Model-based Aquatic Life Criteria for Metals

How May State Criteria Change?

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Objectives

Describe the U.S. Environmental Protection Agency's (EPA) modeling approach for developing aquatic life-based water quality criteria for metals

Discuss how the modeling changes metals criteria developed using the 1985 EPA methodology by incorporating site-specific water chemistry

Describe potential impacts on municipal and industrial wastewater discharges containing metals

Aquatic Life Criteria for Metals

Metals are the most frequent water quality-based effluent limits (WQBELs) in NPDES Permits

Copper, nickel, and zinc, in particular, are present in industrial (and POTW) effluents

When mixing zone allowances are low, e.g., low flow streams, WQBELs for metals are low and costly to achieve

Aquatic Life Criteria for Metals

The U.S. Environmental Protection Agency (EPA) adopts and publishes water quality criteria as authorized by Section 303 of the Clean Water Act

These criteria are **not** the water quality standards that are adopted and implemented by states in NPDES permits

The EPA criteria are guidance for the states and deviations from these must be justified by each state

Aquatic Life Criteria for Metals

EPA's methodology for adopting water quality criteria is published in *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection Of Aquatic Organisms and Their Uses*, PB85-227049, 1985 (updated in 2010)

The methodology is based on protecting >95% of aquatic species (animals, plants) from specific toxic pollutants

Aquatic Life Criteria for Metals

The EPA guidance requires that criteria be based on multiple taxonomic groups of aquatic species and be applied as acute and chronic criteria

- Acute effects – death, immobilization that occurs after short-term exposure
- Chronic effects — reduced growth, reduced reproduction occurring from continuous exposure – these include effects of bioaccumulation if present

Aquatic Life Criteria for Metals

The existing national criteria for metals, which are the basis for state water quality standards (including modified standards) are based on laboratory biological tests for each metal

- Criteria are based on dissolved metals concentrations
- They account for pH and hardness effects on toxicity when data are sufficient
- They are expressed as a criterion maximum concentration (CMC-acute) and a criterion continuous concentration (CCC-chronic)

Aquatic Life Criteria for Metals

In addition to the adjustments to certain metals criteria for receiving water hardness (e.g. copper, zinc, nickel in fresh water), other site-specific adjustments are allowed:

- Dissolved:Total Recoverable metals partitioning
- Water Effects Ratio (WER)
- Recalculation if species are absent locally

Aquatic Life Criteria for Metals

Site-specific adjustments account for differences in bioavailability of a metal in the laboratory water used to develop the criteria and natural waters

- Metals in particulate form tend to have low bioavailability and toxicity – aluminum is a strong example
- Divalent and trivalent metals form ligands (a stable complex) with organic and inorganic materials in receiving waters, reducing their bioavailability and toxicity

Aquatic Life Criteria for Metals

Typically, states will allow adjustment of aquatic life criteria for metals based on site-specific studies conducted by the discharger or state

- Most states have default dissolved-total metals coefficients that are used when WQBELs are developed for a metal
- Site-specific studies are required to change the default coefficients
- The WER is the most commonly used procedure for developing site-specific metals criteria

Water Effects Ratio

WER procedure is widely used for site-specific metals criteria

- Compares toxicity of a chemical in site water to toxicity of the chemical in lab water that is similar in quality to that used by EPA to set the national criterion
- Calculates a ratio (>1) of the site-specific criterion to the national criterion
- Only usable for constituents with standards based on aquatic toxicity data
- Because EPA criteria for metals such as aluminum, copper, nickel, lead and zinc were developed using very clean fresh and marine waters (Lake Superior, Narragansett Sound), the WER procedure often produces higher site-specific limits

Water Effects Ratio

Examples of completed WERs in Texas

- Houston Ship Channel-San Jacinto River Estuary – copper =1.8X > state criterion for salt water
- Neches River segment – zinc = 2.88X > state criterion for salt water
- Turkey Creek – copper = 4.55X > state criterion for fresh water
- Sabine River segment – copper = 6.7X > state criterion for fresh water and hardness = 40 mg/L
- Papermill Creek to Neches River – aluminum = 8.39X > state criterion for fresh water

Modeling to Predict Metals Toxicity

The 1985 EPA Guidance does allow adjusting metals criteria for water chemistry such as hardness and pH

- Hardness adjustments of a few fresh water metals criteria have been in use since the original adoption of EPA's criteria
- EPA also provided default adjustments for dissolved:total metals partitioning in the 1990's as a result of criticism of using dissolved criteria for WQBELs

Modeling to Predict Metals Toxicity

EPA has conducted research for a number of years to develop criteria for metals that can better describe the effects of receiving water chemistry

This research resulted in the proposal and subsequent adoption of the biotic-ligand model (BLM) for copper in fresh water environments

The current BLM-based freshwater aquatic life criterion is EPA’s Aquatic Life Ambient Freshwater Criteria – Copper 2007 Revision (EPA-822-R-07-001)

Biotic Ligand Model

The BLM uses site-specific chemistry to calculate a site-specific aquatic life criterion

- pH, calcium, magnesium, sodium, potassium, sulfate, chloride, dissolved organic carbon, alkalinity are variables in the model
- Collect upstream/downstream samples for one year or more
- Use model to recalculate copper standard – if successful, state will establish a site-specific standard
- Hardness, pH and DOC are most influential parameters in the copper BLM

