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RE: Washington State Surface Water Quality Standards Triennial Review

I. Introduction

These comments to the Washington State Surface Water Quality Standards Triennial Review are submitted by the Center for Biological Diversity (the "Center"). The Center is a nonprofit environmental organization dedicated to the protection of imperiled species and their habitats through science, education, policy, and environmental law. The Center's Oceans Program aims to protect marine life and ocean ecosystems in United States and international waters. The Center has over 300,000 members and online activists throughout the United States and submits these comments on its own behalf and on behalf of its members and staff with an interest in protecting the ocean environment.

The Center urges Washington State Department of Ecology (the "Department of Ecology") to revise Washington State's Aquatic Life pH Criteria in Marine Water, (WA ADC 173-201A-210(1)(f)), so that waters may not deviate measurably from naturally occurring pH levels as a result of the marine waters' absorption of anthropogenic carbon dioxide resulting in ocean acidification.[1] Washington's current pH criterion conforms to the minimum national recommended standard of 0.2 units. We contend, however, this amount of ocean acidification is insufficient to protect water quality and Washington's designated uses.

[1] This phenomenon is referred to herein as "ocean acidification." The absorption of atmospheric carbon dioxide (CO_2) into the ocean lowers the pH of the waters, which is commonly referred to as "ocean acidification." (Feely 2008). Ocean acidification is "primarily caused by increasing CO_2 levels in the atmosphere." (Memo. from Denise Keehner, Dir., EPA Office of Wetlands, Oceans and Watersheds, to EPA Water Division Directions, Regions 1-10, *Integrated Reporting and Listing Decisions Related to Ocean Acidification* (Nov. 15, 2010) (available at http://water.epa.gov/lawsregs/lawsguidance/cwa/tmdl/upload/oa_memo_nov2010.pdf).

The U.S. Environmental Protection Agency ("EPA") recently issued a memorandum noting the adverse environmental consequences of ocean acidification and stating that "waters should be listed for [ocean acidification] where data are available." (Memo. from Denise Keehner, Dir., EPA Office of Wetlands, Oceans and Watersheds, to EPA Water Division Directions, Regions 1-10, *Integrated Reporting and Listing Decisions Related to Ocean Acidification* (Nov. 15, 2010) (available at http://water.epa.gov/lawsregs/lawsguidance/cwa/tmdl/upload/oa_memo_nov2010.pdf) (hereinafter "Keehner Memo")). Sufficient data now exist for Washington to list any waters with a measurable human-caused deviation of pH as threatened or impaired waters under its Clean Water Act ("CWA") § 303(d) listing. By adopting a "no deviation" criterion for pH levels, Washington State and EPA will better be able to identify and track waters impaired by ocean acidification and, ultimately, manage CO_2 emissions that lead to such pollution (Keehner Memo).

II. Background: Effects of Ocean Acidification on Biological Resources

Addressing ocean acidification is now listed a top priority of the Federal government (Keehner Memo), with the prognosticated effects of ocean acidification becoming increasingly grim: The scientific community's comprehension of the dangers of ocean acidification reveals that immediate action is essential if the irreversible loss of marine ecosystems is to be avoided (Carnegie Institution for Science 2007, Hoegh-Guldberg 2007).

Globally, the ocean's daily uptake of 22 million metric tons of CO_2 has a sizable impact on its chemistry and biology (Feely 2008). This absorption of CO_2 is directly polluting ocean waters and results from human activity, namely fossil fuel burning. Since the beginning of the industrial era, the oceans have absorbed between 109 and 145 billion metric tons of carbon as CO_2 from the atmosphere, or about one-third of the total anthropogenic carbon emissions released (Feely 2008). Due to the fact that the ocean has a carbonate buffer system, an increase in aqueous carbon dioxide reduces the concentration of carbonate while increasing the concentration of bicarbonate. The result is a decrease in ocean pH.

Carbon dioxide pollution has already lowered average ocean pH by 0.11 units,[2] with a pH change of 0.5 units projected by the end of the century under current emission trajectories (Feely 2008). While this might seem fairly innocuous, the environmental impacts of such a deviation from normative pH levels are likely to be devastating on sensitive marine ecosystems.

