Managment of Phosphates in Recreational Waters for Optimum Algae Control

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Phosphorous is a significant contributor to the development of green colored water in both natural and recreational waters. It is a growth limiting nutrient to both algae and cyanobacteria. Phosphorous enters water in a variety of forms and its absence is paramount to preventing algae blooms. Various chemical treatments can be effective in removing phosphates from both natural and recreational water and each offers their own advantages and disadvantages. The use of lanthanum compounds has recently been shown to be quite successful in removing orthophosphates from recreational water.

The green, red or brown colored water observed in various types of recreational water including natural lakes, ponds, reservoirs and swimming pools often results from high density growth of phytoplankton. Phytoplankton are free floating small microscopic organisms that include both algae and cyanobacteria (*Standard Methods* 1985, Villee et al. 1989, Mlot 1997). They are responsible for many of the so–called red and green tides occurring along coastal waters and estuaries worldwide and are common indicators of fresh water lake eutrophication (*Lake* 1988). The unsightly green scum seen on the surface of these lakes is due to the filamentous growth of these phytoplankton species. As mentioned above and shown in Table 1, the two major phytoplankton forms are algae and cyanobacteria. Algae are plants and exhibit a cell structure which is of the eukaryotic type. Cyanobacteria on the other hand are bacteria and therefore exhibit the cell structure typical of prokary-

otes. Cyanobacteria were formerly referred to as blue–green algae but are in fact a bacteria that contain chlorophyll, endowing them with the ability to pho-

Kingdom: *Protista*
- Algae (aquatic plants)
- Eukaryotic (cell structure, plants & animals)
- Photosynthetic (chlorophyll)

Kingdom: *Monera*
- Cyanobacteria (formerly referred to as blue-green algae)
- Prokaryotic (cell structure, bacterial)
- Photosynthetic (chlorophyll)
- Fix Nitrogen

Table 1 – Phylogenetic Relationship Between Algae and Cyanobacteria

Common Name	Common Habitat
Green Algae	*fresh water, damp soil, tree bark, salt water*
Red Algae	*saltwater, some freshwater*
Brown Algae	*saltwater, seaweeds, kelp*
Dinoflagellates	*saltwater, freshwater*
Euglenoids	*freshwater*
Golden Brown Algae	*freshwater, saltwater, soil*
Diatoms	*freshwater, saltwater*
Yellow-green algae	*freshwater, saltwater*

Table 2 – Major Algae Groups

tosynthesize. Although both algae and cyanobacteria convert carbon dioxide to glucose through the process known as photosynthesis, the cyanobacteria are unique in their ability to fix or utilize gaseous nitrogen.

Of the major algae groups listed in Table 2, the green algae are the most common and contain over 6000 species. Most algae groups are common to both fresh and salt water. The dinoflagellate group are the culprits often responsible for numerous fish and shellfish kills occurring in tributaries of the Chesapeake Bay and North Carolina estuaries (Mlot 1997, Anderson 1994). These particular algae are responsible for the so called red tides commonly reported in the news. Their toxicity is due to the release of potent neurotoxins which can result in the death of land mammals that drink the water or consume the fish and shellfish harboring these toxins (Metting 1986). Interestingly, various cyanobacteria species also produce toxins similar to those of the marine algae dinoflagellates (Metting 1986,Carmichael 1994). These toxins can be released following killing of the bacteria by chlorination or copper sulfate. As previously mentioned, the cyanobacteria are able to convert nitrogen into usable forms. This property is absent in algae. Some of the characteristic properties of cyanobacteria are:

- Present in ponds, lakes, swimming pools, and oceans
- Contain chlorophyll and are photosynthetic
- Fix nitrogen gas into usable forms
- Grow in nitrogen and phosphorous rich water and are responsible for most water blooms
- Commonly form the colored scums on water surfaces
- Contain carotenoid, phycocyanin and phycoerythrin pigments
- Poisonous genera include *Anabaena, Microsystis, Nodularia*
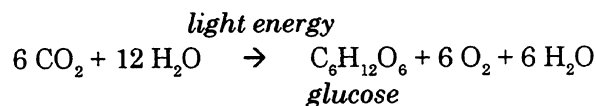- Produce toxins in drinking water that have resulted in death of animals and humans

Nutrient Requirements of Phytoplankton

The nutrient requirements of phytoplankton are similar to those of plants (Villee et al. 1989, South and Whittick 1987). They require the elements carbon, hydrogen, oxygen, nitrogen, phosphorous, calcium, potassium, magnesium, sulfur, molybdenum, copper, iron, zinc, manganese, silicon sodium and boron. Carbon and nitrogen are the building blocks of amino acids (build protein), sugars, DNA, RNA and fatty acids. Phosphorous is required for energy transfer in the form of ATP. It is also incorporated into the str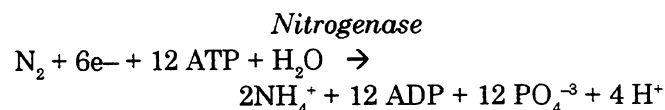ucture of nucleic acids such as DNA, RNA and membrane lipids. Sulfur is found in certain amino acids and forms the active site of various enzymes used to catalyze metabolic reactions within the cells. Magnesium is part of the photosynthetic pigments such as chlorophyll, and calcium helps form the structural components of cell walls.

