Facts in Support of Changing Water Quality Standards for Sulfate, Total Dissolved Solids and Mixing Zones

I. 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 A) gives the following account for sulfate:

Sulfate (SO_4^{2-}) is widely distributed in nature and may be present in natural waters at concentrations ranging from a few to several thousand milligrams per liter. Mine drainage wastes may contribute large amounts of SO_4^{2-} 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 4 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 V), 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 B, 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 document, 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 Exhibit B 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 V), 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.

II. 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 C).

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 D. 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 is 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.

III. 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	AS93-8	Akzo Chemical	Sulfate	1,000

Creek			TDS	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.

IV. 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.

V. 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 C) 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 E. 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 F) 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 G) 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 H) found that exposure to water with 2,500 mg/L sulfate results in poor conception of cattle. Patterson et al. (2004, See Exhibit I) 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 J). 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 has performed consultations for livestock operations throughout the State and has often dealt with the issue of sulfate in livestock water and feed. Dr. Meerdink was supplied with the data from Exhibit E 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 Exhibit E. 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 (Na_2SO_4) to a standard medium (as defined by USEPA and ASTM). The medium contains various cations, Na, K, Mg, and Ca, and anions, HCO_3, chloride and sulfate. All of these ions are necessary for normal functioning of cells. Raising the sulfate level is not just a matter of increasing the level of the specific substances, sodium and sulfate. It also involves increasing the ionic strength of the solution as a whole. Also, the balance or ratios of some of the ions are being changed as Na_2SO_4 is raised. Thus, sulfate toxicity (as for other ions) is a complex phenomenon with toxicity dissimilar to most other kinds of substances.

Sulfate is a conventional pollutant, therefore, information concerning it has been in the literature for many years. This means there may be information in older, sometimes difficult-to-find, literature. Tests done decades ago would not have been standardized in ways that are routine now. The most important problem encountered in the older studies

was that heavy metal contamination in the reagents might have exerted a toxic effect when a high level of the salt of interest is necessary to produce a response. Researchers prior to the 1980's were probably unaware that the purity of the sodium sulfate reagent used in their tests could have been a factor in the results obtained. Toxicity studies now use the most pure form available. The Agency also found that the literature contained studies done on unusual species that live in habitats with very little natural sulfate. In particular, a Canadian study was rejected because the test species was unique to an unusual mountain habitat, and was apparently very intolerant of what would be a normal level of sulfate in the Midwest. A complete list of all literature with comments on pertinence is found in Exhibit K.

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 L) requires gathering all data available and assessing their suitability to determine the water quality criterion. The Agency narrowed the search to Na_2SO_4 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 Exhibit M.

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 N). 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 O). 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 to 10% of exposed organisms) for the most sensitive organisms would be used in derivation

of the sulfate standard. However, this approach was met with opposition from USEPA, therefore, a modified approach of the Guidelines was utilized in its place. Details and justification for use of this sulfate-specific approach is summarized below in the equation formulation section.

Research conducted by Dr. Soucek was vital to the standard derivation, as the sensitivity of several organisms was thoroughly studied and greatly increased the amount of acceptable sulfate data. Possibly of greater significance was the finding that sulfate toxicity is dependent on water chemistry, thereby emphasizing the need for a water quality-based equation rather than a statewide numerical standard derived from typical procedures. Data obtained from research conducted by Dr. Soucek is summarized in Exhibit P, final and quarterly reports summarizing this research are found in Exhibits Q, R, S, T and U. 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 S), 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 P). 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:

AATC = [-57.478 + 5.79 (hardness) + 54.163(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.

VI. 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.

VII. 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 Exhibit V. 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.

VIII. 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.