



Canadian Water Quality Guidelines for the Protection of Aquatic Life

pH
(Marine)

The pH is the negative logarithm (base 10) of the chemical activity (concentration in mol·L⁻¹) of the hydrogen ion in solution. The pH scale indicates a neutral solution at pH 7.0, an acidic solution below 7.0, and an alkaline (basic) solution above 7.0. A unit change in pH corresponds to a tenfold change in the hydrogen ion concentration; thus, small changes in pH can significantly alter the chemistry of marine and estuarine waters.

The pH of marine waters is usually quite stable (between 7.5 and 8.5 worldwide) and is similar to that of estuarine waters because of the buffering capacity provided by the abundance of strong basic cations such as sodium, potassium, and calcium and of weak acid anions such as carbonates and borates (Wetzel 1983). Higher pHs are usually found in near-surface waters because of solar radiation. The effect of solar radiation on pH is twofold: it promotes photosynthesis and increases surface temperatures, both of which decrease the amount of free carbonic acid and consequently raise the pH (Skirrow 1965; Wetzel 1983). For example, at a depth of 23 m in the Beaufort Sea, an average pH of 7.79 was recorded, whereas surface pH measurements averaged 8.1 (Thomas et al. 1982). Such effects can be the result of both diurnal and seasonal fluctuations (Skirrow 1965). The longer periods of daylight experienced in June, for instance, have caused surface pH in the Beaufort Sea to average 8.1, whereas in February, the average surface pH dropped to 7.84 (Thomas et al. 1982).

Even in estuaries and embayments, where considerable dilution of seawater from freshwater sources occurs, buffering is sufficient to maintain stable pH values, usually in the slightly alkaline range. Reported ranges of pH for brackish areas of the Fraser River estuary (Swain and Holms 1985, 1988), the Burrard Inlet (Nijman and Swain 1990), and the Mackenzie River delta (Thomas et al. 1982) were 7.3–8.3, 7.4–8.8, and 7.85–8.6, respectively.

Fluctuations in pH due to anthropogenic influences in aquatic environments are largely the effects of industrial activities. Acid precipitation caused by SO₂ and NO_x emissions from industries and vehicles can depress the pH of surface waters, especially after spring snowmelt, when significant amounts of accumulated acid deposition (i.e., in the snow pack) are flushed into marine and estuarine

waters (Knutzen 1981; Kaufmann et al. 1992). Deposition of atmospheric CO₂ emissions from fossil fuel combustion can also lead to decreases in the alkalinity and pH of marine waters (Jones and Levy 1981). In addition, the pH of aquatic environments can be altered as the result of direct inputs of acid, through acid mine drainage, and some industrial waste leachates (McNeely et al. 1979).

Biological Effects

A broad spectrum of marine and estuarine organisms have been shown to be adversely affected by pH fluctuations, many of these effects being physiological. A decrease in pH was correlated with a reduction in carapace weight, increased magnesium content (with constant calcium content), and a slight decrease in strontium content of the marine prawn *Penaeus monodon* (Wickins 1984). In the marine octopus *Octopus dofleini*, a pH below 7.2 was correlated with a decrease in maximum oxygen saturation of hemocyanin, a blood oxygen transporter (Miller and Magnum 1988). At pH below 7, reduced growth, weight loss, reduced shell size, shell dissolution, and suppressed feeding occurred in four species of bivalves (Bamber 1987, 1990). Significant mortalities occurred in the same four species after a 60-d exposure to similar test conditions.

An increase in acidity can affect physical processes in organisms. Cell aggregation of sea urchin embryos (*Hemicentrotus pulcherrimus*) was found to be affected by low pH and was obliterated at a pH lower than 4.0 (Tonegawa et al. 1990). Fluctuations in pH can also affect photosynthetic processes. Inhibition of photosynthesis was observed in the seagrass *Zostera muelleri* at pH less than 7.8, while maximum photosynthetic activity occurred at pH 8.4 (Millhouse and Strother 1986). A combined increase in pH and oxygen concentration and a decrease in dissolved inorganic carbon concentration inhibited photosynthetic activity in five species of marine macroalgae (Gordon and Sand-Jensen 1990).

In the marine environment, pH changes can also significantly affect the chemical forms and toxicity of other substances. In water, ammonia exists in two forms: a non-ionic species, NH₃, and an ionic species, NH₄⁺. The toxicity of ammonia to marine species is largely

determined by the concentration of the non-ionic species. The relative concentration of NH_3 in seawater is influenced in part by pH; with a reduction of one pH unit, the amount of NH_3 in water diminishes by a factor of 10 (Miller et al. 1990). Responses of marine organisms to alterations in ambient NH_3 concentrations as a result of pH fluctuations will vary between species. Juvenile mysids (*Mysidopsis bahia*) experienced decreasing acute toxicity to ammonia as pH increased from 7.0 to 9.0. In contrast, acute toxicity of ammonia to the inland silverside (*Menidia beryllina*) was greatest at pH 7.0 and 9.0 and lowest at pH 8.0 (Miller et al. 1990). The speciation of metals and the solubility of some organic chemicals are also strongly influenced by pH (Bengtsson 1978; Kaiser and Valdmanis 1982; Drever 1988).

Interim Guideline

The pH of marine and estuarine waters should fall within the range of 7.0–8.7 units unless it can be demonstrated that such a pH is a result of natural processes. Within this range, pH should not vary by more than 0.2 pH units from the natural pH expected at that time. Where pH is naturally outside this range, human activities should not cause pH to change by more than 0.2 pH units from the natural pH expected at that time, and any change should tend towards the recommended range (CCME 1996).

Rationale

The interim guideline for an acceptable pH range in Canada is based largely on the guideline of British Columbia (McKean and Nagpal 1991). This guideline is representative of the pH range commonly observed in Canadian coastal waters. To provide additional guidance when pH naturally exceeds the recommended guideline range, the proviso of the Alaskan guideline (State of Alaska 1989), which permits induced changes in pH only towards the specified range, has been adopted.

Unrestricted variation in pH due to human influences within the specified range may not be protective of organisms with narrow pH tolerances. The limit on induced pH changes (0.2 pH units) within this range is recommended to reduce the potential for impacts on organisms. Similar recommendations have been adopted in several jurisdictions, including Australia, California, the United States, Washington, and Western Australia.

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