Photosynthesis

Both algae and most cyanobacteria are photosynthetic and can use energy from the sun to convert carbon dioxide gas (CO_2) into organic carbon (glucose) with the generation of oxygen as described in the reaction below:

$$\text{6 CO}_2 + \text{12 H}_2\text{O} \xrightarrow{\textit{light energy}} \underset{\textit{glucose}}{\text{C}_6\text{H}_{12}\text{O}_6} + \text{6 O}_2 + \text{6 H}_2\text{O}$$

Cyanobacteria, in contrast to algae, are capable of converting nitrogen gas in the atmosphere to usable nitrates according to the following reaction:

$$\text{N}_2 + \text{6e}- + \text{12 ATP} + \text{H}_2\text{O} \xrightarrow{\textit{Nitrogenase}} \text{2NH}_4^+ + \text{12 ADP} + \text{12 PO}_4^{-3} + \text{4 H}^+$$

Primary Growth Limiting Nutrients

Phosphorous and nitrogen are the two major growth limiting nutrients for phytoplankton (Fisher et al. 1992, Seitzinger and Sanders 1997, Jensen and Sicko–Goad 1976, Falkner et al. 1984, Schindler 1977). Nitrogen is more commonly rate limiting in marine environments while phosphorous is primarily rate limiting in freshwater and is responsible for the increase in growth of various phytoplankton resulting in the eutrophication of lakes (*Lake* 1988, Schindler 1977). Recent studies have shown that phosphorous is also the rate limiting nutrient for bacterial species in drinking water (Miettinen 1996). Controlling phosphorous is easier than controlling nitrogen because nitrogen and its numerous chemical forms can be assimilated by a variety of different biochemical reactions. The fact that nitrogen in the atmosphere can be converted by bacteria into chemical forms usable by both algae and cyanobacteria presents a major disadvantage in trying to control nitrogen (Lipschultz and Owens 1996).

Phosphorous

Phosphorous is a vital and essential element in all living systems and can exist in a variety of forms (Villee et al. 1989, Sawyer 1962, Hamm 1969, Stryer 1975, Alberts et al. 1994):

- Phosphate salts and esters of phosphoric acid
  H_3PO_4 *orthophosphoric acid*

$H_4P_2O_7$ *pyrophosphoric acid*
$H_5P_3O_{10}$ *triphosphoric acid*
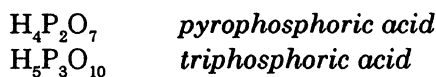
- Igneous Rocks *(calcium phosphates)*

- Inorganic phosphates *(orthophosphates, form used by algae & cyanobacteria)*
  PO_4^{-3}
  HPO_4^{-2}
  $H_2PO_4^{-}$

- Condensed Phosphates *(can be hydrolyzed to orthophosphate)*
  HPO_3 *metaphosphate*
  $H_4P_2O_7$ *pyrophosphate*
  $H_5P_3O_{10}$ *triphosphate*

- Organic Phosphates *(contain 1–3 organic groups in ester linkage to oxygen)*
  $C_6H_{18}O_{24}P_6$ *inositol hexaphosphoric acid*
  $C_6H_{13}O_9P$ *inositol monophosphate, glucose-6–phosphate*
  $C_{10}H_{16}N_5O_{13}P_3$ *adenosine triphosphate, incl. numerous other organic–bound phosphates*

The orthophosphates are the forms utilized by both algae and cyanobacteria (Jensen and Sicko–Goad 1976). Orthophosphates are primarily used as fertilizers and are obtained by mining phosphate rock. Condensed phosphates can be converted to orthophosphates by enzymatic processes carried out by microorganisms. They also slowly hydrolyze to the orthophosphate forms when added to water (Shannon and Lee 1966). Condensed phosphates are utilized in water treatment and in detergents as commercial cleaning agents (*Standard Methods* 1985, Bunce 1991). The organic phosphates are produced through biological processes from orthophosphates and can be utilized directly by microorganisms.

Maintaining Low Phosphate Levels
Orthophosphates in pool water can come from a number of different sources including:

- Soil
  Mineral forms (apatites)
  Organic forms (nucleotides, phospholipids, inositols)
- Plant debris
  leaves, bark, pollen and seeds
- Water– phosphate leached from rock (Florida)
- Insects
- Microorganisms
- Pool chemicals
- Soaps & detergents
- Hair conditioners, shampoo's (natural plant extracts & oils)
- Body waste
  feces, urine, perspiration
- Lawn and agricultural fertilizers
- Rainwater
  10 –10 µg phosphate/L (particulates in air)

Controlling and managing phosphorous in pool water is best accomplished by:

- Minimizing dirt entering the pool
- Routinely removing dead plant & insect matter
- Maintaining proper pool balance
- Regularly backflushing the filter
- Minimizing input of phosphate–containing chemicals
- Regularly using phosphate precipitants & clarifiers
- Routinely vacuuming debris from pool bottom

The importance of keeping dirt out of the pool water is obvious since it is a high source of both orthophosphates and organic phosphates. Maintaining proper pool balance is critical, particularly with respect to sanitizer concentrations. As mentioned earlier, microbes can convert condensed phosphates to orthophosphates which feed both algae and cyanobacteria. Proper pH and alkalinity are also important in minimizing dissolved carbon dioxide which is utilized by growing phytoplankton during photosynthesis. Low pH shifts the bicarbonate equilibrium to higher concentrations of dissolved CO_2 (carbon dioxide) according to the following reaction:

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O$$
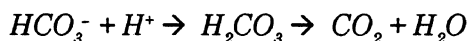
Backflushing of the filter is important for removing both organic debris and trapped condensed phosphates which can leach organic phosphates into the water as a result of both enzymatic and microbial degradation. The use of phosphate–containing chemicals should be minimized for obvious reasons. Regular use of clarifiers is important for continual removal of suspended phosphate–containing organic colloid. Cationic clarifiers such as those containing chitosan are particularly effective in removing the anionic inositol phosphates which are abundant in plant matter.

