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Barr Report

Barr Report

with Tom Barr

Magnesium's role in aquatic macrophyte nutrition

Special points of interest:

- Feature Article "Magnesium's role in aquatic macrophyte nutrition"
- Magnesium—the "blood" pigment of plants
- Magnesium is far more important to in terms of plant health and growth than many aquarist may realize, but plants do not need large amounts to grow well.

Inside this issue:

Magnesium was shown to be an essential nutrient for plant growth in 1839 by Carl Sprengel. Magnesium is absorbed by plants as the divalent cation Mg^{2+} from the soil pore water and in the case of aquatic macrophytes through their leaves from the water column. Like calcium, magnesium reaches plant roots by mass flow and diffusion. Root interception contributes much less to Mg^{2+} uptake than Ca^{+}. The quantity of Mg^{2+} taking up by plants is usually less than Ca^{2+} or K^{+}. Magnesium in the chlorophyll molecules represents only about 10% of the total leaf Mg^{2+}. Most plant Mg^{2+} is found in plant sap and in the cell cytoplasm, not in the chloroplast. The highest Mg^{2+} concentration in plants are found in meristematic (new growth) areas for most plants (Adamec, 1995). The Mg^{2+} content of plants varies not only with species and varieties, but also somewhat at different age stages of the same plant. *Aldrovandra vesiculosa* continued to increase the calcium content as each part aged but the magnesium remained fairly stable with age of each plant part (Adamec, 1995).

Chlorophyll is essential for photosynthesis, the process by which green leaves synthesize carbohydrate, fats, proteins, etc. in the presence of sunlight. Iron is to hemoglobin as is magnesium to chlorophyll, the "blood" pigment of plants. They both actually have very similar structures and it's easy to see where the evolution of blood came from with a simple metal cation change. Plant dry matter usually contain 0.2-0.5% Mg^{2+}. It is relatively mobile in the plant. Magnesium plays an important role in the formation of carbohydrates, fats and vitamins, activates the formation of the polypeptide chain from amino acids and also aids in a number of physiological and biochemical functions including phosphate transport. It is required for maximum activity of energy phosphorylating enzyme in carbohydrate metabolism. Magnesium is also known to be essential for many energy reactions constantly taking place in plant cells and as an activator of several enzymes. Mg^{2+} ions are needed for enzymatic activity as well as for DNA and RNA synthesis (Horlitz and Klaff, 2000). Correct positioning of Mg^{2+} in the active site of the carbon fixing Rubisco enzyme involves addition of an "activating" carbon dioxide molecule to a lysine in the active site forming a carbamate. Formation of the carbamate is favored by an alkaline pH. The pH and the concentration magnesium ions in the fluid compartment (in plants, the stroma in the chloroplast) releases in the light. Upon illumination of the chloroplasts, the pH of the stroma rises from 7.0 to 8.0 because of the proton (hydrogen ion, H^{+}) gradient created across the thylakoid membrane. At the same time, magnesium ions (Mg^{2+}) move out of the thylakoids, increasing the concentration of magnesium in the stroma of the chloroplasts. Rubisco has a high optimal pH (can be >9.0, depending on

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Iron is to hemoglobin as is magnesium to chlorophyll, the "blood" pigment of plants. ....

"Magnesium plays an important role in the formation of carbohydrates, fats and vitamins, activates the formation of the polypeptide chain from amino acids and also aids in a number of physiological and biochemical functions ..."

the magnesium ion concentration) and thus becomes "activated" by the addition of carbon dioxide and magnesium to the active sites as described above. Generally, if the plant is deficient in magnesium, additions should correct the problem dramatically in most cases.

The exact mechanism of Mg uptake is not certain, but it seems likely to be via metabolically generated carriers. The general idea is that energy is used to carry ions across or through root membranes inside the plant. Magnesium is extremely mobile in plants but its movements into and within the plant is also affected by other ions. Potassium can hinder magnesium, not only in uptake at the soil-root contact level but also within cells at the enzyme level. The form of nitrogen in rooting medium has an influence on absorption and distribution of Mg. Ammonium (NH_4^+) may lower the Mg content in plants (Peet *et al,* 1985). The anion NO_3^-, in contrast may stimulate Mg uptake. The implication is that a nitrogen source containing some nitrate nitrogen may be preferable when other conditions are conductive to low magnesium uptake by plants. Generally low soil pH decreases Mg availability, and high soil pH increases availability. Stable isotopes such as Mg 25 may be used to track the movement of magnesium in plants by enriching the nutrients solution, but this has rarely if ever been done in aquatic plants. It would provide a nice tool to investigate many interactions with other nutrients inside the plant.

