PHOSPHORUS IN THE MARINE AQUARIUM

By Adolf F. Klostermann

■ Over the past three years we have experimented with two methods of phosphorus removal from the marine aquarium. The methods used were specifically chosen not to alter the chemical composition of the captive water over prolonged periods of time. Before the experiments are detailed, we'll provide a brief overview of the sources, biological distribution, and chemical speciation of phosphorus in seawater.

A natural source, of course, is organic phosphorus. Because of the element's absolute necessity in many metabolic processes, including photosynthesis, algae, invertebrates and vertebrates incorporate it into many organic compounds; some of the generally known being ADP and ATP, adenosine di-and triphosphate respectively. As organisms die or food substances decay, a large percentage of the phosphorus is released in a form of orthophosphate due to both bacterial oxidation and hydrolysis. However, some of the organic phosphorus does remain bound due to the rather low redox potential of natural waters. As biological activity proceeds within a closed system, phosphorus is constantly recycled. And, more often than not, the producers far exceed the requirements of the consumers, causing an increase in the dissolved concentration of phosphates.

Another source of phosphorus is the direct addition of ionic phosphates from additions of freshwater. Although we have measured the ortho-and polyphosphate concentrations in a number of municipal water sources and found very little present, this should not be considered as the norm. The quality of the water may vary over time and especially from different localities.

A third source is via chemical additives that are purposely introduced into the water. While we were experimenting with different vitamin preparations, we found that some, expecially B_{12}, contained calcium phosphate as a filler. These preparations were not specifically intended for aquarium use, they were prepared for human consumption.

Last, but definitely not least, is the use of activated carbons that contain phosphates. We have found a number of carbons intended for aquarium use that contain a significant amount of phosphates.

Even if we gain control over all external inputs of phosphorus, we still have to contend with the natural and constant generation of phosphates by the biological activity within the system. Although phosphorus is essential, an overabundance is not beneficial. Since the main consumers of mineralized phosphorus are the alga, and their protoplasmic makeup has an average atomic ratio [1] of 1 part phosphorus, 16 parts nitrogen and 106 parts carbon, the surrounding water should exhibit that ratio approximately. If we use the total carbon available (24mg), the phosphorus concentration becomes 1.8mg/1 as phosphate. If we only use the free carbon dioxide available, the phosphate concentration becomes 0.008mg/1. The latter is probably more appropriate and closely simulates measured data from unpolluted water. When the C/N/P ratio is varied, some species of algae are discouraged while others may flourish. Generally speaking, conditions are considered less eutrophic when high N/P ratios are present, although the actual concentrations are also of importance. Also of importance is the ability of phosphate to change the surface of calcite to apatite at the pH normally encountered in the marine environment. This definitely interferes with the normal calcification process of stony corals.

If we disregard the organic and polyphosphates, the form (species) of mineralized inorganic phosphorus present in the water is pH dependent. The total phosphorus may be expressed by the following relationship:

$$P_T = H_3PO_4 + H_2PO_4^{-1} + HPO_4^{-2} + PO_4^{-3} \quad (1)$$

Where H_3PO_4 is molecular phosphoric acid, $H_2PO_4^{-1}$ is dihydrogen phosphate, HPO_4^{-2} is hydrogen phosphate and PO_4^{-3} is phosphate. With the use of dissociation constants, adjusted for saltwater, the concentration of the species may be determined for a given pH. At a pH of 8.3, salinity and temperature of 35°/oo and 25°C respectively the percentages of the different species are as follows:

$$H_3PO_4 = 0$$
$$H_2PO_4^{-1} = 0.37$$
$$HPO_4^{-2} = 64.5$$
$$PO_4^{-3} = 35.1$$

When the pH is raised to ten, phosphoric acid and dihydrogen phosphate are nearly zero. Hydrogen phosphate drops to 3.5% and phosphate increases to 96.5%. At a pH of 6 the concentration percentages become:

$$H_3PO_4 = 0.002$$
$$H_2PO_4^{-1} = 53.4$$
$$HPO_4^{-2} = 46.5$$
$$PO_4^{-3} = 0.1$$

At the pH of standard seawater, 65% of the phosphate is present as hydrogen phosphate (HPO_4^{-2}). As the pH falls, both hydrogen phosphate and phosphate decreases. As the pH rises, all species except PO_4^{-3} decrease. The percentages thus calculated are the expected concentrations of the species at equilibrium and are comprised of both bound and free ions. This speciation is most likely of biological importance; some forms being preferred over others by consumer organism. It is of definite significance when the elimination of excess phosphate is to be considered.

