

## **Chapter 3. Managing Algal Productivity**

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The preceding overview on biological productivity and physical processes sets the stage for a closer look at what makes algae grow. It should be clear that algal primary productivity is the driving force behind secondary productivity in a fertilized pond. By understanding what algae require to grow efficiently, we can direct our pond management towards creating the most favorable environmental conditions for algal productivity. This chapter first discusses those algal nutrients we are most concerned with in pond fertilization, and then presents the concept of nutrient limitation as a means of controlling algal productivity with greater fertilizer utilization efficiency.

### **Algal Nutrient Dynamics**

As a general principle, algae require a supply of inorganic nutrients, sufficient light, and favorable temperatures to grow (Fogg, 1975; Bold and Wynne, 1978). The primary inorganic nutrients are P, N, and C. Of course hydrogen (H) and oxygen (O) are also essential for algal growth, but water (H<sub>2</sub>O) provides an abundance of these elements and no further discussion of H and O is necessary in regards to algal nutrient requirements. Many other elements are needed for algal growth in lesser or often trace amounts, and are collectively referred to as micronutrients. For example, silica (Si) is needed by diatoms as a structural component for their rigid cell walls. Other micronutrients required for growth and enzymatic activity include calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), iron (Fe), manganese (Mn), sulfur (S), zinc (Zn), copper (Cu), and cobalt (Co) (Goldman and Horne, 1983).

It is also important to understand that different algal species do not have identical nutritional needs. The fertilization approach in this book, however, addresses the needs of the algal community as a whole. No attempt is made here to manipulate interspecific competition for algal nutrients, or to promote a particular algal species by managing resource availability. With that in mind, the following section examines in more detail the three primary algal nutrients: P, N, and C. Discussions focus on their sources, biological availabilities, and recycling dynamics in a productive pond.

## Phosphorus

Of the three primary nutrients, phosphorus (P) is the most scarce in the natural environment. Weathering of phosphorus-containing rocks, agricultural and urban drainage, and atmospheric dust are the principal mechanisms for P to reach the aquatic environment. Phosphorus is also found in the waste products of animals and is released during the decomposition of organic matter (Boyd, 1971).

Once in the pond, however, P can be very dynamic (Hepher, 1958; Hepher, 1966; Syers et al., 1973). To best understand P dynamics it is important to recognize the different forms in which P can be found. Most broadly, P can be found either in particulate matter or in a soluble form (Table 1). Particulate forms can either be organic, such as phytoplankton, zooplankton, bacteria, fish, or detritus, or inorganic. Inorganic particulate P is represented largely by P adsorbed (i.e., attached by chemical ionic bonding) to suspended and settled sediments in the pond, or as precipitates formed with phosphate ( $\text{PO}_4$ ) and iron (Fe), aluminum (Al), and calcium (Ca) (Hepher, 1965; McKee et al., 1970; Syers et al., 1973). Soluble P is also found in both organic and inorganic forms. The organic form consists of dissolved organic molecules such as polypeptides, enzymes (e.g., alkaline phosphatase), adenosine triphosphate (ATP), and organophosphates released into the water through decomposition, excretions, and secretions from

	Organic	Inorganic
Particulate	Living biomass Detritus Feces, etc.	P adsorbed to suspended sediments P precipitated in Ca, Fe, and Al complexes
Soluble	Enzymes Amino acids Waste products	Orthophosphate Polyphosphates

**Table 1. Different forms of phosphorus (P) commonly found in ponds.**

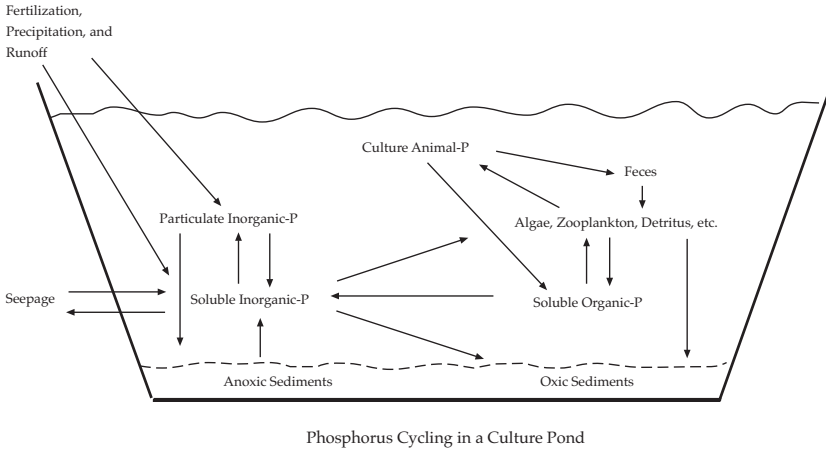
algae and the rest of the aquatic biological community. Inorganic forms of dissolved P are principally orthophosphate ( $\text{PO}_4$ ) and, to a lesser degree, polyphosphates (Syers et al., 1973; Goldman and Horne, 1983; Brabrand et al., 1990).

Analytically, P is first separated into particulate and soluble fractions by filtering the water through a filter with an effective pore size of between 0.45 and 1.0  $\mu\text{m}$  (APHA, 1985). It was once generally believed that only orthophosphate passed through the filter, and represented the only utilizable form of P for algae. However, neither assumption has endured. It is now known that many forms of soluble and colloidal P can pass through the filter, and for the last several decades the conventional term for the dissolved fraction has been soluble reactive phosphorus (SRP) (APHA, 1985). This is the most appropriate term because it describes only the amount of analytically measured P which passes through the filter.

