



DEPARTMENT OF  
**ECOLOGY**  
State of Washington

## **Washington State's Marine Dissolved Oxygen Criteria: Application to Nutrients**

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*Understanding the Purpose and Application of  
the Criteria in the Surface Water Quality  
Standards*

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## Purpose & Background

This paper is intended to provide a history and rationale for marine dissolved oxygen (DO) criteria within the Surface Water Quality Standards for Washington State, and the role of DO criteria in limiting nutrients. The purpose of DO criteria are to protect aquatic life from exposures to low DO concentrations and also to indirectly limit excessive nutrients in waters that would otherwise lead to low DO concentrations. This document describes the rationale for applying the DO criteria to limit excessive nutrient inputs into Washington State marine waters. The interrelationship between nutrients and DO are described to provide context to applying DO criteria for the purpose of limiting nutrients.

This information can be used to guide the application of the State's marine DO criteria, and use of nutrient reductions as a surrogate for improving DO for the Puget Sound Nutrient Source Reduction Project and other applicable projects. This will help define model outputs as compared to the criteria for projects that use complex computer modeling to evaluate the DO response to changes in nutrients. This understanding provides the basis from which to interpret the results and to relate the criteria to protection of the aquatic life designated uses.

# Regulatory Framework for Water Quality Standards

## Federal Clean Water Act Requirements

Under Section 303(c) of the Clean Water Act (CWA) and federal implementing regulations at 40 CFR § 131.4, states and authorized tribes have the primary responsibility for reviewing, establishing, and revising water quality standards (WQS), which consist primarily of the designated uses of a waterbody or waterbody segment, the water quality criteria that protect those designated uses, and an antidegradation policy to protect high quality waters. This statutory and regulatory framework allows states and authorized tribes to work with local communities to adopt appropriate designated uses (as required in 40 CFR § 131.10(a)) and to adopt criteria to protect those designated uses (as required in 40 CFR § 131.11(a)).

The EPA has compiled a list of nationally recommended water quality criteria for the protection of aquatic life and human health in surface waters. These criteria are published pursuant to Section 304(a) of the CWA and provide guidance for states and tribes to establish water quality standards and provide the foundation for controlling the release of pollutants and identifying impaired waters. The state WQS are federally approved by the Environmental Protection Agency (EPA) and describe the level of protection for Waters of the State.

The Marine Water Quality Standards were developed under this federal regulatory framework.

## Washington State Water Quality Standards

The Washington State surface water quality standards are established under Washington Administrative Code (WAC) 173-201A. The water quality standards set limits on pollution in our lakes, rivers and marine waters in order to protect beneficial uses, such as aquatic life and swimming. The statutory authority for the water quality standards is the revised code of Washington (RCW) 90.48, which mandates the state of Washington to maintain the highest possible standards to insure the purity of all waters of the state consistent with public health and public enjoyment thereof, the propagation and protection of wild life, birds, game, fish and other aquatic life, and the industrial development of the state, and to that end require the use of all known available and reasonable methods by industries and others to prevent and control the pollution of the waters of the State of Washington. All surface waters are protected by numeric and narrative criteria, designated uses, and an antidegradation policy. Based on the use designations, numeric and narrative criteria are assigned to a water body to protect the existing and designated uses. Surface waters of the state include lakes, rivers, ponds, streams, inland waters, saltwaters, wetlands, and all other surface waters and water courses within the jurisdiction of the State of Washington.

## Purpose of DO Criteria in the Water Quality Standards

**Dissolved oxygen levels established in the water quality standards are intended to set levels that protect healthy, robust aquatic communities, including the most sensitive species.**

The influence of human and biologic factors that affect DO concentrations as well as hydrologic characteristics, can have implications on meeting the established water quality criteria for DO, and introduce serious practical and scientific challenges for the state in setting and applying water quality criteria for DO. Aquatic systems are often spatially heterogeneous in DO concentrations and limited by natural conditions and processes. Thus, the needs of aquatic species may not be fully met in all portions of a waterbody even under natural conditions.

Factors that influence DO concentrations in aquatic systems are described within this document.

