

## **NPDES Implementation of Instream Dissolved Metals Standards – Freshwater Standards**

The NC 2007-2015 Water Quality Standard (WQS) Triennial Review was approved by the NC Environmental Management Commission (EMC) on November 13, 2014. The US EPA subsequently approved the WQS revisions on April 6, 2016, with some exceptions. Therefore, metal limits in draft permits out to public notice after April 6, 2016 must be calculated to protect the new standards - as approved.

**Table 1. NC Dissolved Metals Water Quality Standards/Aquatic Life Protection**

Parameter	Acute FW, µg/l (Dissolved)	Chronic FW, µg/l (Dissolved)	Acute SW, µg/l (Dissolved)	Chronic SW, µg/l (Dissolved)
Arsenic	340	150	69	36
Beryllium	65	6.5	---	---
Cadmium	Calculation	Calculation	40	8.8
Chromium III	Calculation	Calculation	---	---
Chromium VI	16	11	1100	50
Copper	Calculation	Calculation	4.8	3.1
Lead	Calculation	Calculation	210	8.1
Nickel	Calculation	Calculation	74	8.2
Silver	Calculation	0.06	1.9	0.1
Zinc	Calculation	Calculation	90	81

Table 1 Notes:

1. FW= Freshwater, SW= Saltwater
2. **Calculation** = Hardness dependent standard
3. Only the aquatic life standards listed above are expressed in dissolved form. Aquatic life standards for Mercury and selenium are still expressed as Total Recoverable Metals due to bioaccumulative concerns (as are all human health standards for all metals). It is still necessary to evaluate total recoverable aquatic life and human health standards listed in 15A NCAC 2B.0200 (e.g., arsenic at 10 µg/l for human health protection; cyanide at 5 µg/L and fluoride at 1.8 mg/L for aquatic life protection).

**Table 2. Dissolved Freshwater Standards for Hardness-Dependent Metals**

The Water Effects Ratio (WER) is equal to one unless determined otherwise under 15A NCAC 02B .0211 Subparagraph (11)(d)

Metal	NC Dissolved Standard, µg/l
Cadmium, Acute	$WER * \{1.136672 - [\ln \text{hardness}](0.041838)\} \cdot e^{\{0.9151 [\ln \text{hardness}] - 3.1485\}}$
Cadmium, Acute Trout waters	$WER * \{1.136672 - [\ln \text{hardness}](0.041838)\} \cdot e^{\{0.9151 [\ln \text{hardness}] - 3.6236\}}$
Cadmium, Chronic	$WER * \{1.101672 - [\ln \text{hardness}](0.041838)\} \cdot e^{\{0.7998 [\ln \text{hardness}] - 4.4451\}}$
Chromium III, Acute	$WER * 0.316 \cdot e^{\{0.8190 [\ln \text{hardness}] + 3.7256\}}$
Chromium III, Chronic	$WER * 0.860 \cdot e^{\{0.8190 [\ln \text{hardness}] + 0.6848\}}$
Copper, Acute	$WER * 0.960 \cdot e^{\{0.9422 [\ln \text{hardness}] - 1.700\}}$
Copper, Chronic	$WER * 0.960 \cdot e^{\{0.8545 [\ln \text{hardness}] - 1.702\}}$
Lead, Acute	$WER * \{1.46203 - [\ln \text{hardness}](0.145712)\} \cdot e^{\{1.273 [\ln \text{hardness}] - 1.460\}}$
Lead, Chronic	$WER * \{1.46203 - [\ln \text{hardness}](0.145712)\} \cdot e^{\{1.273 [\ln \text{hardness}] - 4.705\}}$
Nickel, Acute	$WER * 0.998 \cdot e^{\{0.8460 [\ln \text{hardness}] + 2.255\}}$
Nickel, Chronic	$WER * 0.997 \cdot e^{\{0.8460 [\ln \text{hardness}] + 0.0584\}}$

Silver, Acute	$WER * 0.85 \cdot e^{\{1.72[\ln \text{hardness}] - 6.59\}}$
Silver, Chronic	Not applicable
Zinc, Acute	$WER * 0.978 \cdot e^{\{0.8473[\ln \text{hardness}] + 0.884\}}$
Zinc, Chronic	$WER * 0.986 \cdot e^{\{0.8473[\ln \text{hardness}] + 0.884\}}$

### **General Information on the Reasonable Potential Analysis (RPA)**

The RPA process itself did not change as the result of the new metals standards. However, application of the dissolved and hardness-dependent standards requires additional consideration in order to establish the numeric standard for each metal of concern of each individual discharge.