Because of the relative scarcity of phosphorus in the aquatic environment, algae have become quite adept in extracting it from its various forms for nutrient uptake. Determining biological availability of the different forms of P, therefore, can be quite difficult. Algae are certainly capable of taking up soluble inorganic P from the water, as well as many forms of soluble organic P produced by the enzymatic breakdown of organic molecules. Algae colonizing detrital particles utilize dissolved organics released from the microbial decomposition of the detritus (Rodina, 1963; Rodina, 1966; Fry, 1987). Furthermore, some algae are capable of extracting P adsorbed to sediments resuspended in the water column (Grobbelaar, 1983).

After recognizing the various forms of P suitable for algal uptake, the next step is to examine a few of the more important dynamic processes which affect P availability in the pond. Many of these processes have already been mentioned above, and the more basic pathways are illustrated schematically in Figure 3. In addition to intentional fertilization, P enters pond water from runoff from pond banks and atmospheric precipitation, groundwater seepage, and from pond sediments.

The aim in culture ponds, of course, is to get as much fertilizer-P into algal biomass as possible. The recycling of P between dissolved and particulate forms through uptake, excretion, secretion, and decomposition benefits algal productivity (Brabrand et al., 1990). Biological competition for P, however, is complicated by the two



**Figure 3. Schematic diagram showing major ecological pathways of phosphorus (P) transformations and cycling in a culture pond. For purposes of illustration, pond sediments are simultaneously represented as both anoxic and oxic.**

chemical processes of adsorption and precipitation, which can take soluble P out of solution.

Phosphorus adsorption, as used here, refers to the chemical bonding of P to particulate matter suspended in the water or in the sediments (Boyd, 1971; Boyd and Musig, 1981). Phosphorus adsorption is affected by pond water and sediment characteristics. Soluble P adsorbs primarily to  $\text{CaCO}_3$ , and to Al and Fe oxides (McKee et al., 1970; Syers et al., 1973; Furumai and Ohgaki, 1989). Adsorption is greater when water has dissolved oxygen present (i.e., the water is said to be oxic), and when P is in the presence of particulate inorganic matter, especially fine clays (Stumm and Morgan, 1970; Syers et al., 1973; Boyd, 1995a; Shrestha and Lin, 1996). Adsorption of soluble P can take as little as 30 seconds to occur, with the rate of adsorption increasing as the pH of the water increases (Furumai et al., 1989).

In newly dug ponds, the relatively large exposure of inorganic sediments to overlying water facilitates P adsorption and removal from the water column. The rate of P removal by sediments decreases as bonding sites are filled and as organic matter (e.g., detrital particles) settles on the bottom. Organic matter reduces the crystallization

of Al and Fe oxides, and proportionally greater amounts of input-P remain in solution, available for algal uptake (Borggaard et al., 1990). In a statistical analysis of 16 culture ponds with widely varying fertilization histories, Knud-Hansen (1992) found that those ponds which had previously received greater organic (chicken manure) inputs required significantly less P input to maintain high algal productivities. Therefore, newly dug ponds generally require more P input to stimulate algal productivity than older ponds (Boyd, 1971; Boyd and Musig, 1981; Knud-Hansen, 1992).

On the other hand, when the environmental conditions are more acidic (i.e., pHs around 5.0) and void of dissolved oxygen (i.e., the water is anoxic), P desorption occurs and P becomes more soluble again (McKee et al., 1970; Stumm and Morgan, 1970; Furumai and Ohgaki, 1989). These conditions are often found in the interstitial or pore water, which surrounds the particulate matter in pond sediments. Decomposition of settled organic matter strips the oxygen out of the interstitial water, and the release of organic acids and carbon dioxide creates more acidic conditions (see following discussion on inorganic carbon). If the pond is thermally stratified, these more acidic and anoxic conditions may occur in the overlying bottom water as well. When this water is mixed with surface water, more P becomes available for algal growth through this internal fertilization mechanism (i.e., nutrients coming from within the pond).

The second mechanism which removes soluble P from solution is precipitation of phosphate by calcium, iron, and aluminum as  $\text{CaPO}_{4(s)}$ ,  $\text{FePO}_{4(s)}$ , and  $\text{AlPO}_{4(s)}$ , respectively. Calcium phosphate precipitates out in waters with high pHs and high Ca concentrations, and becomes more soluble at lower pHs, particularly with the addition of carbon dioxide ( $\text{CO}_2$ ) (Hepher, 1965). In a productive pond, therefore,  $\text{CaPO}_{4(s)}$  precipitated during the daytime when pHs are high and  $\text{CO}_2$  concentrations are low becomes soluble again during the night when respired  $\text{CO}_2$  accumulates and lowers the pH.

In contrast,  $\text{FePO}_{4(s)}$  and  $\text{AlPO}_{4(s)}$  are least soluble at pHs of around 5 to 6 (Stumm and Morgan, 1970; Syers et al., 1973). Therefore, the high soluble P concentrations found in anoxic bottom waters with pHs of around 6 come from the desorption of P from metal oxides (and the solubilization of  $\text{CaPO}_{4(s)}$  in ponds with high Ca concentrations), rather than from the solubilization of Al and Fe precipitates. With more acidic waters (pHs of 3 to 4) associated with acid sulphate soils, however, the solubility of Fe and Al increases. When these acidic

waters in the sediments mix into oxygenated pond water, Fe and Al oxides form and remove soluble P from solution through adsorption (Gaviria et al., 1986). Except perhaps in waters with very high calcium concentrations, P adsorption to metal oxides is likely a more significant cause of P loss than by precipitation (Syers et al., 1973). This is in part due to the relatively slow chemical reactions causing precipitation, and the higher solubility of Al and Fe precipitates at the higher daytime pHs normally found in productive freshwater ponds (Stumm and Morgan, 1970).

