The Role of pH, Alkalinity, and Calcium Carbonate in Shellfish Hatcheries

Emma Gaines[1], Leslie Sturmer[1], Natalie Anderson[1], Susan Laramore[2], and Shirley Baker[1]

Introduction

This document describes the interaction of pH, alkalinity, and calcium carbonate in water chemistry and their effects on the production of molluscan shellfish seed in hatcheries. Optimal values to maintain in hatchery culture waters are recommended and a buffering system is described to adjust values.

What are pH and alkalinity?

The pH is a measure of the concentration of hydrogen ions in water. The pH scale runs from 0 to 14, with 7 a neutral value (Figure 1). Anything higher than 7 is basic (or alkaline) and anything lower than 7 is acidic. The scale is an inverse of hydrogen ion concentration, so more hydrogen ions translate to higher acidity and a lower pH. Rapid pH changes can cause stress to aquatic organisms. Alkalinity is a measure of the capacity of water to neutralize acids, and to buffer rapid changes in pH. Alkaline compounds, such as bicarbonates, carbonates, and hydroxides, remove hydrogen ions by combining with them to form new compounds. This lowers the acidity of the water. A proper alkalinity level can help prevent stress in aquatic organisms brought on by rapid pH changes.

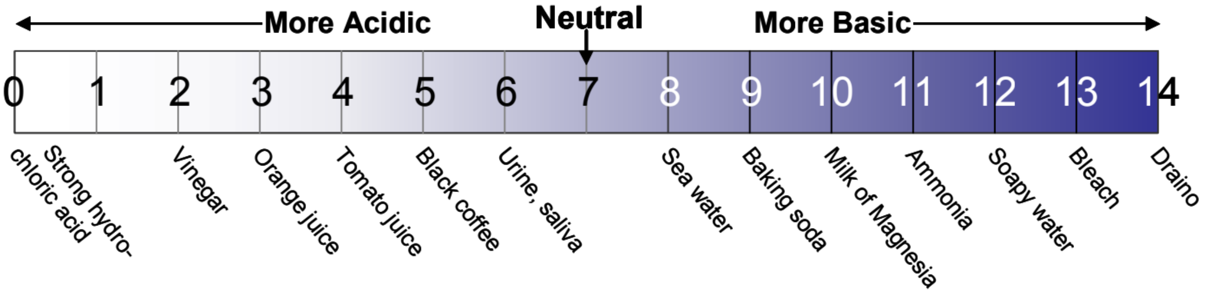

Figure 1. pH scale and examples of solutions at various levels from acidic to basic.

How are pH and alkalinity related to calcium carbonate?

Calcium carbonate ($CaCO_3$), also referred to as lime, is a source of alkalinity that is present in rocks, especially limestone. Parts per million (ppm) of calcium carbonate is a common measurement used to express the alkalinity of water. Alkaline substances, like calcium carbonate, react with acids and neutralize them in the process. Recall that pH is a measure of hydrogen ions in solution. Acidic hydrogen ions have a positive charge, which is attracted to the negative charge of basic carbonate ions. When these two ions combine, they neutralize each other. A proper alkalinity level helps to buffer rapid changes in pH. Liming, or addition of calcium carbonate in the form of calcite, will increase alkalinity of water and help buffer the water against pH changes.

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[1] University of Florida, Institute of Food and Agricultural Sciences

[2] Florida Atlantic University, Harbor Branch Oceanographic Institute

Why do these parameters vary?

The pH of water varies throughout the day due to photosynthesis of phytoplankton living in ambient water used by hatcheries. During daylight hours, photosynthesis is taking place and carbon dioxide is being used, which causes an increase in pH. At night, photosynthesis stops, and respiration occurs, which creates carbon dioxide (CO_2) and decreases the pH (Figure 2). Low pH may alleviate metal-induced oxidative stress. Other factors that influence pH include geology of a location (bedrock), acid rain, water use, and wastewater discharge.

Calcium carbonate may increase as crushed coral or limestone is added to water. Rainwater, which is slightly acidic, or acid rainwater, which is more acidic, may contribute to dissolution of calcium carbonate as well. This addition of dissolved calcium carbonate helps to maintain a constant pH because the minerals react with excess acid. Calcium carbonate may decrease when water softeners or lime softening are used to adjust pH levels. Dilution of water by significant rainfall, freshwater or anthropogenic inputs, and other sources may also cause pH, alkalinity, and calcium carbonate to vary.