The hardness-based standards require some knowledge of the effluent and instream (upstream) hardness and so must be calculated case-by-case for each discharge.

Metals limits must be expressed as ‘total recoverable’ metals in accordance with 40 CFR 122.45(c). The discharge-specific standards must be converted to the equivalent total values for use in the RPA calculations. We will generally rely on default translator values developed for each metal (more on that below), but it is also possible to consider case-specific translators developed in accordance with established methodology.

### **RPA Permitting Guidance/WOBELs for Hardness-Dependent Metals - Freshwater**

The RPA is designed to predict the maximum likely effluent concentrations for each metal of concern, based on recent effluent data, and calculate the allowable effluent concentrations, based on applicable standards and the critical low-flow values for the receiving stream.

If the maximum predicted value is greater than the maximum allowed value (chronic or acute), the discharge has reasonable potential to exceed the standard, which warrants a permit limit in most cases. If monitoring for a particular pollutant indicates that the pollutant is not present (i.e. consistently below detection level), then the Division may remove the monitoring requirement in the reissued permit.

- To perform a RPA on the Freshwater hardness-dependent metals the Permit Writer compiles the following information:
  - Critical low flow of the receiving stream, 7Q10 (the spreadsheet automatically calculates the 1Q10 using the formula  $1Q10 = 0.843 (s7Q10, cfs)^{0.993}$ )
  - Effluent hardness and upstream hardness, site-specific data is preferred
  - Permitted flow
  - Receiving stream classification
- In order to establish the numeric standard for each hardness-dependent metal of concern and for each individual discharge, the Permit Writer must first determine what effluent and instream (upstream) hardness values to use in the equations.

The permit writer reviews DMR’s, Effluent Pollutant Scans, and Toxicity Test results for any hardness data and contacts the Permittee to see if any additional data is available for instream hardness values, upstream of the discharge.

If no hardness data is available, the permit writer may choose to do an initial evaluation using a default hardness of 25 mg/L (CaCO<sub>3</sub> or (Ca + Mg)). Minimum and maximum limits on the hardness value used for water quality calculations are 25 mg/L and 400 mg/L, respectively.

If the use of a default hardness value results in a hardness-dependent metal showing reasonable potential, the permit writer contacts the Permittee and requests 5 site-specific effluent and upstream hardness samples over a period of one week. The RPA is rerun using the new data.

The overall hardness value used in the water quality calculations is calculated as follows:  
 Combined Hardness (chronic)

$$= \frac{(\text{Permitted Flow, cfs} * \text{Avg. Effluent Hardness, mg/L}) + (s7Q10, \text{ cfs} * \text{Avg. Upstream Hardness, mg/L})}{(\text{Permitted Flow, cfs} + s7Q10, \text{ cfs})}$$

The Combined Hardness for acute is the same but the calculation uses the 1Q10 flow.

- The permit writer converts the numeric standard for each metal of concern to a total recoverable metal, using the EPA Default Partition Coefficients (DPCs) or site-specific translators, if any have been developed using federally approved methodology.

EPA default partition coefficients or the “Fraction Dissolved” converts the value for dissolved metal at laboratory conditions to total recoverable metal at in-stream ambient conditions. This factor is calculated using the linear partition coefficients found in *The Metals Translator: Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion* (EPA 823-B-96-007, June 1996) and the equation:

$$\frac{C_{\text{diss}}}{C_{\text{total}}} = \frac{1}{1 + \{ [K_{\text{po}}] [SS^{(1+a)}] [10^{-6}] \}}$$

Where:

ss = in-stream suspended solids concentration [mg/l], minimum of 10 mg/L used, and

K<sub>po</sub> and a = constants that express the equilibrium relationship between dissolved and adsorbed forms of metals. A list of constants used for each hardness-dependent metal can also be found in the RPA program under a sheet labeled DPCs.