Main function and role in plants:

- Chlorophyll Formation**:** Chlorophyll is essential for food production process by every plant. Magnesium occupies the centre-spot in the chlorophyll molecule and thus is indispensable for photosynthesis by plants.
- Activation of Enzymes: In higher plants some important enzymes such as AMP pyro-phosphorylase, IMP-pyro-phosphorylase, Hexokinase, Glucokinase, Fructokinase and Phospho-Glycerate Kinase etc. are found to be activated by Mg^{2+}.
- Synthesis of Proteins and Chromosomes formation: Magnesium is a component of chromosomes (DNA and RNA) and polyribosomes (which are required for protein synthesis). This role makes Mg^{2+} a very important nutrient for plant growth.
- Carbohydrate Metabolism and Energy Transfer: Mg^{2+} takes part actively in the metabolism of carbohydrates and transfer of energy in the plant body. Its role in phosphate metabolism and plant respiration is well known.

Besides of all these activities magnesium also act as a catalyst in many oxidation-reduction reactions inside the plant tissues. It supports movement of iron (Fe) and helps plants in countering the bad effect of poor aeration. By exerting a positive influence on the strength of cell walls and permeability of membranes, Mg may increase crop resistance to drought and diseases. Magnesium exerts a synergistic effect of N uptake by crops. This is likely due to the ionic balance of $NH4^+$ and $NO3^-$. Too much of any nutrient ion can influence the plant's ability to photosynthesize at optimal levels. For example: the plant can block K^+/H^+'s inside the chloroplast with Mg^{2+}, this is markedly different than Mg blocking K^+ uptake from a solution(say your aquarium's water), or $NH4^+$ blocking Mg^{2+} uptake from a solution outside the plant cell. Plants need to be able to block ions to allocate them where they are needed once inside the plant, but that is quite different than internal regulation. This same type of confusion caused a misunderstanding with respect to K^+ blocking Ca^{2+} uptake in plants. A simple test adding high levels of K^+ with low Ca^{2+} on the same plant showed no evidence of inhibition of calcium uptake.

In recent years, considerable attention has been paid to the appearance of Mg deficiency by the application of potassium fertilizer. It is paradoxical in the sense that on one hand, application of fertilizer K^+ increases the yield and thereby the magnesium requirement of the plant and on the other hand there is an antagonistic effect of K^+ on Mg^{2+} uptake. In the literature, the antagonistic effect of K^+ on Mg^{2+} is widely reported. But reports of antagonistic effect of Mg^{2+} on K^+ are few. The antagonism between K and Mg^{2+} seems to be confined to the deficiency of the other. In soils deficient in K^+ and Mg^{2+}, the deficiency of Mg^{2+} should be corrected before

Magnesium is also known to be essential for many energy reactions constantly taking place in plant cells and as an activator of several enzymes.

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applying K+ fertilizer. With adequate Mg^{2+} in the medium, even though Mg^{2+} concentration in the plant falls with increasing rate of K+ application, it can stay above the critical level. There was a strong positive relationship between the P and Mg^{2+} concentration in rice ($r = 0.70$ to 0.97). These results suggest that the P deficiency in soil does not only affect the P nutrition of rice, but may also affect the uptake of other nutrients, especially that of K+ and Mg^{2+}. When deficiencies occur, the older leaves are generally affected first. The deficiency symptoms may include the following: (1) loss of color between the leaf veins (*Anubias sp*), beginning at the leaf margins or tips and progressing inward. This can give the leaves a striped appearance. (2) Leaves may become brittle and cup or curve upward and they may become thinner than normal (more common in aquatic plants). (3) Tips and edges of leaves may become reddish-purple in cases of severe deficiency (especially with cotton). (4) Low leaf Mg can lead to lowered photosynthesis and overall plant stunting (common in a few aquatic species). After 20 days of initial growth, Mg deficiency in sago pondweed grown from turions is evidenced by reduced weight and slight chlorosis; this reflects the function of Mg in the chlorophyll molecule (Devlin et al.1972).

