 mg/L Hardness)			
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), *Sphaerium simile*	740 (678-807)	1100[a] (1040-1164)
Planorbid snail (mixed ages), *Gyraulus parvus*	3,078 (2,771-3,418)	3,009 (2,728-3,318)
Tubificid worm (mixed ages), *Tubifex tubifex*	4,278 (3,848-4,717)	6,008 (5,563-6,489)

[a] 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^a = 35)	B (N = 35)	C (N = 23)	D (N = 29)
Acute Value (CMC)	574	$283.17(\text{hardness})^{0.205797}(\text{sulfate})^{-0.07452}$	$254.3(\text{hardness})^{0.205797}(\text{sulfate})^{-0.07452}$	$195.7(\text{hardness})^{0.217736}$
Chronic Value -1 (CCC1)	238	$117.36(\text{hardness})^{0.205797}(\text{sulfate})^{-0.07452}$	$105.4(\text{hardness})^{0.205797}(\text{sulfate})^{-0.07452}$	$81.1(\text{hardness})^{0.217736}$
Chronic Value -2 (CCC2)	360	$177.70(\text{hardness})^{0.205797}(\text{sulfate})^{-0.07452}$	$159.6(\text{hardness})^{0.205797}(\text{sulfate})^{-0.07452}$	$122.8(\text{hardness})^{0.217736}$
Chronic Value -3 (CCC3)	342	$168.77(\text{hardness})^{0.205797}(\text{sulfate})^{-0.07452}$	$161.5(\text{hardness})^{0.205797}(\text{sulfate})^{-0.07452}$	$120.7(\text{hardness})^{0.217736}$

[a] 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 8th, 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.

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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 (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		
	50th percentile	90th percentile	Maximum value
TDS	360	510	1,640
Chloride	23	40	170
Sulfate	**37**	**97**	**400**
Hardness (as $CaCO_3$)	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 (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, *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 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, S*phaerium 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 $CaCO_3$) 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:

   Sulfate Criterion = [1276.7 + 5.508 (hardness) – 1.457 (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:

   Sulfate Criterion = [-57.478 + 5.79 (hardness) + 54.163 (chloride)] * 0.65

3) The following sulfate standards must be met at all times when hardness (in mg/L as $CaCO_3$) 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 $CaCO_3$	$Cl^- < 5$ mg/L	5 < = Cl^- < 25	25 <= Cl^- < =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

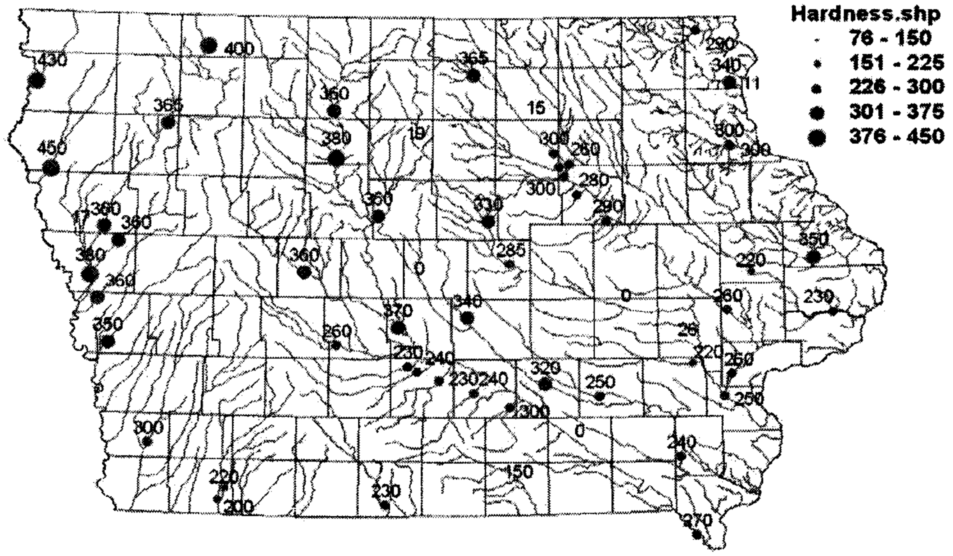
Based on the similarities in surface water quality and aquatic life species distributions between Iowa and Illinois, the same approach for TDS, sulfate and chloride criteria can be applied, that is replacing the current site-specific TDS approach with numerical sulfate and chloride criteria for aquatic 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

