## Nitrogen Reactions in Soil

The amount of nitrogen (N) that is in an available or soluble form at any one time is small. Very little is found in the rocks or minerals from which soils are formed. Most of the N in the environment is located in the atmosphere. About 80% of the air is made up of nitrogen gas. The largest "pool" of N in the soil is found in the organic matter. This organically bound N must undergo several transformations to become plant available or soluble in water. Plants take up this available or soluble N in their process of growing. At the end of the growing season dead or discarded plant material returns to the soil surface or is incorporated into the soil. This dead plant residue replenishes the soil organic matter pool.

Various methods are used to get N from the air to the plant. Legume plants have the ability to "fix" N from the air in rhizobia containing root nodules, which is then translocated and used by the plant for growth. Man has invented a process that manufactures N containing fertilizers by capturing nitrogen from the air. This fertilizer N supplements organic matter N in growing plants. This entire process is cyclic in nature and involves a recycling of N in the environment.

## Soil organic nitrogen

The largest "pool" of N in the soil is contained in the soil's organic matter. This represents about 97 to 98% of the total N. In Kentucky, the average soil has about 3% organic matter in the surface 6-7 inches, or about 60,000 lbs in a one acre slice of 2,000,000 lbs soil. With about 5 % of the organic matter being N, the total N in this "pool" is about 3000 lbs. This unavailable and insoluble form must be converted by soil microbes to more available or soluble forms.

## **Nitrogen Mineralization**

Mineralization involves the process of microbially converting unavailable organic N to inorganic N. Inorganic forms of N make up only about 2 to 3 % of the total N in soils. The first step in this process is that fungi, actinomycetes, and bacteria break down the larger residue pieces into very small pieces, releasing carbon dioxide in the process. A small amount of available or soluble N is required for these microbes to begin this process. Usually about 1 part of N is required for 30 to 40 parts of carbon.

The second step is for bacteria to further decompose these very small pieces of organic matter (proteins, amino acids, etc.) into their basic chemical compounds, one of which is ammonium N (inorganic form). This process is often called ammonification. The ammonium exists in a cation form that is rapidly attached to clays or other organic matter by the exchange process in soils.

Organic N ====> Ammonium (NH4+)

## Nitrification

The third step in mineralization is called nitrification. The source of ammonium ions could either be from organic matter mineralization, supplementation from ammonium containing N fertilizers, or animal waste. This process uses bacteria to convert ammonium to soluble nitrate which is the major form taken up by growing plants. This process requires oxygen and it releases

hydrogen ions in the soil.

Ammonium = Nitrate (NO<sub>3</sub>-)

The nitrate form is soluble in water and can move with soil moisture deeper into the soil profile (leaching) or upward to the soil surface as water is evaporated. When a soil lacks sufficient oxygen to maintain normal bacteria growth, the oxygen can be separated from the N of a nitrate molecule in denitrification.

## Immobilization

This term applies to any process that converts inorganic N in the available or soluble forms to plant unavailable or insoluble forms. This happens in several soil and plant processes: (1) when legume plants "fix" N from the atmosphere with rhizobia in root nodules that is converted to plant proteins; (2) when plant available or soluble forms are taken up by plants through the roots and metabolized into plant compounds; and (3) when soil microbes have insufficient available N, they will "grab" available or soluble N near their sites of growth to combine with carbon in plant residue during the early stages of mineralization.

Depending on the process, immobilized N can be a significant amount, and the length of time N is immobilized can be from a few weeks to a few years. The amount contained in plant residues can be returned to the organic N "pool" of the soil while that portion of plant removed from the land is lost to the natural soil recycling of N. Listed below are amounts of N that are immobilized in a growing plant and amounts that can be returned to the soil in plant residue.

or removed as usable feeds.					
	Ν	N	Ν	Ν	
Crop	Uptake	Fixed	Removed	in Residue	
150 bu Corn	150 lb		95 lb	55 lb	
50 bu Soybeans		250 lb	150 lb	100 lb	
60 bu Wheat	92 lb		72 lb	20 lb	
5T Alfalfa		250 lb	250 lb		
4T Fescue	140 lb		140 lb		
7T Bermuda grass	280 lb		280 lb		
NO3 - ====	ngan kaning mata kanin mining sanat waka manin Mana alaya ya ita kanin salini ikalia mana minin	=>		==>Removed	
		PLAN	ГS		
N2 ======		=>		=> Residue	

Nitrogen amounts taken up or fixed by plants, and amounts contained in residue

#### Denitrification

This process occurs when any part of the soil containing nitrate becomes deficient in oxygen (<5 % of soil air) so that bacteria metabolize the nitrate ion in order to get the oxygen for survival. The result is a release of gaseous forms of N into the atmosphere. Denitrification can begin within a few hours after the onset of oxygen deficiency and can proceed rather rapidly.