## Current Marine DO Numeric Criteria

The water quality standards apply year-round to all surface waters unless otherwise noted in WAC 173-201A. The DO criteria are 1-day minimum values. The aquatic life designated uses are based on the presence of, or the intent to provide protection for, the key uses identified (see table below). The water quality standards are intended to protect all indigenous fish and nonfish aquatic species in waters of the state.

### Aquatic life DO criteria in marine waters, WAC 173-201A-210(1)(d).

Aquatic Life Use	DO Criteria (1-day min.)	General Description
<b>Extraordinary</b>	7.0 mg/L	Extraordinary quality salmonid and other fish migration, rearing, and spawning; clam, oyster, and mussel rearing and spawning; crustaceans and other shellfish (crabs, shrimp, crayfish, scallops, etc.) rearing and spawning.
<b>Excellent</b>	6.0 mg/L	Excellent quality salmonid and other fish migration, rearing, and spawning; clam, oyster, and mussel rearing and spawning; crustaceans and other shellfish (crabs, shrimp, crayfish, scallops, etc.) rearing and spawning.
<b>Good</b>	5.0 mg/L	Good quality salmonid migration and rearing; other fish migration, rearing, and spawning; clam, oyster, and mussel rearing and spawning; crustaceans and other shellfish (crabs, shrimp, crayfish, scallops, etc.) rearing and spawning.
<b>Fair</b>	4.0 mg/L	Fair quality salmonid and other fish migration.

## DO Concentrations in Aquatic Systems

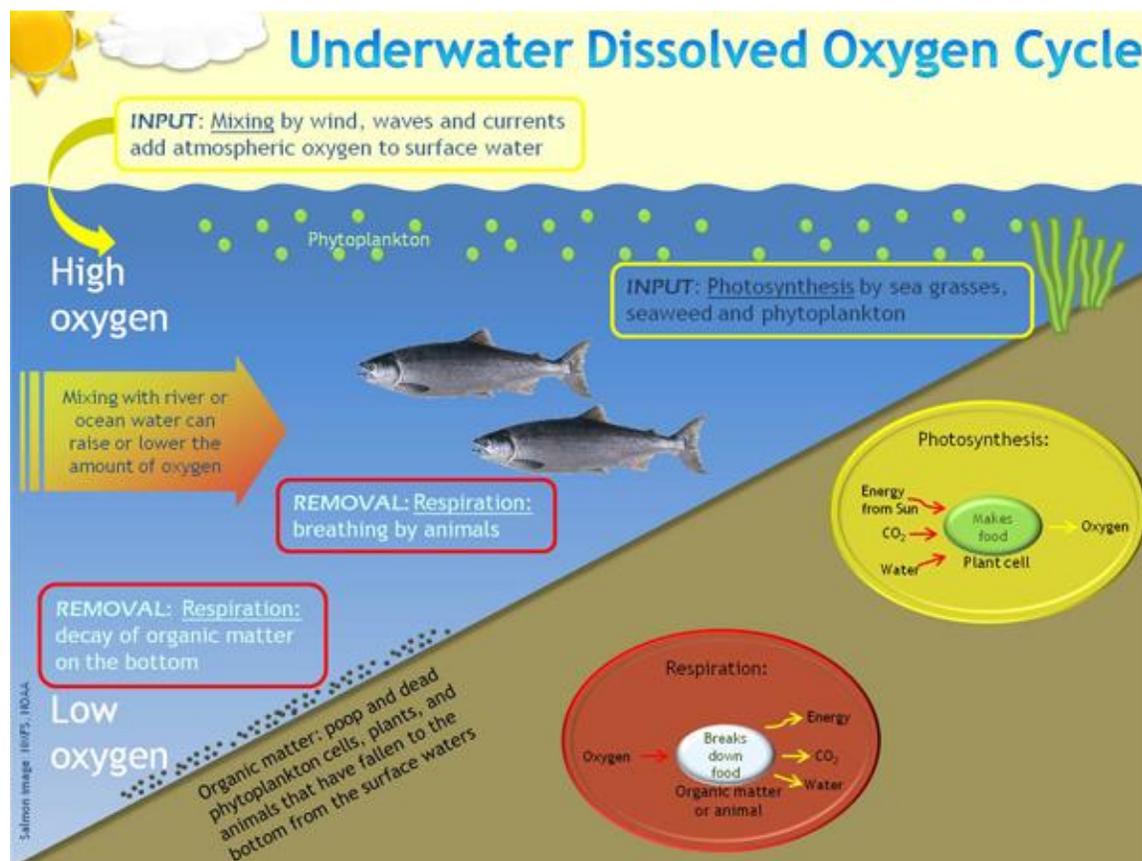
Dissolved oxygen concentrations in aquatic systems are a balance of several factors including: the exchange of atmospheric oxygen with surface waters; hydrologic processes; oxygen produced by aquatic plants during photosynthesis; and aquatic animals, plants and bacteria that consume DO through respiration (see figure below). Among water quality parameters, DO can be significantly affected by human actions. Human actions can increase the biological oxygen demand via contributions of organic and inorganic materials that are metabolized by organisms