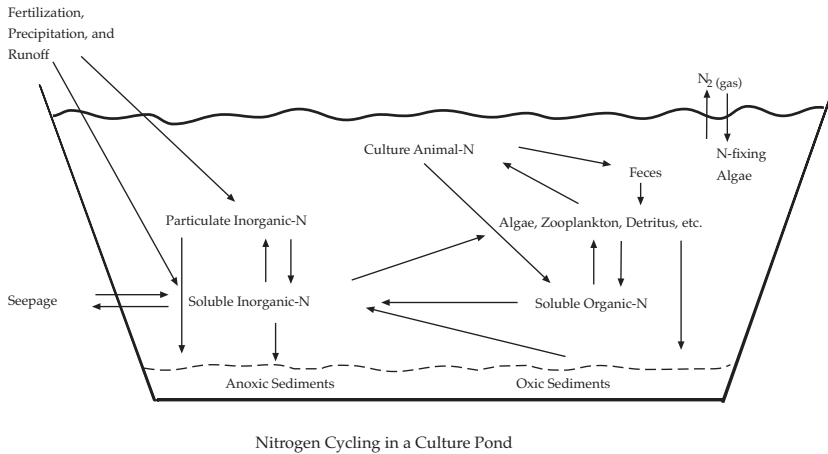
### Nitrogen

Nitrogen is a major component of proteins and amino acids, and is, after C, H, and O, the most abundant element in living cells. Similar to P, the different forms of N can be separated into organic and inorganic, as well as particulate and dissolved components (Table 2). Particulate organic N is found in living biomass and detritus, while soluble organic nitrogenous materials are released into the water from excretions, secretions, and decomposition processes (Keeney, 1973). Soluble inorganic nitrogen is represented primarily by four different molecules: nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), ammonia ( $\text{NH}_3/\text{NH}_4^+$ ), and nitrogen gas ( $\text{N}_2$ ). Particulate inorganic N is largely represented by ammonium ( $\text{NH}_4^+$ ) ions adsorbed to suspended sediments.

Figure 4 presents a simplified version of the nitrogen cycle in ponds. Nitrogen can enter the pond water through atmospheric

	Organic	Inorganic
Particulate	Living biomass Detritus Feces, etc.	Ammonia adsorbed to suspended sediments
Soluble	Enzymes Amino acids Organic acids Waste products	Nitrate Nitrite Ammonia Dissolved $\text{N}_2$ gas

**Table 2. Different forms of nitrogen (N) commonly found in ponds.**



**Figure 4. Schematic diagram showing major ecological pathways of nitrogen (N) transformations and cycling in a culture pond. For purposes of illustration, pond sediments are simultaneously represented as both anoxic and oxic.**

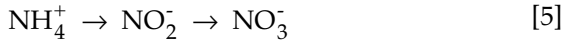
precipitation and dry fallout, through runoff into the pond, from groundwater seepage, and through the chemical solubility and biological incorporation of atmospheric nitrogen gas ( $N_2$ ). For relatively leaky culture ponds, the continual addition of source water can also contribute a significant amount of algal nutrients. For example, aquaculture ponds in Indonesia received an average of about  $0.4 \text{ kg N ha}^{-1} \text{ d}^{-1}$  from the additional source water needed to compensate for daily evaporation and seepage losses (Knud-Hansen et al., 1991b).

The three primary N molecules utilized for algal growth are ammonia, nitrate, and nitrogen gas (Fogg, 1975; Bold and Wynne, 1978). Essentially all algae can take up nitrate and ammonia, and ammonia is the preferred form for plant growth because the incorporation of nitrate requires additional metabolic energy and enzymatic activity (Goldman and Horne, 1983). Both algae and bacteria incorporate ammonia very rapidly (Sugiyama and Kawai, 1979). In addition, some algae can metabolize various forms of dissolved organic N, as well as remove ammonium ions adsorbed to suspended particulate matter (Grobbelaar, 1983).

The incorporation of  $N_2$  into algal biomass occurs through a process known as nitrogen fixation. The only algae capable of

extracting and fixing  $N_2$  are certain blue-green algae, and they can do so only under limited environmental conditions (Fogg, 1975; Bold and Wynne, 1978; Oláh et al., 1983; Paerl and Tucker, 1995). These algae often have gas vacuoles which enable them to float to the water's surface. Not only does flotation provide these algae with direct access to atmospheric nitrogen and carbon dioxide, but it also gives them a competitive advantage for solar radiation. The importance of N-fixation as a mechanism for nitrogen input in fertilized ponds is generally quite limited. El Samra and Oláh (1979) reported fixation rates of  $< 0.005 \text{ g N m}^{-2} \text{ d}^{-1}$  ( $= 0.05 \text{ kg N ha}^{-1} \text{ d}^{-1}$ ), while Lin et al. (1988) observed rates from  $0.06$  to  $0.57 \text{ kg N ha}^{-1} \text{ d}^{-1}$ . These rates are relatively low when compared to typical fertilization input rates.