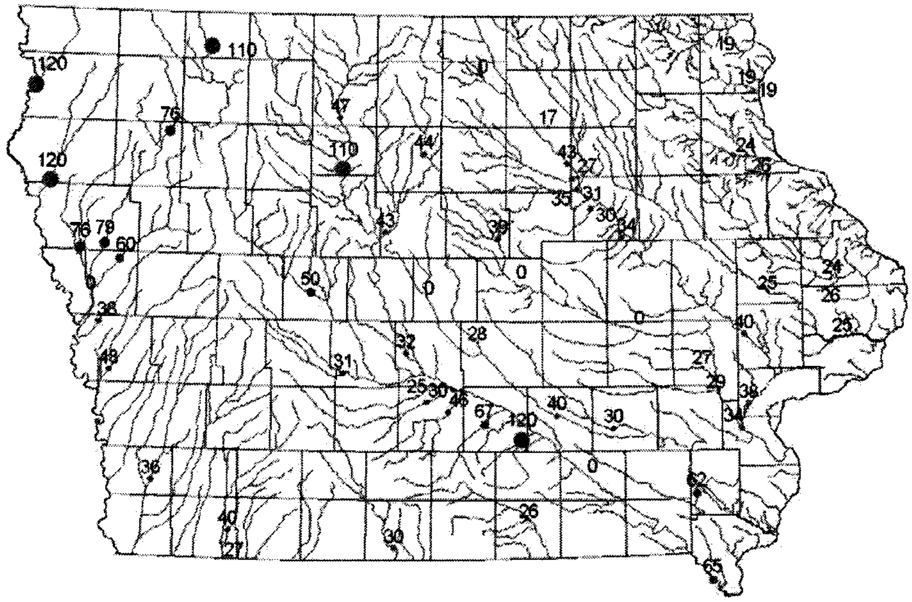
Sulfate is not a toxicant in the category of heavy metals, pesticides or other toxic natural or man-made substances, but rather is a common salt necessary for life at some concentrations. It is usually diluted in the waterbody rather quickly and is non-bioaccumulative. Also, since the sulfate standard 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

