

Barr Report

Barr Report

Dissolved Inorganic Carbon (DIC)

Special points of interest:

- Feature Article "Dissolved Inorganic Carbon"
- "Carbon exists in inorganic and organic forms ..."
- "Dissolved inorganic carbon (DIC) is the sum of all carbon present as CO_2 , H_2CO_3 , and CO_3 and represents the primary source of carbon for photosynthesis by aquatic organisms ..."

Carbon is required for life on Earth, including life in aquatic ecosystems (Rheinheimer 1992). All living organisms need carbon as a food source. The importance of carbon cycling is that the processes involved form important links between the abiotic (non-living) and biotic (living) components of the aquatic ecosystem (or any ecosystem). This is in large part due to the ability of carbon to form strong bonds to other non-metals such as hydrogen, nitrogen, oxygen, sulfur and the halogens (Zumdahl 1993). Under certain conditions metals such as iron and manganese, or nutrients such as phosphorus or nitrogen, can become adsorbed (or attached) to carbon molecules, temporarily rendering these unavailable to aquatic organisms (Figure 1).



The cycling of carbon involves transitions of carbon between organic and inorganic states.

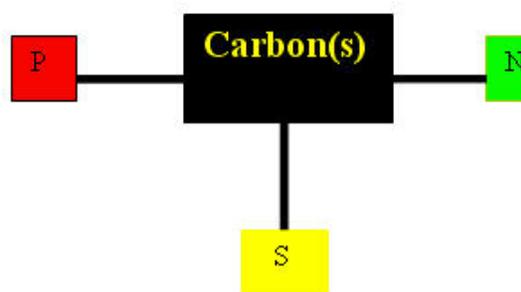


Figure 1

Carbon exists in inorganic and organic forms. Organic forms typically consist of long chains or rings of carbon atoms which constitute a part of living matter or part of substances derived from living matter such as decaying vegetation and humic acids. Compounds such as the oxides

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In fully planted aquariums, free CO₂ becomes limiting to aquatic macrophytes under higher light intensity.

“All Organisms need carbon as a food source.”

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of carbon (e.g. CO₂) and carbonates (CO₃) are considered to be inorganic substances (Zumdahl_1993). The cycling of carbon involves transitions of carbon between organic and inorganic states. These transitions are influenced by, and themselves influence, a number of physico-chemical factors such as light, temperature, dissolved oxygen, pH, redox potential, ionic composition of the water, as well as biological factors such as productivity. Next month’s issue of the Barr Report will discuss organic carbon. Figure 2 shows a carbon cycle within a typical wetland (adapted from Reddy 2004).