Washington State is hardly immune from these effects. One of the primary known impacts of acidification is impairment of calcification,[3] the process whereby corals, crabs,

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[2] A 0.11 pH unit increase is equivalent to an overall increase in the hydrogen ion concentration in surface waters of approximately 30% (OCB 2009).

[3] "The reaction of CO2 with seawater reduces the availability of carbonate ions that are necessary for calcium carbonate ($CaCO_3$) skeleton and shell formation for marine organisms

abalone, oysters, sea urchins, and other animals make shells and skeletons. Many species of phytoplankton and zooplankton, which form the basis of the marine food web, are also particularly vulnerable to ocean acidification (Feely 2006).

The North Pacific aragonite (a form of calcium carbonate, or $CaCO_3$) saturation horizons are now among the shallowest in the global ocean (Feely 2008). Pteropods, which form their shells from aragonite, are at risk of having their shells dissolved as seawater becomes undersaturated with aragonite (Orr 2005). Measurements have shown that upwelled coastal water (discussed below) is corrosive enough to dissolve aragonite and literally eat away at the shells of many animals on the continental shelf off the coast of Washington and Oregon (Feely 2008, Barton et al. 2009). Krill, whales, salmon, and other fish eat pteropods, and they contribute significantly to marine production. Similar animals feed many of the major fish species in Alaska's North Pacific, which supports the billion-dollar Seattle-based fishing industry (Craig Welch, *Oysters in deep trouble: Is Pacific Ocean's chemistry killing sea life?* The Seattle Times (June 15, 2009)).

Fish themselves are also affected by ocean acidification. When fish are exposed to high concentrations of CO_2 in seawater, cardiac failure can result and directly cause mortality (Ishimatsu 2004). At lower concentrations, sublethal effects can be expected that can seriously compromise the fitness of fish. Juvenile and larval stages of fish were found to be the most vulnerable (*Id*.).

Additionally, many threatened and endangered species depend on the ocean ecosystem and are extremely vulnerable to changes in marine habitat. Ocean acidification jeopardizes the continued existence of some of these species. For example, ocean acidification may dissolve the shell of the endangered white abalone or inhibit shell formation and growth. Also, there are numerous threatened and endangered species such as blue, humpback, and fin whales, and sea otters that prey on calcifying species. Declining fitness of fish due to acidification could not only impact depleted fish populations, but also already imperiled fish-eating species such as the brown pelican, marbled murrelet, Steller sea lion, Guadalupe fur seal, Kemps Ridley Sea Turtle, and orca. Similarly, impacts to squid, among the most sensitive of marine species to changes in pH, would likely impact squid-eating species such as sperm whales.

The effects of ocean acidification are likely to only increase in the years to come. This is especially true for coastal waters, including those of Washington State. The seasonal upwelling of subsurface waters along the coast contains anthropogenic CO_2 sequestered by the water when it last came in contact with the atmosphere half a century ago (Feely 2008, OCB 2009). Unfortunately, the atmospheric concentration of CO_2 has increased markedly since then and is

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such as corals, marine plankton, and shellfish. The extent to which the organisms are affected depends largely on the $CaCO_3$ saturation state (Ω), which is the product of the concentrations of Ca^{2+} and CO_3^{2-} divided by the apparent stoichiometric solubility product for either aragonite or calcite." (Feely 2008). The Ω value can also be used as a proxy for the ease with which organisms can produce $CaCO_3$ (Miller et al. 2009).

expected to continue to rise at an increasing rate (Feely 2008). The consequence of this that in each ensuing year, the upwelling water that has been exposed to the atmosphere still more recently will yield yet higher CO_2 levels (OCB 2009).

Recent research has also shown that this upwelling of anthropogenically acidified coastal waters is also responsible for the decrease of pH in the Puget Sound estuary complex (Feely 2010). It is estimated that ocean acidification is responsible for up to 49% of the pH decrease in the deep waters of the Hood Canal sub-basin of Puget Sound (compared to pre-industrial pH values). Over time, however, ocean acidification could account for up to 82% of the subsurface pH declines if CO_2 emissions continue to increase on their current trajectories (*Id*.). And, because they are shallower, less saline, and have lower alkalinity, estuaries and coastal marine habitats have been shown to be even more susceptible to changes in pH than the open ocean (Miller at al. 2009); the input of "acidified" low-pH upwelled water from the ocean combines with estuaries' natural processes to produce very low pH conditions (Feely 2010.)

