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Managing High pH in Freshwater Ponds

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The term "pH" is a mathematical transformation of the hydrogen ion (H^+) concentration; it conveniently expresses the acidity or basicity of water. The lowercase letter "p" refers to "power" or exponent, and pH is defined as the negative logarithm of the hydrogen ion concentration. Each change of one pH unit represents a ten-fold change in hydrogen ion concentration. The pH scale is usually represented as ranging from 0 to 14, but pH can extend beyond those values. At 25 °C, pH 7.0 describes the neutral point of water at which the concentrations of hydrogen and hydroxyl ions (OH^-) are equal (each at 10^{-7} moles/L). Conditions become more acidic as pH decreases and more basic as pH increases.

The pH of freshwater ecosystems can fluctuate considerably within daily and seasonal timeframes, and most freshwater animals have evolved to tolerate a relatively wide environmental pH range. Animals can, however, become stressed or die when exposed to pH extremes or when pH changes rapidly, even if the change occurs within a pH range that is normally tolerated. In addition to the direct effects of pH on aquatic animals, the hydrogen ion concentration affects aqueous equilibria involving ammonia, hydrogen sulfide, chlorine and dissolved metals. The interactions of pH with these variables are often more important than the direct effects of pH on aquatic animals. Direct "pH toxicity" is relatively rare in aquaculture ponds because farm sites and water supplies are selected to provide a desirable environment for culture, which should include a pH of approximately 6 to 9. However, certain conditions may cause pH to rise or fall outside the tolerable range, killing the animals being cultured. This publication addresses the most common of these situations—when excessive underwater photosynthesis causes pH to rise to high, basic levels. There are no precise guidelines for high pH tolerance, but pH values above 9.5 or 10 are generally considered undesirable in aquaculture ponds.

pH of natural waters

Pure water exposed to air has an acidic pH of about 5.6 because carbon dioxide hydrates in water to form carbonic acid, which dissociates to hydrogen ion and bicarbonate (HCO_3^-):

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

Natural waters are never pure, though, because water is a powerful solvent. Water dissolves some of every gas or solid it contacts, and some of these dissolved substances affect the water's pH. Bicarbonate and carbonate (CO_3^{2-}) are negatively charged ions (anions) common in most waters. These basic anions are derived from the dissolution of limestone and they increase the pH of water. Bicarbonate and carbonate are also the anions primarily responsible for the property of water called "alkalinity," which is the capacity of water to neutralize acid.

Chemical interactions among carbon dioxide, hydrogen ions, and the anions that produce alkalinity buffer the pH of most natural waters in a range of about 6 to 8.5. In the absence of processes that add or remove carbon dioxide, the initial pH of water in contact with air depends on its alkalinity. Waters with low alkalinities have an initial pH at the low end of that range, while waters of higher alkalinities have higher pH.

Although alkalinity establishes the initial pH of water, adding or removing carbon dioxide causes pH to rise or fall from that initial value. Adding carbon dioxide "pushes" the previously defined chemical reaction toward the right-hand side, forming carbonic acid and hydrogen ions and causing pH to decrease. Removing carbon dioxide "pulls" the reaction to the left, thereby removing hydrogen ions and causing pH to increase. The magnitude of variation from the initial pH depends on 1) the amount of carbon dioxide added or removed and 2) alkalinity, which tends to buffer, or reduce, the effect of changes in carbon dioxide concentrations.

High pH problems in ponds

Underwater biological activity controls carbon dioxide concentrations in most surface waters, including aquaculture ponds. All living organisms continuously

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produce carbon dioxide as a product of respiration. During daylight, algae and underwater plants remove carbon dioxide from the water as part of the sunlight-driven process of photosynthesis. The relative rates of respiration and photosynthesis within the pond determine whether there is a net addition or removal of carbon dioxide, and therefore whether pH falls or rises. Respiration rates are affected by water temperature and the biomass of plants, animals and microorganisms in the water and bottom sediment. Rates of photosynthesis are controlled primarily by sunlight intensity, plant biomass and water temperature.

During the day, underwater photosynthesis usually exceeds respiration, so pH rises as carbon dioxide is extracted from the water. As the sun begins to set in late afternoon, photosynthesis decreases and eventually stops, so pH falls throughout the night as respiring organisms add carbon dioxide to the water. When the sun rises, plants resume photosynthesis and remove carbon dioxide from water, causing pH to rise again. The daily interplay of respiration and photosynthesis causes pH to cycle up and down during a 24-hour period.