To reduce phosphorus we must use a substance that, when added to the water, causes a high degree of saturation and

TABLE 1

	Start	$Ca(OH)_2$ Dose	Finish	
pH	8.3	10	8.9	
Alk	10	19	9	grains/gal.
Ca	400	460	392	mg/l
Mg	1200	1200	1200	mg/l
C_T	35	35	24	mg/l
P_T (as PO_4^{-3})	3.5	3.5	0.2	mg/l

EQUATIONS 2-6

$Sr(NO_3)_2$	=	$Sr^{2+} + 2NO_3^{-1}$	(2)
$NO_3^{-1} + 1/2H_2O + 5/4(C)^*$	=	$1/2N_2(gas) + 5/4CO_2 + OH^{-1}$	(3)
$5/4CO_2 + 5/4H_2O$	=	$5/4H_2CO_3$	(4)
$5/4H_2CO_3 + OH^{-1}$	=	$1/4H_2CO_3 + HCO_3^{-1} + H_2O$	(5)

If equations (2) through (5) are combined we obtain:

$Sr(NO_3)_2 + 3/2H_2O + 5/2(C)^* = Sr^{2+} + 1/2H_2CO_3 + 2HCO_3^{-1}$ (6)

*(C) is the carbon used as the electron donor for nitrate reduction, and for this example, is at an oxidation state of zero.

EQUATIONS 7 & 8

$1/2Sr^{2+} + 1/2HPO_4^{-2}$	=	$1/2SrHPO_4$(solid)	(7)
$1/2Sr^{2+}$ $1/2CO_3^{-2}$	=	$1/2SrCO_3$(solid)	(8)

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induces precipitation. If calcium is used as the cation there are a number of solids that may be formed that are generally insoluble. Calcium orthophosphate ($Ca_3(PO_4)_2$), and a number of forms of apatite. $Ca_5(PO_4)_3OH$, $Ca_{10}(PO_4)_6(OH)_2$, or $Ca_{10}(PO_4CO_3)_6F_2$. Each compound contains phosphorus in the form of PO_4. However, the PO_4^{-3} ion accounts for only 35% of the total phosphorus at a pH of 8.3. If a considerable amount of phosphorus is to be eliminated the pH has to be elevated to nearly ten, where the PO_4^{-3} ion is 95% of the total.

In our experiments we used a five gallon denitrification chamber to elevate the pH. We did not proceed much beyond ten to prevent the precipitation of magnesium. The chemical used was calcium hydroxide. The initial phosphorus concentration, all expressed as if it were PO_4^{-3}, was 3.5mg/1 in a 55 gallon tank set up in May of 1986. The tank has a deep gravel (calcerous) bed, and when a small amount was dissolved with hydrochloric acid to liberate any chemisorbed phosphate, the resulting concentration was 7mg of phosphate per gram of calcerous gravel. If all the calcerous substrate, roughly 30 kg, contained the same percentage of phosphate, we would have to deal with a considerably greater quantity than 3.5mg/1, because precipitates would re-equilibriate as the dissolved concentration drops.

In April of 1988 we commenced to add sufficient calcium hydroxide to the denitrification chamber to raise the pH to between 9.5 and 10. Initially we experienced very little precipitation. After a 24 hour period the pH had fallen off only slightly, as had the alkalinity and phosphates. This led to the conclusion that the bulk of the phosphates and carbonates were generally bound and could not readily precipitate. However, as we repeated the cycle at 24 hour intervals the alkalinity and phosphates started to decline. The concentrations of the ions in question at the beginning and end of a cycle are listed in Table 1 (see page 27).

