State of Oregon
Department of Environmental Quality Memorandum

To: DEQ Water Quality Staff **Date:** Oct. 21, 2014

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Subject: Implementation Instructions for Selenium (CAS #7782492)

This memo clarifies how DEQ interprets selenium concentrations in effluent and surface water to determine compliance with water quality criteria.

Criteria Summary

Oregon water quality standards include numeric criteria for selenium to protect human health and aquatic life (OAR 340-041-0033(3) and (4), and Tables 30 and 40). The human health criteria are based on total selenium, while the aquatic life criteria are based on dissolved selenium. Table 1 below reflects the selenium criteria as published in the rule.

Table 1: Water Quality Criteria

Pollutant	Table 40		Table 30			
	Human Health Criteria		Aquatic Life Criteria (Freshwater)		Aquatic Life Criteria (Saltwater)	
	Water + Org (µg/L)	Org Only (µg/L)	Acute (µg/L)	Chronic (µg/L)	Acute (µg/L)	Chronic (µg/L)
Selenium	120	420	See C, L	4.6[C]	290[C]	71[C]

Notes
[C] Criterion is expressed in terms of "dissolved" concentrations in the water column.
[L] The CMC*****=(1/[(f1/CMC1)+(f2/CMC2)]µg/L) * CF where f1 and f2 are the fractions of total selenium that are treated as selenite and selenate, respectively,and CMC1 and CMC2 are 185.9 µg/L and 12.82 µg/L,respectively.

***** The CMC (criterion maximum concentration) is the acute aquatic life criterion.

Key Issues

EPA approved new aquatic life criteria for selenium on April 18, 2014. The criteria values are more stringent than previous criteria and are based on dissolved selenium, rather than total selenium. Furthermore, based on current EPA recommendations, the freshwater acute criterion depends on the fraction of total selenium that is comprised of selenate and selenite. DEQ and dischargers do not typically collect dissolved selenium data, or analyze results for selenate or selenite. Therefore, this memo describes how to apply the selenium criteria depending on what kind of selenium data are available.

Additional Background

Selenium is composed of selenite and selenate. Selenate is the more toxic form of selenium, but both forms are toxic. Therefore, Oregon's updated acute freshwater criterion for selenium is equal to the sum of the fractions of total selenium that are treated as selenite and selenate. These fractions are then divided by their respective acute criteria values. DEQ multiplies this result by a conversion factor to convert a metal criterion expressed as a total recoverable fraction in water to a criterion expressed as a dissolved fraction. The selenium footnote for the freshwater acute criterion in Table 30 is:

Acute Criterion (CMC) = (1/[(f1/CMC1) + (f2/CMC2)] ug/L) * CF

The terms are defined as follows:

f1 = fraction of total selenium that is selenite, measured
f2 = fraction of total selenium that is selenate, measured
CMC1 = acute criterion for selenite (185.9 ug/L)
CMC2 = acute criterion for selenate (12.82 ug/L)
CF = Conversion Factor for total to dissolved selenium (0.996)

According to the above equation, both selenite and selenate should be measured to determine if the acute criterion is met. Currently, it is fairly uncommon to analyze for both selenate and selenite and DEQ's lab does not have the capability of measuring these analytes. In addition, EPA is currently reviewing its national recommended criteria for selenium. Based on EPA's draft criteria, it is very likely that any future final recommendations will not be based on selenite and selenate analyses.[1]

Recommended Analytical Method

Selenate and selenite are customarily analyzed by ion chromatography (IC), but this method does not always provide for low enough detection to determine attainment with the water quality criteria. Advanced methodologies have been developed using IC coupled with ICP-MS (IC-ICP-MS) that allow for lower detection, but the DEQ Laboratory has yet to obtain this capability. Other labs in the northwest may have this technology.

Table 2 contains the list of applicable pollutant species and recommended analytical method. To determine the applicable quantitation limits for individual permit holders, please refer to Schedule B of the relevant permit. For older permits without quantitation limits in Schedule B, please refer to Revision 3.0 of the Reasonable Potential Analysis for Toxic Pollutants IMD to determine applicable quantitation limits.

[1] EPA. External Peer Review Draft Aquatic Life Ambient Water Quality Criterion for Selenium--Freshwater 2014. Federal Register Volume 79, Number 93 (Wednesday, May 14, 2014). EPA-HQ-OW-2004-0019. http://water.epa.gov/scitech/swguidance/standards/criteria/aqlife/selenium/index.cfm

Table 2: Monitoring Guidance

Pollutant	Criteria Type	Pollutant Species	Recommended Analytical Method
Selenium	Human Health	Total Recoverable	200.8
Selenium	Aquatic Toxicity	Dissolved	200.8 + 0.45 µm filtration
Selenium	Freshwater Acute Aquatic Toxicity	Dissolved Selenite and Selenate	200.8 + 0.45 µm filtration

Implementation Instructions for NPDES Permits

Freshwater Selenium Acute Aquatic Life Criterion

Unless selenite and selenate data is available, dischargers and DEQ staff will conservatively assume that a total selenium sample is 100 percent selenate to assess compliance with the acute freshwater criterion. Selenate is more toxic than selenite.The acute criterion for selenate is then multiplied by its conversion factor to convert the total recoverable criterion to a dissolved criterion:

Acute criterion (CMC) for selenium =(1/[(0/185.9) + (1/12.82)] ug/L) * 0.996
=12.77
=13 µg/L (two significant figures)

If representative selenite and selenate data are available from the receiving stream, the equation to derive acute criteria based on the fraction of selenite and selenate may be used. For example, if a total selenium sample is comprised of 80 percent selenite and 20 percent selenate, then the criterion would be calculated as:

Acute criterion (CMC) for selenium =(1/[(0.8/185.9) + (0.2/12.82)] ug/L) * 0.996
=50.3
=50 µg/L (two significant figures)

If Tier I analysis results in no Reasonable Potential based on assuming selenate is 100 percent of the sample, then no further analysis is needed. If the analysis results in Reasonable Potential, then the permittee may conduct followup monitoring and analysis for selenite and selenate in the effluent and receiving stream.

Total Versus Dissolved Effluent Selenium Data for Aquatic Life Criteria:

- Total selenium data results from the effluent may first be multiplied by the applicable conversion factor before comparing it to the aquatic life dissolved criteria. Note that the conversion factors assume almost all of a total selenium sample is in the dissolved form.
- Dissolved selenium data results from the effluent may be directly compared to the aquatic life dissolved criteria. Comparing dissolved effluent data to the dissolved selenium aquatic life criteria most accurately measures compliance.

Selenium Human Health Criteria

DEQ staff and dischargers must compare total selenium data from the effluent to the total recoverable criteria stated in Table 40.

Refer to the Dissolved Metals Water Quality Criteria in Reasonable Potential Analysis and Water Quality-Based Effluent Limits Calculation implementation memo for instructions on how to convert metals criteria based on dissolved to effluent limits based on total recoverable.

Conclusion

When evaluating the freshwater acute criterion for dissolved selenium and in the absence of selenite and selenate data, DEQ staff should assume that all selenium in a total selenium data result is selenate, the more toxic form. This assumption results in an acute criterion of 13 ug/L. Where selenate and selenite data are available, the acute criterion is calculated based on the fraction of these forms according to the equation in the footnote.