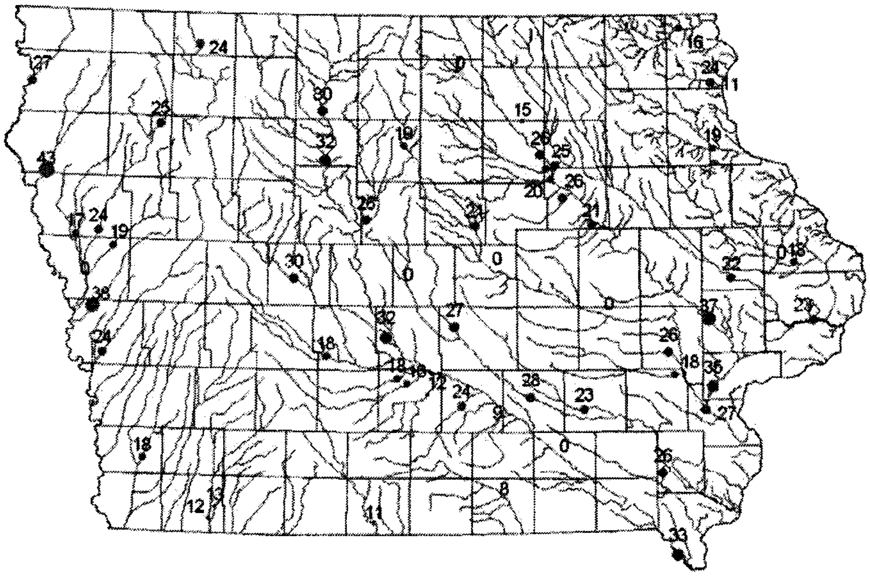
Statewide Hardness as CaCO3



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 (SO42-) 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 SO42- 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 (Na2SO4) to a standard medium (as defined by USEPA and ASTM). The medium contains various cations, Na, K, Mg, and Ca, and anions, HCO3, 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 Na2SO4 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 Na2SO4 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_{10} (lethal concentration to10% 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, S*phaerium 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_{50} (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-Karber 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(hardness) - 1.457(chloride)
H. azteca: LC50 = 1464 + 5.508(hardness) - 1.457(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.

AATC = [1276.7 + 5.508 (hardness) – 1.457 (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.

Animal	Treatment	Sulfate (mg/L)	Effect	Reference
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

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

Meyer, JS et al. 1985. Chemistry and Aquatic Toxicity of Raw Oil Shale Leachates from Peceannce 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.

Reference	**Comment**
Abraham, T.J., K.Y.M. Salih, and J. Chacko. 1986. Effects of Heavy Metals on the Filtration Rate of Bivalve Villorita cyprinoides (Hanley) Var. Cochinensis. Indian J. Mar. Sci. 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 Daphnia magna. Sewage Works J. 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 Daphnia magna. Sewage Works J. 18(1):82-87. (A: 2130)	Test results with D. magna but they probably are not useful.

Reference	**Comment**
Anderson, B.G. 1948. The Apparent Thresholds of Toxicity of Daphnia magna for Chlorides of Various Metals When Added to Lake Erie Water. Trans. Amer. Fish. Soc. 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, Musculium transversum. 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 Allium cepa L., Lepidium sativum L. and Daphnia magna St.: Comparative. Water Res. 29(2):497-503. (A: 13712)	Test results with D. magna 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. Nature 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 Chlorella. Proc. W. Va. Acad. Sci. 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. J. Fish Dis. 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. Sewage Ind. Wastes 29:53-75.	No results concerning sulfate.

Reference	**Comment**
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 (Anguilla anguilla) in a constant temperature culture. Ann. Inst. Michel Pacha, Lab. Marit. Physiol. 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 (Anguilla anguilla) during thermal stress. Ann. Inst. Michel Pacha, Lab. Marit. Physiol. 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 (Salmo gairdneri R.) maintained at constant temperature. Cah. Lab. Hydrobiol. Montereau No. 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 (Salmo gairdneri R.) after the production of thermal shocks. Cah. Lab. Hydrobiol. Montereau No. 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. Gesund. Ing. 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.), Comparative Leukemia Research 1973, Leukemogenesis, Bibl. Haematol. No. 40, 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, Mysidopsis bahia. Arch. Environ. Contam. Toxicol. 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. Proc.13th Ind. Waste Conf., Purdue Univ, Eng. Bull 43:243-252. (A: 930)	All relevant test results are acceptable.

Reference	**Comment**
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. Environ. Toxicol. Chem. 19:210-214.	All tests were on synthetic effluents.
Davies, T.D. 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.	All relevant tests with D. magna and H. azteca 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: www.trcr.bc.ca/docs/2003-davies_etal.pdf	Same data as Davies (2002).
Den Dooren de Jong, L.E. 1965. Tolerance of Chlorella vulgaris for Metallic and Non-Metallic Ions. Antonie Leeuwenhoek J. Microbiol. Serol. 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. Environ. Toxicol. Chem. 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 Dreissena polymorpha Using a Simi-microassay. Can. J. Zool. 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 polymorphia: 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 Na2SO4 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: Heterohabditidae) 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.
Khangarot, 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 Daphnia magna Straus. Ecotoxicol. Environ. Saf. 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. Can. J. Fish. Aquat. Sci. 52:464-469.	Sodium-sulfate waters limit the hatching success of several species of fish.