In most aquatic environments, daily photosynthesis is about equal to respiration and pH will usually remain within a range tolerated by most animals. However, when plants or algae are growing rapidly, more carbon dioxide is removed each day by photosynthesis than is added each night by respiration. As a result, pH may rise to abnormally high levels during the afternoon and may even remain high through the night (Fig. 1). This condition may last for many days, until photosynthesis decreases or respiration increases.

Problems with high pH are common in fry nursery ponds and in ponds used to grow freshwater prawns (*Macrobrachium rosenbergii*) because fertilization practices used to prepare ponds for stocking are designed to promote fast-growing phytoplankton blooms that rapidly take up carbon dioxide. Unfortunately, the early life stages of fish and crustaceans are particularly susceptible to pH toxicity and juveniles are less able than older animals to "enviroregulate" by moving to areas of lower pH in the pond (such as deeper waters).

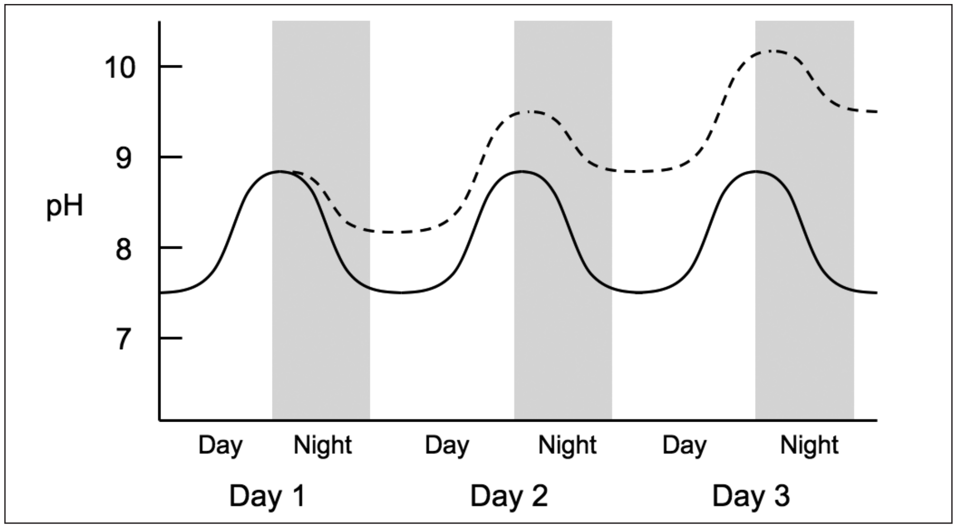

Figure 1. Idealized depiction of pH cycling during a 3-day period in two ponds. In both ponds, pH rises during the day as carbon dioxide is removed through photosynthesis and falls at night (shaded vertical bars) as carbon dioxide is added to the water through respiration. The solid line represents pH changes in a pond where carbon dioxide taken up in photosynthesis is offset by carbon dioxide respired at night. The dashed line represents pH changes in a pond where more carbon dioxide is fixed in photosynthesis than is produced at night, and pH values increase from day to day.

Although high pH is most common in recently filled and fertilized ponds, ponds with established phytoplankton blooms are also susceptible. Phytoplankton in fertile aquaculture ponds often cycles through periods of bloom and collapse. When large numbers of algal cells die, the nutrients released during decomposition stimulate the growth of a new bloom. When plants are growing quickly, their rapid carbon dioxide uptake may cause high pH until the phytoplankton community comes to a new equilibrium.

Extended episodes of high pH are particularly common in ponds where filamentous algae dominate the plant community. Ponds with filamentous algae usually have clear water, allowing sunlight to penetrate deep into the water column and promote intense photosynthesis by underwater or floating mats of algae.

High pH in aquaculture ponds appears to occur more frequently and with greater severity in waters with low total hardness and moderate to high total alkalinity. The reason for this is not completely understood.