Reduction of High Phosphate Levels
High orthophosphate concentrations in pool

water can be reduced by dilution (i.e., partial draining and refilling) or by precipitation of the phosphate using metal salts followed by filtration.

Phosphate Precipitation

Orthophosphates can be precipitated using metal salts containing aluminum, iron or lanthanum. Aluminum and iron are used to remove phosphates during tertiary treatment of wastewater and each has it's disadvantages (Sawyer 1962, Vollenweider 1968).
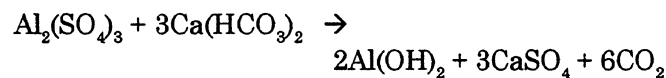
Alum

The most common aluminum –containing compound used for phosphate precipitation is alum [aluminum sulfate, $Al_2(SO_4)_3$]. When added to water, it forms acidic aqueous solutions containing insoluble aluminum hydroxide [$Al(OH)_3$] colloids according to the following reaction (*Lake* 1988, Sawyer 1962):

$$Al_2(SO_4)_3 + 6 H_2O \xrightarrow{pH>5} 2 Al(OH)_3 + 3 H_2SO_4$$
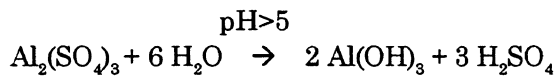
The acidity (H^+) is neutralized by the bicarbonate (alkalinity) in the water which acts as a buffer according to the reaction:

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O$$
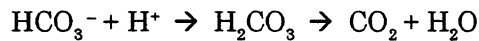
Neutralization of the acid generates carbonic acid which is in equilibrium with carbon dioxide. Increased carbonic acid shifts the equilibrium to increased carbon dioxide which can be utilized by growing algae and cyanobacteria in the process of photosynthesis. Since calcium is present as hardness, and exists in equilibrium with bicarbonate (HCO_3^-), it is available to react with the sulfate (SO_4^-) to form calcium sulfate ($CaSO_4$) or gypsum. Calcium sulfate is only very slightly soluble in water and contributes to an increase in turbidity. The combination of reactions can be described as follows (Sawyer 1962):

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow$$
$$2Al(OH)_2 + 3CaSO_4 + 6CO_2$$

The removal of orthophosphate by alum is an <u>adsorption process</u>. The insoluble aluminum hydroxide [$Al(OH)_3$] formed at pH>5 when alum is added to water, tends to adsorb orthophosphate to form an insoluble gelatinous precipitate (*Lake* 1988). This gelatinous precipitate can result in inefficient filtration. At pH values below 5, insoluble aluminum phosphate is the predominant species present, due to the reaction of trivalent aluminum cations with orthophosphate anions.

$$Al^{+3} + PO_4^{-3} \rightarrow AlPO_4$$
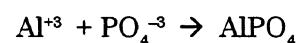
Although alum is effective in reducing orthophosphate concentrations, the disadvantages include:

- Reduction of alkalinity
- Formation of gelatinous precipitates that are difficult to filter
- Generation of carbon dioxide utilized by phytoplankton which enhances growth

Ferric Sulfate

The iron salt, ferric sulfate [$Fe_2(SO_4)_3$], exhibits similar chemistry to alum. The formation of insoluble iron hydroxide [$Fe(OH)_3$] occurs when ferric sulfate is dissolved in water (*Lake* 1988). $Fe(OH)_3$ adsorbs orthophosphates similar to $Al(OH)_3$ resulting in gelatinous precipitates. While the enhanced uptake of carbon dioxide by phytoplankton is a disadvantage, the potential for iron staining can also pose a problem. Recent marine studies have shown that iron appears to stimulate photosynthesis in marine phytoplankton leading to algae blooms (Monastersky 1995).

Lime

Lime or calcium hydroxide [$Ca(OH)_2$] has been used to precipitate orthophosphate by precipitation as calcium phosphate [$Ca_3(PO_4)_2$]. The primary disadvantage to its use in pools is the requirement for high pH ~10.

Lanthanides (trivalent rare earth metals)

The use of lanthanides in phosphate removal from recreational water is relatively new and quite effective. Two major lanthanide salts are currently being used to treat pool water.

> *Lanthanum carbonate – $La_2(CO_3)_3$*
> ion exchange

> *Lanthanum chloride – $LaCl_3$*
> direct precipitation

The major advantage in the use of lanthanide salts is the extremely low solubility of the lanthanum phosphate formed. Due to the low solubility product constant (K_{sp}) of lanthanum phosphate ($LaPO_4$), orthophosphate concentrations can be reduced to significantly low levels. Since orthophosphate is the primary growth limiting nutrient to phytoplankton, the use of lanthanides in managing phosphates can be very effective in controlling algae and cyanobacteria.
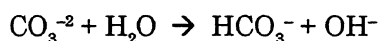
Lanthanum Carbonate

Orthophosphate removal using the insoluble carbonate salt of lanthanum is principally an ionic

exchange reaction.