Reference	**Comment**
LeBlanc, G.A., and D.C. Surprenant. 1984. The influence of mineral salts on fecundity of the water flea (Daphnia magna) and the implications on toxicity testing on industrial wastewater. Hydrobiologia 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 (Alburnus alburnus) and the Harpacticoid. Chemosphere 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 Scenedesmus obliquus. Water Res. 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 Ceriodaphnia dubia, larval Fathead Minnow, and the Freshwater Mussel Anodonta imbecilis. Environ. Toxicol. Chem. 14:1913-1920.	All toxicity tests were on a synthetic mine effluent.
McKee, J.E., and H.W. Wolf. 1963. Water Quality Criteria, 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 Peceannce Basis, Colorado. Environ. Toxicol. Chem. 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 Ceriodaphnia dubia, Daphnia magna and Pimephales promelas (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. Prog. Fish-Cult. 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. Aquatic Toxicity Workshop, Quebec City.	All relevant test results are acceptable.

Reference	**Comment**
Pillard, D.A. et al. 2000. Predicting the Toxicity of Major Ions in Seawater to Mysid Shrimp (Mysidopsis bahia), Sheepshead Minnow (Cyprinodon variegatus), and Inland Silverside Minnow (Menidia beryllina). Environ. Toxicol. Chem. 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 (Carassius auratus) After Sublethal Exposure to Hexachlorobutadiene. Aquat. Toxicol. 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. Limnol. Oceanogr. 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. Cumbria Sea Fish. Comm., Sci. Rep. No.74/1, 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. Sewage Ind. Wastes 22:1157-1187(?).	No results concerning sulfate.
Saliba, L.J., and M. Ahsanullah. 1973. Acclimation and Tolerance of Artemia salina and Ophryotrocha labronica	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 Phytoplankon 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 Biotoxicity 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).

Tomiyama, 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. Rocz. 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 Mytilus edulis: Effects of Diatom Chemical Composition. Mar. Biol. 125:715-724. (A: 7332)	No toxicity test results.
Wang, W. 1986. Toxicity Tests of Aquatic Pollutants by Using Common Duckweed. Environ. Pollut. (Ser. B) 11(1):1-14. (A: 11789)	All tests were with duckweed.