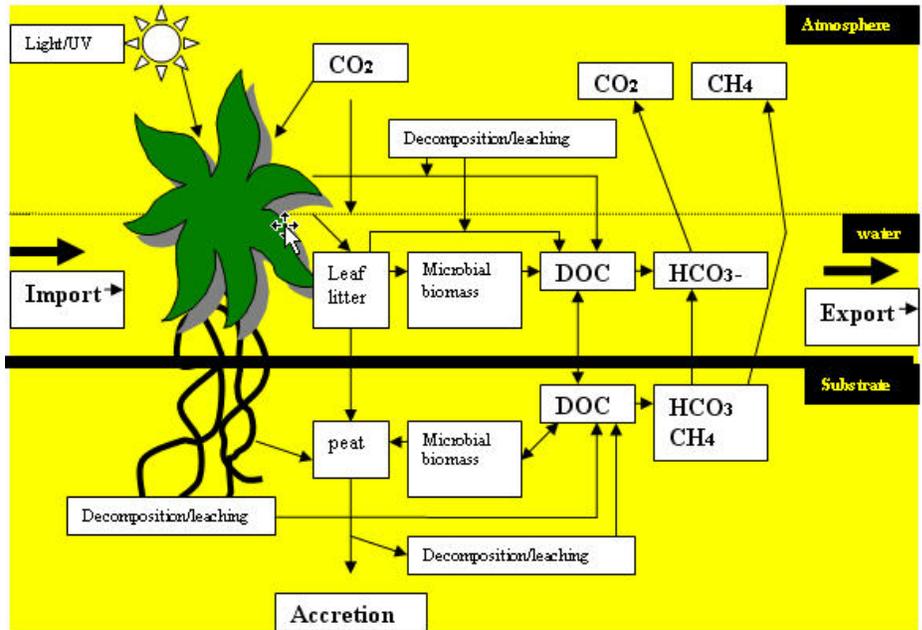


Figure 2



It's not a missile, but a Submersed Aquatic Macrophyte

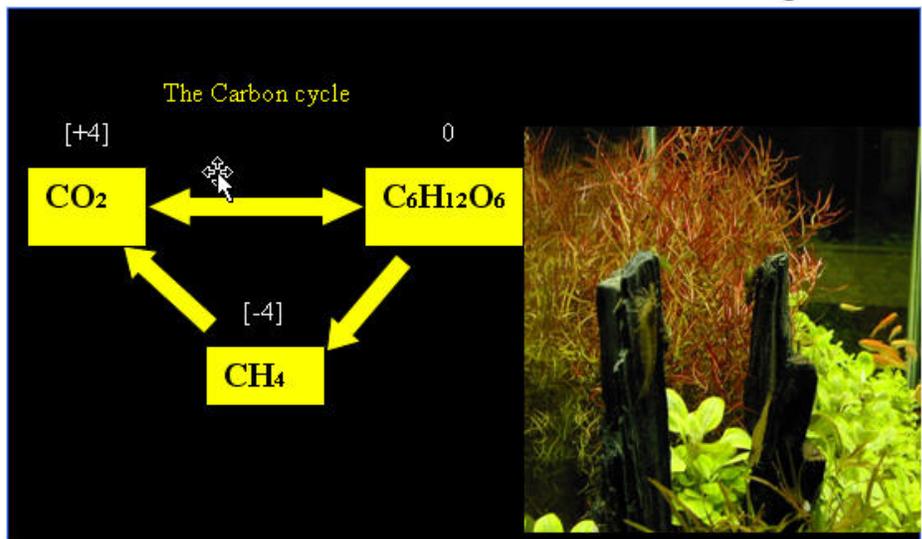


Figure 3

Continued on page 3

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Figure 3 shows the various carbon transformations in a wetland. CO₂ enters the cycle and is incorporated into submersed aquatic Macrophytes (and other plants and algae); the other forms of carbon will be addressed in next month's issue of the Barr Report. Figure 3 shows that plants assimilate and reduce CO₂ into sugars. When these sugars [C₆H₁₂O₆] are decomposed without oxygen, they yield CH₄ (methane) through microbial processes and oxidized into CO₂ as it travels up into the aerobic zone. If they are decomposed in the presence of oxygen, then it yields CO₂ which can be reassimilated by the plants.

DIC

Dissolved inorganic carbon (DIC) is the sum of all carbon present as CO₂, H₂CO₃, HCO₃⁻ and CO₃²⁻ and represents the primary source of carbon for photosynthesis by aquatic organisms. In most bodies of water, there is ample carbon available for use in photosynthesis and only under certain conditions (such as soft water or extremely high productivity) does DIC become limiting. Where there is high SAM density, CO₂ is removed rapidly in the presence of light. There is a close correlation between ample DIC and distribution of SAM's in natural ecosystems (Raven 1970). In fully planted aquariums, free CO₂ becomes limiting to aquatic macrophytes rapidly under higher light intensity. When this occurs, many SAM's utilize bicarbonates, HCO₃⁻, as a source for carbon (Equation 1). It is estimated that 50% of submersed aquatic macrophytes can utilize HCO₃⁻ under high light low CO₂ conditions.



All plants and algae *prefer* CO₂ over HCO₃⁻ and it takes approximately one week for both to acclimatize to a given steady level of CO₂ (Bowes 2003, Taiz and Zieger 1998). Bicarbonate can be used under limiting conditions and plants can do this directly as with the case using carbonic anhydrase(CA) which is *direct* bicarbonate use or they can utilize indirect bicarbonate use. *Indirect* bicarbonate utilization uses a proton pumping mechanism where the plants pumps out large amounts of H⁺ on the abaxial surface of the leaf(the bottom surface) and which lowers the pH and reduces the bicarbonate to free CO₂ whereby the SAM then takes up the carbon in the CO₂ form (Bowes 2003).

Free CO₂ is usually present in surface waters at concentrations of < 10 ppm and is often present in well and tap water at higher concentrations. This is due to microbial CO₂ release in the soil as the water from the surface accumulates the respired CO₂ and has no way to escape or equilibrate underground. Additionally, cooler water possesses more dissolved gases than warmer aquarium water. High excess CO₂ in water can have deleterious effect on locomotion and metabolic activity in many animals so measurement of total inorganic carbon is an important variable in water management. While excess CO₂ is often considered a negative parameter for aquatic ecosystems, when SAM's are present in high density, it allows rapid growth and high levels of the by product O₂. This high O₂ level mitigates the effect of the elevated CO₂ levels (within



"Bicarbonate can be used under limiting conditions and plants can do this directly ..."