Similar to P, transformations between different forms of N in ponds are influenced by pond environmental conditions (Keeney, 1973). For example, ammonia is the principal nitrogenous by-product of organic decomposition, and experiences different fates depending on where in the pond the ammonia is produced. In waters containing dissolved oxygen, ammonia not incorporated by algae can be oxidized (i.e., add oxygen) through microbial processes. The oxidation of ammonia first to nitrite and then to nitrate is called nitrification, and is schematically shown in Equation 5:

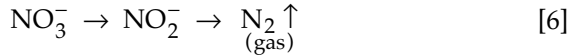


In this two-step process, the microbial transformation of ammonia to nitrite is much slower than the subsequent microbial transformation of nitrite to nitrate (Cavari, 1977; Goldman and Horne, 1983). This fact has two implications. First, algal uptake of ammonia can be relatively fast, and competition for ammonia between algae and bacteria is predominantly in favor of the algal community. Second, the relatively rapid oxidation of nitrite to nitrate means that very little nitrite accumulates in oxic waters. Analytically, nitrite and nitrate are commonly measured together, and reported as  $\text{mg l}^{-1} \text{NO}_3\text{-NO}_2\text{-N}$  (APHA, 1985). If analyzed separately, the actual percentage of nitrite in such measurements should be negligible in most surface waters, and proportionally higher in the more chemically reduced conditions often found in anoxic pond sediments (Cavari, 1977).

Anoxic water with sufficient organic matter, an environment often found in pond sediments and in the bottom waters of a produc-

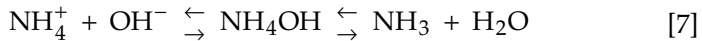


tive pond experiencing persistent thermal stratification, creates a biochemically reducing condition. Ammonia is already in a chemically reduced form and accumulates under these conditions. On the other hand, oxidized forms of N, such as nitrate and nitrite, become reduced (i.e., lose oxygen) as by-products of another two-step, biological process. This process is called denitrification, and is schematically represented in Equation 6.



First,  $\text{NO}_3^-$  loses an atom of oxygen to form  $\text{NO}_2^-$ . Then, the nitrite produced in the first step is further reduced to nitrogen gas ( $\text{N}_2$ ), which may go back into solution or escape from the pond's surface water (schematically shown in Figure 4 and Equation 6) (Bouldin et al., 1974). The bacterial metabolic processes responsible for denitrification occur in anoxic pond sediments worldwide.

The last transformation of nitrogen to be mentioned is the purely chemical transformation between two forms of ammonia, namely the ionized ( $\text{NH}_4^+$ ) and the un-ionized ( $\text{NH}_3$ ) forms. The equilibrium reaction is shown in Equation 7:



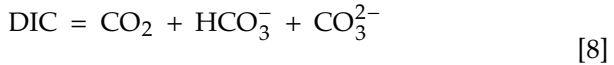
The implications of this transformation in aquaculture systems are great because whereas the ionized form is generally safe for culture organisms, the un-ionized form can be highly toxic (Colt and Armstrong, 1981; Meade, 1985). A more thorough discussion of ammonia toxicity and the environmental factors which affect this chemical transformation is presented in the subsection on maintaining a favorable growth environment in Chapter 4.

### Inorganic Carbon

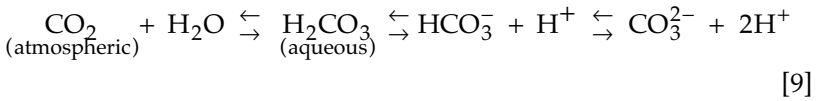
Carbon is the dominant element in organic matter. Recall from the last chapter that primary producers such as algae incorporate inorganic carbon, while secondary producers such as fish incorporate organic carbon from biological sources (e.g., algae, algae-derived

detritus, zooplankton). In pond fertilization we are trying to optimize algal productivity, so our focus on carbon dynamics will naturally focus on inorganic carbon.

The three principal forms of dissolved inorganic carbon (DIC) are carbon dioxide (CO<sub>2</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>), as indicated in Equation 8:

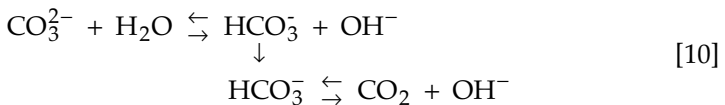


The three major sources of soluble CO<sub>2</sub> are the solution of atmospheric CO<sub>2</sub> into surface water, equilibrium reactions of dissolved CO<sub>2</sub> in the water with bicarbonate and carbonate, and the decomposition of organic matter in the pond. The solution of atmospheric CO<sub>2</sub> into water and the corresponding equilibrium reactions are presented below in Equation 9:



As illustrated in Equation 9, two things happen when CO<sub>2</sub> is added and dissolves into water. First, bicarbonate and carbonate are produced. Second, hydrogen ions (H<sup>+</sup>) are released, increasing their concentration in the water.

In addition to CO<sub>2</sub> solubility, primary sources of carbonate and bicarbonate are from the dissolution of the common rock limestone, which consists primarily of calcite (calcium carbonate [CaCO<sub>3</sub>]) and may contain magnesium carbonate (MgCO<sub>3</sub>). Once in the water, the carbonate and bicarbonate become part of the same equilibrium relationship described in Equation 9. Equation 10 illustrates this equilibrium by showing what happens when carbonate and/or bicarbonate are added to water.