Managing problems with high pH

Managing high pH in aquaculture ponds is difficult and no specific management practice is always successful. Difficulties arise because the term "high pH" describes not only a chemical property, but also the outcome of many interacting chemical and biological processes. As a measure of water's hydrogen ion concentration, high pH can be corrected simply by adding an acid to increase that concentration. However, "high pH" also describes the net result of many individual processes that add or remove carbon dioxide. Reducing pH with an acid does not alter these processes and, therefore, cannot address the underlying causes of high pH. So while adding an acid may temporarily reduce pH, high pH will probably occur again unless other environmental conditions also change.

The long-term solution to high pH problems in ponds is to alter pond biology so that the net daily carbon dioxide uptake is near zero. This can be done by reducing photosynthesis or increasing respiration. But changing the metabolism of the pond community is difficult because biological processes have considerable "ecological momentum." This momentum is based upon a given set of environmental conditions that strongly favor a particular ecological outcome. For example, when a newly filled pond contains lots of nutrients, receives bright sunshine and has warm water temperatures, conditions strongly favor the development of a biological community that produces a high afternoon pH. Altering those conditions to change the outcome is difficult. In general, preventing or managing around pH problems will be more effective than trying to correct problems after they occur.

Fill and prepare ponds early

Problems with high afternoon pH commonly arise in the first few weeks after aquaculture ponds are filled. At that time, plant nutrients derived from feeds or fertilizers promote fast-growing algal blooms and the biomass of respiring organisms is comparatively low. After this first flush of rapid plant growth, high afternoon pH values typically abate as the production and removal of carbon dioxide come into balance. And, as ponds age, organic matter begins to accumulate in the pond (particularly in the sediment). The carbon dioxide produced as organic material decomposes helps reduce peak pH values.

Accordingly, one way to minimize problems caused by high pH is to prepare ponds as early as possible, preferably several weeks before stocking. This may not always be possible, because some animals must be stocked relatively soon after ponds are filled and fertilized to avoid losses from predatory insects or to ensure that the proper natural foods are available. For example, hybrid striped bass fry should be stocked when rotifers are most abundant (see SRAC Publication #302). Rotifers are the preferred food for young bass fry, and peak rotifer populations occur at predictable times after pond fertilization is begun. When possible, however, delaying stocking until after the initial flush of plant growth can help prevent losses caused by excessively high pH.

Balance the hardness and alkalinity

Problems with high pH seem to occur most often in ponds where total alkalinity (the amount of bicarbonate and carbonate in the water) far exceeds water hardness (the amount of calcium and magnesium in the water). For example, it is common for freshwater prawn ponds at the Mississippi State University aquaculture unit in Starkville to have high pH in late spring. The groundwater supply for these ponds has a hardness of about 30 mg/L as $CaCO_3$ and an alkalinity of about 90 mg/L. An even wider disparity between hardness and alkalinity is found in many other waters, particularly those in the southeastern coastal plains where many groundwaters have alkalinities exceeding 150 mg/L and hardness values of less than 10 mg/L.

Deficiencies in hardness relative to alkalinity can be corrected by adding gypsum (calcium sulfate). The effectiveness of gypsum treatment in reducing pH is subject to debate; at best, it is a preventive procedure rather than an emergency treatment. Hardness deficiencies should, therefore, be corrected before stocking, preferably as soon as the pond is filled in the spring.

The amount of gypsum needed to roughly balance hardness and alkalinity can be calculated by subtracting hardness from alkalinity and multiplying that value by two. For example, if hardness is 30 mg/L as $CaCO_3$ and alkalinity is 90 mg/L as $CaCO_3$, then 120 mg/L of gypsum will be needed. This would require about 2,500 pounds of gypsum in a 2-acre pond that is 4 feet deep. This is a large amount of gypsum, but the results of treatment should be long-lasting because calcium is lost from ponds only when waters are diluted by excessive rainfall or by the addition of water with a low calcium content.

Increasing the calcium level in a pond by adding gypsum may help reduce the occurrence of high pH and benefit animals by helping them respond better physiologically to pH extremes and other environmental stressors. Relatively high levels of calcium also help crustaceans, such as freshwater prawns, to replace calcium lost during molting.

Add alum or an organic substance

It is difficult to reduce pH significantly by adding an acid to the water because pond waters are usually buffered by bases of the alkalinity system. Relatively large amounts of acid are therefore needed to achieve a meaningful decrease in pH. Also, adding an acid to water is only a short-term solution because it addresses the result rather than the cause of the problem, which is rapid plant growth.