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limits) within the respiration cycle of other organisms. High densities of fish and animals are found in naturally occurring waters where elevated CO₂ levels are present (Florida and Brazilian freshwater springs) and this has a pronounced effect on the plant production.

Table 1 shows the various forms and uses for carbon. The primary focus initially will be the DIC fraction. The second chapter in the two part series will address the organic fraction, DOC (Dissolved organic carbon) and POC (Particulate organic carbon).

"In locations where there is ample rich CO₂ in the water, there are often vibrant stands of [Aquatic Life] growing actively ."

	<u>Particulate</u>	<u>Dissolved</u>
<u>Organic</u>	Living organisms Dead organic material	<u>Soluble organics:</u> amino acids sugars DOC (dissolved organic carbon)
<u>Inorganic</u>	CaCO ₃ carbonates of Mg, K, Na, etc.	DIC (dissolved inorganic carbon): CO ₂ H ₂ CO ₃ HCO ₃ ⁻ CO ₃ ²⁻

Table 1

Some research will mention the ratio of CO₂:H₂CO₃. This is roughly 400:1 and most treat this fraction as all CO₂ (Lea 2000).

Photosynthesis

Photosynthesis consists of light reactions and dark reactions. This is the overall pathway simplified from light to sugar:

Light → produces light reactions in the autotroph → produces ATP, NADPH, O₂ → for use in reductive pentose cycle or Calvin cycle → to reduce CO₂ → to sugars.

We will be looking at the [CO₂ → "sugars"] portion of this process: CO₂ + ribulose 1,5-bisphosphate (5-Carbon) → the enzyme: D-ribulose 1,5-bisphosphate carboxylase → produces two 3-C sugars (6 total Carbons from

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the original 5) Rubisco catalyzes the reaction between ribulose biphosphate (RuBP: a five-carbon sugar biphosphate) and CO₂ to give two molecules of 3-P-glyceric acid (PGA: a three-carbon acid). The PGA then goes on with ATP and NADPH to form sugar-phosphates in the PCRC cycle.

RuBP + CO₂ → 2 x PGA → photosynthesis (PCRC Cycle).
Rubisco

This process is called the photosynthetic carbon reduction cycle(PCRC). This involves electron and proton transfer reactions, complex membrane systems, protein complexes, electron carriers, lipid molecules, all surrounded by water. Submersed Aquatic Macrophytes (SAMs) use Carbon dioxide (CO₂) to make sugar phosphates by using the products of the light reactions: ATP and NADPH. ATP and NADPH are used to reduce CO₂ to sugar phosphates. These sugar phosphates are the subunits used to synthesize *all the plant's organic molecules*. This cycle is found in all autotrophs organisms (except for a few bacteria). The key enzyme in this process is rubisco (ribulose biphosphate carboxylase-oxygenase). With the exception of the carbon fixed by some prokaryotic organisms, most of the carbon fixed on Earth is processed by the Calvin cycle.

“High [O₂], low [CO₂], high temperature and irradiance enhance photorespiration, and thus reduce net photosynthesis...”

Adaptation to available CO₂ concentrations

The concentration of rubisco, the carboxylating enzyme of the Calvin cycle, is generally high. For example, it accounts for 50% or more of the total protein in plant leaves, and its concentration within chloroplasts is extremely high (approximately 0.2 g/ml). It constitutes some 30% of the total protein in many leaves for which reason it is of considerable interest in relation to the nitrogen nutrition of plants. Plants from elevated CO₂ had significantly higher (52%) rubisco than plants from ambient CO₂ when measured in their respective growth CO₂ concentrations. Elevated CO₂ decreased leaf soluble protein (40-52%) and rubisco (30-55%) contents, increased soluble sugar (52%) and starch (44%) (Jacob and Drake, 1994). This means that SAMs adapt under high CO₂ levels allocate their resources to the production of food and storage sources of energy rather than uptake enzymes. This adaptation takes approximately one week's time (Madsen, Bowes, Maberly, 1996). This shows how plants are able to adapt to *different* aquatic environments allowing aquarist to grow SAM's in non Carbon and Carbon enriched aquariums (an important issue for aquarist is maintaining a stable supply of the form of carbon as well as the concentration) as well as how they can adapt their enzymes.