When carbonate is added, bicarbonate and the hydroxyl ion (OH<sup>-</sup>) are produced. Bicarbonate in the water either from carbonate or added independently (e.g., as sodium bicarbonate, NaHCO<sub>3</sub>) produces CO<sub>2</sub> and another OH<sup>-</sup> molecule.

The H<sup>+</sup> produced with the addition of CO<sub>2</sub> (Equation 9) and the OH<sup>-</sup> produced with the addition of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> (Equation 10) demonstrate the very important role of pH in carbonate equilibria. The pH is a measure of the H<sup>+</sup> concentration, which is a product of the equilibrium between water (H<sub>2</sub>O) and concentrations of H<sup>+</sup> and OH<sup>-</sup> (Equation 11).



Theoretically, pH ranges between 0 and 14 pH units. A pH value between 0 and 7 indicates chemically acidic water (i.e., H<sup>+</sup> concentration > OH<sup>-</sup> concentration); a value from 7 to 14 indicates water which is chemically basic (i.e., H<sup>+</sup> concentration < OH<sup>-</sup> concentration), and a pH of 7 is considered chemically neutral (i.e., H<sup>+</sup> concentration = OH<sup>-</sup> concentration). Adding H<sup>+</sup> or removing OH<sup>-</sup> increases the concentration of H<sup>+</sup> in the water, and consequently lowers the pH. Similarly, removing H<sup>+</sup> or adding OH<sup>-</sup> decreases the concentration of H<sup>+</sup> in the water, and increases the pH.

These pH shifts due to carbonate equilibria are clearly demonstrated in a productive pond. For example, when CO<sub>2</sub> is produced through respiration, total DIC concentrations increase and the corresponding release of H<sup>+</sup> causes a decrease in pH. In fact, CO<sub>2</sub> produced from organic decomposition is a major reason (along with the production of organic acids) why pond sediments are generally more acidic than overlying waters. On the other hand, algal uptake/removal of CO<sub>2</sub> during photosynthesis increases OH<sup>-</sup> concentrations and raises the pH of the water. This relationship is shown in Equation 10; as CO<sub>2</sub> is removed by algae, the reaction moves to the right and OH<sup>-</sup> are produced from the reactions involving HCO<sub>3</sub><sup>-</sup> and water. This equation demonstrates why surface-water pHs of productive ponds increase during sunny afternoons.

In the same way adding and removing any of the three forms of DIC can affect the pH, adding and removing H<sup>+</sup> or OH<sup>-</sup> (i.e., changing the pH) can affect the relative amounts of CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> in the water (Stumm and Morgan, 1970). As the pH shifts, the

pH	CO <sub>2</sub>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>
5	95.7	4.3	0.0
6	69.2	30.8	0.0
7	18.3	81.6	0.0
8	2.2	97.4	0.5
9	0.2	95.3	4.5
10	0.0	68.1	31.9
11	0.0	17.6	82.4

**Table 3. Relationship between pH and approximate relative percentages of total dissolved inorganic carbon (DIC), based on equilibrium reactions between dissolved carbon dioxide (CO<sub>2</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>), and carbonate (CO<sub>3</sub><sup>2-</sup>) at 25°C (see text and Equations 8 to 10).**

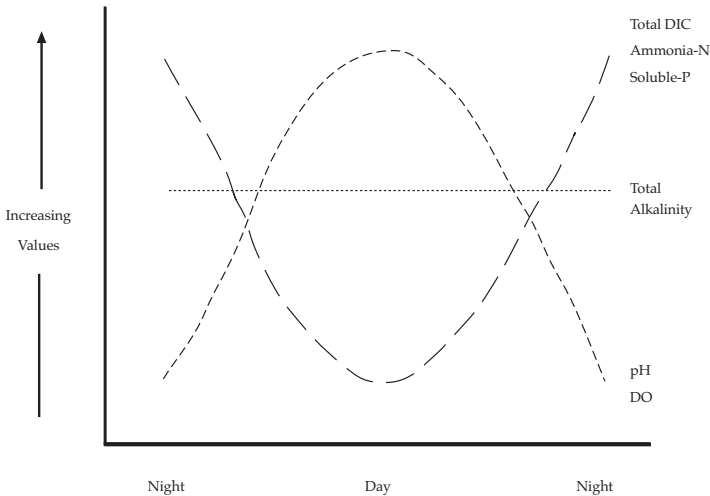
percent of total DIC represented by each of the three inorganic forms also changes (Table 3). At pHs below 5, dissolved CO<sub>2</sub> represents about 100% of the DIC; at pH of about 8.3, nearly 100% of the DIC is HCO<sub>3</sub><sup>-</sup>; and at pH 12, approximately 100% of the DIC is in the form of CO<sub>3</sub><sup>2-</sup>. Total DIC concentrations generally remain the same as the pH shifts, unless some CO<sub>2</sub> is lost to the atmosphere when surface water CO<sub>2</sub> concentrations become saturated at low pHs, or if some carbo-

	CO <sub>2</sub>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>
DIC	X	X	X
Alkalinity		X	X
Utilized by Algae	X	X	

**Table 4. Identification of different forms of dissolved inorganic carbon (DIC) in relation to total alkalinity and forms of inorganic carbon generally available for algal uptake. The three forms of DIC are dissolved carbon dioxide (CO<sub>2</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>), and carbonate (CO<sub>3</sub><sup>2-</sup>).**

nates precipitate out of solution (e.g., with calcium, discussed below) at high pHs (Stumm and Morgan, 1970).