<u>The Role of Magnesium in aquatic systems</u>:
Natural sources contribute more magnesium to the environment than do all human activities combined. Magnesium is found in algal pigments and is used in the metabolism of plants, algae, fungi, and bacteria. Freshwater organisms need very little magnesium compared to the amount available to them in water. Because there is such little biological demand for magnesium compounds and because they are highly soluble, magnesium concentrations in water bodies fluctuate very little. Florida lakes had average magnesium concentrations ranging from 0.02 to over 600mg/L. Magnesium concentrations are higher in water bodies where inflowing water has been in contact with dolomite. Numerous studies have shown that Mg^{2+} availability to the plant decreases at low pH values. On acid soils with a pH below about 5.8, excessive hydrogen and aluminum can influence Mg^{2+} availability and plant uptake. At high pH values (above 7.4), excessive calcium may have an overriding influence on Mg^{2+} uptake by plants. Although no ideal basic cation saturation range in soil has been scientifically proven at which crop yields are maximized, a rule of thumb may be used to ensure that Mg^{2+} is not limiting. For soils with a cation exchange capacity (CEC) higher than about 5 milliequivalents (ME) per 100 grams, it may be desirable to maintain the soil Ca^{2+} to Mg^{2+} ratio at about 10 to 1. Most aquatic references point to a ratio of 3:1 to 4:1. Ca: Mg The need for this "ideal" ratio has never been verified by various research efforts. Therefore, as fertilizer recommendations are developed, emphasis should be placed on providing adequate amounts of magnesium in soils and water rather than the maintenance of a ratio.

"Freshwater organisms need very little magnesium compared to the amount available to them in water. ..."

<u>Table 1: Common Magnesium Sources</u>

Material	Mg%	Water Solubility
Dolomitic lime	6-12	No
K-Mag	10-11	Yes
Magnesium chloride (solution)	7.5	Yes
Magnesium hydroxide	40	No
Magnesium nitrate	16	Yes
Magnesium oxide	56-60	No
Magnesium sulfate	10-16	Yes

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Magnesium's role in aquatic macrophyte nutrition and horticulture.

Generally aquarist use MgSO4 * 7H2O (Do not forget the water when making dosing ppm calculations!), their tap water (somewhat variable) or Dolomite for Mg2+ sources. The preferred source of some nutrients such as potassium (K), calcium (Ca), magnesium (Mg), sulfate (SO4), sodium (Na), and (Cl) appears to be the water column (Barko et al, 1991). Submersed macrophytes make use of both aqueous and sedimentary nutrient sources, and sites (roots vs. shoots) of uptake are related, at least in part, to nutrient-specific differences in sediment compared to overlying water nutrient availability. In other words, submersed plants are operating like good opportunistic species should operate; they take nutrient supplies from the most available source.

Figure 1. Biopathways of various types of Chlorophyll a, b, c, d, e and g

Mg-Protoporphyrin IX

↓

Protochlorophyllide → **Chl-c_2** → **Chl-c_1**

↓

Chlorophyllide *a*

↓

Chl-*b* ← **Chl-*a*** → **BChl-*a*, BChl-*b*, BChl-*g***

↓

BChl-*c*, BChl-*d*, BChl-*e*

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Table 2. Absorption spectrum of various chlorophyll types.

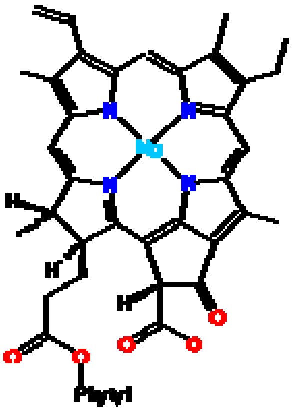
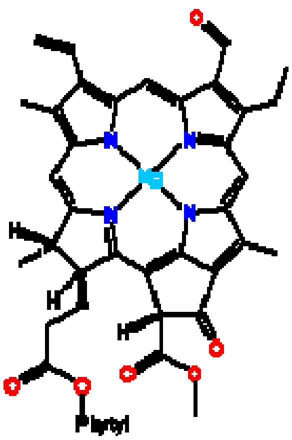
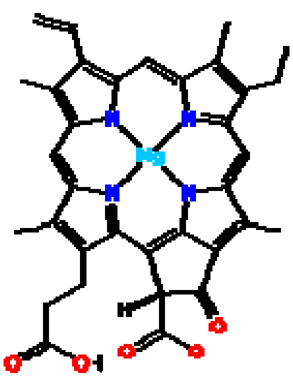
Chlorophyll type / LIGAND entry	Occurrence	Absorption maxima (nm)
 Chl-*a*	• Photosystem I of algae and higher plants • Photosystem II of algae and higher plants	660-725
 Chl-*b*	• Photosystem I of algae and higher plants • Photosystem II of algae and higher plants	640-695
	• Light harvesting proteins in diatoms, dinoflagellates, brown macrophytic algae and cryptophytes	630-740

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Table 2 Continued. Absorption spectrum of various chlorophyll types.