The Rubisco enzyme is the first step in the carbon reduction cycle and is the way by which inorganic carbon enters the biosphere as organic carbon. It is

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a large, sluggish enzyme with a turnover time of 2 s^{-1} . It occurs in the stroma of the chloroplast and is a major limiting factor in terrestrial photosynthesis (part of mesophyll resistance). Microphytes (algae) such as epiphytic algae on the surface of SAM's leaves and blades increase this diffusional distance, thus resistance (as well as reduce the available CO_2 and foliar nutrient and light availability). Additionally, most microphytes (algae) possess only one cell layer surface between the environment, while SAM's typically have several cell layers distance to transport CO_2 to the photosynthetic cells. It should be noted that microphytes are epiphytes upon each other as well as SAM's, therefore they can cause availability declines within both groups much like SAM's can with one another. This resistance is further increased in the thick viscous liquid water medium, although SAM's make up for this a number of ways through thin finely dissected leaf morphology, reduced cuticle thickness, no requirement to close stomata aperture (effectively keeping the stomatal resistance at its lowest level) for water evapotranspiration (we assume there is ample water in an aquarium or lake!), root uptake of CO_2 and CAM and C4 photosynthetic pathways. Adding to the problem of low CO_2 for Rubisco to fix CO_2 efficiently is gas diffusion from the atmosphere into the water. Water is a dense polar solvent. CO_2 and O_2 diffuse 10,000 times slower than in air. This greatly reduces the plant's ability to make the basic building blocks and is often the main limitation in natural lakes and streams. In locations where there is ample rich CO_2 in the water, there are often vibrant stands of SAMs growing (Raven 1970).

Photorespiration

Since CO_2 and O_2 are similar rubisco's active site, the enzyme has a hard time distinguishing between them, and so O_2 can become a competitive inhibitor of rubisco with respect to CO_2 . So in the presence of atmospheric $[\text{O}_2]$ and $[\text{CO}_2]$ the enzyme (and photosynthesis) is inhibited by up to 50% (Chollet, 1977). In addition, rubisco catalyzes the reaction of O_2 with RuBP to form one molecule of PGA and one of P-glycolate (a two-carbon acid). When this happens, no C is added to the organic-C pool of the plant, and even worse the P-glycolate is metabolized in the Photorespiratory Carbon Oxidation (PCO) Cycle and releases previously fixed CO_2 .



Organic-N is released as ammonium and has to be refixed into organic-N – an energetically very expensive process (uses lots of ATP) in photorespiration. Plants that just use the PCR cycle, and thus also photorespire, are called C3 plants (C3 photosynthesis), because the first compound formed is PGA (a three-carbon acid). They constitute the majority of autotrophic species on the planet. High $[\text{O}_2]$, low $[\text{CO}_2]$, high temperature and irradiance enhance photorespiration, and thus reduce net photosynthesis. One of my studies (Barr 2003) involved various combinations of O_2 and CO_2 gas to investigate whether high O_2 levels had a significant impact on epiphytic attached algae growth on glass slides. The results show similar Chlorophyll *a* levels, but different algae species compositions in each of the various combinations

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Test one	Ambient low CO ₂	Ambient low O ₂
Test two	Ambient low CO₂	High O ₂ [150% saturation at 25C]
Test three	High CO₂ (25ppm)	Ambient O ₂
Test four	High CO ₂ (25 ppm)	High O ₂ [150% saturation at 25 C]

Table 2

In aquariums, high CO₂ and O₂ levels are the most commonly found conditions where CO₂ or carbon enrichment is used. It would appear that algae epiphytes are adapted photorespiration and these conditions can change the algae species composition but not the production significantly under these conditions. SAM's also adapt well to high levels of O₂ and photorespiration (Bowes 2004).

CO₂ and O₂ differences

An understanding of the mechanism of CO₂ fixation requires knowledge of the physical and chemical properties of CO₂, particularly those related to its interaction with water. The amount of any gas dissolved in water is proportional to its partial pressure (P_{gas}) above the solution (Henry's law) and its Bunsen absorption coefficient (α). The Bunsen absorption coefficient is the volume of gas absorbed by one volume of water at a pressure of 1 atmosphere and is temperature dependent, decreasing as the temperature rises. The solubility of a gas therefore decreases with increasing temperature. Thus, for a given temperature,