Because algae can not utilize all forms of DIC equally (Table 4), these changes in the forms of DIC as the pH shifts can have great importance to algae. Carbon dioxide is readily taken up by algae, and  $\text{HCO}_3^-$  can be utilized by many algal species (Talling, 1976; Boston et al., 1989; Prins and Elzenga, 1989). Carbonate, however, is generally



**Figure 5. Typical diel (24-hour) curves of total dissolved inorganic carbon (DIC), ammonia-N, alkalinity, pH, and dissolved oxygen (DO) in a productive pond. Ecological reasons for curves and potential factors which could cause diel alkalinity values to vary are discussed in the text.**

an unusable form and not available for algal uptake. In most waters this is not a problem, since about 95% of the DIC in waters with pHs below 9 is in the form of either  $\text{CO}_2$  or  $\text{HCO}_3^-$ , and  $\text{HCO}_3^-$  still represents approximately 50% of the total DIC (the other 50% is  $\text{CO}_3^{2-}$ ) at pHs of around 10.4 (Table 3). Nevertheless, DIC availability can be an issue in highly productive rain-fed ponds, where pond water is naturally low in both DIC concentration and total alkalinity (i.e., buffering capacity, see discussion below).

It is useful at this point to summarize DIC transformations in light of pond dynamics. When algae remove  $\text{CO}_2$  and  $\text{HCO}_3^-$  from pond water during daytime photosynthetic activity, the pH goes up, dissolved oxygen concentrations go up, and total DIC concentrations go down (Equations 9 and 10) (Talling, 1976; Goldman et al., 1974). As the pH goes up, forms of the remaining DIC shift towards a higher percentage of  $\text{CO}_3^{2-}$ , a form not useful to algae. Then, as nighttime respiration dominates DIC activity, dissolved oxygen is consumed and  $\text{CO}_2$  is released back into the water, increasing DIC while decreasing pH. Figure 5 illustrates these diel cycles, or cycles which occur over a 24-hour period. The two main points to remember from the above discussion are: 1) the forms of DIC shift with changing pH values (Table 3); and 2) the typical diel cycles of pH, DIC, and dissolved oxygen (Figure 5) are due to the fact that photosynthetic uptake of DIC occurs only during daylight hours.

The DIC equilibrium equations discussed above illustrate another very important concept in aquatic ecology. Notice that if an acid (i.e.,  $\text{H}^+$ ) is added to water containing bicarbonate and carbonate (i.e., water with a pH above 5), the  $\text{H}^+$  concentration does not increase by the exact amount that is added. Some of the  $\text{H}^+$  is used to convert  $\text{CO}_3^{2-}$  to  $\text{HCO}_3^-$ , and then to convert  $\text{HCO}_3^-$  to  $\text{CO}_2 + \text{H}_2\text{O}$  (Equation 9). Likewise, adding a base (i.e.,  $\text{OH}^-$ ) will result in the conversion of  $\text{CO}_2$  to  $\text{HCO}_3^-$ , and of  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-} + \text{H}_2\text{O}$  (Equation 10). In this way, carbonate equilibria act as a buffer to prevent large changes in pH when an acid or base is added to the water. This buffering capacity is also referred to as total carbonate alkalinity.

Although other negatively charged molecules such as phosphate ( $\text{PO}_4^{3-}$ ), borate ( $\text{B}(\text{OH})_4^-$ ), nitrate ( $\text{NO}_3^-$ ), and the hydroxyl ion ( $\text{OH}^-$ ) are also part of total alkalinity, concentrations of these compounds are nearly always substantially less than 1% of the concentration of carbonate and bicarbonate in fresh water (Stumm and Morgan, 1970). For that reason, total alkalinity measurements are conveniently given in terms of  $\text{mg l}^{-1}$  of  $\text{CaCO}_3$  (APHA, 1985). The simplified equation for total alkalinity can be expressed as follows:

$$\text{Total Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

[12]

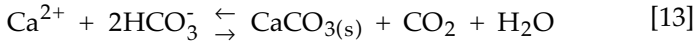
Equation 12 illustrates the loss of alkalinity when acid is added to water. If enough  $H^+$  is added to the water, all the carbonate and bicarbonate molecules are converted to  $CO_2$  and there is no more carbonate alkalinity left in the water (Equation 9). This is precisely what happens with acid rain or with alkalinity measurements using acid titration (APHA, 1985). The pH will decrease slowly due to carbonate alkalinity until the buffering capacity is gone at about pH of 5—then the pH drops rapidly and proportionally to acid input.

It is important to appreciate that  $CO_2$  is not a part of alkalinity, and adding  $CO_2$  to water has no impact on total alkalinity (Stumm and Morgan, 1970). Recall from Equation 9 that adding  $CO_2$  to water produces equal amounts of  $HCO_3^-$  and  $H^+$ . Although DIC will increase with the addition of  $CO_2$ , for every molecule of  $HCO_3^-$  produced there is also a molecule of  $H^+$  produced, canceling any net increase in alkalinity (Equation 12). Therefore, there are typically no diel changes in alkalinity with  $CO_2$  removal during photosynthesis or with  $CO_2$  production during respiration (Figure 5).