$$La_2(CO_3)_3 + 2PO_4^{-3} \rightarrow 2LaPO_4^{-3} + 3CO_3^{-2}$$
lanthanum phosphate   lanthanum   carbonate
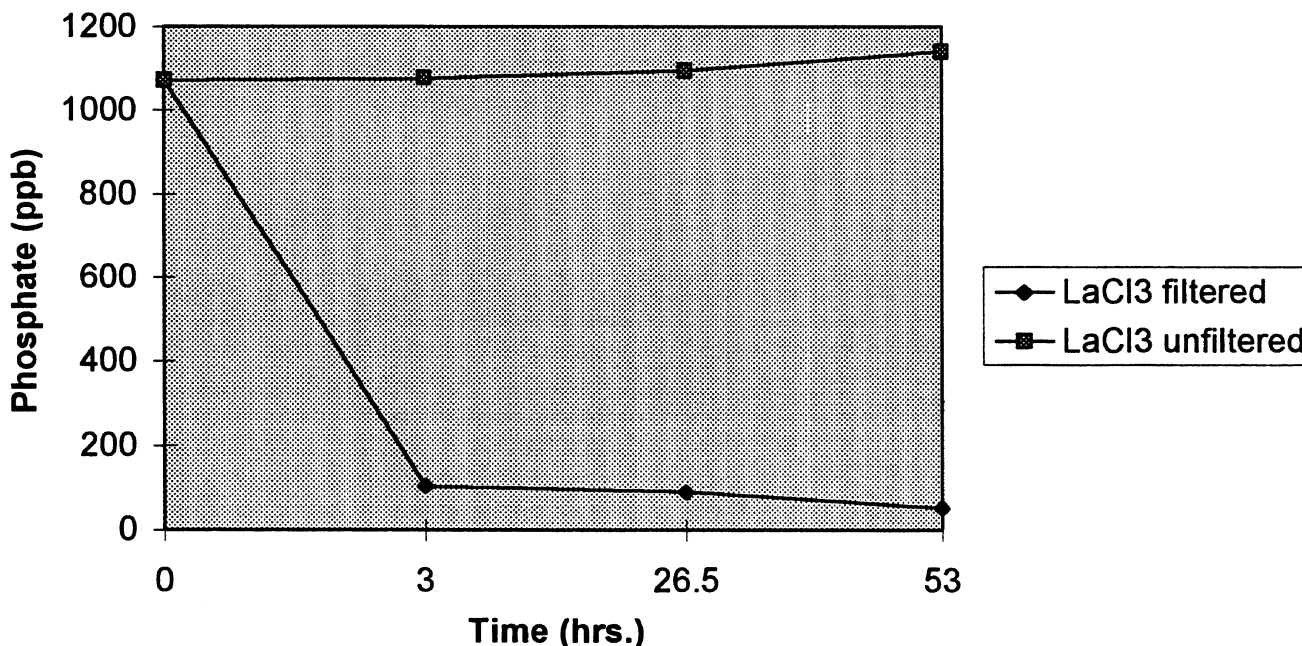*carbonate   phosphate*
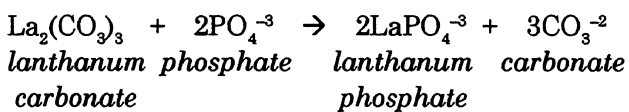
The insoluble carbonate associated with lanthanum is replaced or exchanged by phosphate resulting in the formation of insoluble lanthanum phosphate followed by the release of soluble carbonate ions. The carbonate is exchanged for the phosphate due to the lower solubility product of lanthanum phosphate compared to lanthanum carbonate. The removal mechanism is by ion exchange followed by filtration of insoluble lanthanum phosphate particles. This type of mechanism requires an insoluble fine particulate of lanthanum carbonate (high turbidity) to come in contact with soluble phosphate ions while suspended in water. This can be less than efficient compared to soluble lanthanum ions coming in contact with soluble orthophosphate ions. The addition of carbonate ions to water tends to increase pH due to the generation of hydroxide as described by the following equation:

$$CO_3^{-2} + H_2O \rightarrow HCO_3^- + OH^-$$

At high pH, calcium ions (contributing to hardness) combine with carbonate ions resulting in the precipitation of calcium carbonate.

$$Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3$$
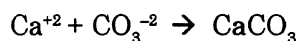
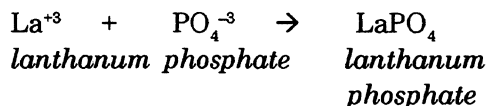This tends to raise turbidity and contributes to