$$[\text{gas}] \mu\text{M} = P_{\text{gas}} \times \alpha \times 10^6/V_0$$

Where V_0 is the normal volume of an ideal gas at standard temperature and pressure ($V_0 = 22.4 \text{ L mol}^{-1}$). We can calculate the partial pressure of a gas by multiplying the mole fraction of the gas by the total pressure. The mole fraction of a gas is its partial volume divided by the total volume of all the gases present. Thus, the mole fractions of CO₂ and O₂ in air are 0.0345% and 20.95%, respectively. At sea level, atmospheric pressure is about 0.1 MPa, yielding the partial pressures of CO₂ and O₂ at 3.4×10^{-5} and 2.1×10^{-2} MPa. From these values and those of α , the corresponding solution concentrations of CO₂ and O₂ can be computed by the equation given above. The table below presents values for these concentrations at different temperatures (Table 3). These values place considerable constraints on carboxylation. As a carboxylase, rubisco must be capable of operating efficiently even at the rather low concentrations of CO₂ available to it. Rubisco also functions as an oxygenase in photorespiration, so the solution concentration of O₂ is also important. Because of the different temperature dependences of the Bunsen absorption coefficients $\alpha(\text{CO}_2)$ and $\alpha(\text{O}_2)$, the concentrations of these two gases vary with temperature such that the ratio of CO₂ to O₂ decreases as the temperature increases. This effect is important biologically, because as the temperature increases, the ratio of carboxylation to oxygenation catalyzed by rubisco decreases and the ratio of photorespiration to photosynthesis thus increases. This slows plant growth.

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Temperature (°C)	α (CO ₂)	[CO ₂] (μ M in solution)	α (O ₂)	[O ₂] (μ M in solution)	$\frac{[\text{CO}_2]}{[\text{O}_2]}$
5	1.424	21.93	0.0429	401.2	0.0515
15	1.019	15.69	0.0342	319.8	0.0462
25	0.759	11.68	0.0283	264.6	0.0416
35	0.592	9.11	0.0244	228.2	0.0376

Solubility of CO₂ and O₂ as a function of temperature. Table 3

For reference to ppm and mole conversions of CO₂: CO₂ 1 mmol/l = 44 mg / l. The incorporation of CO₂ (gas) into a solution comprise two reactions:

The solubilization CO₂ (gas) → CO₂ (aq)

and the hydration CO₂ (aq) + H₂O → H₂CO₃, K = 2 x 10⁻³.

Partial pressure is the mole fraction multiplied by the total pressure. For example, at sea level, where the atmospheric pressure is about 10⁵ Pa, the partial pressure of oxygen is 2.1 × 10⁴ Pa (21% × 10⁵), and the partial pressure of CO₂ is 36 Pa (360 ppm = 0.036%; 0.036% × 10⁵ = 36). At the top of a 1500 m mountain, where the atmospheric pressure is about 8.5 × 10⁴ Pa, the partial pressure of oxygen is 1.8 × 10⁴ Pa and that of CO₂ is 30.6 Pa. This is the reason that it is harder for people to breathe and for leaves to photosynthesize at higher altitudes.



“As the buffering effect is overcome, a continued increase in CO₂ lowers pH because more carbonic acid is formed....”

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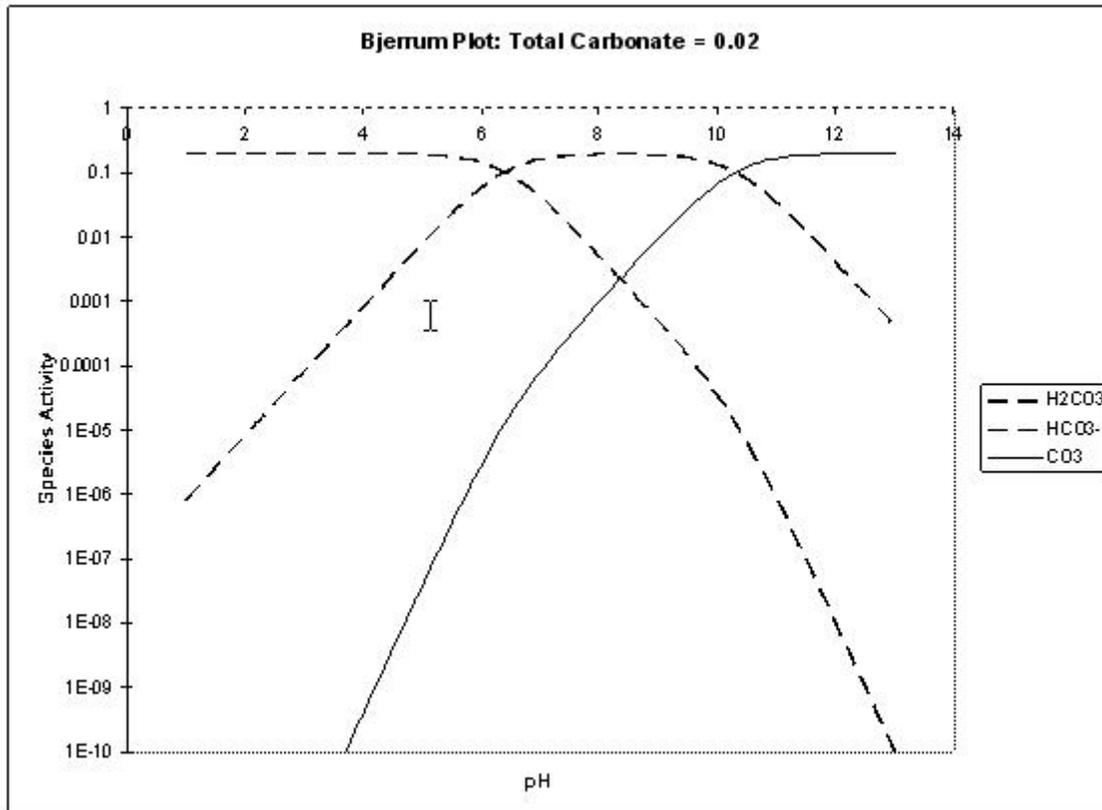