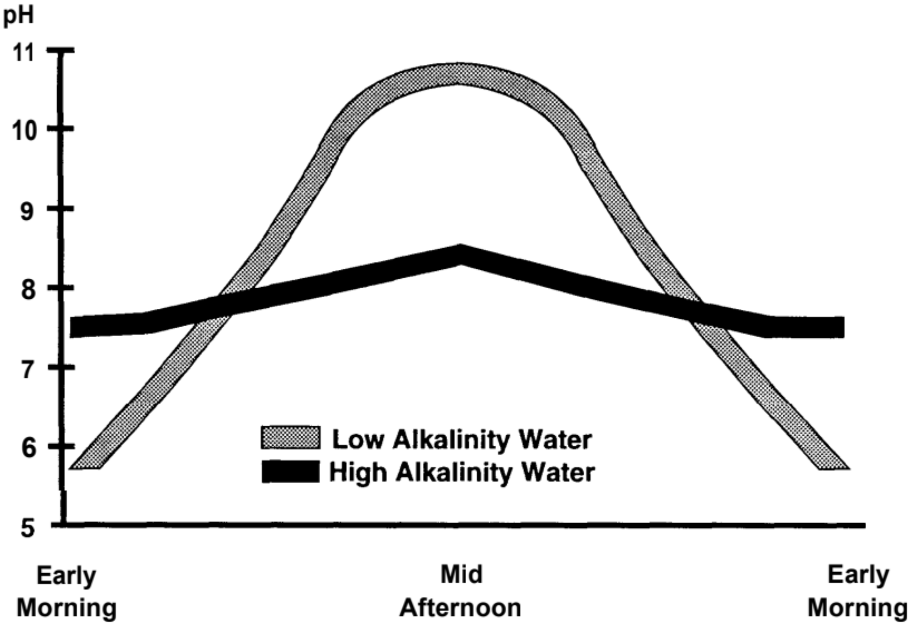


Figure 2. Changes in pH over a 24-hour period in waters of high and low alkalinities.

How are these parameters measured?

There are multiple ways to measure each of these parameters. Aquarium or field test kits or meters for pH and alkalinity are readily available and easy to use. It is best to monitor these parameters at the same time every day due to normal pH changes during the day (see Figure 2).

pH

Water quality probe: A water quality probe may have one or multiple probes used to measure water chemistry parameters. The probe is dipped directly into the water and provides a digital readout of pH.

Indicator tests or strips: Also referred to as the colorimetric method, indicator tests use a reagent in the form of test strips or drops that change color according to the pH. The intensity of the color is proportional to the pH in the sample, and colors are compared on a provided chart.

Grab samples: Grab samples are taken in the field and then sent to a laboratory for analysis. This method offers the highest degree of accuracy and precision but takes more time and may be expensive.

Alkalinity

Titration of a reagent: A water sample taken in the field has small, precise amounts of acid added to it until the sample reaches a certain pH. The amount of acid required to reach the pH value determines the alkalinity of the sample. A digital titrator is recommended.

Calcium carbonate

Saturation state: Calcium carbonate levels can be measured by calcium carbonate saturation state (Ω) using the equation below, where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are concentrations of ions in solution and K_{sp} is the solubility product at a given temperature, salinity, and pressure.

$$\Omega = \frac{\left[Ca^{2+}\right]\left[CO_3^{2-}\right]}{K_{sp}^{*}}$$

If the calcium carbonate saturation state is less than one, calcium carbonate can readily dissolve. If it is greater than one, then calcium carbonate does not readily dissolve.

Why are these parameters important for shellfish hatcheries?

Calcium carbonate is used by molluscan shellfish to build their shells, so it is crucial for proper shell development. Inadequate pH and alkalinity levels can cause larval shell deformities and poor survival. Research has shown the importance of carbonate chemistry for best bivalve larval performance. Thus, larval rearing water should mimic seawater chemistry. It is recommended that shellfish hatcheries maintain a pH of 7.8 to 8.4 with an optimal value of 8.2. An alkalinity level of 150 to 180 mg/L is also recommended. Hard clams *Mercenaria mercenaria* and oysters *Crassostea virginica* typically live in conditions where the calcium carbonate saturation state is greater than one and thrive in conditions where it is much greater than one.