As time progressed, the phosphate concentration dropped to nearly zero (in the denitrification chamber) within 8 hours. The cycle was stopped when the alkalinity was equal to the alkalinity just prior to the calcium hydroxide dose. This prevented any net loss of calcium, and the loss in carbon was automatically replaced with respiratory and atmospheric carbon dioxide as the five gallons of water were remixed with the 55 gallons after each cycle. This process was continued from April until October of 1988 and the phosphate concentration flattened out at 0.2mg/1. We were not able to reduce the concentration any further since, during mixing of the two waters, the pH drop in the denitrification chamber allowed some of the metastable solids to redissolve. Also, it became somewhat cumbersome trying to combine the denitrification rates with the precipitation rates.

We searched for an alternate method. Looking through the solubility tables of

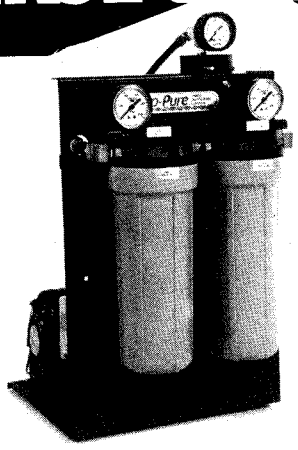
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Bicarbonate	92%	Phosphate	99%
Calcium	98%	Polyphosphate	99%
Copper	99%	Potassium	96%
Iron	99%	Silica	90%
Magnesium	98%	Sodium	96%

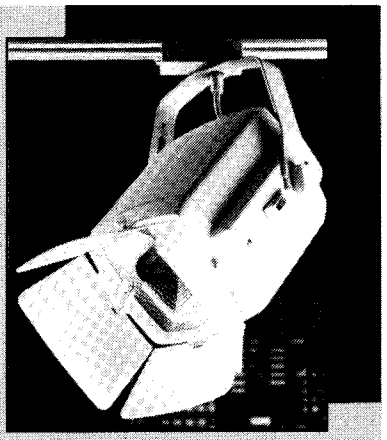
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chemical compounds we found that strontium hydrogen phosphate was generally insoluble. And, since 65% of the dissolved phosphates are in that form at a pH of 8.3, the pH would not have to be raised. Also, strontium carbonate is less soluble than either calcite or aragonite, and the excess would precipitate as the carbonate. If we used the proper anion there would be no net change in the water chemistry with prolonged use of this method. The nitrate was chosen as the anion. As strontium nitrate is added to the denitrification chamber the nitrates are converted to N_2 (nitrogen gas) along with a generation of hydroxyl (OH^-) ions. The latter, in contact with dissolved carbon dioxide, generate carbonate alkalinity (HCO_3^{-1}). The overall process is detailed in Equations 2 through 6.

(See page 27.)

This shows that by adding one molecule of strontium nitrate, via denitrification, we produce one strontium ion, two bicarbonate ions and one half molecule of dissolved carbon dioxide. The strontium precipitates as the hydrogen phosphate and as the carbonate as shown by equations (7) and (8) (see page 27).

If we add 1/2 of an ion of HPO_4^{-2}, which was initially present, to the right hand side of equation (6) and subtract the right hand side of equations (7) and (8) we obtain a result of:

$$H_2CO_3 + HCO_3^{-1}$$

The H_2CO_3 represents the dissolved carbon dioxide and can be expelled, leaving only water. Therefore, during the process of removing the hydrogen phosphate ion we have added two bicarbonate ions. If the phosphorus was initially introduced via biological oxidation, each hydrogen phosphate ion must have been associated with two hydrogen ions. If we combine the two hydrogen ions with the remaining two bicarbonate ions we obtain two molecules of dissolved carbon dioxide. This CO_2 may be expelled or used for photosynthesis, and the net change in water chemistry is zero.