Figure 3

The Bjerrum plot shows the relative ratios of the various species of DIC at different pH's. H₂CO₃ is assumed to be free CO₂. Losses and additions of CO₂ from either photosynthesis and respiration or enrichment will change the pH of the water column. However, the carbonate species as well as other ions dissolved in the water act as buffers and pH changes will be resisted as long as the buffering compounds are not used up. As the buffering effect is overcome, a continued increase in CO₂ lowers pH because more carbonic acid is formed. Correspondingly, as CO₂ is depleted, pH rise and are inversely proportional.

Depletion and Primary Production

Free CO₂ is the "species of choice" used by microphytes (algae) and SAMs. Many aquatic plants and mosses can only utilize free CO₂ as a carbon source. However, some plants can utilize bicarbonate (HCO₃⁻) in situations where free CO₂ is low and bicarbonate is abundant. Many microphytes that are adapted to grow in low-light conditions (*Oscillatoria*) can stay alive in the absence of light if conditions are relatively bacteria-free by utilizing organic compounds (glucose) as a carbon source much as do respiring organisms. These organisms are said to be photoheterotrophic. Carbon utilization by this route is at much lower levels in these organisms compared with normal photosynthesis. This maybe a reason as to why *Oscillatoria* blooms occur when the filters are not cleaned regularly.

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Marl Formation

If sufficient loss of CO₂ occurs, such as during periods of high CO₂ uptake in a high light planted aquarium, chemical equilibrium between the carbonate species is lost and insoluble calcium carbonate or marl precipitates:



This reaction continues until equilibrium is reestablished. Often other substances will co-precipitate with the marl such as phosphate a limiting nutrient in primary production. As these substances precipitate, they sink out of the photic zone and primary productivity may be adversely affected.

Alkalinity

Alkalinity (also carbonate alkalinity, alkaline reserve, titratable base, or acid-binding capacity) has little to do with how alkaline water is. Rather, it refers to the quantity and kinds of compounds present in natural waters that act as buffers. It is a measure of the buffering capacity of natural waters. These substances are important as most aquatic organisms are sensitive to pH changes. The term alkalinity comes from the fact that these compounds, mostly the carbonate species, collectively shift the pH to the alkaline side of the pH scale. Alkalinity is measured as equivalents of carbonate or bicarbonate. This term also has little to do with hardness, waters may be very soft (low hardness) yet have high alkalinity. Another way to consider alkalinity is as the acid neutralizing capacity (ANC), which refers to the capacity to neutralize strong acids such as HCl, H₂SO₄, and HNO₃. In other words, alkalinity is the ability of an aquatic system to accept protons (H⁺).

Borate (H ₄ BO ⁻ , mostly in sea water and desert lakes)
Humic and Fulvic Acids (in bog environments)
Phosphate species (PO ₄ ⁻³ , HPO ₄ ⁻² , H ₂ PO ⁻)
Arsenates (AsO ₄ ⁻²)
Silicates
Aluminates

Other Contributors to Alkalinity

Table 4

Table 4 discusses several other components that influence alkalinity besides bicarbonates and carbonates. Other factors that will influence and lower alkalinity: seasonal and diel variations in alkalinity (as alkalinity is determined mainly by carbonates and bicarbonates) and seasonal depletions of these species such as marl precipitation. As with the CO₂ species, these situations are seen mainly in highly productive lakes and the littoral zones. *Potamogeton* species often form marl in aquariums due to this bicarbonate usage forming a visible white crust.

