

**COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF ENVIRONMENTAL PROTECTION
BUREAU OF POINT AND NON-POINT SOURCE MANAGEMENT**

**RATIONALE FOR THE DEVELOPMENT OF
AMBIENT WATER QUALITY CRITERIA FOR**

SULFATE

PROTECTION OF AQUATIC LIFE USE

A state-wide aquatic life criterion for sulfate would provide an appropriate level of protection for all of Pennsylvania's waters. The existing sulfate criterion was developed primarily for the protection of potable water supplies. Although this criterion, a maximum of 250 mg/l, may be protective of instream aquatic life uses when applied, it is not applied in all waters of the Commonwealth, but rather only at the point of water supply intake, pursuant to 25 Pa. Code § 96.3(d) (relating to water quality protection requirements). Elevated levels of sulfate are toxic to aquatic life in freshwater environments. Therefore, the Pennsylvania Department of Environmental Protection (Department) is recommending additional sulfate criteria to be applied in all freshwaters for the protection of aquatic life.

Pertinent scientific literature and historical data were reviewed and are discussed in detail in the following sections. This document presents the rationale and results of analyses conducted by the Department during development of an aquatic life criterion for sulfate.

Characteristics of Sulfate

Sulfate occurs naturally in the aquatic environment or it can have an anthropogenic origin. When sulfate naturally occurs in aquatic environments, it can be the result of the decomposition of leaves, atmospheric deposition, or the weathering of certain geologic formations including pyrite (iron disulfide) and gypsum (calcium sulfate). The processes involved with coal extraction greatly increase the effects of weathering by exposing the pyrite to more air and water which raises the dissolved sulfate level. Effluent waste from the extraction of coal varies widely in composition but it is typified by high concentrations of total dissolved solids. Sulfate is a primary constituent of the effluent waste (Rose and Cravotta, 1998). A USGS Report on the Water Quality in the Allegheny and Monongahela River basins names sulfate as an indicator of coal-mining activity and the report reveals that sulfate yields were 5 times greater in stream basins where coal mining occurred (Anderson, et al. 1996-98). The sulfate anion is the most prevalent specific dissolved solid in the effluent waste associated with Pennsylvania's coal extraction industry. In addition to coal mining, sulfate levels can be artificially elevated by discharges from municipal treatment plants, agricultural runoff, and industrial discharges including tanneries, pulp mills, and textile mills.

Freshwater fish and aquatic communities cannot survive in elevated concentrations of sulfates. Maintaining a proper salt-to-water balance in a freshwater environment challenges most aquatic life, and in particular, aquatic insects. Macroinvertebrates maintain an internal ionic concentration that is higher than the surrounding environment by actively transporting ions in and out of their bodies through osmoregulation (Buchwalter and Luoma, 2005). Osmoregulation can be disrupted by large increases in certain ions (including sulfate). This disruption in water balance and ion exchange is capable of causing stress or death to the organism (Pond et al. 2008).

Discussion / Rationale of Sulfate

There are currently no national ambient water quality criteria for sulfate which are designed to be protective of aquatic life. The Illinois Environmental Protection Agency (IL EPA) worked with the US EPA to conduct a multi-year project researching the toxicity of sulfate to aquatic life.

Dr. David Soucek of the Illinois Natural History Survey conducted the laboratory toxicity testing. His work included a determination of the sulfate level which corresponded with the acute toxicity for invertebrate species. The species that were part of the study included the water flea *Ceriodaphnia dubia*, an amphipod *Hyaella azteca*, a midge fly *Chironomus tentans*, fingernail clam *Sphaerium simile*, and a freshwater mussel *Lampsilis siliquoidea*. The toxicological results obtained using these species are applicable in Pennsylvania waters as this collection of species is representative of Pennsylvania. Dr. Soucek's work also revealed that the level of sulfate toxicity is driven by the concentrations of chloride and hardness.

To ensure that aquatic life is protected from sulfate throughout the Commonwealth, chloride and hardness need to be considered on a site-specific basis. This can be accomplished in Pennsylvania by using the Illinois sulfate criteria. The derivation of the aquatic life criteria for sulfate is based upon acute toxicity data only. This research indicated that the chronic toxicity of sulfate is not more sensitive than the acute effect, therefore, the sulfate criteria are implemented as both an acute and a chronic criterion with the corresponding durations of one hour and ninety-six hours, respectively (Connie Dou, pers comm, 2011). The end result of this work was the development of the Illinois equation-based sulfate criteria for the protection of aquatic life.

The Illinois sulfate criteria accounts for the relationship of chloride and hardness to sulfate toxicity, therefore chloride and hardness can be measured and entered into that equation to determine the maximum amount of sulfate allowable for that water body. At low chloride concentrations between 5 and 25 mg/l chloride ameliorates the toxic effect of sulfate but above 25 mg/l it adds to the toxicity, hence the two equations where chlorides are added in one and subtracted in the other. Soucek and Kennedy (2005) found that hardness ameliorates the toxicity of the sulfate.

Illinois aquatic life criteria consists of the equations for the low chloride (greater than or equal to 5 mg/L and less than 25 mg/L) and high chloride (greater than or equal to 25 mg/L but less than or equal to 500 mg/L) conditions when hardness is greater than or equal to 100 and less than or equal to 500 mg/L. Naturally occurring chloride levels never exceed 500 mg/L in Pennsylvania, therefore the sulfate equation for high chloride conditions will be applied whenever the chloride

is greater than or equal to 25 mg/L at the specified hardness conditions. Additionally, there are numerical standards that are used when chloride and hardness are extremely high or low. These numerical standards must be implemented because very little sulfate toxicity data is available at these extreme conditions (IL EPA, 2007).

The Illinois sulfate criteria also includes a protective standard for livestock in Illinois that is equal to 2,000 mg/l and applicable at any point where water is withdrawn or accessed for purposes of livestock watering. The naturally occurring concentrations of hardness and chloride throughout Pennsylvania preclude the possibility that the sulfate standard resulting from the equations would ever exceed 2,000 mg/l, therefore it is not necessary to adopt this standard for the protection of livestock.

Illinois and Iowa have both adopted this standard and it was approved by the USEPA for both states. Indiana has also promulgated this equation as their aquatic life criterion for sulfate.

The Department has reviewed the IL EPA ambient water quality criteria development document (ILEPA, 2007) for sulfate and agrees with the data analysis, interpretation, and development of the criterion. The Department recommends that the sulfate criteria, as summarized below, should be included in Pennsylvania’s water quality standards.

Proposed Sulfate Criteria for Pennsylvania Waters			
	Ch < 5 mg/L	5 ≤ Ch < 25	25 ≤ Ch
H < 100 mg/L	500	500	500
100 ≤ H ≤ 500	500	$S = [-57.478 + 5.79 (\text{hardness}) + 54.163 (\text{chloride})] * 0.65$	$S = [1276.7 + 5.508 (\text{hardness}) - 1.457 (\text{chloride})] * 0.65$
H > 500	500	2000	2000

H = hardness (in mg/L as CaCO₃). **Ch** = chloride (in mg/L). Hardness and chloride values used in the determination of the sulfate water quality standard shall be based on receiving water natural quality.

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