Losses ranging from 10 % to as high as 90 % of fertilizer nitrate have been reported within a few days under oxygen deficient conditions.



## Fertilizer Nitrogen

Several N fertilizer materials are manufactured that are used to supplement the release of N from organic matter for producing several crops. Most of the manufactured sources start with the production of ammonia (NH<sub>3</sub>). This is a gas made by combining hydrogen from natural gas with N from the air in the presence of a metal catalyst.

N2 + CH4 ===> NH3 Nitrogen Natural gas Anhydrous ammonia (82 % nitrogen)

This basic product must be stored under pressure in sealed containers. It is used directly for soil application in many areas of the state, primarily for corn production. From this basic product, several other N fertilizer materials are manufactured:

NH3	+ HNO <sub>3</sub> ====================================	Ammonium nitrate (34 % nitrogen)
NH3	+ CO <sub>2</sub> ====== Carbon dioxide	> CO(NH2)2 Urea (46 % nitrogen)
NH3	+ H2SO4 ====== Sulfuric acid	=====> (NH4)2SO4 Ammonium sulfate (21 % nitrogen)

#### **Nitrogen Fertilizer Reactions**

<u>Anhydrous ammonia</u>. When anhydrous ammonia is injected into the soil under pressure it reacts rapidly with soil moisture to form an ammonium ion. This ammonium attaches to the exchange complex of the soil. It then goes through the nitrification process (outlined above) to form nitrate. This process usually starts within a day or two and can be completed with a few weeks.

<u>Ammonium nitrate.</u> This material is dissolved in the soil moisture giving rise to two separate ions: ammonium and nitrate. The ammonium ion attaches to the exchange complex and is converted to nitrate by the nitrification process. The fertilizer nitrate is directly available for plant uptake thus this material has one-half of its N available rather quickly.

<u>Urea.</u> This material when applied to the surface with adequate moisture, soil temperature above 50 degrees F, and in the presence of urease enzyme will rapidly convert to ammonia. This ammonia can be lost to the atmosphere through volatilization if not incorporated or moved into the soil via rainfall within a few hours, or if the surface temperature is above 50 degrees.

<u>Ammonium sulfate.</u> This material dissolves in soil moisture leaving two ammonium ions and a sulfate ion. As with the other materials, the ammonium goes through the nitrification process to produce nitrate. The sulfate is readily available to plants as a source of needed sulfur.

## Nitrogen from Animal Manure

In recent years, more animal manure has been applied to the land as a source of N. Forms of N found in animal manure include organic N, ammonium and a small amount of nitrate. The ratio and amounts of organic N and ammonium N depends on the animal species and the storage or treatment prior to land application.

The reactions of N from animal manure are essentially the same as discussed above for any other related N form. Organic N is mineralized to the ammonium form followed by nitrification. This process will delay release of some of the total N during the first year after application and will usually result in some N being carried over into the following 2 to 3 years (residual N). Ammonium N is available for nitrification to nitrate just as any source of ammonium, and any nitrate present with application will be immediately available for plant uptake or leaching.

Storage methods like deep lagoons (> 8 ft) promote greater amounts of ammonium since oxygen diffusion to depths greater than 8 ft is low, favoring mineralization to ammonium but not any further to nitrate. In some cases, small amounts of nitrate will be formed above the 8 ft depth but become a small portion of the total N when the lagoons are stirred prior to land application. Shallow lagoons or holding ponds (< 8 ft) will have slightly higher amounts of the nitrate form. Both types of storage will have much larger portions as organic N.

Stacks of manure solids will have primarily organic N but will tend to have some more ammonium if stacks remain in place for a long period and significant amounts of ammonia are trapped in the stack and not volatilized. Bacterial activity does take place as C:N ratios are most favorable. With C:N being below 20:1, volatilization of some N is quite likely as the bacteria release ammonia N. However, when bedding material such as straw, sawdust or wood shavings are part of the total mixture, the effective C:N ratio may be much higher and thus much less or no ammonia is volatilized during bacterial decomposition while piled. Research at UK with stacking poultry litter, after whole house clean out containing wood shavings, indicated that very little N as ammonia was lost. The C:N ratio of the stacked litter was about 12:1, which is about the same ratio as contained in soil organic matter.