the formation of scale. The precipitation of calcium carbonate will eventually reduce hardness through the depletion of calcium ions. Carbonate is in equilibrium with carbon dioxide and bicarbonate and the species which predominates is influenced by the pH, salinity, partial pressure of atmospheric CO_2 and temperature. Because algae can utilize both carbon dioxide and bicarbonate (South and Whittick 1987), the alkalinity and pH of the water needs to be carefully monitored and properly balanced when using chemicals containing carbonate or bicarbonate.
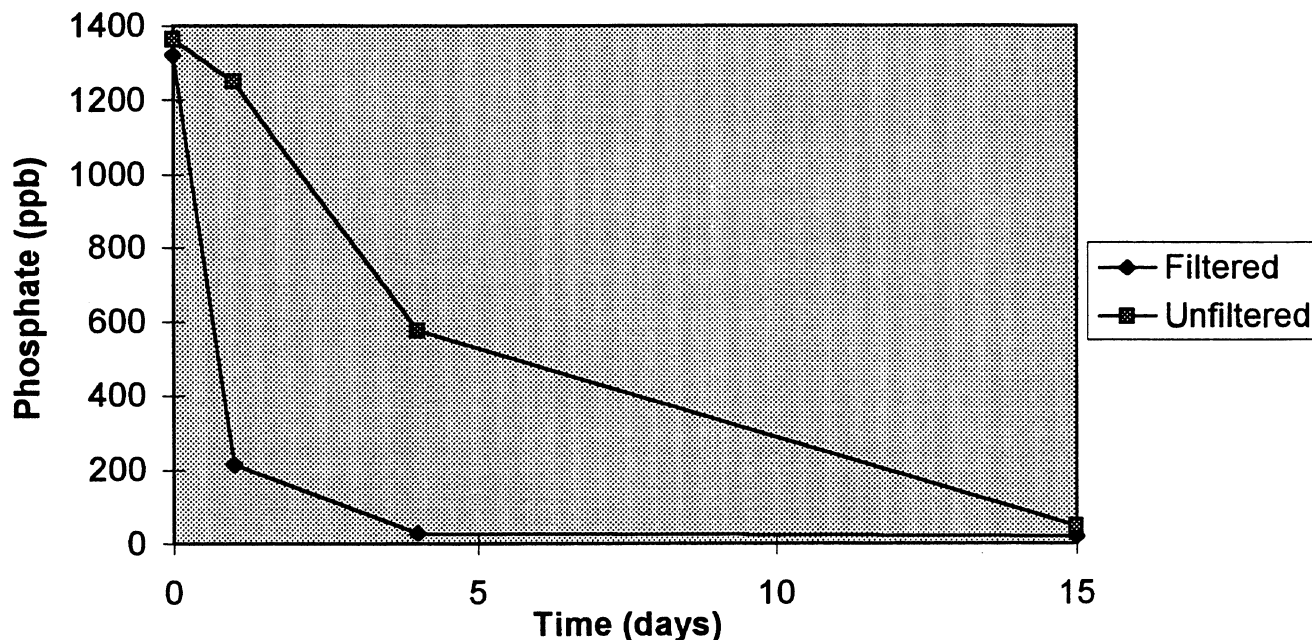
Although the use of lanthanum carbonate for phosphate removal does offer distinct advantages to using aluminum (alum), iron (ferric sulfate or ferric chloride) and calcium salts, the disadvantages include:

- High turbidity, long clarification times
- Potential for decreased hardness
- Potential for increased scale
- Potential for increased CO_2 allowing increased phytoplankton growth
- Insolubility of lanthanum carbonate contributing to slow removal efficiencies
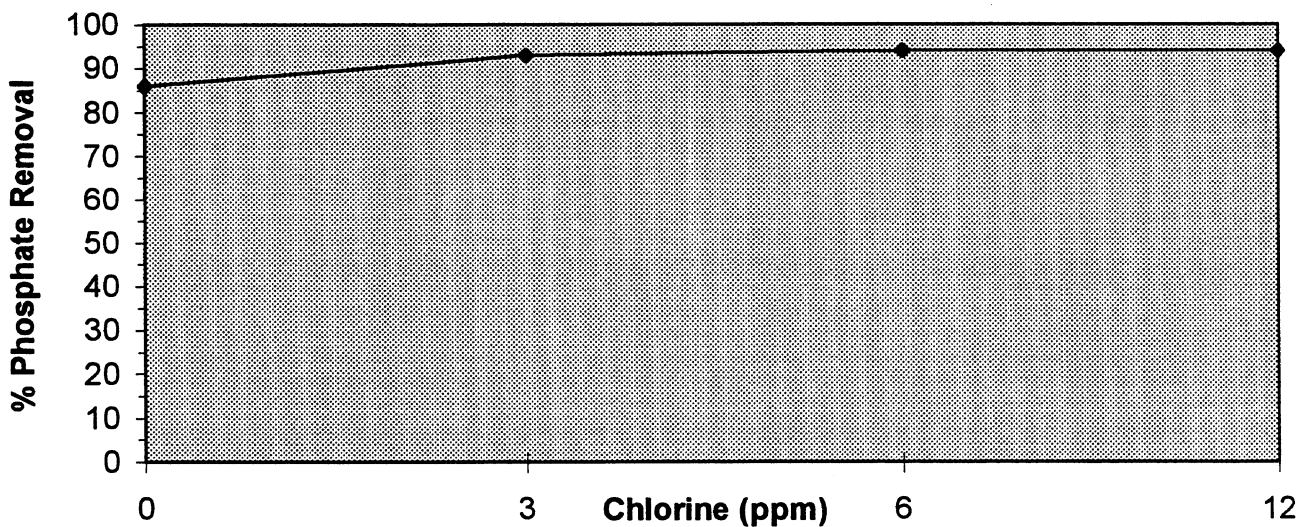
Lanthanum Chloride

Orthophosphate removal using the soluble chloride salt of lanthanum, is principally a direct chemical precipitation between soluble lanthanum ions and soluble orthophosphate ions.

$$La^{+3} + PO_4^{-3} \rightarrow LaPO_4$$
lanthanum phosphate   lanthanum
                        phosphate

Figure 1 – Reduction of Phosphate by Lanthanum Chloride

Figure 2 – Reduction of Phosphate by Lanthanum Chloride in a Swimming Pool

Figure 3 – Effect of Chlorine Concentration on Phosphate Reduction by Lanthanum Chloride

Lanthanum chloride is water soluble (no significant turbidity) resulting in release of free lanthanum ions and free chloride ions when added to water. The reaction of soluble trivalent lanthanum ions with soluble orthophosphate ions is rapid and results in the immediate precipitation of lanthanum phosphate. Although not utilized by phytoplankton, the insoluble lanthanum phosphate is subsequently removed by filtration. The advantages of lanthanum chloride–mediated removal of orthophosphate are:

- Minimal interference with alkalinity

- No significant increase in turbidity
- Low potential for scale
- Fast removal efficiencies due to soluble reactant (lanthanum ions)

