Total Phosphorus and Phosphate Impact on Surface Waters

Phosphate Cycle
Phosphorus occurs naturally in rocks and other mineral deposits. During the natural process of weathering, the rocks gradually release the phosphorus as phosphate ions which are soluble in water and the mineralize phosphate compounds breakdown. Phosphates PO₄³⁻ are formed from this element. Phosphates exist in three forms: orthophosphate, metaphosphate (or polyphosphate) and organically bound phosphate each compound contains phosphorous in a different chemical arrangement. These forms of phosphate occur in living and decaying plant and animal remains, as free ions or weakly chemically bounded in aqueous systems, chemically bonded to sediments and soils, or as mineralized compounds in soil, rocks, and sediments.

Orthophosphate forms are produced by natural processes, but major man-influenced sources include: partially treated and untreated sewage, runoff from agricultural sites, and application of some lawn fertilizers. Orthophosphate is a readily available to the biological community and typically found in very low concentrations in unpolluted waters. Poly forms are used for treating boiler waters and in detergents. In water, they are transform into orthophosphate and available for plant uptake. Organic phosphates is typically estimated by testing for total phosphate. The organic phosphate is the phosphate that is bound or tied up in plant tissue, waste solids, or other organic material. After decomposition, this phosphate can be converted to orthophosphate.

Phosphate rock is commercially available form is called apatite and the phosphate is also present in fossilized bone or bird droppings called guano. Apatite is a family of phosphates containing calcium, iron, chlorine, and several other elements in varying quantities. The most common variety contains fluorine, and fluorapatite is the main constituent in bones and teeth! Huge quantities of sulfuric acid are used in the conversion of the phosphate rock into a fertilizer product called "super phosphate". Small amounts of certain condensed phosphates are added to some water supplies during treatment to prevent corrosion and this chemical is used extensively in the treatment of boiler waters. Larger quantities of these compounds can be found in laundrying and commercial cleaning fluids. Orthophosphates applied to agricultural or residential lands as fertilizers are carried into the surface water during storm events or snow melt. In addition, storm events can cause the vertical migration of the phosphates into the groundwater system, but because of soils affinity for phosphate, the soil mantle acts as a storage media.

Why Phosphorus Is Important
Phosphorus is one of the key elements necessary for growth of plants and animals and in lake ecosystems it tends to be the growth limiting nutrient and is a backbone of the Kreb's Cycle and DNA. The presence of phosphorus is often scarce in the well-oxygenated lake waters and importantly, the low levels of phosphorus limit the production of freshwater systems (Ricklefs, 1993). Unlike nitrogen, phosphate is retained in the soil by a complex system of biological uptake, absorption, and mineralization.

Phosphates are not toxic to people or animals unless they are present in very high levels. Digestive problems could occur from extremely high levels of phosphate. The soluble or bio-available phosphate is then used by plants and animals. The phosphate becomes incorporated into the biological system but the key areas include: ATP, DNA, and RNA. ATP, adenosine triphosphate, which is important in the storage and use of energy and a key stage in the Kreb's Cycle. RNA and DNA are the backbones of life on this planet, via genetics. Therefore, the availability of phosphorous is a key factor controlling photosynthesis.
Photosynthesis - KEY Factor At the Base of the Food Chain

Photosynthesis is a complex series of reactions carried out by algae, phytoplankton, and the leaves in plants, which utilize the energy from the sun. The simplified version of this chemical reaction is to utilize carbon dioxide molecules from the air and water molecules and the energy from the sun to produce a simple sugar such as glucose and oxygen molecules as a byproduct. The simple sugars are then converted into other molecules such as starch, fats, proteins, enzymes, and DNA/RNA, i.e., all of the other molecules in living plants and animals. All of the of a plant or animal is ultimately produced as a result of this photosynthesis reaction. The equation governing photosynthesis is:

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\text{CO}_2 + \text{H}_2\text{O} + \text{energy} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2
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Environmental Impact:
Phosphate will stimulate the growth of plankton and aquatic plants which provide food for larger organisms, including: zooplankton, fish, humans, and other mammals. Plankton represent the base of the food chain. Initially, this increased productivity will cause an increase in the fish population and overall biological diversity of the system. But as the phosphate loading continues and there is a build-up of phosphate in the lake or surface water ecosystem, the aging process of lake or surface water ecosystem will be accelerated. The overproduction of lake or water body can lead to an imbalance in the nutrient and material cycling process (Ricklefs, 1993). Eutrophication (from the Greek - meaning "well nourished") is enhanced production of primary producers resulting in reduced stability of the ecosystem. Excessive nutrient inputs, usually nitrogen and phosphate, have been shown to be the main cause of eutrophication over the past 30 years. This aging process can result in large fluctuations in the lake water quality and trophic status and in some cases periodic blooms of cyanobacteria.