(consuming available oxygen), and by actions that raise the temperature of waterbodies, thus reducing the solubility of oxygen.

Waterbodies come in a wide range of sizes and flow characteristics. Source waters may be cold and plentiful or alternatively, fed only by infrequent rains. They may be supplied by well-established surface water streams or dominated by shallow or deep ground water seeps and upwellings. The soil substrate and geologic features that shape the water body may be rich in biologically and chemically active materials or may be composed mostly of inert rock types. Air temperature, which influences water temperature and thus DO concentrations (the solubility of DO in water increases with decreasing water temperatures), can vary considerably based on a given waterbody's altitude.

In marine waters, salinity and depth play an important role in oxygen concentrations and the distribution of oxygen throughout the water column. Upwellings can have a significant influence on oxygen levels. Upwellings are driven by surface winds that results in the movement of deep, cold, nutrient rich water to move into the upper water column resulting in increases in productivity and changes in the DO regime. The climatic, hydrologic, and geological characteristics of aquatic systems are important factors in evaluating natural water quality conditions.

The following figure demonstrates the DO cycle for marine waters.



## History and Rationale of Marine DO Numeric Criteria

Washington State first adopted marine DO numeric criteria into rule in 1967 and they continue to be the applicable water quality standards. In order to provide background information on the development of the marine DO standards, Ecology staff searched through historical archival records in an attempt to find the origin of the current marine DO numeric criteria. Unfortunately, no definitive records were found that confirmed the origin of Washington's 1967 water quality standards for marine DO criteria.

In the absence of a definitive historic record, Ecology staff searched for studies and reports available during that timeframe and found relevant information in a Department of Interior (DOI) 1968 "Water Quality Criteria Report of the National Technical Advisory Committee to the Secretary of the Interior." Based on the similarities in the report to the marine DO criteria adopted by Washington, Ecology believes that the marine DO water quality standards for Washington State are most likely based upon this federal report.

As background, the Water Quality Act of 1965 required states to adopt water quality criteria applicable to interstate waters or portions thereof by June 30, 1967. According to the DOI, an interim report of the "Water Quality Criteria Report of the National Technical Advisory Committee to the Secretary of the Interior" was printed and presented to the Secretary of the Interior on June 30th, 1967. Washington State subsequently adopted water quality standards, including marine DO criteria, on December 4th, 1967. Washington's 1967 water quality standards state that they were adopted to comply with Section 10 of the Federal Water Pollution Control Act via Public Law 84-660 as mandated by the DOI. Ecology is not aware of any other water quality recommendations for interstate waters by the DOI's Federal Water Pollution Control Administration during this time.

The final 1968 DOI recommendations were written on the basis of maintaining native populations of fish and other aquatic life. The 1968 DOI recommendations state that marine DO levels between 5.3 and 8 mg/L were satisfactory for survival and growth of fish. At the time of the DOI recommendations, studies demonstrated DO concentrations between 5 to 8 mg/L were adequate for all species of fish. The DOI recognized that DO in deeper marine waters are often considerably less than 5.0 mg/L and in some estuaries may reach 4.0 mg/L at infrequent intervals for limited periods of time. The DOI concluded that surface DO concentrations in coastal waters should not be less than 5.0 mg/L and DO concentrations in estuaries and tidal tributaries should not be less than 4.0 mg/L at any time or place, precluding natural conditions (USDOI, 1968). Washington's marine DO criteria (ranging from 4.0 to 7.0 mg/L) aligns well with the 1968 DOI recommendations. The DOI stressed that the marine DO recommendations were based on limited studies that were available at the time.