A simple laboratory experiment illustrates the relationship between alkalinity and  $CO_2$ . Measure alkalinity in a pond water sample before and after blowing bubbles (we exhale  $CO_2$  produced from our own respiration) with a straw through the water for about a minute. The pH drops and a higher percentage of the DIC is in the  $CO_2$  form (Table 3), but the alkalinity remains unchanged. Total DIC measurements, however, show an increase due to  $CO_2$  added from blowing bubbles. The added  $CO_2$  is available for algal uptake, but this increased DIC availability is not reflected in the alkalinity measurements, which stay the same.

A decrease in pond water alkalinity can occur, however, when  $HCO_3^-$  is removed by algae, as might occur during periods of high photosynthetic activity (Boston et al., 1989). Under these conditions, total DIC will still exhibit the same diel variability shown in Figure 5, but alkalinity may gradually decrease over time. Bicarbonate incorporated into decomposable algal biomass is subsequently released as  $CO_2$ , thus increasing DIC concentrations, but alkalinity will remain low until additional alkalinity is provided (e.g., adding lime to the pond).

Productive ponds with high calcium concentrations may show daytime losses of alkalinity through the formation and precipitation of  $CaCO_3$  following high afternoon pHs (Boyd, 1990). The equilibrium reaction is given in Equation 13:



This white precipitate can be seen around the pond's edges below the water surface, or as a fine suspension of  $\text{CaCO}_3$  particles (a phenomenon known as lake whitening), which can significantly reduce light penetration in the water (Goldman and Horne, 1983). However, the lower pHs and higher  $\text{CO}_2$  concentrations resulting from nighttime respiration activity cause the precipitate to dissolve, restoring water clarity and alkalinity.

Competition for carbonates from other aquatic organisms can also reduce alkalinity and carbon availability in a pond. For example, organisms which incorporate calcium carbonate ( $\text{CaCO}_3$ ) in their shells, such as snails and clams, are capable of seriously lowering alkalinity measurements in the pond water. This was observed with both snails and clams in culture ponds in Thailand (Knud-Hansen et al., 1993). The impact on algal productivity varies, depending upon the initial amount of alkalinity present and whether other sources of DIC are provided. Fertilization strategies designed to minimize this potential problem are discussed in Chapter 5.

A practical problem for aquaculturists is how best to quantify DIC availability for algal uptake. We have seen that algae utilize  $\text{CO}_2$  and bicarbonate ( $\text{HCO}_3^-$ ), but not carbonate ( $\text{CO}_3^{2-}$ ). Therefore, neither total alkalinity nor total DIC can be automatically assumed to accurately represent DIC availability for algal growth since they both include carbonate, and alkalinity measurements do not include  $\text{CO}_2$  (Table 4). Total  $\text{CO}_2$  and bicarbonate concentrations can be calculated directly by using carbonate equilibrium equations together with water pH, water temperature (which affects solubility rate constants), and either total alkalinity or total DIC measurements (Stumm and Morgan, 1970). However, this approach is often not very practical.

Under certain environmental conditions, total DIC and alkalinity measurements can also provide reasonably accurate indications of DIC availability for algae. Total DIC measurements are very good approximations in waters with pHs below about 9, where > 95% of the DIC is  $\text{CO}_2$  and bicarbonate (Table 3). On the other hand, total alkalinity can accurately indicate DIC availability for algae only in waters with pHs close to 8.3 under equilibrium conditions, when essentially 100% of DIC is in the form of bicarbonate, and assuming



only an insignificant amount of non-carbonate alkalinity (e.g., silicates, borates, nitrates) is present in the water. However, pHs in productive fertilized culture ponds are quite dynamic, and diel pH shifts of several units are common (Figure 5). Waters with pHs above 8.3 contain carbonate, and waters with pHs below 8.3 contain CO<sub>2</sub>, so alkalinity measurements alone do not accurately indicate DIC availability for algal uptake.

Total alkalinity may directly indicate dissolved CO<sub>2</sub> and bicarbonate concentrations in some natural waters where nearly all the DIC enters from the dissolution of carbonaceous rocks. But this assumption is not appropriate when additional organic matter (e.g., compost, manures, wastewater, and pelleted and other feeds) is added to a pond. These organic materials decompose, adding CO<sub>2</sub> to the pond and increasing DIC availability for algae. When lime (calcium carbonate) has been added to animal manures to reduce odors, a common practice with chicken manure, manure fertilization contributes both alkalinity and DIC. Lime increases pond alkalinity, and both the added carbonate from lime and carbon dioxide from manure decomposition increase total DIC availability to algae.

Although pond alkalinity has serious limitations regarding its ability to quantitatively assess DIC availability for algae, it can still be a useful measurement qualitatively. Recall that adding CO<sub>2</sub> to water does not affect total alkalinity, but adding carbonate alkalinity does increase CO<sub>2</sub> availability through equilibrium reactions. Statistical analyses of nutrient limitation in dozens of very productive fertilized ponds in Thailand suggest that alkalinities above about 75 mg l<sup>-1</sup> of CaCO<sub>3</sub> provided sufficient algal DIC so as not to limit algal productivity (Knud-Hansen and Batterson, 1994; Knud-Hansen, unpublished data). It has been suggested that alkalinities below 100 mg l<sup>-1</sup> of CaCO<sub>3</sub> may still be insufficient (Boyd, 1997). On the other hand, a pond with low alkalinity (e.g., 10 to 20 mg l<sup>-1</sup> of CaCO<sub>3</sub>) may still have sufficient DIC for algae if enough DIC is provided from organic decomposition and release of CO<sub>2</sub>. Alkalinity measurements above an experimentally established threshold value *should* indicate sufficient DIC, whereas values below *may* indicate potential carbon limitation with high algal productivities.