The collective availability of N in animal manure is less than N availability from fertilizer sources. First, research with animal manure N has compared its availability to N fertilizer sources, and secondly, the presence of significant amounts of organic N offers a natural delay in availability. First year N availability has ranged from as low as 30 % to as high as 75 % of the total N applied. Part of this wide range is attributed to potential volatilization of ammonia, part to species differences as it affects the proportions of organic and ammonium, and part to storage method prior to land application.

Poultry manure (broiler, layer and turkey) has a much higher fraction in either the ammonium form or another form that is easily converted to ammonium. The organic N is often a lower percentage of the total nitrogen. This manure will have greater potential volatilization losses and higher first year availability to plants.

Cattle (beef and dairy) manure will have higher organic N portions resulting from the dietary components (more forage based) and the digestion process (bacterial activity in a rumen).

This will be reflected in a reduced first year availability of N to plants.

First year N availability from swine manure will be slightly higher than from cattle manure but usually less than from poultry manure. The dietary makeup is usually oriented to feedstuffs that are ground finer, have a higher energy content, and greater reduced forage makeup. When both feces and urine are collected, stored and handled together, the N availability is at its maximum.

## **Residual nitrogen**

Residual N is a term used to define N that will remain in the soil for more than one cropping season, and become available following bacterial action in succeeding years. Sources of residual N include soil organic matter, undecomposed crop residue, active bacterial mass, and undecomposed animal manure. The overlying characteristic of these sources is that N is part of an active or undecomposed organic material. The length of potential residuality depends on the complexity of the organic material. The more complex the organic compounds containing the N, the longer the potential residuality. The more complex compounds take longer for natural bacterial breakdown. Therefore, there is really a built-in length of time for N carryover due to the amount of complex materials containing N.

Soil organic matter is the largest pool in the soil of more complex N containing compounds. Some of the crop residue, especially those materials containing cellulose and lignin, are more complex. Some fraction of animal manures also contain these more complex compounds. In some soils receiving annual animal manure applications, the active bacterial mass will have significant N "tied up" (immobilized) in their bacterial bodies that will only be released when bacterial activity is reduced due to low amounts of readily available carbon. This is the reason that some soils receiving annual manure applications may have long-term (5-6 years) availability of N after several annual applications (higher percentages of residual N for more years).

In planning for crop growth, the amount of potential residual N should be taken into account. Current recommendations usually only account for residual N for up to two years but, as mentioned above, long-term annual manure applications can extend this residual nitrogen availability for several years. The best correction is to increase (by 2x) the amount of residual N available to crops in years 2 and 3 following 4-5 years of annual manure applications.



## **Phosphorus Sources and Soil Reactions**

Phosphorus is a very chemically reactive element, so it is not found in nature in the pure state. It is found only in combinations with other chemical elements. The upper 6 to 7 inches of soil may contain from 400 to 1,600 lbs of total phosphorus in combination with other elements. Most of this phosphorus is not readily available to plants or is not in a soluble form.

Native soil phosphorus amounts for plant growth as measured by a soil test come largely from weathering of apatite, a mineral containing both calcium and phosphorus plus small amounts of fluoride and chloride. As the apatite slowly breaks down, several other chemical compounds are formed. Two soluble phosphorus compounds (called orthophosphates) are contained in the soil solution in very low amounts (0.01 to 0.1 % of total phosphorus). In order to provide a soluble source for adequate plant uptake, research has indicated that a P concentration of 0.025 to 0.04 ppm must be in soluble form in the soil solution at all times to prevent phosphorus deficiency. This indicates that only small amounts of the total soil phosphorus are soluble at any one time and that the soil solution must be replenished 250 to 350 times during the growing season.

As a corn crop grows during the season, 150 bu will remove about 25 lb of phosphorus in the grain per acre. If we assume most of the phosphorus comes from the top 6 inches of the soil and the soil solution contains about 0.08 lbs of phosphorus per acre at any one time, the soluble phosphorus must be replenished approximately 312 times during the growing season. Therefore, it is not only the solubility of phosphorus containing compounds that controls phosphorus availability in the soil, but more important, the rate at which these compounds dissolve to maintain phosphorus in the soil solution.

Phosphorus has been supplemented with mined and manufactured fertilizer sources during the last 60 or more years. These supplemental sources contain more soluble compounds of phosphorus following the manufacturing process. The need for supplemental sources has been based on observations of phosphorus deficiency in plants, the need to produce higher crop yields, and the ability of soils to keep large amounts of phosphorus in unavailable and insoluble forms. More recently, animal manures and other wastes containing relatively high amounts of phosphorus have become available for land application. Some of the phosphorus (10 to 12 %) in animal manure is considered water soluble, a large portion (40 to 55 %) is in organic forms, and the remainder exists as relatively insoluble inorganic compounds.