These equations may be somewhat cumbersome, but they do demonstrate that the phosphorus removal utilizing this technique does not leave accumulating ions. Furthermore, the precipitates formed do not redissolve at the pH normally encountered in the marine environment. If strontium chloride or sulphate is used in lieu of the nitrate, either chlorides or sulphates accumulate and the alkalinity is reduced as strontium carbonate precipitates. We have used strontium nitrate in the experimental tank since March of 1989 and the phosphate level at this date is less than can be detected with wet chemistry analysis having a resolution of 0.01 mg/l of phosphate. The daily input of strontium is equivalent to 100mg as the ion, and translates to 0.48 mg/l per day in the 55 gallon tank. This dose is roughly one twentieth of the typical seawater strontium concentration. We also have taken another assay of the calcerous gravel and found no trace of phosphate.

to page 208

ADVERTISERS INDEX

Advanced Aquatic Technologies 185
American Acrylic 47, 70-71
American Fish Farming Research 114
American Marine Inc. 182
Anchor Bay Aquarium 110
AquArt 185
Aqua Haven 110
Aquanetics 40, 159, 182
Aquarium Design & Engineering 51
Aquarium Instruments 108
Aquarium Lights 141
Aquariums Plus 64, 115
Aquarium Products 15, 39, 87, 169
Aquarium Systems ..... 4th Cover
Aqua Rock Co. 99
AquaSys Reg'd 14
Aquatic Gardens 164
Aquatic Life 3, 36
Aquatic Maestro 183
Aquatic Specialists 199
Aquatic Supply House 41, 52, 200-201
Aquatronics 37, 148
Aquatropics 149
Aquatropics Marinelife Supply Inc. 124
Back To Nature Filtration 54
Baytech 20
Bay View Aquariums 4
Biotope Life Support Systems 131
Bob Kelton 6
Boyd Enterprises 22-23
Brantana Aquatics 114
Buckaroo Marine 24
By-Rite Pet Supplies 203
California Reef Specialists 128, 145
Caribbean Creatures 150
CaribSea 184
C & B Distributors 44
C.F. Bowman 136
Champion Supply Co. 143
Charles C. Thomas — Publisher 44
Clear Choice Filters 101
Coral Fish Hawaii 94
Coral Sea Filter 137
C & S Services 168
Cumberland Pictures 948
Custom Sealife 151
Daleco Master Breeder Products 154-155
Dale Jordan 46
Dan Ogrizek 65
Debron Aquatics 62
Delaware Aquatic Imports 184
D.G. Enterprises 101
Discount Aquarium 196-197
Discus Haven 46, 140
DKM Products 29
DLS Aquatics ..... 77, 105 thru 107
Dream Filtters Co. 36
Emperor Aquatics 12
Endich, Inc. 30
Energy Savers Unltd., Inc. ..... 49, 78 thru 81, 122, 206
Eugene G. Danner, Inc. 82
Exotic Aquaria Inc. 58
Exotic Aquatics of Utah 132-133
Exotic Fish 198
Exotic Specialists 164
FAMA Anthology 162
FAMA Subscription 63
Filtronics 85
Fin & Feathers Pet Shop 86
First Class Marine Fish 44
Florida Aqua Farms 11
Florida Bay Brand 11
Florida Brine Shrimp 25
Florida Exotic Fish Sales 86
Gull Mfg. 104
Gwynnbrook Farm 195
Rolf C. Hagen (USA) Corp. ..... 3rd Cover
Hamilton Technologies 88
Hawaiian Marine Imports, Inc. ..... 2nd Cover
HBH Plastics 160-161
Icetronics, Inc. 99
Ichthy Tech 44
Imperial Discus 141
Imperial Reef 183
Innovate Corp. 146-147
John Shilton 89
Joseph Gargas 28
J.P. Burleson 13, 109
Keith Wolos, Inc. 183
Kent Marine 3
Kordon 26, 121
Lifeline 95
Lifereef Filter Systems 125
Life Support Live Line 76
Little Ocean Prod. 45
Living Reef 188-189
Living Sea Aquarium 183
Lower Keys Aquatics 46
Lumar International 112
Mac's Discus 91
Mail Order Pet Shop 166-167
Majestic Pet Supply 186-187
Mandrin Care Specialties, Inc. 69
Marc Weiss 10, 68
Mardel Laboratories, Inc. 73
Markus Products 125
Marine Invertebrates 74-75
Marineland Aquarium Products 31
Marine Technical Concepts 98
Marck's Aquarium Pet World 142
Mark's Marine Fish, Inc. 120
Mid-Jersey Pet Supply 111
Mile High Aquarium Products 202
Mini-Reef Traps 12
Motorsport 51
Natural Aquariums 152
Nature Pet Centres Inc. 139
Nature Reef 181
Natures World 112
Nautilus Aquarium Supply, Inc. 38
North Olmstead Aquarium 168
Now Playing With Fish 194
Ocean Nutrition 55, 57, 159
Oceanic Systems 61
O.S.I. Marine Lab, Inc. 42
Peirce Enterprises, Inc. 100
PEP Engineering 156-157
Pet Warehouse ..... 192 thru 194
Pisces Coral & Fish 110
Poly-Bio Marine 67
Precision Aquarium Testing 90
Python Products 21
Quality Live Rock 142
Quality Marine 190
Rainbow Plastics 97
Redi Oxygen 168
Reef Aquarium Designs 64
Reef Concepts 194
Reef Displays 129
Reef Encounter 5
Reef Island Aquarium Corp. 115
Reefline By Leon and Sons 68, 72
Reef Patterns 163
Reef Scapers 51
Reef Supply, Inc. 46
Reef Tech 102
Regal Discus 104
Salt Watr Solutions 84, 136
Sandpoint Aquarium Products 72
Savko Plastic Pipe 51
Sea Chem 130
Sealife Imports 174
Sea of Cortez Handcaught Marines, Inc. 180
Sea-Thru 53
Shamrock Aquatics 153
Shangrila Discus 198
Simos Aquaria 120
S & S Aquarium 14
Spectacular Sea Systems 92-93
Summit Aquatics, Unltd. 30
Superior Aquatic Technology ..... 116 thru 118
Tetra Sales USA 103
That Fish Place ..... 170 thru 173
The Aquarium 178-179
The Art Game 18
The Discus Expert 120
The HowTo Co. 195
The Lettuce Clip 190
The Pet Book Shop 174
Thiel Aqua Tech 50, 144, 165
Tideline 28
Today's Aquarist 120
Tropical And Marine Paradise 151
Tropical Fish Environment 165
Tropical Imports 140
Tropical Pumps Co. 126
Tropic Reef Products 35
Two Little Fishies 89
Ultramarine Enterprises 60
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from page 206