The reaction of soluble lanthanum chloride with soluble orthophosphate results in the formation of insoluble lanthanum phosphate which is filterable as shown in Figure 1. Simulated balanced pool water was spiked with defined amounts of orthophosphate followed by the addition of lanthanum chloride. At

various time points following the addition of lanthanum chloride, a sample of water was filtered through 12 micron filter paper and tested for the presence of orthophosphate using a standard commercial phosphate test kit. A non–filtered sample corresponding to each time point was also assayed for orthophosphate in the same fashion. As shown in Figure 1, orthophosphate concentration was significantly reduced within the first three hours following addition of the lanthanum chloride. These results also demonstrate that filtration is necessary to remove the insoluble lanthanum phosphate formed. The non–filtered samples contain precipitated lanthanum phosphate as evidenced by its removal following filtration. When analyzing for orthophosphate, the reaction involves an acid solubilization step that dissolves the insoluble lanthanum phosphate allowing free orthophosphate to react with the chemicals used to detect it. If lanthanum phosphate is not removed by filtration, free orthophosphate will be detected in the sample as a result of this acid solubilization step.

The requirement for filtration is also observed in a 25,000 gallon swimming pool spiked with orthophosphate as shown in Figure 2. Orthophosphate was added to a 25,000 gallon swimming pool and allowed to reach equilibrium concentrations. A known amount of lanthanum chloride was then added and samples of water were removed at various time points and filtered in the laboratory (12 micron) prior to assay. Additional samples were also assayed without filtering. At each time point, orthophosphate was measured

on both the laboratory filtered (12 micron) and non–laboratory filtered swimming pool water. Orthophosphate concentration decreased in a time dependent fashion in both laboratory– filtered and non–laboratory filtered swimming pool water as seen in Figure 2. The difference in phosphate concentrations between laboratory filtered and non–laboratory filtered water demonstrate the time required for the pool filter to remove the insoluble lanthanum phosphate formed. From these experiments, it is clear the rate of removal of insoluble lanthanum phosphate is influenced by the efficiency of filtration. It is also clear that orthophosphate concentrations are reduced significantly within the first 24 hours following the addition of lanthanum chloride to a swimming pool.