- The numeric standard for each metal of concern is divided by the default partition coefficient (or site-specific translator) to obtain a Total Recoverable Metal at ambient conditions.

In some cases, where an EPA default partition coefficient translator does not exist (ie. silver), the dissolved numeric standard for each metal of concern is divided by the EPA conversion factor to obtain a Total Recoverable Metal at ambient conditions. This method presumes that the metal is dissolved to the same extent as it was during EPA’s criteria development for metals. For more information on conversion factors see the June, 1996 EPA Translator Guidance Document.

- The RPA spreadsheet uses a mass balance equation to determine the total allowable concentration (permit limits) for each pollutant using the following equation:

$$Ca = \frac{(s7Q10 + Qw)(Cwqs) - (s7Q10)(Cb)}{Qw}$$

Where: Ca = allowable effluent concentration (µg/L or mg/L)

Cwqs = NC Water Quality Standard or federal criteria (µg/L or mg/L)

Cb = background concentration: assume zero for all toxicants except NH<sub>3</sub>\* (µg/L or mg/L)

Qw = permitted effluent flow (cfs, match s7Q10)

s7Q10 = summer low flow used to protect aquatic life from chronic toxicity and human health through the consumption of water, fish, and shellfish from noncarcinogens (cfs)

\* Discussions are on-going with EPA on how best to address background concentrations

Flows other than s7Q10 may be incorporated as applicable:

1Q10 = used in the equation to protect aquatic life from acute toxicity

QA = used in the equation to protect human health through the consumption of water, fish, and shellfish from carcinogens

30Q2 = used in the equation to protect aesthetic quality

6. The permit writer enters the most recent 2-3 years of effluent data for each pollutant of concern. Data entered must have been taken within four and one-half years prior to the date of the permit application (40 CFR 122.21). The RPA spreadsheet estimates the 95th percentile upper concentration of each pollutant. The Predicted Max concentrations are compared to the Total allowable concentrations to determine if a permit limit is necessary. If the predicted max exceeds the acute or chronic Total allowable concentrations, the discharge is considered to show reasonable potential to violate the water quality standard, and a permit limit (Total allowable concentration) is included in the permit in accordance with the U.S. EPA Technical Support Document for Water Quality-Based Toxics Control published in 1991.
7. When appropriate, permit writers develop facility specific compliance schedules in accordance with the EPA Headquarters Memo dated May 10, 2007 from James Hanlon to Alexis Strauss on 40 CFR 122.47 Compliance Schedule Requirements.
8. The Total Chromium NC WQS was removed and replaced with trivalent chromium and hexavalent chromium Water Quality Standards. As a cost savings measure, total chromium data results may be used as a conservative surrogate in cases where there are no analytical results based on chromium III or VI. In these cases, the projected maximum concentration (95th %) for total chromium will be compared against water quality standards for chromium III and chromium VI.
9. Effluent hardness sampling and instream hardness sampling, upstream of the discharge, are inserted into all permits with facilities monitoring for hardness-dependent metals to ensure the accuracy of the permit limits and to build a more robust hardness dataset.
10. Hardness and flow values used in the Reasonable Potential Analysis for this permit included:

Parameter	Value	Comments (Data Source)
Average Effluent Hardness (mg/L) [Total as, CaCO <sub>3</sub> or (Ca+Mg)]		
Average Upstream Hardness (mg/L) [Total as, CaCO <sub>3</sub> or (Ca+Mg)]		
7Q10 summer (cfs)		
1Q10 (cfs)		
Permitted Flow (MGD)		

Date: \_\_\_\_\_

Permit Writer: \_\_\_\_\_