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Andrea Matzke, *WQ Standards and Assessment Section***Subject:** Implementation Instructions for the Water Quality Criterion Chlorine (CAS #: 7782-50-5)

This memo clarifies how chlorine concentrations in effluent and surface water are measured to determine compliance with water quality criteria.

Criteria Summary

Oregon water quality standards include numeric criteria for chlorine to protect human health and aquatic life (OAR 340-041-0033(3), and Tables 30). Table 1 below reflects the selenium criteria as published in the rule.

Table 1: Water Quality Criteria

| Chemical | 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) |
| Chlorine | --- | --- | 19 | 11 | 13 | 7.5 |

Key Issues

There are several forms of chlorine. The chlorine aquatic life criteria do not include any clarifying footnotes as to which form of chlorine is targeted by the criteria. Therefore, DEQ staff referenced a 1984 EPA criteria support document¹ to address this question:

When chlorine is added to fresh water, the solution will usually contain two forms of free chlorine: hypochlorous acid (HOCl) and the hypochlorite ion (OCl⁻). If the water contains ammonia, the solution will probably also contain two forms of combined chlorine: monochloramine and dichloramine. Because all four of these are quite toxic to aquatic organisms, the term "total residual chlorine" is used to refer to the sum of free chlorine and combined chlorine in fresh water. However, because salt water contains bromide,

¹ EPA. Ambient Water Quality Criteria for Chlorine - 1984. EPA 440/5-84-030. January 1985. See pg. 1: (also see pgs. 17-18 of that support document in direct reference to the criteria).

http://water.epa.gov/scitech/swguidance/standards/upload/2001_10_12_criteria_ambientwqc_chlorine1984.pdf

addition of chlorine also produces hypobromous acid (HOBr), hypobromous ion (OBr), and bromamines (Dove, 1970; Johnson, 1977; Macalady, et al. 1977; Sugam and Helz, 1977). The term “chlorine-produced oxidants” is used to refer to the sum of these oxidative products in salt water (Burton, 1977). Consequently, the freshwater and saltwater data herein will be expressed as total residual chlorine (TRC) and chlorine-produced oxidants (CPO), respectively, although both terms are intended to refer to the sum of free and combined chlorine and bromine as measured by the methods for “total residual chlorine” (U.S. EPA, 1983a).

This excerpt indicates that the aquatic life criteria for chlorine are based on total residual chlorine.

Recommended Analytical Method

There are three basic methods used for the determination of free and total residual chlorine in environmental samples; amperometric titration (including a low level method), DPD titration method and DPD colorimetric method. These are well described in the Standard Methods compendium and listed as 4500-Cl D, E, F and G. Samples must be analyzed immediately in the field. Laboratory analysis can be done, but the recommended holding time is 15 min, so the laboratory must be located near the source of the samples.

The measurement of chlorine in saltwater cannot be accomplished using any methods currently recommended by EPA because of the complex reactions that occur between chlorine and bromide naturally present in all saltwater. Any result using the above methods applied to saltwater must be reported as mg/L “chlorine-produced oxidants”.

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.

Implementation Instructions for NPDES Permits

For the purposes of effluent and ambient characterization, determining “reasonable potential”, establishing effluent limits and compliance monitoring, the water quality criteria for “chlorine” will be interpreted as “total residual chlorine”.

Conclusion

In summary, the aquatic life criteria for chlorine in freshwater are expressed as “total residual chlorine” which is the sum of free and combined chlorine. The aquatic life criteria for chlorine in saltwater are expressed as “chlorine-produced oxidants”, which is the sum of free and combined chlorine and bromine. The “total residual chlorine” analytical methods described above apply to both freshwater and saltwater criteria.