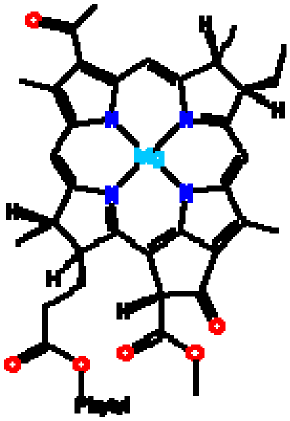
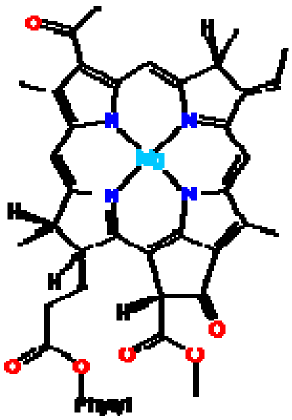
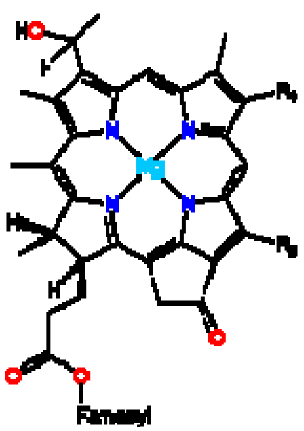
Chlorophyll type / LIGAND entry	Occurrence	Absorption maxima (nm)
 BChl-*a*	• Fenna-Matthews-Olson complex • Light harvesting complex II of purple bacteria • Photosynthetic reaction centre of purple bacteria (*Rb. sphaeroides*)	800-910
 BChl-*b*	• Photosynthetic reaction centre of purple bacteria (*Rps. viridis*)	1020-1035
	• Light harvesting complexes of filamentous photosynthetic bacteria and green sulfur bacteria	745-760

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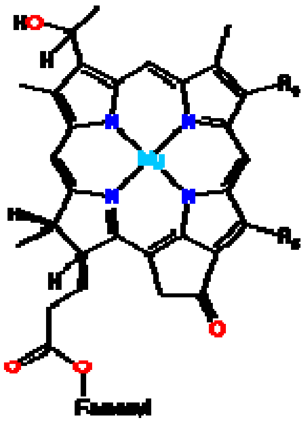
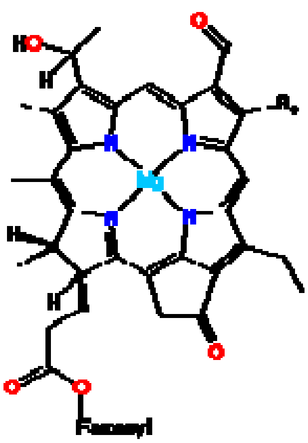
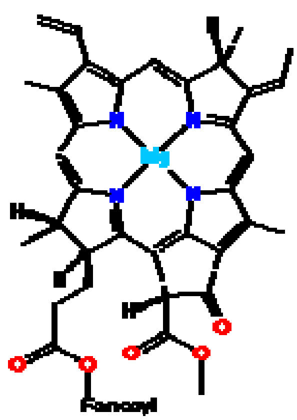
Table 2 Continued. Absorption spectrum of various chlorophyll types.

Chlorophyll type / LIGAND entry	Occurrence	Absorption maxima (nm)
 BChl-*d*	• Light harvesting complexes of green and brown sulfur bacteria	725-745
 BChl-*e*	• Light harvesting complexes of green and brown sulfur bacteria	715-725
 BChl-*g*	• Photosynthetic proteins of *Heliobacterium*	788

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Magnesium's role in aquatic macrophyte nutrition and horticulture.