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Plant adaptations

Species adapted to high light intensity are called shade intolerant. Those adapted to shade environments are called shade tolerant (most SAMs fall into this group). Shade tolerant species show little difference in their survival and growth rates under shaded or sun. Shade intolerant species were, however, greatly impaired when growing in shaded conditions. This is due to the difference in light compensation point between and carbon allocation between the two species: Shade tolerant plants can maintain a positive carbon uptake under limited light. Shade intolerant plants continue high rate of photosynthesis under low light intensity thus affecting their ability to survive, due to a deficit in carbon uptake. When ample CO₂ is present less carbon is lost and less uptake takes place resulting in a lower compensation point. In general, leaves grown in reduced light tend to be larger and thinner than those grown in full light. Changes in carbon allocation also occur, e.g. decrease ration of root mass to leaf area. These morphological changes increase the chances to capture light, the limiting factor with respect to light.

Responses to UV radiation.

Laboratory experiments show that UV-B radiation can damage DNA, partially inhibit photosynthesis, alter the growth form of plants, and reduce yield (Tevini et al., 1990, 1991a; Mark, 1992). Plants defend themselves against UV damage by having anthocyanins, colorless flavonoids and other phenols that absorb UV-B radiation **but transmit PAR** to the interior of the leaf. It should be noted that these flavonoids are an antiherbivory agent as well and tend to be highest in the apical growing tips (the most nutritious portion of the SAM). There is debate as to why these secondary compounds are present in plants and there are likely multiple and separate reasons that provide advantages to SAMs. For example, many red anthocyanin rich plants are found in the understory of tropical rainforest where the light levels are very low and herbivory pressure is high. Growing tips of many plant species also possess high concentrations of anthocyanins which are rich in carbon and possess no nitrogen (often a limiting nutrient) and low Chlorophyll (rich in Nitrogen). Therefore adding stable carbon levels allows a SAM to produce ample anthocyanins which yield red color even at low light intensities. Reducing nitrogen levels will also allow the red color from anthocyanins to appear more but care must be given to not reduce the nitrogen levels since the rubisco which fixes the CO₂ is also a major role player in production of the anthocyanin subunits.

Problems with CO₂ measurements and practical matters with enrichment

Supplying adequate CO₂ or carbon to prevent limitation is a goal of many aquarium plant hobbyists.

Stray current can cause measurement problems, such as those from lighting ballast and submersed pumps. Turning off all electrical components when using an electronic pH monitor or pen is a wise approach here. Stray current can give false positives with respect to CO₂, showing that there is more CO₂ than is really present. While many assume that pH controllers will make the system more stable, often times due to things such as variations in tap water alkalinity and electrical current, they can also cause problems when other changes occur that influence the CO₂ level. Compounding the measurement problems associated with CO₂ are

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large differences between most alkalinity test kits (the KH test kits) in their wide 17.9ppm per degree units. Some test kits measure in degree units while some measure ppm. The more accurate the alkalinity test kit, the better the final measurement. Utilizing a chemical test kit for pH that has a narrow range can be useful and satisfactory for most cases but more precise electronic meters will provide more accurate CO₂ measurements when used properly.

There is no practical need for adding CO₂ gas at night, microphytes and macrophytes do not use CO₂ at night, only a very few CAM plants can do this. Some arguments exist with respect to pH fluctuations and additions of CO₂ at night to maintain pH. Performing large water changes frequently also changes the pH dramatically yet the organisms respond well to this, the main difference is the amount of gas between the tap source water and the aquarium's water. pH changes can cause problems with livestock health due to other factor other than CO₂ levels which have been traditionally view as a waste product (and something to keep as low as possible) by fish aquarist not keeping SAMs. Long term chronic levels of CO₂ may build up in the aquarium without turning off the CO₂ at night when it's not needed which can arguably do more harm than pH variations. In natural systems with high SAM densities, large pH fluxes occur daily and animals are present without harmful effects. The higher O₂ levels appear the issue in terms of animal livestock health rather than pH nor CO₂ levels under practical usage. Therefore, allowing the aquarium to off gas the excess CO₂ at night allows fewer maintenance problems and an increased margin of safety. It also allows higher levels of CO₂ during the photoperiod when the CO₂ is needed without impacting animal health with long term **chronic** high CO₂ concentrations when the O₂ levels are at their lowest at night.