In a review of minimum DO requirements of aquatic life in Canadian waters, Davis (1975) reported mean ( $\pm 1$  standard deviation) incipient oxygen thresholds of  $6.72 \pm 2.12$  mg/L for marine nonanadromous fish,  $6.43 \pm 2.57$  mg/L for marine anadromous fish including salmonids,  $3.38$  mg/L for marine anadromous fish excluding salmonids, and  $6.94 \pm 2.39$  mg/L for marine anadromous salmonids. The oxygen thresholds listed represent levels where the fish community begin to exhibit symptoms of oxygen distress (often defined as changes in metabolic activity) and represent some risk if the oxygen minimum period lasts beyond a few hours. Davis (1975)

noted that there was a lack of knowledge on the effects of low DO on the physiology of marine invertebrates but that it is reasonable to assume that levels of protection proposed for fish are protective of most aquatic invertebrates.

In a more recent review of 872 published experiments spanning 206 species, Vaquer-Sunyer and Duarte (2008) concluded that DO concentrations of 4.6 mg/L would be expected to maintain populations for most species and conserve marine biodiversity, while 5.0 mg/L would be expected to be protective of sub-lethal effects for most aquatic species. However, 4.6 and 5.0 mg/L DO concentrations represented median lethal concentrations (LC50s) and median sub-lethal concentrations (SCL50), respectively, of the 90<sup>th</sup> percentile of reported species (all but the 10% most sensitive species protected). Given that the 10% most sensitive species are not protected at 4.6 and 5.0 mg/L levels, full protection of uses would equate to DO concentrations greater than 5.0 mg/L.

Vaquer-Sunyer and Duarte (2008) indicated that some experiments in their analysis evaluated thresholds of hypoxia in the presence of additional stressors (e.g. temperature). The influence of multiple stressors may alter the sensitivity of organisms to oxygen reductions, thus providing some uncertainty around the oxygen thresholds reported. However, the authors state that the majority of experiments evaluated used reductions in oxygen as the single treatment variable. Furthermore, many of the species examined in Vaquer-Sunyer and Duarte (2008) are not indigenous to Washington State. However, surrogate species are often used when data on species from a particular region are not available. When evaluating robust datasets, elements of uncertainty can be expected but still provide a valuable tool to evaluate biological effects.

Overall, Davis (1975) and Vaquer-Sunyer and Duarte (2008) conclusions generally align with the 1968 DOI recommendations of marine DO concentrations of 5 to 8 mg/L for protection of survival and growth of fish.

## **Aquatic Life Designated Uses**

To determine DO limits for designated uses, Ecology used scientific literature to set limits that provide protection for salmonid and other fish migration, rearing, and spawning as well as rearing and spawning for clams, oysters, and mussels, crustaceans, and other shellfish (crabs, shrimp, crayfish, scallops, etc.). Where appropriate, Ecology used minimum DO requirements of individual life stages of aquatic species to create synthesis recommendations that protects all life stages including the most sensitive species (e.g. salmonids, clam, oyster, mussel, crustaceans, crabs, shrimp, crayfish, scallops, etc.). Adherence to the proposed minimum DO criteria should be expected to provide protection (which is required under the Clean Water Act) for Washington's native aquatic life communities.

## **Single Criterion versus Multiple Criteria**

Ecology adopted a single DO criterion for each aquatic life designated use rather than separate criteria for individual species rearing, migration, and spawning or seasonal-based criteria. This simplifies application of the criteria and also avoids the complex task of needing to identify spawning seasons for all of the state's aquatic life for different water bodies. Furthermore, setting

a single criterion protects for all conditions as oxygen fluctuates throughout the year. A single criterion ensures that the depression of DO in summer is adequate to support aquatic life and as fall and winter approach and oxygen levels improve, concentrations are adequate for spawning in preferred marine habitats (e.g. intertidal and shallow zones for species such as forage fish).