An emergency treatment that quickly reduces high pH is the application of alum (aluminum sulfate). This is a safe, relatively inexpensive chemical that reacts in water to form an acid. Besides reducing pH, alum also flocculates and removes algae by sedimentation, thus decreasing algal biomass and reducing photosynthesis. Alum may also help to reduce pH indirectly by removing phosphorus—an important nutrient for plant growth.

Alum does not have a permanent effect and it may need to be applied more than once until plant or algal growth decreases. A precise reduction of pH through the addition of alum is difficult because response is influenced by a number of conditions in the pond, especially the water's total alkalinity. Overtreatment with alum can cause a dramatic decrease in pH, possibly to levels more dangerous than the original high pH problem.

Experience dictates a cautious approach, starting with an initial dose of 10 mg/L alum (27 pounds of alum per acre-foot of water) followed by additional applications in 5- to 10-mg/L increments as needed. Alum should not be used in waters with total alkalinities of less than 20 mg/L as $CaCO_3$ because even small amounts may reduce pH to dangerous levels.

A safer, longer lasting way to reduce high pH is to add carbon dioxide, which acts as an acid in water. Carbon dioxide levels can be increased by adding organic matter such as cracked corn, soybean meal or cottonseed meal to ponds. As organic matter decays, it releases carbon dioxide. This method does not reduce pH immediately, but it is a safe and relatively dependable practice that yields results rather quickly. Generally, applying about 15 pounds per acre daily for about 1 week should prevent pH from rising to undesirable levels. This amount would be in addition to any daily application of organic fertilizer already planned. The total daily application of organic matter should not exceed 50 pounds per acre. The decay process that releases carbon dioxide into the water also uses dissolved oxygen, so adding too much organic matter could reduce dissolved oxygen concentrations to dangerous levels. Dissolved oxygen concentrations must therefore be measured regularly and the pond aerated, if necessary, to maintain satisfactory oxygen levels.

Reduce plant growth

The rapid removal of carbon dioxide during periods of rapid plant growth is the basis of all high pH problems in ponds. Waiting for fast plant growth to decrease naturally is an option, as described previously, but if pH must be reduced quickly, the rate of plant growth must be slowed by adding a herbicide or restricting the amount of light penetrating the water column.

Using herbicides to kill algae and plants will eliminate high pH problems, but the benefits are often not worth the risks and costs. The decomposition of plants killed by herbicides causes oxygen depletion and the accumulation of carbon dioxide and ammonia. Some herbicides are also relatively toxic to juvenile aquatic animals. Copper-containing products, for example, have a relatively low margin of safety between concentrations that kill plants and those lethal to juvenile fish or prawns. Reducing plant growth to manage high pH also conflicts with the goal of fertilization, which is to increase the production of natural foods in the pond to support aquaculture production. Thus, using herbicides to reduce high pH is usually a poor substitute for proper pond management.

In general, herbicides should be used only to change one type of plant community to a more desirable type. For example, mats of filamentous algae are often responsible for excessively high pH in recently filled ponds used for fry or prawn culture. Filamentous algae are also undesirable because they interfere with pond management, particularly feeding and harvest. Certain herbicides can be used cautiously to eliminate these algae in favor of a phytoplankton bloom. In prawn ponds, some success has been achieved with Hydrothol 191®. Hydrothol® appears to be safe for juvenile prawns at an application rate of not more than 0.2 ppm, but there is still the danger of oxygen depletion. The Aquaplant Web site (*http://aquaplant.tamu.edu*) contains more information on selecting and using aquatic herbicides.

A safer (but less effective) alternative to herbicides is to reduce the amount of sunlight available for photosynthesis. One approach is to add an approved aquaculture dye to the pond. These dyes are sold as weed-control agents and tint the water blue to reduce light penetration. The dye is usually effective for several weeks. Note, however, that using dyes may favor the growth of mat-forming filamentous algae that float high in the water column where there will be adequate light even in dye-treated water. Another way to reduce light penetration is to keep the pond water turbid (with suspended sediment) by using aerators or other devices to stir up mud from the pond bottom.