Some species of algae, namely a red alga, *Audouinella* appear when the CO₂ level is low or variable. Adding more CO₂ will stop their growth and these make good indicators of poor CO₂ levels even if the testing method appears to show adequate CO₂ concentrations. Therefore adding more CO₂ gas will help eliminate new growth. This should be done slowly and carefully and noting the animal's response. *Riccia* is also a good indicator of good CO₂ levels when pearls of O₂ bubble appear roughly 2-6 hours into the photoperiod. CO₂ should be checked often and the aquarist should not become complacent even if they are well experienced and considered advanced. While testing is one method of monitoring, noting the plant's health and looking for signs of algae of a lull in the growth rates are often good signs that something is slowing plant growth and the environmental conditions should be checked. While many have assumed excess nutrients causes algae in the past, the reverse appears to be the case due to the differences between SAM's and microphytes (algae) ecologically in their respective niches. Therefore adding more CO₂ often addresses any limitations with respect to the SAMs and DIC.

Why add so much CO₂ only during the day?

If the CO₂ is kept stable, the plants will catch up, but most aquarist that have CO₂ issues also have CO₂ stability issues. By adding enough CO₂ to reach the **maximum saturation level for plants** (say 25-35ppm) at a high level of light irradiance, the target is much wider to hit for aquarist than say keeping the CO₂ at 8ppm constantly. That is much more difficult but overall, the plants will do well if the CO₂ is stable. For example: A target of CO₂ is 25-35 ppm, that gives you a + or - 10 ppm target to hit versus a target of + or - 1ppm with the 8ppm. Less light places less demand on CO₂ so reducing the light is an effective means of providing more stability in terms of all nutrients including CO₂. Most SAMs fully saturate their rubisco and their production pathway at 30ppm of CO₂ (Van et al 1976)

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CO₂ added to excess levels:

CO₂ (like PO₄, NO₃, Fe) dosing recommendations often suggested assumes that excess levels of nutrients will not cause algae. Yes, the aquarist can get away with less than this certainly and this is *easier to achieve with less light*. CO₂ dosing at high levels is no different than adding 1-2ppm of PO₄ versus maintaining a close tolerance between 0.1ppm and 0.2ppm. Both are SAM and microphyte nutrients. Which would be easier to maintain and dose on a practical level? This concept is supported with the Estimative index : <http://www.barrreport.com/forums/showthread.php?t=1> and applies to CO₂ as well as PO₄ or other nutrients. Aquarists have traditionally made this target so small that achieving the balance has been very difficult for many/most. As the skills of an aquarist improve, they can reduce the level of nutrients or CO₂ as they chose but it offers little practical use in terms of horticulture. Many have suggested adding **barely just enough** to provide for plant growth. Why place a self imposed hardship or barrier in the way when it's not needed?

Other's have suggested adding just enough nutrients for the plants for specific tanks as the nutrients are consumed, while possible and relatively easy, it requires more testing and management and given the wide range above the minimal need and variations in CO₂ measurements and light measurements, it is more arguable that the two main inputs into plant growth (light and CO₂) should also be closely controlled if that is the conceptual goal. Taking this concept further, adding barely enough light would seem the most prudent if limitation is the goal or not adding CO₂ at all, since SAMs can and do grow well enrichment. Light and CO₂ are far more **significant components** to SAM growth than say PO₄. Without addressing these major players in SAM growth, these routines ignore the primary components and focus on relatively minor constituents. Less light at these concentrations will provide more stability and still not cause algae, as algae prefers CO₂ like plants. It's much more an issue of **stable levels** of nutrients or adding enough to fully saturate the nutrients for the plant's needs for any commonly used light level in planted aquariums. The aquarist can choose add just enough or they can add to a wider excess level. The target becomes more and more difficult to hit as it gets closer to the threshold of limitation. Non CO₂ tanks possess less light and do not dose CO₂. They also are more stable than CO₂ enriched aquariums and need virtually no resetting, water changes and no testing due to this stability. The issue of stability becomes an issue when nutrients become low enough to become limiting. Fortunately, SAM's ranges are very wide allowing the aquarist to dose easily without such careful management. When SAMs are provided with stable DIC levels, they adapt quite well and grow successfully.

Further reading of the role of CO₂ enrichment and cycling is provided for a basic overview:

http://www.csd.net/~cgadd/aqua/art_plant_co2chart.htm

<http://www.brainyday.com/jared/aquarium/discus/co2.htm>

<http://www.thekrib.com/Plants/CO2/>

<http://www.floridadriftwood.com/whyCo2.htm>

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Summary

- Difference between organic and inorganic carbon
- Role and types of DIC
- Photosynthetic processes
- Photorespiration and CO₂ and O₂ differences
- Partial pressures
- Bjerrum plot for DIC species
- Depletion and primary production
- Marl formation
- Alkalinity
- Response to UV radiation
- Problems with CO₂ measurements and practical matters with enrichment

Note: Next Month's Barr Report will focus on the organic carbon fraction.

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