The effects of different pool parameters on phosphate removal by lanthanum chloride was also examined using simulated pool water that was adjusted appropriately. Chlorine concentration was examined over a range of 0 – 12 ppm as shown in Figure 3. For each concentration, lanthanum chloride was allowed to react in simulated pool water containing approximately 1,200 ppb orthophosphate. After 3 hours, a sample of water was removed and the chlorine neutralized by the addition of thiosulfate. The water was filtered and assayed for orthophosphate. The percent phosphate removed was calculated relative to the control water containing the same concentration of phosphate and chlorine but no lanthanum chloride. The results presented in Figure 3 demonstrate no significant effect of chlorine on removal efficiencies over a
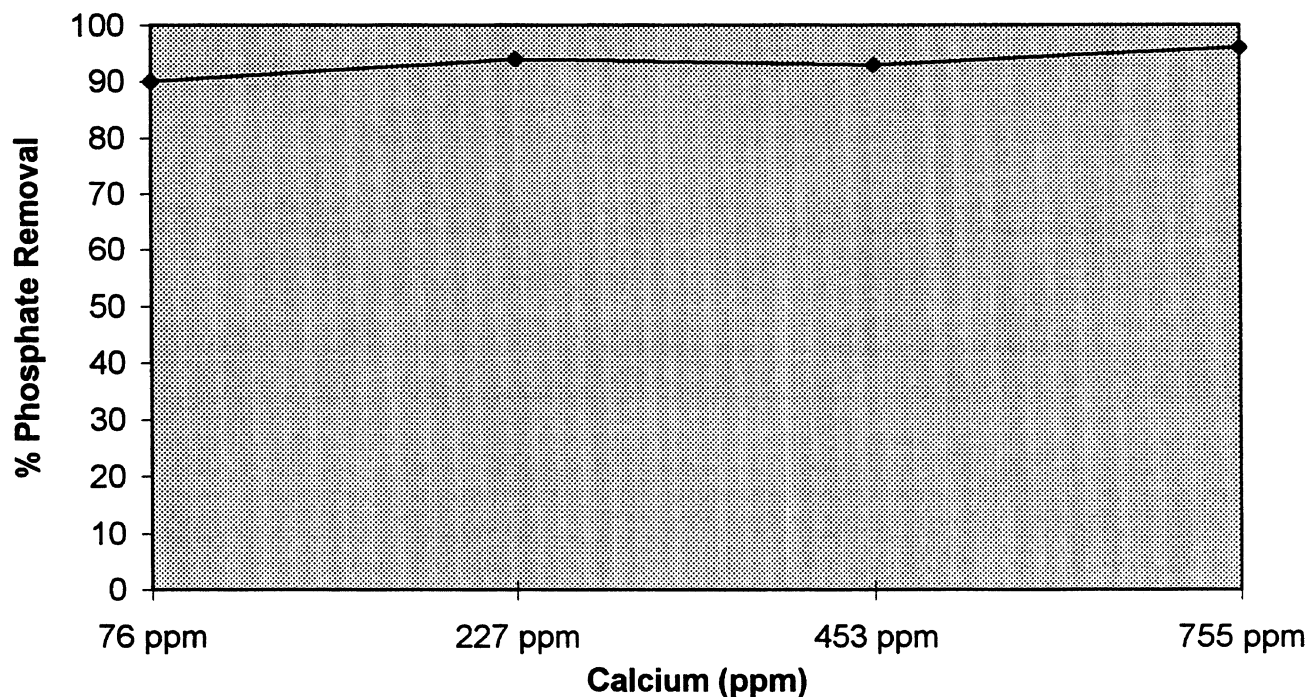
Figure 4 – Effect of Calcium Concentration on Phosphate Reduction by Lanthanum Chloride
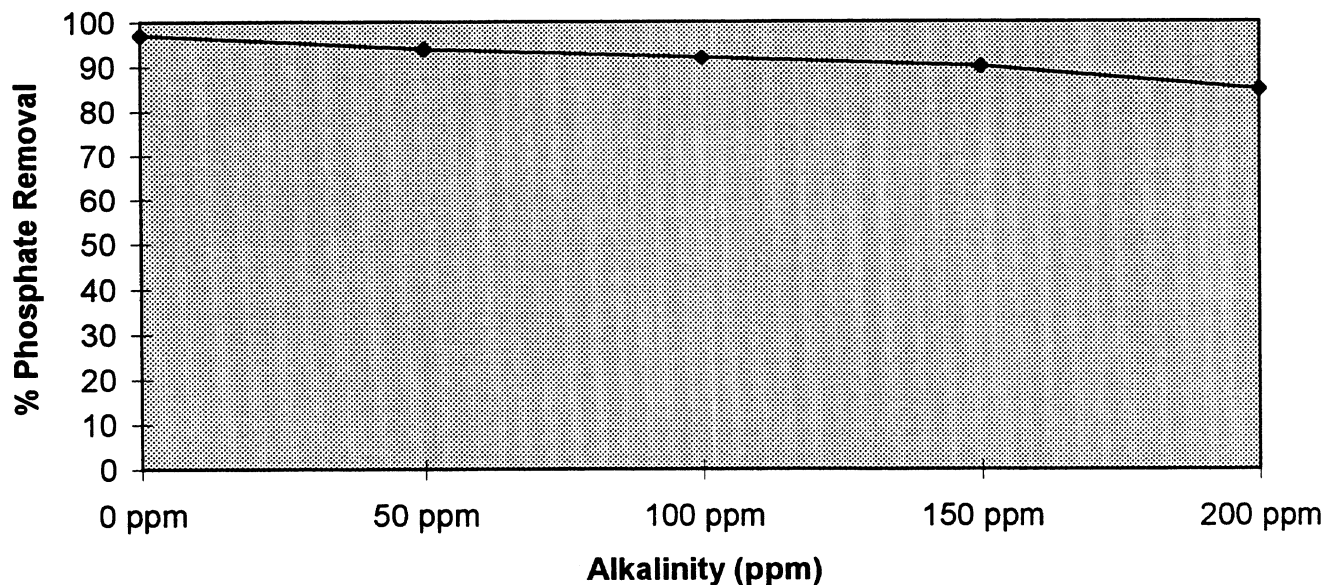
Figure 5 – Effect of Alkalinity on Phosphate Reduction by Lanthanum Chloride
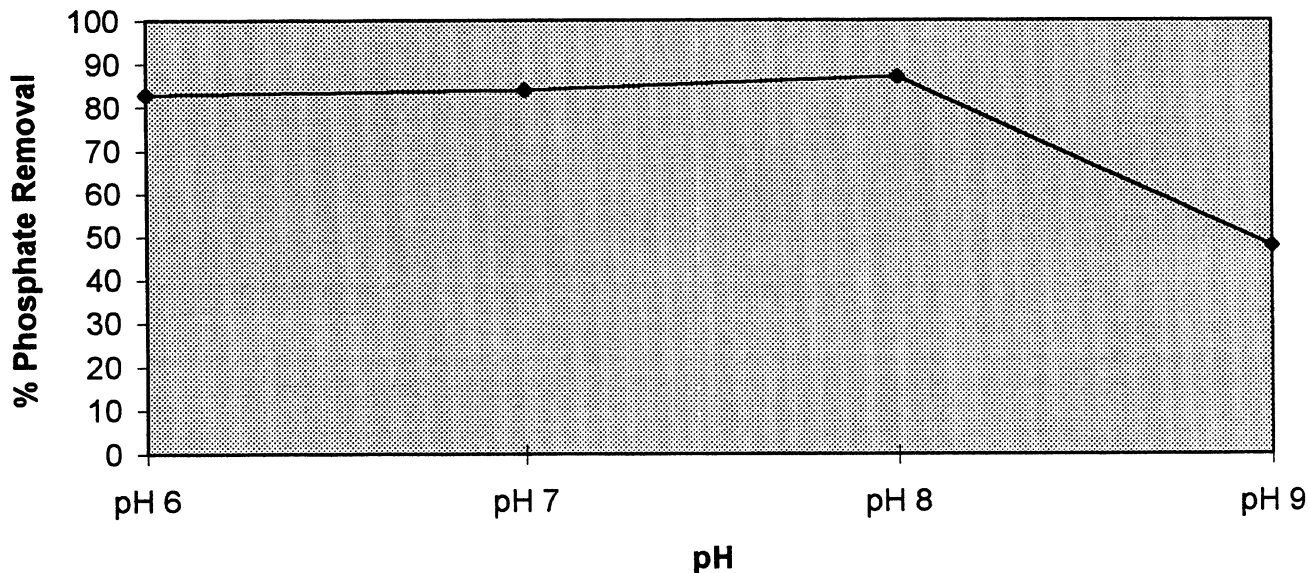
Figure 6 – Effect of pH on Phosphate Reduction by Lanthanum Chloride

concentration range of 0 – 12 ppm.