The fallacy of using sodium bicarbonate

Oddly, one of the most frequently recommended treatments for high pH—sodium bicarbonate (also called bicarbonate of soda or baking soda)—is the least effective. Sodium bicarbonate reduces high pH in water because it neutralizes either acids or bases. (Compounds with this property are called *amphoteric*.) Sodium bicarbonate is, however, a weak acid and large amounts must be added to significantly reduce pH, especially in waters with high total alkalinities (Table 1). For example, if water has a total alkalinity of 200 mg/L as $CaCO_3$ and a pH of 10.0, then adding 100 mg/L of sodium bicarbonate will reduce the pH to only about 9.9. At this rate, a 2-acre pond that is 4 feet deep would need about 270 pounds of chemical per acre-foot, or a little more than 2,000 pounds. The same amount of sodium bicarbonate (100 mg/L) added to water with an initial alkalinity of 50 ppm as calcium carbonate will reduce pH to about 9.6.

Information in Table 1 was derived from a laboratory study and the small decreases in pH measured under controlled laboratory conditions will probably be undetectable under field conditions. The ineffectiveness of sodium bicarbonate treatment was verified in a study of pH management in hybrid striped bass nursery ponds in Arkansas. In that study, sodium bicarbonate treatments of 8, 16 and 32 mg/L had no apparent effect on afternoon pH values.

In addition to the relatively large amount of chemical needed to reduce pH significantly, there is another drawback to using sodium bicarbonate—its inability to prevent subsequent increases in pH. This is true for any acid. Therefore, sodium bicarbonate is neither an effective emergency treatment for high pH nor a long-term solution.

Table 1. Final pH of waters with an initial pH of 10.0 and three different total alkalinities after treatment with different amounts of sodium bicarbonate.

Initial alkalinity (mg/L as $CaCO_3$)	Amount of sodium bicarbonate added		
	25 mg/L	50 mg/L	100 mg/L
50	9.9	9.8	9.6
100	9.9	9.9	9.7
200	9.9	9.9	9.8

Sudden increases in pH

Sudden changes in pH can stress or kill aquatic animals even when those changes occur within a pH range they normally tolerate. Studies at the National Warmwater Aquaculture Center in Stoneville, Mississippi, have shown that channel catfish fry are very sensitive to sudden increases in pH. Catfish fry acclimated to waters with pH near optimum (pH 7.5 to 8.5) can withstand sudden transfer to water with pH values 4 units lower without being killed. However, fish will be killed when abruptly transferred to waters with pH values more than 1 unit higher than the water to which they were acclimated. Sudden transfer to waters 1.5 pH units higher will kill about 50 percent of the fish, and transfer to water 2.2 pH units higher will kill almost all the fish.

This intolerance of catfish to abrupt increases in pH has important practical considerations. Most newly hatched catfish fry are held for several days in hatchery tanks supplied with flow-through groundwater with a pH near 8.0. Fry are then transferred to a transport tank (usually filled with water from the same source used in the hatchery) and then stocked into a nursery pond for further growth. Nursery pond pH cycles daily, and if fish are transferred to the nursery pond during the afternoon when pH is usually highest, many fish may quickly die. The solution is simple: First measure the pH of the water in both the transport tank and the pond, and then transfer fish only when the pH of the receiving water is very near, or below, that of the transport tank water. Pond pH is usually lowest a few hours after dawn, so this is usually the best time to transfer fry.

The physiological basis for the insensitivity of catfish fry to rapid increases in pH is unknown and a similar response may occur in other fish or crustacean species. In the absence of additional information farmers should assume that this response is common to all species of fish and crustaceans and avoid transferring animals to waters with higher pH.

Summary

Different management practices can be used to reduce high pH and minimize the risk of pH toxicity to freshwater fish and crustaceans. The choice of method should be based upon the specific need, and a combination of approaches might be most effective. Planning ahead can help avoid many problems. Pond water should have adequate levels of alkalinity and hardness for the species under culture, and those levels should not be widely disproportionate. Stocking should be done at the right time of year and right time of day to reduce risks. Adding small amounts of easily decomposable organic matter can be an effective preventive measure because its decomposition produces carbon dioxide and reduces pH for a longer period. Emergency treatments to rapidly reduce high pH are fraught with problems and most have only temporary benefits because the underlying cause of the problem is not being properly addressed. The careful use of alum is probably the safest and most dependable emergency treatment.

Additional Reading

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