In situations where eutrophication occurs, the natural cycles become overwhelmed by an excess of one or more of the following: nutrients such as nitrate, phosphate, or organic waste. The excessive inputs, usually a result of human activity and development, appear to cause an imbalance in the "production versus consumption" of living material (biomass) in an ecosystem. The system then reacts by producing more phytoplankton/vegetation than can be consumed by ecosystem. This overproduction can lead to a variety of problems ranging from anoxic waters (through decomposition) to toxic algal blooms and decrease in diversity, food supply and habitat destruction. Eutrophication as a water quality issue has had a high profile since the late 1980s, following the widespread occurrence of blue-green algal blooms in some fresh waters. Some blue-green algae can at times produce toxins, which are harmful to humans, pets and farm animals.

Under aerobic conditions (presence of oxygen), the natural cycles may be more or less in balance until an excess of nitrate (nitrogen) and/or phosphate enters the system. At this time the water plants and algae begin to grow more rapidly than normal. As this happens there is also an excess die off of the plants and algae as sunlight is blocked at lower levels. Bacteria try to decompose the organic waste, consuming the oxygen, and releasing more phosphate which is known as "recycling or internal cycling". Some of the
phosphate may be precipitated as iron phosphate and stored in the sediment where it can then be released if anoxic conditions develop.

In **anaerobic conditions** (absence of oxygen), as conditions worsen as more phosphates and nitrates may be added to the water, all of the oxygen may be used up by bacteria in trying to decompose all of the waste. Different bacteria continue to carry on decomposition reactions, however the products are drastically different. The carbon is converted to methane gas instead of carbon dioxide, sulfur is converted to hydrogen sulfide gas. Some of the sulfide may be precipitated as iron sulfide. Under anaerobic conditions the iron phosphate precipitates in the sediments may be released from the sediments making the phosphate bioavailable. This is a key component of the growth and decay cycle. The pond, stream, or lake may gradually fill with decaying and partially decomposed plant materials to make a swamp, which is the natural aging process. The problem is that this process has been significantly accelerated.

**Non-Point Sources of Phosphate**
The non-point sources of phosphates include: natural decomposition of rocks and minerals, stormwater runoff, agricultural runoff, erosion and sedimentation, atmospheric deposition, and direct input by animals/wildlife; whereas: point sources may include: wastewater treatment plants and permitted industrial discharges. In general, the non-point source pollution typically is significantly higher than the point sources of pollution. Therefore, the key to sound management is to limit the input from both point and non-point sources of phosphate.

Plants may not be able to utilize all of the phosphate fertilizer applied, as a consequence, much of it is lost from the land through erosion, since phosphate has a stronger affinity to binding with the soil compared to nitrogen. The phosphate enters the ecosystem and becomes tied up in the biogeochemical system where it is recycled. The rapid growth of aquatic vegetation and/or increase in the algal population can cause the death and decay of vegetation and aquatic life because of the decrease in dissolved oxygen levels. A large percentage of the phosphate in water is precipitated from the water as iron phosphate or stored in partially decomposed organic material. Through a combination of microbiological action and anoxic conditions, the phosphate may be readily recycled back into the water for further reuse causing the mass of phosphate to build-up in the ecosystem. In deeper environments, the phosphate may be stored in the sediments and then recycled through the natural process of lithophication, uplift, and erosion of rock formations.

**Blue Green Algae**
Blue green algae (or cyanobacteria) are small single celled prokaryotic (having no nucleus or organelles) microorganisms, only a few microns long. When present in large groups or blooms, these algae appear as a blue-green discoloration in the water. This type of algae is usually found in freshwater and are most common in areas with high levels of nutrients and warm, sunny, and calm conditions. Many blue-greens grow attached on the surface of rocks and stones (epilithic forms), on submerged plants (epiphytic forms) or on the bottom sediments (epipelic forms, or the benthos) of lakes. Some species of blue-green algae produce chemicals that are harmful to both animals and humans. These algal blooms have been linked to health problems ranging from skin irritation to liver damage to death, depending on type and duration of exposure. The livelihood of many fish, shellfish, and livestock has also been endangered through contact with this toxin. In addition to causing animal and human health concerns large amounts of blue-green algae can literally suffocate organisms by depleting water of life-sustaining oxygen by causing hypoxic or anoxic conditions.