



# Water quality criteria for an acidifying ocean: Challenges and opportunities for improvement



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## ABSTRACT

Acidification has sparked discussion about whether regulatory agencies should place coastal waters on the Clean Water Act 303(d) impaired water bodies list. Here we describe scientific challenges in assessing impairment with existing data, exploring use of both pH and biological criteria. Application of pH criteria is challenging because present coastal pH levels fall within the allowable criteria range, but the existing criteria allow for pH levels that are known to cause extensive biological damage. Moreover, some states express their water quality criteria as change from natural conditions, but the spatio-temporal distribution and quality of existing coastal pH data are insufficient to define natural condition. Biological criteria require that waters be of sufficient quality to support resident biological communities and are relevant because a number of biological communities have declined over the last several decades. However, the scientific challenge is differentiating those declines from natural population cycles and positively associating them with acidification-related water quality stress. We present two case studies, one for pteropods and one for oysters, which illustrate the opportunities, challenges and uncertainties associated with implementing biological criteria. The biggest challenge associated with these biological assessments is lack of co-location between long-term biological and chemical monitoring, which inhibits the ability to connect biological response with an acidification stressor. Developing new, ecologically relevant water quality criteria for acidification and augmenting coastal water monitoring at spatio-temporal scales appropriate to those criteria would enhance opportunities for effective use of water quality regulations.

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## 1. Introduction

The ocean has absorbed more than a quarter of the carbon dioxide (CO<sub>2</sub>) emissions released into the atmosphere during the last century by burning of fossil fuels, deforestation and agricultural activities (Rhein et al., 2013). This oceanic uptake of anthropogenic

CO<sub>2</sub> lowers the pH and changes the chemical composition of seawater in a process referred to as ocean acidification (OA) (Caldeira and Wickett, 2003; Feely et al., 2009). CO<sub>2</sub> absorbed by seawater forms a weak acid (H<sub>2</sub>CO<sub>3</sub>), which dissociates to lessen pH, carbonate ion (CO<sub>3</sub><sup>2-</sup>) concentration, and calcium carbonate mineral saturation state, while increasing the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) and bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) concentration. As a result, the pH of open-ocean surface waters has decreased by about ~0.1 units and CO<sub>3</sub><sup>2-</sup> concentration has decreased about 16%. By the end of this century, surface ocean pH is expected to decline by another

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0.3–0.4 units and carbonate concentration is expected to decline by ~50% (Orr et al., 2005). Changes in the frequency of low aragonite (a biomineral of calcium carbonate) saturation state events are also occurring (Harris et al., 2013; Hauri et al., 2013).

These acidification changes are already affecting biology in the oceans (Bednaršek et al., 2014a; Somero et al., 2016). The upwelling-dominated shoreline of the North American west coast is particularly vulnerable to OA (Feely et al., 2008, 2012; Barton et al., 2012, 2015; Hauri et al., 2013). Very nearshore waters of Oregon exhibit pH as low as 7.7 (Feely et al., 2008; Barton et al., 2012, 2015) due to the combined effects of atmospheric CO<sub>2</sub> dissolution and upwelling low pH waters onshore. Bednaršek et al. (2014a) found OA hot spots along the entire coasts of Washington and Oregon, as well as northern California, where more than 50% of the upper water column in the very nearshore waters was undersaturated with respect to aragonite during the summer. Declines in oyster hatchery production in this region have been attributed to OA (Barton et al., 2012, 2015; Mabardy et al., 2015), leading to interest in identifying management levers for slowing the effects of OA (Kelly et al., 2011; Strong et al., 2014).

The US Clean Water Act (CWA) contains several mechanisms for protecting water resources, including discharge permits to ensure that water quality standards are met when a discharge is diluted in the ambient water body. However, cumulative effects of multiple permitted discharges and the presence of non-permitted sources can result in waters that violate water quality standards. When water bodies do not achieve their designated beneficial uses, they can be placed on the CWA 303(d) impaired water list. Subsequently, the Total Maximum Daily Load (TMDL) process can be initiated, whereby additional management practices or changes in permitting are employed to improve the water quality.