By altering slight changes in the molecule, plants, algae and bacteria can dramatically change the ability to absorb light, but in each example, they all have the same nitrogenous ring with a central magnesium cation in its center. Certain other ions can be taken up by some plants without being used. Halophytes, for example, take up Na^+ only because they have a stronger resistance against it than other plants. They have thus opened up an ecological niche for themselves. Some plants appear adapted to handle wide ranges of alkalinity whereas some species are sensitive. In general, Mg^{2+} and Ca^{2+} but not Silicon (SiO_2) is found in the ashes of horsetail and in the shoots of grasses sometimes even in considerable amounts. But it is not essential. Only diatoms and some other algae need it for the production of their shells. Some marine algae (especially brown algae) accumulate iodine but nothing is known about its significance.

The average share that the mineral elements have in the dry weight of plants is:

NO_3^-: 1- 3%
K^+: 0.3- 6%
Ca^{2+}: 0.1- 3.5%
HPO_4^{2-}: 0.05- 1%
Mg^{2+}: 0.05- 0.7%
SO_2^{2-}: 0.05- 1.5%.

You will note that these are wide ranges. The range will still produce excellent growth, and may be dependent on the plant species in question. While K+ has been discussed as a Mg2+ blocker in chloroplast, we should also consider relationship between leaf K+ and leaf magnesium because as K+ becomes more available, leaf magnesium concentrations for optimal growth increase. In general, ratios of about 4:1 (K:Mg) or greater are often associated with the appearance of Mg deficiency symptoms. Satisfactory ratios of Ca:Mg on an equivalent basis may range from 1:1 to 20:1, provided that adequate Mg is present.

Mineral ratios in aquatic plants:

Population n= 10	**N**	**P**	**K**	**Ca**	**Mg**	**Na**	**S**	**Fe**	**Ash contents**
Total mean	**2796**	**1076**	**1504**	**1677**	**797**	**732**	**304**	**523**	**13.9**

Aldrovandra mineral weights for nutrients (mg per 100 grams of dry weight). You'll note the high P relative to N, roughly a 2.6 to 1 ratio. This is not surprising, this is a carnivorous plant, living in generally low N aquatic environments and supplementing its nitrogen from insects caught in the traps. K and Ca are rough 2:1 ratios and the Fe content is rather high as well. But like many plants, one species can have marked differences from another. So only by comparisons of several species do we have a representative view of a general consensus about any ratio present, environment plays a role as well but so does the plant, they are able to maintain nutrient homeostasis under a wide range of water column nutrient concentrations.

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Table 4. Mineral nutrient content in shoot segments of successive ages of adult *A. vesiculosa* and in turions. Last living whorls were still yellow-green, while the successive first dead ones were brownish. Data given in % of dry mass.

Shoot segments	N	P	Ca	Mg	K	Na
Apices	1.31	0.48	0.17	0.16	1.86	0.35
1st-6th whorls	0.98	0.30	0.32	0.21	2.11	0.59
7th-10th wh.	0.66	0.23	0.38	0.16	2.36	0.84
11th-14th wh.	0.76	0.21	0.50	0.16	2.56	1.03
15th-18th wh.	0.77	0.16	0.49	0.16	1.93	0.86
last living wh.	0.10	0.10	0.75	0.16	2.30	0.56
1st dead whorls	0.09	0.04	1.10	0.15	0.65	0.19
turions	1.76	0.58	0.13	0.15	0.87	0.05

This is the same table presented for Calcium's section in Dec 2005's BarrReport. Unlike calcium, magnesium is relative stable with only slight build up as the plant ages.

Table 5. Elemental composition of above ground green tissues of sago pondweed.

Element	Unit of measure[a]	Range or single observation (reference[b])
Carbon (C)	%	35.7-39.5 (4)
Calcium (Ca)	%	0.16 (5)-22 (1)
Chlorine (Cl)	%	0.55-2.35 (7)
Cobalt (Co)	ppm	2.8 (8)-26.0 (4)
Copper (Cu)	ppm	8 (8)-103 (3)
Iron (Fe)	%	0.03 (5)-5 0 (1)
Potassium (K)	%	0.59 (1)-5.34 (5)
Magnesium (Mg)	**%**	**0.05 (9~6.08 (1)**
Manganese (Mn)	%	0.01-0.53 (5)
Molybdenum (Mo)	ppm	<65-<110 (4)
Nitrogen (N)	%	1.24 (5~6.01 (10)
Sodium (Na)	%	0.10 (9)-4.00 (5)
Phosphorus (P)	%	0.07 (11)-1.11 (5)
Silicon (Si)	%	0.5-1.05 (1)
Zinc (Zn)	ppm	12 (1~340 (6)