Some of the effects of ocean acidification on estuaries have already been seen in the recent rapid declines of large mussel populations at Tatoosh Island and mass mortalities of oyster larvae in the Pacific Northwest (*Id*.). When the upwelled acidified water is observed in coastal hatcheries, mass mortality events have followed within 24-48 hours (Barton et al. 2009). In such conditions, larvae of all sizes and species (Pacific oysters, Kumamoto oysters, Manila clams, and Mediterranean mussels) are dramatically affected. Experimentally enhanced CO_2 has been shown to decrease the development rate of not only Pacific oyster larvae, but also the early development of sea urchins (Talmage et al. 2009). For six consecutive years, Pacific Coast oysters' yields have collapsed, with commercial hatcheries experiencing alarming and widespread difficulties keeping larvae alive due to the more corrosive water conditions (Craig Welch, *Oysters in deep trouble: Is Pacific Ocean's chemistry killing sea life?* The Seattle Times (June 15, 2009), Miller et al. 2009; Feely et al. 2010).

Larvae are particularly susceptible to acidified waters because their shells are composed of aragonite, with small oyster larvae (1-3 days old) partially forming their shells from calcium carbonate – a compound which is readily dissolved in acidified solutions (Barton et al. 2009, Miller et al. 2009). Larvae that do not perish because of the direct effects of ocean acidification may experience indirect impacts, as they need to expend so much energy building their shells that they are physically weakened, and can more easily succumb to normal stressors like bacteria blooms (*id*.), and prolonged predation due to delayed metamorphosis (Talmage et al. 2009). The overall decreased size (up to 50%) of settled shellfish could generally translate into higher mortality rates for these individuals (Marshall et al. 2003, Talmage et al. 2009).

The leading ocean acidification scientists warn that even a 0.2 pH change – the current EPA and Washington State water quality criteria for pH – will have significantly adverse impacts on marine life (Caldeira et al. 2007). It is for this reason that the Department of Ecology should act prudently and adopt more stringent standards for its pH criteria in marine water in an attempt to reduce the imminent and irreversible degradation of its marine resources, as well as the attendant ecological, recreational, and economic ramifications.

III. The Department of Ecology Should Adopt a More Stringent Standard for its Aquatic Life pH Criterion in Marine Water

Washington State Department of Ecology's current permissible deviation for its pH pollution criterion conforms to the national recommended standard of 0.2 units. As discussed above, however, this variance is impermissibly high given the current impacts that ocean acidification is having on the marine environment. Because the effects of ocean acidification will only intensify in coming years, the Department of Ecology must adopt more stringent pH criterion for marine waters to protect its marine environment.

A. Washington's Water Quality Standard Is Woefully Outdated and Is Insufficient to Protect Aquatic Life from the Adverse Effects of Ocean Acidification

The Clean Water Act's goals to protect the chemical and biological integrity of our nation's waters are being undermined by the water quality criteria that are ineffective at protecting seawater against ocean acidification. The outdated criteria fail to incorporate the latest scientific knowledge about ocean acidification.

Pursuant to section 304's mandate, EPA issued the "Blue Book" of Water Quality Criteria in 1973. In 1976, EPA published the "Red Book" which contained the water quality criteria for pH that is still used today, and adopted by Washington that "the pH should not be changed more than 0.2 units outside the naturally occurring variation."(Quality Criteria for Water 1976: 342-43). This water quality criterion is woefully outdated and fails to reflect the latest scientific knowledge. According to a Comment authored by 25 of the leading researchers of ocean acidification:

> The assumption made by the U.S. Environmental Protection Agency [1976] that a pH decrease of 0.2 units in the ocean will not harm marine biota is fundamental to the conclusions made by Loaiciga [2006]. However, this criterion was established prior to the development of an extensive body of research showing that a decrease of this magnitude would pose a risk to the physiology and health of a variety of marine organisms (much of this research is reviewed by Gattuso et al. [1999], Kleypas et al. [1999], Seibel and Fabry [2003], Portner et al. [2004], and Caldeira et al. [2005]).