## **Anthropogenic Allowance**

Many human actions increase the delivery of nutrients into local waterbodies which theoretically have some impact to the nutrient cycle (e.g. photosynthesis of aquatic plants) and thus on DO levels. For this reason, a small allowable variation from natural oxygen regimes was adopted as an element of the DO standard. The DO criteria includes a provision that a 0.2 mg/L cumulative allowance from human actions (at a given location) be applied when DO concentrations in a given waterbody are naturally lower in DO than the established criteria. This allowance is currently granted in the state water quality standards for marine water oxygen levels.

The anthropogenic allowance of 0.2 mg/L DO value is based on the concept of a measurable change. A measurable change in the physical, chemical, or biological quality of the water is used to determine that a lowering of water quality occurred. The measurable change in relation to the DO anthropogenic allowance represents a detectable change in water quality based on precision of the instrument used to measure the ambient water condition. The 0.2 mg/L limit is based on restricting changes in the DO regime that was, until the last couple of decades, otherwise undetectable using most field methods. The 0.2 mg/L DO allowance does not represent a biologically based value but rather, a detectable or measurable change in water quality.

# Application of Numeric Marine DO Criteria

## Applying DO Criteria in the Water Column

Dissolved oxygen criteria are intended to provide protection for all aquatic species including the most sensitive species (e.g. salmonids, clam, oyster, mussel, crustaceans, crabs, shrimp, crayfish, scallops, etc.). There is uncertainty as to the location to collect representative DO samples from the water column, especially as it applies in deep waters. The water quality standards state that DO measurements should be taken to represent the dominant aquatic habitat of the monitoring site. This indicates that samples should not be taken from shallow stagnant backwater areas, within isolated thermal refuges, at the surface or at the water's edge. In deep marine waters, water column DO can be stratified at varying depths as a result of freshwater inputs (i.e. salinity gradients), tidal fluctuations, ocean currents, thermoclines, biochemical oxygen demand, and climatic influences.

The large variations in DO concentrations throughout the vertical profile in deep marine waters present a challenge for applying DO criteria for the protection of aquatic life uses. In deep marine waters, water quality conditions can vary significantly depending on depth and habitat type. Furthermore, aquatic species present at different depths have varied tolerances to DO. Deep marine waters are often naturally low in DO due to limited photosynthetic activity, high microbial activity, and lack of oxygen diffusivity with the atmosphere. Marine benthos present at deeper depths are often more tolerant to low DO conditions (i.e. mollusks), whereas other benthos sensitive to DO are typically found in shallower, coastal waters (i.e. crustaceans; Diaz and Rosenberg, 1995; Vaquer-Sunyer and Duarte, 2008). However, Vaquer-Sunyer, et. al (2008) asserted that sediment dwelling benthic organisms are vulnerable to hypoxia because interstitial waters of sediments tend to be depleted before the overlaying water column. Fish, the most sensitive taxa to DO concentrations (Vaquer-Sunyer and Duarte, 2008) are found at varying depths at different life stages (Smith, et. al. 2015, Candy et. al. 1999, Duffy, 2005) and have the ability to escape deep waters naturally low in DO, thus allowing for seasonal use.

The physical and biological processes that maintain DO in the upper-to-middle water column (e.g. photosynthesis, atmospheric oxygen diffusion, precipitation, wind driven processes, and freshwater inputs) influence DO concentrations in the lower water column during parts of the year (Figure 1). In the warmer summer months, thermal changes and salinity gradients can stratify waters, hindering mixing of surface and bottom waters, resulting in reductions in DO concentrations in bottom waters. Compliance points should be directed at locations that represent the dominant aquatic habitat of the most sensitive marine species. If the compliance point represents a large range of depths within the vertical profile, then water samples should be assessed within portions of the waterbody demonstrating relatively homogenous conditions (e.g. euphotic zone; waters below or above the pycnocline; bottom waters) in the various dominant aquatic habitat of communities (e.g. benthic, fish, phytoplankton, zooplankton communities). Since the criteria must protect all indigenous fish and nonfish aquatic species (WAC 173-201A-210), the assumption is that if the numeric criteria are met for the most sensitive organisms of each habitat, then the ambient condition of the waterbody as a whole will protect all other species.

