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Iowa's Water Quality Standard Review – Total Dissolved Solids (TDS)

I. Background

The TDS is a measure of all constituents dissolved in water. The inorganic anions dissolved in water could include carbonates, chlorides, sulfates and nitrates. The inorganic cations could 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 is 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 provided by a 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 six recommendations made by the EPC, as specified in ARC 3281B, published in the April 14, 2004, Iowa Administrative Bulletin. The Department will utilize the information gathered during the three-year period to propose a new standard by April 1, 2007. The six recommendations by EPC were:

1. Sample and monitor chlorides and TDS for adequate data to make an informed decision including the possible costs and returns associated with clean and healthy water.
2. Monitor aquatic ecosystem impacts through biological surveys, particularly where aquatic life may be impacted as a result of current effluent levels of cations and anions. Coordinate with and utilize fisheries personnel where possible.
3. Utilize the U.S. Environmental Protection Agency (EPA) to make sure options being considered are consistent with the Federal Clean Water Act including court directives.
4. Review stream classifications to be sure that the uses of streams are properly classified.
5. Sponsor a workshop with help from EPA and Iowa scientists on alternative solutions to hard water, solutions for managing effluent during low-flow

conditions, new technology in waste treatment, and health considerations of effluent when reentering the drinking water supply.

6. Continue consideration of site-specific Whole Effluent Toxicity (WET) tests but with maximum standards to protect aquatic ecosystems, livestock and wildlife watering, and other uses in current rules.

II. Interim TDS Site-Specific Approach as Adopted in 2004

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.

For point sources that discharge directly into a general use stream (undesignated), based on the site-specific TDS approach, if a facility's discharge causes the in-stream TDS concentration above 1000 mg/l, acute toxicity tests would be required 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 will 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 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.

III. Implementation Issues with the Interim TDS Site-Specific Approach

The current site-specific TDS approach uses the 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.

Implementation Problems:

1. Chronic testing with *Ceriodaphnia* has shown inconsistent testing results for the same discharge.
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 samples 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.

IV. 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. 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 2006. This data set provides an indication of what typical ion and TDS concentrations are for Iowa streams. Table 1 shows a summary of TDS, chloride, sulfate and hardness values for the Iowa ambient monitoring data from 2000-2005. These monthly monitoring data represent different stream flow conditions.

Table 1. TDS and Ion Concentrations in Iowa Streams

Chemicals	Iowa Ambient Monitoring Data from 2000-2005, units in mg/l		
	50^{th} percentile	90^{th} percentile	Maximum value
TDS	360	510	1640
Chloride	23	42	170
Sulfate	39	99	400
Hardness (as CaCO3)	300	410	820

V. 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 limited.

VI. The Analysis of TDS Toxicity Data Submitted by Facilities in Iowa

After EPA approved the interim site specific TDS approach on December 6, 2006, the Department started to implement the adopted standard. Since December 7, 2006, the Department has received TDS toxicity test data from approximately 50 facilities among the 307 NPDES permits issued. All 50 facilities conducted acute toxicity tests. Chronic toxicity test data was submitted by 23 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 2. 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.	5098	1980
	Min.	325	29
Chloride	Max.	1200	930
	Min.	14	5.0

VII. Literature Review on TDS Toxicity Data

See Appendix B.

VIII. Proposed Options

Option 1: Revised Site-Specific Toxicity Test Approach

The current site-specific approach requires facilities to conduct acute toxicity testing if the receiving stream is a general use, and both acute and chronic toxicity testing if the receiving stream is designated (when the in-stream threshold values are exceeded for TDS and/or chloride). The toxicity test results are used to develop water quality based limits for TDS as follows. For the acute test, either the ½ LC50 value or the No-Observed-Adverse-Effect concentration (NOAEC) for TDS is used as the daily maximum limit. For the chronic test, either the No-Observed-Adverse-Effect concentration (NOAEC) or the IC25 for TDS is used as the average limit. Both NOAEC and IC25 are defined in Appendix C. The current approach assumes that the toxicity in the effluent is from TDS or chloride only. In reality, several factors could affect effluent toxicity test results, including other pollutants, potential interactions among different pollutants, etc.

According to the EPA procedure, WET test results are recorded as percentages, representing how much dilution, if any, of an effluent sample is required for a certain effect to occur (*e.g.*, for the "No Observable Effect Concentration" data points, the percentage represents the level of dilution at which the mixture ceases to affect the organisms). Effluent that must be diluted to a 25% concentration before it ceases to cause demonstrable harm is more toxic than effluent that need only be diluted to 50%. In order to simplify the expression and application of these test results, EPA devised a scale of chronic toxicity units ("TU_c"), equal to 100 divided by the measured percentage value, such that the 25% sample above would translate to 4 TU_c, while the 50% sample would be 2 TU_c.

The use of TDS concentrations as end points is not the recommended measurement unit for WET testing. The question becomes, "can a WET limit be used to replace a TDS concentration limit for the site-specific TDS approach?" A WET limit is a permit control required where the reasonable potential exists for an exceedance of the State water quality criteria for the protection of aquatic life where a specific toxicant has not been identified and controlled via a toxicity reduction evaluation (TRE). It is probably not appropriate to use Toxic Unit as the end point for TDS if the toxicity failed because of other pollutants rather than TDS.

