Phosphate - What is it and why should you care?

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By Randy Holmes-Farley

Mention phosphate to a reefkeeper and the images that come to mind are often those of a tank overrun with algae. In truth, phosphate can be a difficult nutrient to limit in a closed reef system. But what exactly is phosphate, where does it come from and how can one deal with it?

Inorganic Phosphate
Let's start with the "simplest" form of phosphate: inorganic orthophosphate (sometimes called Pi by biologists). Figure 1 shows the various forms of orthophosphate that exist in water. In more acid solutions (low pH), those on the left predominate, and in more basic solutions, those on the right predominate.

In seawater, we are stuck smack dab in the middle, and orthophosphate takes all three of the right-hand forms (with very little present as phosphoric acid). In fact, seawater at pH 8.1 contains 0.5 percent H2PO4-, 79 percent HPO4- and 20 percent PO4--, although one should keep in mind that all of these forms interconvert many times per second. Consequently an individual phosphate ion will probably take all of these forms faster than you can say phosphate. The relatively large proportion of PO4-- is important and may surprise many people, as less than 0.1 percent would be present in freshwater at pH 8.1.

Why the difference? That's a bit complicated. A small part of the effect has to do with the presence of all of the other ions in solution (in other words, the ionic strength). These other ions effectively stabilize the more highly charged forms of phosphate. In a sense, as the salt concentration is increased, it is increasingly more likely that one or more positively charged ions are in close proximity to the highly negatively charged PO4--, thereby stabilizing it through ionic interactions. The more highly charged the species, the more it is stabilized by this effect, causing PO4-- to increase in concentration relative to the other forms of phosphate.

This general ion effect, however, does not fully explain the large amount of PO4-- present. More specific interactions with calcium and magnesium also stabilize the PO4--, and help to explain the large concentration. In fact, in seawater only 0.2 percent of the PO4-- is in the form of "free" phosphate ions. The remainder is ion-paired to either calcium (73 percent of the PO4--) or magnesium (27 percent of the PO4--). Both H2PO4- and HPO4-- also form such ion pairs, but to lesser extents. Consequently, in natural seawater at pH 8.1 we have the breakdown of phosphate species that is shown in the table below.Table ISpeciesRelative
ConcentrationH3PO4<0.1H2PO4-0.46H2PO4-Ca++0.04H2PO4-Mg++0.004HPO4--39.0HPO4--Ca++3.8HPO4--Mg++36.3PO4---0.04
100

Phosphate can also take other inorganic forms (Figure 2). While these are not typically of significance in natural seawater, they may be present in things that get added to our tanks. There are dozens of these compounds, the most common of which are the short linear polyphosphates (such as pyrophosphate and tripolyphosphate) and the three- and four-membered rings (such as trimetaphosphate and tetrametaphosphate). Any of these that get into your tank will likely break down into orthophosphate.

These polyphosphates are used industrially to bind metals, as was done historically in laundry detergents. In that use, they form soluble complexes with calcium and magnesium, softening the water and permitting greater cleaning action. The amount of such phosphates getting into natural waterways from laundry detergents, however, was high enough that algae blooms resulted, and the practice is now illegal in many places.

Unfortunately for those of us trying to master phosphate chemistry, the world of organic phosphates is far larger than inorganic phosphates. Many common biochemicals contain phosphate esters, and every living cell will contain some. Such molecules as DNA, ATP, phospholipids such as lecithin, and many proteins contain phosphate. In these molecules, the basic phosphate structure is covalently attached to the remainder of the organic molecule through one or more phosphate ester bonds. These bonds are stable for some period of time in water, but will eventually break down to release inorganic phosphate from the organic part of the molecule, a process that can be sped up through the action of acids, bases or enzymes. Addition and removal of phosphate from ATP, for example, is a highly regulated process taking place in all organisms.

A few other points about organic phosphates. Many of these compounds will be readily removed from a tank by skimming. This is, in my opinion, one major way that a skimmer can result in reduced inorganic phosphate levels in a tank. It is not because phosphate ions are themselves directly skimmed (they are not because they do not adsorb onto an air/water interface), but because organic phosphates are removed before they can be converted into inorganic phosphate.