Ocean acidification (OA) is the result of an imbalance in pH buffering that occurs as the result of excess carbon dioxide (CO_2) input. As dissolved CO_2 levels increase, pH and mineral stability (i.e., saturation state) decline due to disequilibrium in the carbonate chemistry of water causing an excess of hydrogen ions (H^+) in solution. OA has been shown to affect bivalve hatchery production. For example, oyster hatchery success has been compromised due to inadequate shell formation associated with coastal OA (Barton et al. 2012, Hettinger et al. 2013). Likewise, larval hard clam and bay scallop *Argopecten irridians* growth, development, and survival have been shown to be affected by acidification (Talmage and Gobler 2010). Changes in carbonate chemistry, both pH and mineral saturation, affect larval bivalve development, growth, and/or survival; however, the synergistic effects of other stressors, both abiotic and biotic, have not been as well studied. Temperature is a key abiotic factor known to affect the ocean's carbonate chemistry through its influence on pH and alkalinity via thermodynamic influence on dissolved CO_2. As temperatures rise, pH decreases due to increased CO_2, the primary driver of carbonate equilibrium. Increased temperatures also affect alkalinity by increasing the ratio of carbonate to bicarbonate and thereby increasing buffering capacity. Talmage and Gobler (2011) found that production of hard clams and bay scallops was compromised at higher temperatures and CO_2 levels. The complex interactions of the carbonate system are well documented, however, interactions between multiple abiotic and biotic factors are not well defined within aquaculture operations.

Although the primary cause of OA is considered to be anthropogenic (i.e., fossil fuel combustion, deforestation) in coastal regions, other factors, such as watershed inputs, oceanic upwelling events, and even respiration, enhance this process (Cai 2011). The drivers of coastal OA have been shown to vary depending on location. Oceanic water in the Pacific Northwest is CO_2-rich and seasonal upwelling events are the primary driver of OA in this region (Barton et al. 2015). As such, incoming hatchery waters fall below the minimum calcium carbonate saturation state threshold required for normal larval shell development and has resulted in devastating seed production failures from 2007 to 2009, see Box 1 (Barton et al. 2015). Recently, oyster hatcheries in the Northeast and mid-Atlantic states began experiencing oyster larval production problems. In contrast to the Pacific coast, it was observed that decreased saturation states resulted from a combination of increased atmospheric CO_2 and freshwater runoff from heavy precipitation events. Buffering incoming hatchery seawater by adding alkaline chemicals to balance acidic chemistry has since resulted in fast larvae growth, high survival rates, and high conversion to juveniles (Schreiber 2018). Results of a water chemistry study conducted at oyster hatcheries in the Chesapeake Bay identified potential solutions, including installation and use of specialized filtration systems to remove pollutants and balancing water chemistry through the addition of salts to increase carbonate saturation state (VMRC 2013).

Box 1. Production problems in West coast oyster hatchery linked to ocean acidification.

Whiskey Creek Shellfish Hatchery, located on the U.S. west coast in Oregon, has been producing shellfish since 1978. Like most hatcheries, Whiskey Creek uses local seawater to supply their hatchery. When the hatchery began experiencing mortalities of oyster larvae, they recruited the University of Oregon to examine their water chemistry. The mortalities turned out to be the result of an aragonite issue. Aragonite is the primary form of calcium carbonate used by oysters and other shellfish to build their shells. Whiskey Creek began adjusting the pH of their water by creating a system to add soda ash to their water supply source. The pH was brought up to and maintained at 8.25, thus improving hatchery production. The low pH in Whiskey Creek Shellfish Hatchery is closely linked to ocean acidification. Ocean acidification is caused by a decrease of the ocean's pH. As pH decreases, so do carbonate ion and aragonite concentrations. Aragonite is one of the more soluble forms of calcium carbonate and is widely used by marine calcifiers to build their skeletons and shells. Without proper levels of aragonite, shellfish are unable to form hard structures like shells, which impacts larval and juvenile development By adding soda ash to their water supply before using in their hatchery, Whiskey Creek was able to maintain adequate amounts of aragonite.

In contrast, subtropical coastal waters in the Southeastern US tend to be well buffered, with lower CO_2 partial pressure (pCO_2) and higher alkalinity (Robbins and Lisle 2017).