Biotic Ligand Model

EPA released its “*Draft Technical Support Document: Recommended Estimates for Missing Water Quality Parameters for Application in EPA’s Biotic Ligand Model*” in March 2016

The technical support document (TSD) provides default values for 8 of the 10 parameters and is intended to facilitate the use of the BLM

- Many potential users, including states, are not using the BLM due to its complexity and lack of available stream-specific data
- TSD uses ecoregion WQ values from monitoring programs, recommends 10^{th}-percentile values (very low) for DOC
- Currently states use less stringent percentiles (typically 15 – 25^{th} bands) for adjusting water quality standards

Biotic Ligand Model

EPA issued draft revised water quality criteria for copper in marine and estuarine waters in July 2016

- The revised copper criteria are based on a marine copper BLM model that predicts numeric criteria based on pH, DOC, salinity, and temperature
- Because seawater has a consistent ion composition, salinity is used as BLM variable rather than individual cations/anions
- The BLM is designed to achieve the same level of protection (95% of species) as the existing criteria methodology
- The draft criteria document gives an example calculation based on the following inputs: pH 8.0 SU, 22°C, DOC 1 mg/L and Salinity 32 ppt

Biotic Ligand Model

The proposed final acute value (FAV) example calculated with the BLM was lowered from 9.1 µg/L to 3.9 µg/L to protect the red abalone, a commercially important species

- States that do not have populations of red abalone would use a 4.5 µg/L CMC
- The chronic criterion (CCC) is based on adjusting the FAV by an acute:chronic ratio (ACR) of 3.022, which in this example, results in a 1.3 µg/L CCC
- Using the unadjusted BLM of 9.1 µg/L, the CCC would be 3 µg/L

Biotic Ligand Model

The most influential factor in the BLM model for marine/estuarine copper criteria is DOC

DOC concentrations in estuaries and harbors would be expected to be greater than the 1 mg/L used in the previous EPA example

- At a pH = 8 SU, 20°C, 15 ppt salinity and 4 mg/L DOC
  - CMC = 7.1 µg/L
  - CCC = 4.7 µg/L

Biotic Ligand Model

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- At a pH = 8 SU, 20°C, 15 ppt salinity and 4 mg/L DOC
  - CMC = 7.1 µg/L
  - CCC = 4.7 µg/L
- These criteria would be more typical of most estuaries and are consistent with current copper WQS

Biotic Ligand Model

EPA believes that both the fresh water and marine/estuarine BLMs provide improved copper criteria because they use site-specific data

EPA Region 6 has recently taken the position that it will compare WER-based site-specific copper criteria to the BLM-predicted values for the same site on the belief that the latter may be more protective

In several cases evaluated by T/K, the BLM gives a higher multiplier than the WER when the effluent percentage is high (>50%), because most treated effluents have TOC concentrations > 10 mg/L

Biotic Ligand Model

EPA has not proposed BLMs for other metals

- The focus on copper is because it is the metal that has most often been identified as causing impairments in state 303(d) listings
- Some states have looked at BLMs for zinc

The EU Water Framework Directive (WFD) directs members to use a BLM approach for metals criteria

- Simplified BLMs (fewer input parameters than in US) are available for Ag, Al, Cd, Co, Cu, Mn, Ni, Pb and Zn
- Acute and chronic BLMs are available for all but Co and Mn that have only chronic BLMs
- Parameters are pH, Ca concentration and DOC and the BLMs are only applicable to fresh water

Multiple Regression Model

July 2017 EPA published the *Draft Aquatic Life Ambient Water Quality Criteria for Aluminum – 2017* (EPA-822-P-17-001)

- The proposed model is based multiple linear regression (MLR) curve fitting to chronic test data for an invertebrate (*Ceriodaphnia dubia*) and a vertebrate (*Pimephales promelas*).
- The MLR variables are pH, hardness and dissolved organic carbon (DOC)
- The MLR calculates a CCC using these site-specific variables
- The acute criterion (CMC) is estimated using an acute:chronic ratio

Multiple Regression Model

EPA considered a BLM approach but decided on the MLR method because:

- It is less complex than a BLM model
- Although it is a statistical approach, it incorporates the same parameters effecting toxicity as a BLM
- It requires fewer input variables – i.e. only pH, hardness and DOC
- It applies to fresh water only

Multiple Regression Model

The proposed MLR-based aluminum criteria is a substantial improvement over the single number 1988 criteria

- Example for pH = 7 SU; hardness = 100 mg/L; DOC = 1 mg/L
  - CMC 1988 = 750 µg/L; CCC = 87 µg/L
  - CMC 2017 = 1,400 µg/L; CCC = 390 µg/L
  - Note: 1988 criteria are single numbers for all conditions of hardness, pH and DOC

While a significant improvement over the 1988 criteria, there are still substantial issues

Multiple Regression Model

Issues identified by commenters include:

- Hardness maximum is 150 mg/L
- DOC maximum is 5 mg/L
- Model allegedly is for total aluminum but all supporting data are essentially for dissolved aluminum

Thus, the proposed MLR model is not acceptable for streams with high natural hardness and DOC and for use in mixing zones for high TOC effluents

Conclusions

Future aquatic life criteria and standards for metals will be model based to better account for site-specific chemistry

Because of limitations on water chemistry data for aquatic toxicity tests, simpler models like the MLR model or the European BLMs are likely

While model-based metals criteria will assure aquatic life protection while accounting for water chemistry, it should not replace the WER for site-specific criteria of individual discharges which is a direct measurement of toxicity