Recommended approach: if the effluent TDS concentration causes an in-stream concentration above a threshold level of 1000 mg/l (only the TDS threshold level is needed since IDNR will adopt chloride criteria separately), WET tests would be required. If the facility passes a WET test, no limits are imposed. If a facility fails a WET test, options would include: conducting WET tests using site-specific species, using the ambient water as dilution water, and performing a rapid bioassessment of the downstream biota to demonstrate no impact from the elevated TDS discharge.

Option 2: Site-Specific Toxicity Test Using Mock Effluent

Another option would be to require WET testing if the effluent TDS concentration causes an in-stream concentration above a threshold level of 1000 mg/l (only TDS threshold level is needed since IDNR will adopt chloride criteria separately). However, in order to eliminate effluent toxicity from pollutants other than TDS, a mock effluent based on ion analysis of the effluent TDS can be used to conduct the required toxicity tests. The mock effluent samples can be prepared with de-ionized water and reagent-grade salts to match the effluent TDS and specific ion concentrations for the toxicity tests. The mock sample would eliminate other sources toxicity such as ammonia toxicity and only include the potential toxicities from TDS and specific ions. Then, the toxicity test results can be applied as the current approach without the consideration of chloride since IDNR will adopt chloride criteria separately.

Option 3: Numerical Criteria for TDS

Mount *et al*. (1997) indicates that the toxicity results for TDS show a wide range of LC50 values, depending on ionic composition. It is difficult to establish a TDS numerical criterion based on toxicity variability for different ion constituents of TDS. However, Goodfellow et al. (2000) states "as a general screening tool, if the conductivity of a freshwater effluent is above 2,000 µS/cm, the concentration of dissolved solids can be high enough to adversely affect freshwater test species". Thus, a screening conductivity criterion value of 2,000 µS/cm could be applied to all waters of the state. If the effluent conductivity causes an in-stream conductivity above this value, different implementation approaches can be used.

1) Mixing zone study. If the facility can show a higher mixing zone than the default values are achieved, the conductivity limits can be revised to reflect the site-specific mixing zone when water quality based limits are developed for conductivity.
2) Toxicity test: If the facility is willing to conduct toxicity tests, the new conductivity limits would be set based on the toxicity test results.
3) Flow variable limits: The limits would be calculated based on a certain stream flow value below which no discharge occurs.

Conductivity limits have advantages over TDS concentration limits as it is easy to measure conductivity and the results can be determined quickly on site.

Option 4: Specific Ion Criteria

As the literature review indicates, individual ions rather than TDS criteria/limits probably are more appropriate to characterize toxicity related to TDS. This discussion below explores the option of developing specific ion criteria for TDS.

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. The examination of STORET monitoring data and the analysis of effluent ion concentrations submitted to IDNR indicate that the concentrations of K^+, $HCO3^-$, and Mg^{2+} usually are not elevated to a level of concern. The ambient monitoring program usually does not monitor for K^+, $HCO3^-$, and Mg^{2+}, however some data has been collected. The limited ambient monitoring data available from STORET indicates that potassium concentration is usually below 100 mg/l (95th percentile is 78 mg/l). The 95th percentile concentration from the effluent ion analysis is below 67 mg/l. For magnesium, 95% of the ambient concentrations are below 60 mg/l. The 95th percentile concentration for magnesium from the effluent ion analysis is below 225 mg/l. The median effluent magnesium concentration is about 43 mg/l.

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 a hardness below 100 mg/l as CaCO3. However, the median hardness for Iowa streams is 300 mg/l as CaCO3.

Based on the examination of available effluent ion analysis and literature review, the TDS site-specific approach could 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 could be recalculated based on the national toxicity database and new toxicity data. The proposed chloride criteria are summarized in the chloride criteria work element report.

For sulfate, the Illinois approach could be used. The State of Illinois has proceeded through a thorough process to collect sulfate toxicity data. Thus, the following sulfate standard is proposed:

1) 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 between 100 mg/L and 500 mg/L and the chloride concentration of waters is between 25 mg/L and 500 mg/L:

      [1276.7 + 5.508 (hardness) – 1.457 (chloride)] * 0.65

B) If the hardness concentration of waters is between 100 mg/L and 500 mg/L and the chloride concentration of waters ranges between 5 mg/L and up to 25 mg/L:

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

2) 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 those specified in (h)(2) are present:

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

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

Since the sulfate criteria are derived based on acute toxicity data, the criteria are applied at the end of the Zone of Initial Dilution.

The above four options could be discussed among the Technical Advisory Committee members in order to select the most applicable TDS water quality standard that is approvable by EPA.

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: Literature Review on TDS Toxicity

The purpose of this review was to examine relevant published literature and other technical reports to determine the best approach for the development of specific TDS criteria and/or ion specific criteria for the State of Iowa.

Literature Overview:

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. 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.

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). The elimination of TDS standard is justified as follows:

"Therefore, between the chloride and sulfate water quality standards and the narrative toxics control standard (35 IAC 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. We recommend that the TDS standard be deleted from the Board's regulations."

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. The current TDS standard is replaced with the sulfate standard.

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 four 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, S*phaerium 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.

The Illinois EPA proposed the following numerical standard for sulfate:

1) 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 between 100 mg/L and 500 mg/L and the chloride concentration of waters is between 25 mg/L and 500 mg/L:

[1276.7 + 5.508 (hardness) – 1.457 (chloride)] * 0.65

B) If the hardness concentration of waters is between 100 mg/L and 500 mg/L and the chloride concentration of waters ranges between 5 mg/L and up to 25 mg/L:

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

2) 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 in (h)(2) 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 the sulfate standard is 2,000 mg/L.

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.

Appendix C: 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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