Given the potential for OA ecosystem effects, the Center for Biological Diversity (2013) petitioned the US Environmental Protection Agency (EPA) to list OA-impacted waters as impaired on the CWA 303(d) list. EPA responded by issuing a guidance memo recommending that states should include on their 303(d) lists those marine waters not meeting EPA-approved water quality standards for pH. The goal of this paper is to critically examine scientific issues underlying approaches to a 303(d) assessment for waters affected by OA. We describe the approaches, identify uncertainties associated with each, and indicate the science and data needs to lessen the uncertainties. While OA is a global problem, we focus on US waters where the CWA applies and on the US West Coast, as this region is particularly vulnerable to OA.

## 2. Water quality criteria

Water quality criteria form a quantitative basis for decisions on whether impairment exists. There are two primary types of criteria that potentially can be used to assess OA impacts: (1) numeric pH criteria and (2) narrative criteria to protect biological communities. In addition, antidegradation policies provide protections to waters that meet water quality standards but have declining water quality that is diminishing their beneficial uses. Antidegradation policy can theoretically be used for 303(d) water body listings, but there is no precedent for doing so, even for conventional pollutants. As such, the antidegradation approach is not considered further here.

### 2.1. pH criteria

Many states have pH criteria that are based on EPA's Redbook recommendations, which give an acceptable range of pH for marine aquatic life of 6.5–8.5, but not more than 0.2 units outside the normally occurring range of natural variability, and a range of 6.5–9.0 for freshwater aquatic life (USEPA, 1976). Some states have

modified the Redbook recommendations. Using the US West Coast as an example, Oregon does not include 0.2 unit excursions from natural conditions in their marine pH criteria, only a range of acceptable pH values (State of Oregon, 2014; Table 1). Washington adopted a narrower pH range than that in the Redbook and the range depends on the water body type under consideration (State of Washington, 2012; Table 1). California does not have a specific range of pH values for the marine criteria but instead considers whether pH deviates 0.2 units from natural conditions (State of California, 2004; Table 1). For estuarine waters, California has separate criteria for six regions of the state, which generally follow the range recommended in the Redbook but with minor modifications in each region. These modifications of the Redbook recommendations are representative of a range of modifications made by other coastal states.

States have also adopted assessment methods to determine whether or not a water quality standard is being met. For example, California requires that a minimum of five samples exceed the pH standards, but also employs a binomial statistical approach that could lead to a higher minimum. Oregon requires greater than 10 percent of the samples, and a minimum of two samples, to be outside of the appropriate criterion range. Washington requires a minimum of three samples, and at least 10 percent of values in a given year, not meet the criterion. Similar policies exist in other coastal states.

### 2.2. Aquatic life narrative criteria

States also have aquatic life criteria. These integrate beyond individual chemical perturbations and allow the health of the water to be assessed via the quality of the water's biological communities (Table 2). These generally take the form of narrative criteria that are less quantitatively defined than are water quality criteria, but provide a mechanism for listing a water body as impaired via ocean acidification.

An individual state's 303(d) listing policy defines how narrative criteria are interpreted. For example, California has an open-ended listing policy that allows development of narrative criteria evaluation guidelines if they are demonstrated to be applicable to and protective of the designated beneficial uses for that water body, linked to the pollutant under consideration, well-described, scientifically based, peer reviewed and identify a water quality range above which impacts occur and below which no or few impacts are predicted. Oregon has more prescriptive policies for using biological data to make 303(d) listing decisions, requiring use of invertebrate indices. Washington has prescriptive policies for use of invertebrates, but also has more open-ended policies that allow for use of other biological data.

## 3. Science challenges that arise in using a numerical pH standard for assessing compliance

Standards based solely on a percentage of samples outside of a designated range are straightforward to apply since they do not require determination of natural conditions. However, there are two challenges associated with application of this standard. The first is that the lower end of the acceptable pH range (6.5 in the EPA Redbook) is well below values known to adversely affect biological communities (Kroeker et al., 2013; Waldbusser and Salisbury, 2014; Somero et al., 2016). For example, no pH value less than 7.5 has been measured in more than five years of continuous monitoring at the Whiskey Creek oyster hatchery in Netarts Bay, even though acidification conditions there are poor enough to cause catastrophic shellfish hatchery failure (Barton et al., 2012, 2015).

The second challenge is that pH data quality can be poor for

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