However, regional river water discharges associated with tropical rainfall events and hurricanes as driving factors also contribute to the carbonate chemistry conditions in the Southeast (Hall et al. 2020). Yet, $p\mathrm{CO}_2$ is increasing and pH is decreasing at a rapid pace in the near-shore waters in the Southeast (Reimer et al. 2017). Predicted increases in precipitation events due to the impacts of climate change are likely to result in reduced carbonate ions, which are necessary for carbonate mineral formations, and decreased buffering capacity, due to increased $p\mathrm{CO}_2$ in Florida estuaries (Hall et al. 2020).

How can shellfish hatcheries be managed in response to these parameters?

In the past decade, hatchery and nursery operators across Florida experienced unacceptable losses of clam seed, resulting in an inconsistent and unreliable seed supply and a negative impact on the industry. Hard clam seed production was particularly low in 2013-14, and, again, in 2017-18, which were considered “wet” years. According to the National Climatic Data Center, annual rainfall amounts exceeded 59 inches in those years, see *https://climatecenter.fsu.edu/products-services/data/statewide-averages/precipitation*. A variety of factors, including poor water quality, disease, and toxins, may have accounted for the decline in seed health and subsequent supply. However, it is quite plausible losses can be traced to over-arching causes related to coastal flooding and runoff from land. Yet, until recently, routine monitoring in hatcheries for parameters, such as pH and alkalinity, has not occurred.

A Florida Sea Grant-funded study was conducted in 2020-22 to document variability in water quality at clam hatcheries in various Florida geographic locations during the production cycle to determine how water quality impacts seed production and health. Hatchery pH and alkalinity readings measured weekly as part of that study can be used to deduce the impact of coastal acidification. Table 1 provides a summary of average, minimum, and maximum values measured at several hatcheries over two years. Bivalve hatcheries vary in the water source used and level of water pretreatment. Those that utilize “raw” water sources (e.g., estuarine, surface water) are more likely to experience large swings in pH and temperature than those using saline well water. However, many wells are shallow with varying minerals, pH, and other water chemistry based on geographic location. In the study, hatcheries A, B, and E used well water, while hatcheries C and D used surface (ambient) water. Hatchery A treated tank water through aeration prior to stocking larvae increasing average pH values to 7.9 in year 1 and 7.7 in year 2. Monitoring water chemistry routinely is an important management strategy to determine if coastal acidification is affecting commercial Florida shellfish hatcheries.

Table 1. Summary of average, minimum, and maximum values of pH and alkalinity measured at several Florida shellfish hatcheries over two years (2020-22).

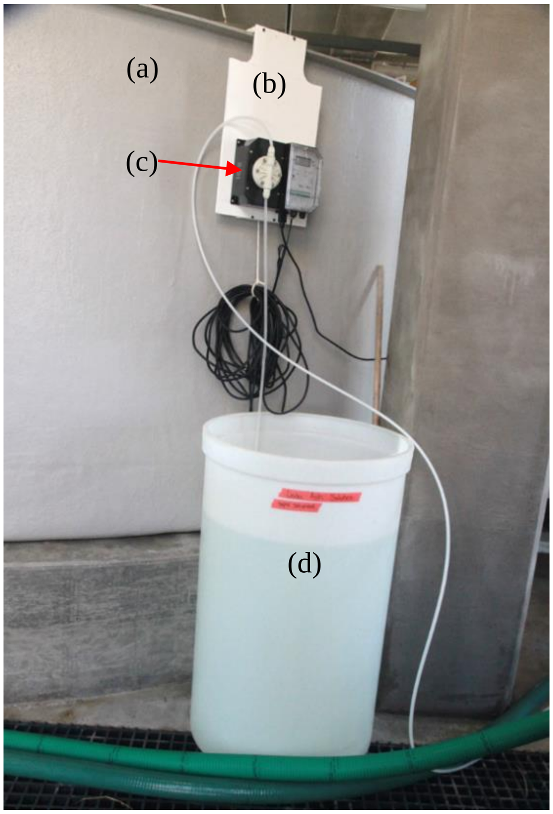
Hatchery and Water Source	**pH**						**Alkalinity (mg/L)**					
	Year 1			**Year 2**			**Year 1**			**Year 2**		
	Ave	**Min**	**Max**	**Ave**	**Min**	**Max**	**Ave**	**Min**	**Max**	**Ave**	**Min**	**Max**
A - Well	7.0	6.7	7.2	7.0	6.4	8.1	160	64	212	121	71	209
B - Well	7.5	7.4	8.0	7.4	7.1	8.1	167	146	179	171	155	178
C- Surface	7.8	6.8	8.7	7.9	7.1	9.0	138	123	150	113	68	146
D - Surface	7.8	7.3	8.1	7.9	7.4	8.5	162	130	195	155	130	182
E - Well	8.0	7.4	8.7	7.7	7.5	8.0	142	129	155	147	139	166