(Caldeira et al. 2007: L18608). In fact, Zeebe et al. (2008) specifically noted the need to reevaluate this stanard with respect to ocean acidification:

> Thus, although the response of different organisms is expected to be inhomogeneous (*9*), current evidence suggests that large and rapid changes in ocean pH will have adverse effects on a number of marine organisms. Yet,

> environmental standards for tolerable pH changes have not been updated in decades. For example, the seawater quality criteria of the U.S. Environmental Protection Agency date back to 1976 and state that for marine aquatic life, pH should not be changed by more than 0.2 units outside of the normally occurring range (*10*). These standards must be reevaluated based on the latest research on pH effects on marine organisms. Once new ranges of tolerable pH are adopted, CO^2 emission targets must be established to meet those requirements in terms of future seawater chemistry changes.

(Zeebe et al. 2008: 52). Washington must comply with its duty under the Clean Water Act regulations 40 CFR § 131.20, which requires that it shall review and revise water quality standards, and here it needs to adopt water quality standards that adequately protect marine waters from the adverse impacts of ocean acidification.

B. "No Deviation" pH Standard

The Center strongly urges that the Department of Ecology adopts a criterion for pH stating: "For marine waters, pH should not deviate measurably from naturally occurring pH levels as a result of absorption of anthropogenic carbon dioxide." This "no deviation" standard addresses key concerns regarding the Department of Ecology's current Aquatic Life pH Criterion in Marine Water:

(1) Marine organisms, especially those that are calcareous, are more sensitive than previously realized to changes of less than 0.2 units in ocean pH. Extensive research shows that a decrease of 0.2 pH could pose a risk to the physiology and health of a variety of marine organisms (Caldeira 2007).

(2) It is possible to make more accurate pH measurements now than in 1976,[4] and thus a narrower range of acceptable values for marine waters is appropriate. In light of this science and the available pH measuring techniques, discussed forthwith, the criterion suggested above is patently reasonable.

(3) Human activity is responsible for recent decreases in marine water pH; the causal linkage is irrefutable. EPA has recently informed the States of the detrimental effects of changes in ocean pH levels caused by the absorption of mass quantities of anthropogenic CO_2 emissions, and has encouraged action where feasible (Keehner Memo.).

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[4] Guidelines for pH were published first in 1976 with the "Red Book", and republished—unchanged—in the "Gold Book" in 1986 (51 Fed. Reg. 43665). The guidelines state that marine waters should have a pH value between 6.5 and 8.5, with no change greater than 0.2 units from normal. Since that time, the state of the science has changed dramatically; scientists now agree that even small reductions in pH may have deleterious effects on marine ecosystems.

(4) Corrosive waters that are presently upwelling along the Washington coast during certain seasons were last at the surface over 50 years ago (Feely et al. 2007). This means that there is already additional carbon dioxide in the pipeline, and ocean acidification we see on the coast now is lagging behind the carbon dioxide absorption.

Washington State should act now and take proactive steps to manage the causes of ocean acidification. The Center's suggested criterion is both prudent and reasonable, and should be adopted as part of Washington State's water quality standard criteria. If pH levels deviate further than they already have, the resulting environmental consequences will not be reversible on human time scales (Caldiera 2007).

C. Measuring pH Levels

In an effort to effectively monitor pH and waters affected by ocean acidification, Washington State and the Department of Ecology should also adopt appropriate methods for detecting and measuring marine water pH. Past impediments to managing acidified waters was the absence of a normally occurring pH baseline to identify variations outside of natural deviations. Because of the now-existing methods for measuring pH levels, these concerns are no longer valid rationales for failing to implementing water quality standards to better address ocean acidification.