Measurements refer to oven-dry matter in whole plants or various tissues, except Va, which refers to ash. High levels of Ca, Fe, and Mg likely are caused by external encrustations. Reference: (1) Kollman and Wali 1976 (2) Peverly 1985;(3) Adams et al. 1973; (4) Neel et al. 19i3; (5) Van Vierssen 1982b; (6) Adams et al. 1980; (7) Ozimek 1978; (8) Varenko and Chuiko 1971, cited in Hutchinson 1975, (9) Riemer and Toth 1968; (10) Ho 1979; (11) Howard-Williams 1981, (12) Petkova and Lubyanov 1969, cited in Hutchinson 1975.

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Conclusion:

Magnesium is far more important to in terms of plant health and growth than many aquarist may realize, but plants do not need large amounts to grow well. Often with imbalances in the GH, generally the GH is all calcium, we will see evidence of magnesium deficiencies. A simple test to see if the plants are deficient in CO2, N, PO4 or Mgt, is to simply add more for 2-3 weeks time and observe the plants. Adding a little bit more will do no harm to plants and will relieve any stress that might be present so the aquarist can rule that nutrient out for the issue they have with aquatic macrophyte growth. In the past, I've suggested using an all in one type of GH builder and K+ salt mix, K2SO4, CaSO4, and MgSO4 works well and targets all 4 macro nutrients that a plant might need. These nutrients can be dosed once a week for good results, whereas some nutrients like N and P and Traces are better dosed in smaller amounts more frequently. Ca, K and Mg are often blamed for many unknown plant related problems, but CO2 and NO3 should be addressed with some absolution prior to dosing more Mg or Ca etc.

More study is needed for Mg's effect on certain plant species in harder and softer waters(KH) as well maximum ppm before toxicity becomes an issue. A number of aquarist have had some issues with their growth and have found adding MgSO4*7H2O has solved their issues, but the plants do not need a great deal and gain little from that. 1.5 grams per 80 liters once a week is adequate. In some cases, it is difficult to induce severe Mg deficiency in many plant species and each has a different response. Rather than attempting to isolate every plant and possible combination, it may be wise to focus on known plants in your tank that are sensitive to variations. These indicator plants are very useful and are better if terms of horticulture than test kits. All you are required to do is slowly manipulate one nutrient over 3-4 weeks to note the effect on each plant species, from then on, you know what to look for and can dose as needed. No test kit is needed but you will need to dose the same consistent amount each time and vary that amount as needed. The aquarist can also use a test kit and measure the Mg and Ca as well in conjunction, but the focus should be on plant health, not some theoretical ideal concentration measured with a cheap hobby grade test kit. It is much easier and consistent for the hobbyists as well as the people helping them to suggest ¼ teaspoon once a week per 80 liters of water. In the EI article and the list of recommended parameters and levels, it is suggested to add SeaChem Equilibrium (Ca:Mg ratio of 3.3:1) or Greg Watson's GH builder(lower ratio, more Mg) if there is a suspected deficiency. Even if the GH is above 3-5 degrees, it may be all calcium, thus lacking Mg and causing an issue. This has caused problems for a few aquarist. Simply adding a little extra Mg SO4*7H2O can quickly rule this out.

Testing: You can test for Mg and Ca but be careful to convert them from CaCO3 equivalents. GH measures the total multivalent ions (mostly Ca^{2+} and Mg^{2+} typically) and assume that they are all from CaCO3 and converts it into CaCO3 ppm in most test kits.

Example:
GH 12*= 213ppm GH 8*=142ppm

Calcium hardness:

Ca 150ppm Ca 120ppm=> Subtract to get Mg

Mg 63ppm Mg 22ppm

Ca 60ppm 48ppm (divide your numbers by 2.5)
Mg 15ppm 5 ppm (divide your numbers by 4.1)

We need little Mg but it's still critical and often times folks over look it or perhaps go overboard with MgSO4, you simply need a little bit weekly to be successful. If you have not tried adding it, try adding a small amount like the ¼ teaspoon once a week just to see, it should not hurt the plants at this dosage and may help. Give it a week or so, you should see a difference fairly quickly due to its highly significant role.

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