Buffering System for Hatcheries

To increase and maintain pH and alkalinity levels in hatchery culture waters, a low-cost buffering system can be developed by using inexpensive meters and controllers. Although similar buffering systems have been developed and tested in other regions of the country, they have not yet been used in Florida hatcheries that operate under a different set of environmental conditions. To obtain recommended levels of pH and alkalinity, soda ash and sodium bicarbonate can be used to adjust larval rearing water in the hatchery (Table 1).

Table 2. Recommended levels of pH and alkalinity for bivalve larval rearing water and chemicals to use in adjusting values.

	Recommended Level	**Chemical to adjust larval rearing water**	**Amount for a 55-gallon tank of saturated solution**
pH	8.2	Soda ash	98.5 lbs
Alkalinity	150-180 mg/L	Sodium bicarbonate	40.0 lbs



A 55-gallon, graduated, neutral color, polypropylene tank is an ideal container to mix a saturated solution of these chemicals. Mixing the chemical into the water can be done easily and applied to the treatment tank of water using a simple submersible pump (not shown) or a metered pump with a specific controller and probe (Figure 3). A meter measures the current pH of the water when tanks are filled and adds buffer to achieve an optimal pH via an injection pump; a controller calculates the required injection rate and activates the system.

When a solute (e.g., soda ash, sodium bicarbonate) will no longer dissolve in a solvent (e.g., seawater), the solution becomes saturated, characterized by undissolved granules at the bottom of the container. Adjusting a tank of seawater to recommended water chemistry is best done using a saturated solution since less is needed to achieve the desired outcome. The solubility of soda ash in water at 20°C is 215 grams per liter, whereas sodium bicarbonate is 96 grams per liter.

Figure 3. Delivering a buffering solution into a water storage tank using a pH controller and pump where (a) water storage tank used to fill larval rearing systems, (b) custom Starboard pump bracket to hang on tank edge, (c) pH controller and pump with long power cord to reach other tanks, and (d) labeled 55-gallon polypropylene tank with saturated soda ash solution.

Glossary

Abiotic - Not associated with or derived from living organisms. Abiotic factors in an environment include such items as sunlight, temperature, wind patterns, and precipitation.

Aragonite ($CaCO_3$) - A carbonate mineral and one of the most common naturally occurring crystal forms of calcium carbonate. It is formed by biological and physical processes, including precipitation from marine and freshwater environments. It is used by calcifying organisms (hard clams, oysters, corals, etc.) to form hard structures like shells and skeletons.

Bicarbonate ($HCO^-{}_3$) - A vital component of the pH buffering system; many bicarbonates are soluble in water at standard temperature and pressure. In particular, sodium bicarbonate contributes to total dissolved solids, a common parameter for assessing water quality.

Biotic - Relating to or resulting from living things, especially in their ecological relations.

Buffer solutions - Used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications.

Calcite ($CaCO_3$) - A white or colorless mineral consisting of calcium carbonate; it is a major constituent of sedimentary rocks such as limestone.

Carbonate (H_2CO_3) - A salt of carbonic acid; most carbonate salts are insoluble in water at standard temperature and pressure. Carbonate minerals are varied and ubiquitous in chemically precipitated sedimentary rock; the most common are calcite or calcium carbonate, $CaCO_3$, the chief constituent of limestone.

Hydroxide (OH^-) - A chemical compound with a negative charge, containing a single hydrogen and a single oxygen; it is a strong base and very caustic.

Liming - Addition of calcite (calcium carbonate) or dolomite (a combination of calcium and magnesium carbonates) to a water body. Liming increases pH and buffers against daily pH fluctuations, but also increases the availability of nutrients and is often used to sterilize ponds prior to stocking of fish.

Photosynthesis - The process by which plants use sunlight to create sugar (energy) and oxygen from carbon dioxide and water.

Physiology - Physiology is the study of normal function within living creatures. It is a sub-section of biology, covering a range of topics that include organs, anatomy, cells, biological compounds, and how they all interact to make life possible.

Phytoplankton - Microscopic plants at the bottom of the food chain, a primary source of food for hard clams and other filter feeders.

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