1. Direct Measurement of pH Levels

There are several means of accurately measuring the pH of marine waters.[5] Direct measurements of pH levels can be conducted by using calibrated pH electrodes or measuring pH spectrophotometrically (OCB 2009). While both methods have their respective benefits and drawbacks, the spectrophotometric technique has a precision of 0.0003 to 0.0004 pH units (Liu 2006); it is also not susceptible to electrode drift throughout the day, as potentiometric methods are, which require buffer calibration (*Id*.) The "calibration-free" characteristic of the spectrophotometric method also makes it particularly well-suited to automatic measurements at pH monitoring stations, buoys, or other platforms using autonomous sensors (OCB 2009).

While it is true that seasonal variables effect the direct measurement of pH levels, existing methods can be used to reliably and accurately predict and correct for seasonal variations (*See e.g.*, Dore 2003). The EPA already has experience dealing with other pollutants that involve seasonal variability, as exemplified by the Region 10 temperature criteria guidance (www.epa.gov/r10earth/temperature.htm). Other empirical approaches, such as multi-linear regression, can be used to accurately fill possible data gaps via interpolation and extrapolation (OCB 2009). As a result, it is fully feasible to adopt and enforce water quality standards that comprise a reduced range of acceptable pH levels through direct measurement of pH.

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[5] *See generally*, Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. *Guide to best practices for ocean CO2 measurements*. PICES Special Publication 3, 191 pp, available at http://cdiac.ornl.gov/oceans/Handbook_2007.html.

2. Alternative Methods for Assessing Whether Waters are Polluted due to Ocean Acidification

Alternative methods that measure pH levels indirectly also exist. Some in the scientific community believe that, due to the natural variables affecting direct pH measurement, other indicators should be considered. Water quality parameters should include: pH, dissolved inorganic carbon (DIC), total alkalinity (TA), partial pressure of CO^2 (ρCO^2), and saturation state with respect to calcite and aragonite (Ω). The U.S. Ocean Carbon and Biogeochemistry (OCB) community of scientists provided useful comments to EPA about how such standards could be developed by looking at a variety of parameters to measure ocean acidification and carbonate saturation states (OCB 2009). For the most accurate results, several methods would be employed (OCB 2009). Washington should review the OCB comments enclosed herein for alternative methods of measuring ocean acidification.

First, Washington should consider adopting saturation state standards in addition to pH standards. Two favored indicators of pH and ocean acidification are the $CaCO_3$ saturation state (Ω) and pCO_2 concentration levels.[6] Second, Washington should consider narrative criteria that aim to protect aquatic life from water quality conditions that stress or decrease organisms' fitness or calcification due to ocean acidification.

Third, Washington should consider implementing biological criteria. The use of biological criteria should also be fully utilized as a supplement to the numeric criteria that can provide a measure against which to evaluate ocean acidification and its impacts on aquatic life. As early as 1990, EPA provided guidance to states to develop biological information and criteria (EPA 1990). Biological criteria are numeric and narrative criteria that define the condition of an aquatic community such as its species richness, presence or absence of indicator taxa, distribution of classes of organisms (*Id.*). Biological assessments and biological criteria can then be used as a measure for determining the impacts of ocean acidification.

IV. Conclusion

It is irrefutable that the health of the ocean declining due to ocean acidification. Marine waters, while valuable carbon sinks, are not immune to the impacts of increased atmospheric concentrations of CO_2. Scientific consensus now shows that a deviation of 0.2 pH units is impermissibly high to avoid the dangerous and irreversible effects of ocean acidification on sensitive marine ecosystems. The Center therefore encourages Washington State to proactively adopt a more stringent standard for its Aquatic Life pH Criteria in Marine Water. A "no deviation" criterion would not only help improve the health of the State's marine ecosystem, but also the economic health of the State and surrounding region. Given the number of reliable and

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[6] Studies have shown that the $CaCO_3$ saturation state rather than the pH or partial pressure of CO_2 controls the response of many calcifying organisms (Langdon et al. 2000).

economically-feasible methods for assessing whether waters have been polluted by ocean acidification, the adoption of this "no deviation" criterion is patently reasonable and scientifically justified.

We appreciate the opportunity to comment on the Washington's triennial review of its water quality standards, and thank you in advance for your consideration of these comments.

Respectfully Submitted,

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enclosure:CD with references

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