Alternatively, inorganic phosphate, being negatively charged, may become ionically bound to positively charged organics that are themselves skimmed. An old literature reference (repeated in several modern hobby books: Baylor et al. 1962. Deep-sea Res 2:120-124) makes the claim that phosphate binds ionically to organics in natural seawater and can be largely removed by simple aeration. In this process the organics and attached phosphate that are adsorbed onto the air/water interface are launched into the air when the bubble bursts, and are thereby removed. Logically, if this were the case, many skimmers might effectively remove inorganic phosphate from aquaria. I tend to not believe this to be a big factor on the basis of extensive research I have carried out on the binding of phosphate by organics (it's harder than it sounds in the presence of high concentrations of chloride and sulfate). Nevertheless, some inorganic phosphate will certainly be removed in this fashion.

Of course, skimmers and skimmate may contain lots of both organic and inorganic phosphate that was skimmed out inside of partial or whole microorganisms.

A second point about organic phosphates is that they will mostly not be impacted by phosphate-binding materials sold to the aquarium hobby. Consequently, while these may do a fine job of reducing inorganic phosphate, they won't help an algae problem that is caused by organic phosphates.

A final point is that organic phosphates will not be detected by any hobby kit unless it is specifically designed to detect them (most do not). Those that do (e.g., Hach PO-24) break the phosphate off of the organic and thereby convert it into inorganic phosphate prior to testing.

Phosphate Sources in Reef Tanks

The organic esters of phosphate are so prevalent in the biological world that any natural food will contain some organic phosphates. That's one of the issues for reefkeepers: what to do with all of that phosphate? Sure, if the food is going directly into tissue mass then there may be no excess phosphate. But much of the food that any organism consumes (including people) goes to provide energy, leaving a residue of CO_2, phosphate and a variety of nitrogen-containing compounds.

As if that weren't enough, many types of seafood that can be bought at the grocery store have various inorganic phosphate salts intentionally added to them as preservatives. This includes canned and frozen foods, as evidenced by the label, and even some fresh seafood (at least that's what someone in the industry told me). In these cases, rinsing the food before using it may help reduce the phosphate load added to the tank.

Finally, tap water can also be a significant source of phosphate. In my case, the water supplied by the Massachusetts Water Resources Authority seems acceptably low in phosphate (though I use RO/DI water due to excessive silica in it). In other cases, however, phosphate levels can be too high. I'd recommend anyone with an algae problem that uses tap water to test to see if phosphate in the water is a possible issue.

Phosphate Sinks in Reef Tanks

So now that we know where phosphate comes from, we can proceed to ask where it goes. Certainly, some of it goes into the bodies of growing organisms, including bacteria, algae, corals and fish. Some of these organisms stay permanently in the tank, and others may be removed by harvesting of algae, skimming of small organisms and even pruning of corals. Further, if you have an algae "problem" you may never detect high levels of phosphate even if phosphate is an issue, because these algae may suck it out of the water column as fast as it enters.

One sink for phosphate may simply be the precipitation of $Ca_3(PO_4)_2$. The water in many reef tanks will be supersaturated with respect to this material, as the equilibrium concentration in seawater is only 0.002 ppm PO_4^{--}, which corresponds to about 0.01 ppm total phosphate. As with $CaCO_3$, the precipitation of $Ca_3(PO_4)_2$ in seawater may be limited by kinetic factors more than equilibrium factors, so it is impossible to say how much might precipitate under reef tank conditions (without, of course, somehow determining it experimentally).

Phosphate Sinks in Reef Tanks: Calcium Carbonate

There are, however, other possible sinks for phosphate. One is precipitation onto the surface of calcium carbonate, such as the sand beds that many people use. The absorption of phosphate from seawater onto aragonite is somewhat pH dependent, with the maximum binding taking place around pH 8.4 (see Millero's link below), with less binding at lower and higher pH values. If the calcium carbonate crystal is not growing, then this process is reversible and the aragonite (or calcite) can act as a reservoir for phosphate. This reservoir may make it difficult to completely remove excess phosphate from a tank that has experienced very high phosphate levels, and may permit algae to continue to thrive despite cutting off all external phosphate sources. If you are experiencing an algae problem, it might even be a reason to want to keep the pH at the high end of normal (say, 8.3 to 8.5) and not at the lower end (7.8 to 8.1). The relationship of CaCO3 to the phosphate cycle is being studied by Frank Millero and his group in relation to the Florida Bay ecosystem (Millero's studies). If the CaCO3 crystals are growing, as they often are in some parts of our systems, then I'd expect some of this phosphate to get buried and locked into the CaCO3 crystals.