## **Applying DO Criteria at Site-Specific Locations**

Marine DO criteria apply to water bodies based on the demarcated boundary descriptions and aquatic life use designations listed in Table 612 of WAC 173-201A. Each area described in Table 612 is required to be in compliance year-round at all assessment sites. Large contiguous water bodies have different aquatic life uses and hence different marine DO criteria based on location.

## **Anthropogenic Allowance of 0.2 mg/L DO**

When a water body's DO concentration is lower than the criteria and the condition is due to natural conditions, then human actions considered cumulatively may not cause DO concentrations of that water body to decrease more than 0.2 mg/L. Human actions (i.e. anthropogenic allowance) are not considered if the water body is in compliance with the DO criteria. Both the DO criteria and the anthropogenic allowance for aquatic life are based on a 1-day minimum concentration. The anthropogenic allowance applies year-round at all locations unless otherwise noted in WAC 173-201A.

# Water Quality Responses to Excess Nutrients

Excess nutrients in marine waters can lead to impairments of water quality including reductions in DO concentrations, ocean acidification (reduced pH), harmful algal blooms (HABs) (Anderson et al., 2002; Howarth et al., 2011) water corrosivity, changes in trophic health and dynamics (Howarth, et. al. 2011), growth of microbial pathogens, and both hypoxia, generally deeper in the water column, and oxygen super-saturation at the surface from enhanced photosynthetic activity. Ecology has determined that the impacts of nutrient enrichment on water quality and hence, aquatic life, can be reasonably measured through changes in DO concentrations. Computer models can be used to assess the response of water bodies to nutrient inputs with the goal of establishing nutrient levels that would ensure meeting the numeric DO criteria.

## Dissolved Oxygen

Nutrient inputs into aquatic systems can lead to increased algal growth that can initially increase DO in the upper portion of a water column via photosynthesis. Scenocystis algae eventually die and provide large amounts of organic matter for respiring (i.e. oxygen-consuming) microorganisms. The proliferation of microorganisms during the decay of algae results in the consumption of DO in the water column. This consumption tends to happen in the lower portion of the water column where the dead algae settles. The relationship between nutrients, algal growth, and depression in DO concentrations can be used to evaluate nutrient levels in water bodies.

## Water Acidification

Nutrient enhancements can result in water acidification (i.e. reductions in pH) through the release of carbon dioxide from respiring organisms feeding on decaying organic matter. Carbon dioxide can combine with water to produce carbonic acid, thereby reducing pH and resulting in ocean acidification. Respiring organisms are dependent on DO concentrations in water, a necessary element of metabolism (i.e. transforming food into energy). Maintaining oxygen levels at optimal levels for all aquatic life should limit nutrients and thwart ocean acidification. The effects of nutrients on water acidification can be directly related to DO concentrations and protected for using the numeric DO criteria.

## Corrosivity

Water corrosivity is an index based on oxidation/reduction reactions linked to the presence of DO. Oxygen is one of the primary electron acceptors in water and therefore a primary factor in oxidation/reduction reactions that take place within the water column, specifically for cellular respiration. Regulating DO concentrations using the numeric criteria will ensure redox equilibrium and protect against low pH conditions that are akin to a reducing (i.e. corrosive) environment.

## **Harmful Algal Blooms**

Harmful algal blooms or HABs release toxins into the water that can have detrimental effects to aquatic life. Algal blooms are formed by nutrients that would otherwise limit primary productivity. Increased primary productivity leads to momentary/brief increases in DO concentrations, followed by decreases in DO concentrations from the consumption of dead organic matter by respiring microorganisms. If DO levels are maintained at levels protective of the most sensitive aquatic life, then algal blooms, along with the potential release of harmful toxins, would likely be minimized. In areas HABs are present when DO criteria are met under natural conditions, the aesthetics narrative water quality criteria is used to designate impairment and control nutrient inputs.