shrimp recently and it ignored them. Aside from the bristleworm problem, everything is doing very well, but I would like to keep anemones and be rid of the worms.

Sincerely,
Larry Clark
Vancouver, Washington.

Hey, if the worms destroy anemones in a few days, you might try baiting a nylon stocking with an anemone! I'm only half serious with that recommendation, Larry. I do have a couple more suggestions for you, but that's all. As for natural predators, I am aware of a couple more you might try, but cannot guarantee that they will be interested in your worms either. The adorable bird wrasse has a reputation for eating bristleworms, so you might want to give it a try. Likewise the arrow crab is also supposed to have a taste for them. Arrow crabs tend to grow large and threaten small fish, but otherwise they are pretty tame. If your rocks are tightly packed, Larry, even if you removed the substrate as I suggested, then there will always be a large refuge area for the worms where the predators can't get at them . . . a more open reef structure helps prevent this. Finally, I have noticed that a sudden drop in specific gravity (say, from 1.022 dropping to 1.018) will sometimes drive worms out into the open where they may be removed easily. I worry about making that kind of recommendation because while I know that I can safely drop the S.G. in an aquarium, I don't know if you have the experience to do it as safely . . . so be careful if you wish to try it.

Well, I had planned to talk about iodine in more detail, but I got a little carried away on the lateral line topic, so you will have to wait, . . . so what else is new?

PHOSPHORUS

from page 30/27

Naturally, no seawater has been replaced in this system since the onset of the experiments. We have since applied this method to a larger system, 275 gallons, and have phosphate levels of less than 0.1. Also, we have a number of systems in the field that have equally good results.

In summary, the two techniques described for phosphate removal do not alter the water chemistry of a captive system. The latter method is more advantageous because precipitation takes place at a nominal pH. Furthermore, strontium is required, to what extent and for what specific function is not completely understood, by some calcifying organism. It is possible that the affinity of strontium for hydrogen phosphate prevents any formation of apatite and, in turn, allows for uninhibited deposition of calcium carbonate. Who knows?

Werner Stumm and J.J. Morgan, Aquatic Chemistry, John Wiley Sons, N.Y. 1981.