The effect of calcium (hardness) concentration was also examined in the same fashion as chlorine. The simulated pool water was adjusted by addition of calcium chloride. As shown in Figure 4, calcium concentration did not significantly affect removal efficiencies over a range of 76 ppm – 755 ppm.

The effect of alkalinity was also examined. The results are shown in Figure 5. Although a slight reduction in phosphate removal efficiency was observed as the alkalinity increased, efficient phosphate removal was attained.

The effect of pH on removal efficiency was pronounced between pH 8 and pH 9 as shown in Figure 6. Reduced phosphate removal may be due to the formation of lanthanum carbonate since the carbonate ion concentration would be higher at pH 9 vs pH 8.

Lanthanum chloride–mediated removal of phosphate was also examined in the presence of potassium monopersulfate, a strong oxidizer. Lanthanum chloride was added to orthophosphate containing simulated pool water as described above, either in the presence or absence of 12 ppm potassium monopersulfate. The results shown in Figure 7 demonstrate that potassium monopersulfate had no ef-
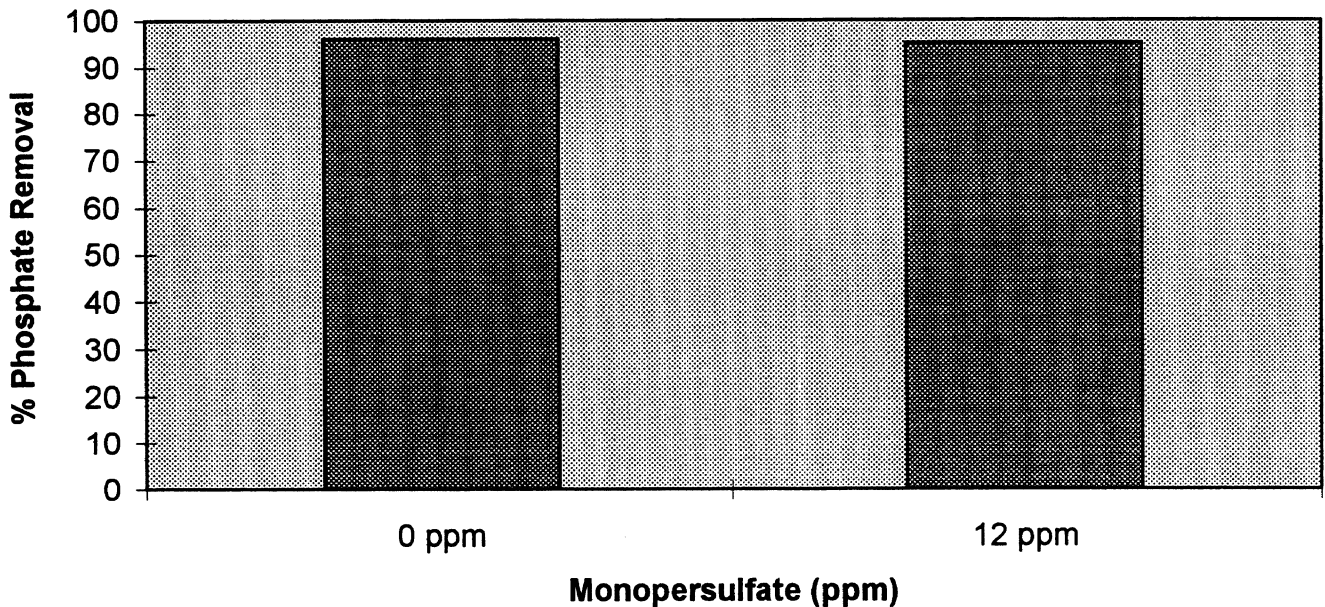
Figure 7 – Effect of Monopersulfate on Phosphate Removal by Lanthanum Chloride

fect on the ability of lanthanum chloride to remove orthophosphate.

These results demonstrate that efficient removal of orthophosphate can be attained by lanthanum chloride under a variety of pool conditions.

Monitoring Phosphate Concentration

Phosphate concentration can be routinely monitored using a variety of phosphate test kits on the market. These tests involve colorimetric determination of dissolved orthophosphate. Organic and condensed phosphates are not measured with the exception of a small percentage that may be hydrolyzed by the test procedure. Measurement of condensed and organic phosphates require oxidative digestion and/ or acid hydrolysis at boiling water temperatures (*Standard Methods* 1985).

The tests involve reacting orthophosphate with molybdate in acidic media resulting in the formation of a molybdophosphoric acid complex that is measured directly or following formation of a colored complex as a result of reduction. The color is measured spectrophotometrically or visually and compared to a standard calibration curve. The three most common test methods in use today are:

- Vanadomolybdophosphoric Acid (1 – 20 ppm)
- Stannous Chloride (10 ppb – 6 ppm)
- Ascorbic Acid (10 ppb – 6 ppm)

The stannous chloride method and the ascorbic acid method both result in a blue color which increases

in intensity at higher orthophosphate concentrations. The vanadomolybdophosphoric acid method yields a yellow color which increases in intensity at higher orthophosphate concentrations.

Conclusions

- Waterblooms are caused by phytoplankton (algae, cyanobacteria)
- Phosphate is the growth limiting nutrient
- Limiting phosphates in pools is effective in preventing phytoplankton blooms
- It is important to maintain proper pool balance
- It is important to monitor phosphate by regular testing
- When phosphates are high, drain pool or precipitate phosphate & remove by filtration
- Regular use of a clarifier is important
- Lanthanide trivalent rare earths are preferred phosphate precipitants
- Lanthanum chloride offers numerous advantages

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