Reference	**Comment**
Wells, M.M. 1915. The reactions and resistance of fishes in their natural environment to salts. Jour. Exp. Zool. 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. J. Exp. Mar. Biol. Ecol. 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. Bull. Environ. Contam Toxicol. 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. Suishitsu Odaku Kenkyu 7(9):576-528. (A: 9715)	All tests were with algae.
Young, R.T. 1923. Resistance of Fish to Salts and Alkalinity. Amer. Jour. Physiol. 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	*Ceriodaphnia dubia*	2,526	10	2.33	100	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,357	10	2.33	100	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,526	10	2.33	102	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,223	15	2.33	92	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,243	15	2.33	94	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,402	15	2.33	94	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,470	20	2.33	94	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,295	20	2.33	94	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,494	20	2.33	94	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,153	25	2.33	100	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,563	25	2.33	96	Soucek 2004
Water flea	*Ceriodaphnia dubia*	1,868	25	2.33	96	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,799	25	2.33	96	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,458	25	2.33	96	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,357	100	2.33	96	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,784	100	2.33	96	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,112	100	2.33	104	Soucek 2004
Water flea	*Ceriodaphnia dubia*	1,895	300	2.33	98	Soucek 2004
Water flea	*Ceriodaphnia dubia*	1,798	300	2.33	102	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,049	300	2.33	102	Soucek 2004
Water flea	*Ceriodaphnia dubia*	1,400	500	2.33	96	Soucek 2004
Water flea	*Ceriodaphnia dubia*	1,933	500	2.33	98	Soucek 2004
Water flea	*Ceriodaphnia dubia*	1,157	500	2.33	94	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,030	1.9	1.46	94	Soucek 2004
Water flea	*Ceriodaphnia dubia*	1,868	1.9	1.46	94	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,269	1.9	1.46	94	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,538	34	5.4	107	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,607	34	5.4	107	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,436	34	5.4	107	Soucek 2004
Water flea	*Ceriodaphnia dubia*	3,059	1.9	1.46	194	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,706	1.9	1.46	194	Soucek 2004
Water flea	*Ceriodaphnia dubia*	3,265	1.9	1.46	194	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,383	1.9	1.46	288	Soucek 2004
Water flea	*Ceriodaphnia dubia*	3,361	1.9	1.46	288	Soucek 2004
Water flea	*Ceriodaphnia dubia*	2,853	1.9	1.46	288	Soucek 2004
Water flea	*Ceriodaphnia dubia*	3,297	1.9	1.46	288	Soucek 2004
Water flea	*Ceriodaphnia dubia*	3,369	1.9	1.46	390	Soucek 2004
Water flea	*Ceriodaphnia dubia*	3,073	1.9	1.46	390	Soucek 2004
Water flea	*Ceriodaphnia dubia*	3,091	1.9	1.46	390	Soucek 2004
Water flea	*Ceriodaphnia dubia*	3,716	1.9	1.46	484	Soucek 2004
Water flea	*Ceriodaphnia dubia*	3,506	1.9	1.46	484	Soucek 2004
Water flea	*Ceriodaphnia dubia*	3,338	1.9	1.46	484	Soucek 2004
Amphipod	*Hyalella azteca*	1,785	33	2.33	96	Soucek 2004
Amphipod	*Hyalella azteca*	1,865	33	2.33	100	Soucek 2004
Amphipod	*Hyalella azteca*	1,749	33	2.33	96	Soucek 2004
Amphipod	*Hyalella azteca*	1,919	100	2.33	98	Soucek 2004
Amphipod	*Hyalella azteca*	1,833	100	2.33	100	Soucek 2004
Amphipod	*Hyalella azteca*	2,062	100	2.33	100	Soucek 2004
Amphipod	*Hyalella azteca*	1,739	300	2.33	98	Soucek 2004
Amphipod	*Hyalella azteca*	1,614	300	2.33	96	Soucek 2004
Amphipod	*Hyalella azteca*	1,721	300	2.33	100	Soucek 2004
Amphipod	*Hyalella azteca*	1,435	500	2.33	98	Soucek 2004
Amphipod	*Hyalella azteca*	1,503	500	2.33	100	Soucek 2004
Amphipod	*Hyalella azteca*	1,472	500	2.33	100	Soucek 2004
Amphipod	*Hyalella azteca*	2,030	25	2.33	106	Soucek 2004
Amphipod	*Hyalella azteca*	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	*Hyalella azteca*	1,615	25	2.33	98	Soucek 2004
Amphipod	*Hyalella azteca*	2,057	25	2.33	102	Soucek 2004
Amphipod	*Hyalella azteca*	2,655	25	2.33	194	Soucek 2004
Amphipod	*Hyalella azteca*	2,076	25	2.33	192	Soucek 2004
Amphipod	*Hyalella azteca*	2,887	25	2.33	196	Soucek 2004
Amphipod	*Hyalella azteca*	2,189	25	2.33	296	Soucek 2004
Amphipod	*Hyalella azteca*	3,358	25	2.33	292	Soucek 2004
Amphipod	*Hyalella azteca*	2,978	25	2.33	292	Soucek 2004
Amphipod	*Hyalella azteca*	2,612	25	2.33	392	Soucek 2004
Amphipod	*Hyalella azteca*	4,026	25	2.33	396	Soucek 2004
Amphipod	*Hyalella azteca*	4,314	25	2.33	396	Soucek 2004
Amphipod	*Hyalella azteca*	4,234	25	2.33	486	Soucek 2004
Amphipod	*Hyalella azteca*	4,320	25	2.33	482	Soucek 2004
Amphipod	*Hyalella azteca*	3,825	25	2.33	482	Soucek 2004
Fingernail clam	*Spherium simile*	1,857	1.9	1.46	89	Soucek 2004
Fingernail clam	*Spherium simile*	2,069	1.9	1.46	81	Soucek 2004
Fingernail clam	*Spherium simile*	2,633	1.9	1.46	83	Soucek 2004
Fingernail clam	*Spherium simile*	2,278	33	5.4	89	Soucek 2004
Fingernail clam	*Spherium simile*	2,122	33	5.4	96	Soucek 2004
Fingernail clam	*Spherium simile*	2,671	1.9	2.33	274	Soucek 2004
Fingernail clam	*Spherium simile*	2,509	1.9	2.33	285	Soucek 2004
Fingernail clam	*Spherium simile*	3,025	33	1.46	90	Soucek 2004
Fingernail clam	*Spherium simile*	2,582	33	1.46	87	Soucek 2004
Fingernail clam	*Spherium simile*	2,343	33	1.46	94	Soucek 2004
Fingernail clam	*Spherium simile*	3,139	1.9	1.46	274	Soucek 2004
Fingernail clam	*Spherium simile*	2,712	1.9	1.46	264	Soucek 2004
Fingernail clam	*Spherium simile*	2,297	1.9	1.46	195	Soucek 2004
Fingernail clam	*Spherium simile*	2,082	1.9	1.46	191	Soucek 2004
Fatmucket	*Lampsilis siliquoidea*	3,377	25	2.33	100	Soucek 2005
Fatmucket	*Lampsilis siliquoidea*	3,525	25	2.33	300	Soucek 2005
Fatmucket	*Lampsilis siliquoidea*	3,729	25	2.33	500	Soucek 2005
Fatmucket	*Lampsilis siliquoidea*	1,727	5	1.46	100	Soucek 2005
Fatmucket	*Lampsilis siliquoidea*	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.