## **Pathogens**

The proliferation of pathogens of the group *Vibrios* have been positively correlated to organic enrichment (Singleton et al. 1982). Nutrient pollution has the ability to promote the growth of pathogens under particular conditions. Associations between *Vibrios* spp. and zooplankton, to whose surfaces the bacteria inhabit, has been noted (Kaneko and Colwell, 1975; Huq et al. 1983). Nutrient enrichment may increase phytoplankton and subsequently zooplankton, leading to outbreaks of *Vibrios* spp. The numeric DO criteria is expected to limit the amounts of nutrients and primary productivity, thus limiting the growth of pathogens.

## **Species Assemblages**

Excess nutrients lead to hypoxic and anoxic bottom waters that result in shifts in benthic and pelagic communities, reduction in available habitat, and a change in trophic level interactions due to the loss of species (Diaz and Rosenberg, 1995). The loss of habitat and suitable species from excess nutrients can be directly related to reductions in DO concentrations. The DO numeric criteria are predicated on maintaining healthy, robust aquatic communities. Given the direct relationship between nutrients and DO concentrations, Ecology supports the use of the DO numeric criteria and narrative criteria for protection against nutrient pollution.

# Protecting Waters from Excess Nutrients

## Nutrient Criteria Alternatives in Marine Systems

The dynamics of nutrient concentrations in marine systems is more complex than in fresh water and lake systems. Setting statewide nutrient criteria in marine waters is challenging due to factors such as tidally reversing and complex currents, upwelling, stratified and well-mixed sections of the receiving water, changes in the limiting nutrient with depth and location, organic carbon inputs, and the variable contributions from freshwater streams and rivers. EPA provides national strategies for developing nutrient criteria but has not issued national recommended numeric criteria for nutrients. Potential reasons for the absence of recommended criteria include data deficiencies in estuaries and the known highly complex relationship between nutrients and trophic health in marine systems. Ecology has chosen an alternative program to control anthropogenic nutrient inputs to marine systems. This program relies on other indicators (e.g. DO concentrations and pH) as triggers for trophic health that are affected by nutrient inputs, and water body specific modeling to select nutrient threshold values. The numeric DO criteria and narrative criteria are used in tandem to protect aquatic life from excess nutrients.

## Application of Numeric Criteria to Nutrients

### DO Criteria

A primary driver for setting the agency's pollution control priorities for nutrients is the failure to comply with DO criteria. Dissolved oxygen is not a pollutant itself but variations in DO concentrations can be attributed to an environmental response associated with excessive nutrient inputs. Paramount to this issue is the role that is played by excessive nutrient contributions from nonpoint and point sources into marine waters. Excessive nutrient inputs lead to increases in algal growth that can initially increase DO in upper portion of a water column via photosynthesis. Algae can also respire (consume DO) in absence of sunlight. To a lesser extent, algae can also undergo photorespiration when stimulated by an increase in temperature or oxygen concentration, resulting in reductions in DO in the water column. However, because daylight hours are longer during the algal growing season (late spring – early fall), there is a net increase in DO in upper water column due to algal metabolism. When algal cells die, they provide large amounts of organic matter for respiring (i.e. oxygen-consuming) microorganisms. Oxygen consumption from the proliferation of respiring microorganisms predominately occurs towards the bottom of the water column where dead algae reside. The result is a lowering of DO concentrations in bottom waters. Given the interrelationship between DO and nutrients, DO levels can be used as an indicator of nutrient pollution. Dissolved oxygen concentrations can be used to develop nutrient reduction volumes needed to restore waters and initiating actions to protect aquatic life.

Ecology develops marine models from water quality studies to assess compliance with water quality standards. Several large areas of Puget Sound have been modeled to focus on areas with DO problems and excess algal production. Ecology has combined internal and external funding to expand the modeled areas of Puget Sound. These models are a priority for the state as they

serve as a tool to understand the most effective actions that will protect water quality in the complex marine environment.