Low alkalinities in water also reflect poor buffering capacity. Carbon dioxide removal during photosynthesis raises the pH more quickly in poorly buffered waters, increasing the percentage of carbonate in the DIC pool (Table 3). Converting part of a pond's DIC

to a form not suitable for algae (i.e., carbonate) furthers the risk of having insufficient inorganic C for algal uptake in waters with low alkalinities. Adding alkalinity increases the buffering capacity as well as available DIC for algae, since algae can utilize bicarbonate.

When the pH is raised, either by adding alkalinity or from daytime CO<sub>2</sub> removal during photosynthesis, then the solubility of CO<sub>2</sub> increases, enabling more atmospheric CO<sub>2</sub> to enter the pond's surface waters (Equations 9 and 10, Stumm and Morgan, 1970). However, any net gain of DIC to a productive pond from increased CO<sub>2</sub> solubility is likely temporary, since some of the nighttime accumulation of respired CO<sub>2</sub> returns to the atmosphere when aquatic concentrations reach saturation levels (Stumm and Morgan, 1970; Talling, 1976). In fact, if the transfer of atmospheric CO<sub>2</sub> into pond water at high pHs was efficient, then DIC availability would not be a concern in culture ponds. Unfortunately, that is not the case.

Finally, and to complete the discussion on terminology regarding DIC, one last concept should be mentioned briefly. Water hardness is the capacity of water to precipitate soap, and is measured by the sum concentration of positive bivalent ions (e.g., Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>) and trivalent ions (e.g., Al<sup>3+</sup>, Fe<sup>3+</sup>) (APHA, 1985). Dissolved ions in the water combine with soap to form insoluble precipitates, which retard the formation of suds.

Alkalinity and water hardness are related terms considering that most of the alkalinity and hardness in natural fresh water usually comes from the dissolution of CaCO<sub>3</sub> and MgCO<sub>3</sub> in the water. For that reason, measurements of hardness, like those of alkalinity, are commonly given in equivalent units of mg l<sup>-1</sup> of CaCO<sub>3</sub>. Both total hardness and alkalinity will decrease in ponds with snails or clams present, due to the incorporation of CaCO<sub>3</sub> in the shells. In ponds with very hard water (i.e., high calcium concentrations), high algal productivity can result in the precipitation of CaCO<sub>3</sub> (Equation 13), again reducing hardness, alkalinity, and DIC.

## Controlling Algal Productivity

The above discussion on the dynamics of P, N, and C in a freshwater pond sets the stage for the key question in pond fertilization: How do you most efficiently make the pond green and abundant with algae? The simple answer is to give the algal community only

what it needs to grow—nothing more and nothing less. We have already seen that algae require:

- Primary nutrients (C, N, P) as well as hydrogen and oxygen;
- Minor and micronutrients;
- Sufficient light energy in the water column; and
- Suitable water temperatures for growth.

Algae will continue to grow rapidly as long as *all* of the above requirements are met. When one or more of the stated requirements are not available for growth, then algal productivity is said to be limited by that condition.

Limitation of algal growth is best described by Liebig's Law of the Minimum, which says that algal productivity will be limited by the element present in least supply relative to algal requirements (O'Brien, 1974; Goldman and Horne, 1983). Note that this principle says "least supply" and not "least concentration." In other words, the *rate* of algal production is determined by the *rate* of nutrient availability. It should be clear from the above discussion on nutrient dynamics that P, N, and C recycle extensively between algae, animals, the water column, and the sediments before becoming ultimately "lost" to the pond system through release into the atmosphere, from water seepage out of the pond, by being permanently bound up in the sediments, or being incorporated into harvestable fish biomass. Therefore, measurements of nutrient concentrations have limited value as indicators of the *supply* of algal nutrients available for uptake.

For purposes of this book, limitation of algal productivity is viewed broadly from an algal community perspective. Although different algal species have widely varying abilities and demands for nutrient uptake and light utilization (Fogg, 1975), here the purpose is to make ponds green without necessarily trying to promote a particular algal species in the pond.

Algal productivities in natural freshwater located in temperate climates are most typically limited by the supply of P (Schindler, 1978), whereas N has been frequently found limiting in tropical fresh water (Setaro and Melack, 1984). Natural nutrient limitation, however, has little practical importance in pond fertilization, where nutrient input rates may be hundreds or thousands of times greater than natural input rates. In pond fertilization, objectives include giving the algal community all it needs to keep growing at high rates, and not

fertilizing when the algae already have a sufficient supply of available nutrients in the water.

From a pond management perspective, however, only a few algal growth requirements need to be met through pond fertilization. Suitable water temperatures can be dealt with by selecting appropriate geographical regions to conduct semi-intensive aquaculture. There is plenty of hydrogen and oxygen in the water, so fertilization of these elements is not necessary. The supply of essential micronutrients has never been shown to limit algal growth in fertilized ponds—although species of diatoms require silica for their cell walls, diatoms are generally found in cooler waters and are not usually a dominant group in warm, freshwater ponds (Fogg, 1975; Goldman and Horne, 1983). Therefore, the only four algal growth factors which the aquaculturist/farmer needs to manage are the availability of suitable forms of P, N, and C, and sufficient light energy. The next chapter examines different types of fertilizers and their relative abilities to efficiently and economically meet these algal growth requirements.