Chloride (mg/L)	Hardness (mg/L)										
	<100	**100**	**150**	**200**	**250**	**300**	**350**	**400**	**450**	**500**	**>500**
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	*302.208g*	*302.208g*	*302.208g*	*302.208g*	*302.208g*	*302.208g*	*302.208g*	*302.208g*	*302.208g*	*302.208g*	*302.208g*

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 16th, 2004 and was approved by EPA on December 6th, 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^+, $HCO3^-$, Mg^{2+}, Cl^-, and $SO4^{2-}$. 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 $HCO3^-$ to D. magna might be the inhibition of the active uptake of 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, Ca^{2+} and 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 $K^+ > HCO3^- = Mg^{2+} > Cl^- > SO4^{2-}$. 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^+ , $HCO3^-$,Mg^{2+}, Cl^- and $SO4^{2-}$, 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)	Concentration 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 10th	 25th	 50th	 75th	 90th	Max Value	Average
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		
	50th percentile	90th percentile	Maximum value
TDS	360	510	1,640
Chloride	23	40	170
Sulfate	37	97	400
Hardness (as CaCO3)	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^+, $HCO3^-$, Mg^{2+}, Cl^-, and $SO4^{2-}$. 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 Cl^-, $SO4^{2-}$ and 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 CaCO3. However, the median hardness for Iowa streams is 300 mg/L as CaCO3. 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.

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2841

From: Kaufman, Kim
Sent: Tuesday, June 15, 2010 9:07 AM
To: Wilmarth, Fiona E.; Gelnett, Wanda B.; Outreach
Subject: Fw: 2841 - 25 PA Code Ch 93 Chlorides
Attachments: PCA Chlorides comments final.doc; Iowa Water Quality Standards Review report.pdf

FYI

From: Josie Gaskey
To: Schalles, Scott R.
Cc: Kaufman, Kim
Sent: Tue Jun 15 08:42:19 2010
Subject: 2841 - 25 PA Code Ch 93 Chlorides

Attached are comments submitted to the EQB earlier today regarding the above.

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