## **pH Criteria**

Another key indicator of nutrient pollution is the state's pH criteria. Carbon dioxide (CO<sub>2</sub>) is a product of respiration and is also a carbon source for photosynthesis by aquatic plants. The relationship between pH and carbon dioxide is inverse and fluctuates from day to night. Increases in primary productivity through photosynthesis results in the removal of carbon from the water and an increase in pH (more alkaline). During times of limited photosynthesis (i.e. "dark" periods), respiring organisms release carbon dioxide into the water and reduce pH (less alkaline). This daily pH fluctuation is a result of the formation and disassociation of hydrogen ions from the bicarbonate buffer system (i.e. measured as alkalinity) in response to algal photosynthesis and respiration in the upper portions of the water column. In the lower portions of the water column, where secondary productivity results from decomposition of settled dead algae, the respiring heterotrophs increase CO<sub>2</sub> and depress pH.

Since small variations in pH measurements may reveal fluctuations in aquatic life health, it provides an important supplementary trigger for initiating necessary water body pollution investigations. Changes in nutrient availability may be inferred by setting pH threshold values known to influence aquatic life health. In conjunction with other water quality parameters, nutrient thresholds can be developed using pH criteria limits established for water bodies. After such problems are identified, the criteria or thresholds serve as targets for restoration and clean up that directly incorporate the causal effect of nutrients. Computer models serve as important tools in this evaluation.

## **Application of Narrative Criteria to Nutrients**

Some situations where the numeric criteria are insufficient to protect all fish and non-fish species, narrative criteria in the standards may need to be applied in order to ensure that aquatic life are not adversely affected.

Narrative criteria, found at WAC 173-201A-260(2)(a), states that toxic, radioactive, or deleterious material concentrations must be below which have the potential, either singularly or cumulatively, to adversely affect characteristic water uses, cause acute or chronic conditions to the most sensitive biota dependent upon those waters, or adversely affect public health.

Narrative criteria, found at WAC 173-201A-260(2)(b), states that aesthetic values must not be impaired by the presence of materials or their effects, excluding those of natural origin, which offend the senses of light, smell, touch, or taste.

Various surrogate indicators such as percent oxygen super-saturation, chlorophyll levels, photographic evidence of algal mats, among others, can be considered to confirm adherence to aesthetic values related to the avoidance of excessive algal blooms due to nutrient enrichment and photosynthetic enhancement.

## **DO Saturation**

For practical purposes, DO concentrations in water at equilibrium with air (i.e., the oxygen concentration at 100% saturation) is a function of temperature, barometric pressure, and salinity. Moisture and other gases in the air, and effects of water density, also play roles, but these factors affect saturation less than the amount of precision in routine measurements (Mortimer, 1981). Measuring percent saturation for DO requires that a minimum percent of gaseous oxygen be present in the water column. Unlike criteria based on DO concentration requirements, percent saturation considers the naturally variable environmental conditions in context to DO. Percent saturation is generally included as a secondary measure when atmospheric pressure and temperature preclude the attainment of a DO concentration criterion (Brown and Hallock, 2009).

While Ecology has traditionally used one-day minimum DO concentration criteria to protect aquatic biota rather than percent saturation criteria, super-saturation may be considered as another indicator of nutrient and photosynthetic enhancement (USEPA, 1988) in surface waters, and may be used as part of the narrative criteria.

Percent saturation of DO identifies the capacity of water to hold DO, and hence, provides a useful metric for determining impairment. A large deviation of oxygen saturation in either direction from 100% may generally indicate impaired conditions. For example, juvenile salmonids may be impacted by both oxygen supersaturation (Jensen, 1986) and low oxygen concentrations (Whitmore, 1960).

With regards to low or hypoxic conditions, DO concentration is a more reasonable and direct parameter than percent saturation from the perspective of protecting aquatic biota. The DO concentration is more critical than percent saturation (though oxygen uptake is more difficult if saturation is low), and critical concentrations are fairly well established (Brown and Hallock, 2009).

## **Other Narrative Criteria**

There are other indicators of excess nutrients that can be used as narrative criteria for purposes of identifying problematic effects of nutrients, such as organic carbon or aragonite saturation. These alternative indicators or thresholds are not discussed in this paper, however, if alternative indicators are used as narrative criteria for purposes of TMDL or other work related to water quality standards, the science behind the alternative would need to be documented.

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