A side effect of the adsorption of phosphate onto aragonite may well be the reported impact of phosphate on calcification of corals. The presence of phosphate may inhibit the formation of calcium carbonate crystals via surface adsorption, and this effect may very well be the factor that inhibits calcification of corals at high phosphate levels. If true, then I would speculate that anything that you do to lower the free PO4-- concentration may limit this impact. Such factors would include normal or lower pH (shifting the PO4-- toward HPO4--) and normal or higher calcium and magnesium (because they complex free PO4--).

Phosphate Sinks in Reef Tanks: Limewater Precipitation

Many reefkeepers accept the idea that limewater addition reduces phosphate levels. This may be true, though the mechanism remains to be demonstrated. Craig Bingman has done a variety of experiments related to this hypothesis and published them in previous Aquarium Frontiers articles. While many may not care what the mechanism is, knowing it would help to understand the limits to this method, and how it might best be employed.

Here are some questions that seem to me to remain unanswered concerning this hypothesis:

Is some sort of insoluble calcium phosphate salt formed immediately on addition of the limewater? If so, where does it eventually go? The skimmer? The bottom? Into the arms of a hungry alga? What is this salt? Ca3(PO4)2? Is it perhaps partly calcium carbonate, or is it a pure phosphate? Is magnesium involved at all? If one's tank cannot handle full strength limewater to replace all evaporation (as mine cannot some of the year), is it better to add full strength limewater plus some pure water, instead of partially saturated limewater?

Is calcium necessary in the additive to see the effect, or does adding any high pH solution (like B-ionic) trigger the precipitation of calcium phosphate by pushing the phosphate equilibrium toward PO4--? For that matter, does adding concentrated calcium additives without a pH spike trigger any calcium phosphate precipitation?

If no phosphate-containing precipitate forms upon the immediate addition of the limewater, then where does the phosphate go? Is the raised pH that typically comes in limewater tanks simply driving more phosphate onto the sand and rock and suspended CaCO3 particulates? If so, do other pH–raising additives (like B-ionic) have a similar effect?

Uptake of Phosphate by Organisms

How organisms obtain phosphate is, in many cases, poorly understood. Even the absorption mechanisms used in the human gastrointestinal tract are largely speculation (one of my occupational research areas involves drugs to modify this absorption). It's not surprising then that such mechanisms in coral reef creatures would also be poorly understood.

One frequently hears that limiting phosphate will limit algae growth in reef tanks. That is almost certainly true, but some species of microalgae will do better under phosphate limitation than others. Some species of microalgae can, in fact, significantly regulate their inorganic phosphate transport capabilities to deal with variable phosphate levels (upregulation of phosphate transport). Add to that the complexity of absorption of organic phosphates and the likelihood that many organisms can enzymatically break down organic phosphates prior to absorption, and we are left not having a very good understanding of what organisms in our tanks use what forms and concentrations of phosphate. And to add insult to injury, our tanks are usually greatly skewed from natural seawater in terms of many other nutrients, so one cannot readily extrapolate from phosphate studies in seawater directly to reef tanks that may have excessive levels of some nutrients and be deficient in others.

This article has obviously posed as many questions as it answered. Perhaps that's good, because it means that we can have years of fun finding out the answers. Hopefully, however, it has provided enough useful information that as a reef or aquarium keeper, you can better understand one of the most talked about issues: phosphate.

As is frequently the case for seawater chemistry issues, I'd recommend Chemical Oceanography by Frank J. Millero (1996. Second Edition, CRC Press) as a very good text on natural seawater. Captive Seawater Fishes by Stephen Spotte (1992. John Wiley & Sons) provides a more practical side to many issues important to aquarium keepers, including phosphate, although it is not focused on reef tanks.