#### Forms and Related Availability

Research has identified up to 60 different phosphorus containing compounds in soils that affect phosphorus solubility and thus plant availability. Many of these are not stable, particularly the ones formed with the addition of more soluble phosphorus containing nutrient sources. The more unstable compounds tend to form and dissolve quite rapidly to form more stable compounds that will persist for some time in the soil. Below is a diagram that denotes the more general forms of phosphorus compounds and a general rating of their solubility.



## Affects of Soil pH

Soil pH is the most important factor in determining formation and solubility of phosphorus compounds. The first stable compound that forms from any inorganic or soluble fraction in slightly acid to calcareous soils is usually dicalcium phosphate dihydrate. In more acid soils the first stable compound is thought to be a noncrystalline aluminum or iron phosphate. These reaction products are slightly soluble and slowly available to plants, and thus largely determine the small amount of phosphorus available in the soil solution.

When a nutrient source like fertilizer phosphorus is applied to soil, the compounds that form are influenced primarily by soil pH, and to a lesser degree, by the properties of the fertilizer itself. The initial, nonstable compounds formed are influenced by the form of fertilizer. However, these compounds may quickly dissolve to form a more stable dicalcium phosphate dihydrate or the

iron and aluminum compounds.

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When a nutrient source such as animal manure is applied, some 10 (normal) to 30% (with phytase) may be water soluble inorganic phosphorus with the remainder being combined with other elements as a precipitate (dicalcium phosphate) or present as organic phosphorus. The water soluble inorganic fraction is subject to formation of the same compounds as described above depending on soil pH. The organic phosphorus is made available as an inorganic source after going through microbial decomposition of the phosphorus containing organic compounds.

## **Phosphorus Sorption**

Many of the soluble or readily soluble phosphorus containing compounds are capable of being sorbed to clay particles. This process appears to involve the attachment of more soluble phosphorus compounds to the hydroxy compounds of iron [Fe(OH)x], manganese [Mn(OH)x] and aluminum [Al(OH)x] that coat the surfaces and edges of clays. Research has indicated that this process can "tie-up" a considerable amount of phosphorus in a soil, and is a major method for many soils to keep phosphorus out of solution. Yet this "tied-up" phosphorus is slowly available to replenish the soil solution. Sorption to these hydroxy compounds occurs more rapidly in acidic soils, and unless the soil is limed or has some source of readily available calcium, the phosphorus will be strongly retained by this mechanism.

As mentioned earlier, the amount of sorbed phosphorus can be considerable in some soils. Research at North Carolina State Univ. indicates that differences in soils is related to clay percentage. A higher clay percentage increases surface area for coating with iron, manganese, and aluminum hydroxy compounds in the soil. Laboratory studies at Auburn Univ. indicated that a Dewey silt loam could adsorb up to 1466 lbs/acre of phosphorus (3357 lbs P<sub>2</sub>O<sub>5</sub>/acre) in the surface 6 inches. If we assume this ability is equally distributed within the entire 6 inch depth, this translates to 122 lbs P/inch of depth. As this value is approached, and certainly when it is exceeded, soluble phosphorus compounds can leach through the soil profile until each inch has sorbed its maximum.

## **Downward Phosphorus Movement**

As indicated by some of the earlier discussion, most sources of phosphorus, except soluble forms, move very little in soils. Given enough time and good water infiltration, movement of soluble phosphorus can contribute to significant changes in phosphorus levels in different layers of soil. For example, when surface applied soluble phosphorus exceeds the sorption capacity of the top 1/4 to 1/2 inch, the surplus soluble P will move downward with soil water until it is held by the next layer of soil. With additional surface applications to an already "saturated" layer, the soluble forms will keep moving downward until they are sorbed by the underlying layers of soil that are not "saturated". Soils in which a high amount of infiltrating water moves downward in large macropores will tend to move phosphorus downward faster. Smaller pores will slow the infiltrating water that allows the soluble phosphorus to sorb to clay more readily.

Phosphorus that is combined with other compounds tends to exist as fine precipitates. These compounds move very little in soils with smaller pores, as the pores tend to act like filters. In the case of large pores, the rapid movement of infiltrating water can carry fine precipitates to lower depths before it is filtered or slowed. In most cases, this is not a major source of downward moving phosphorus.

## **Soluble Phosphorus**

As previously mentioned, the amount of phosphorus that is soluble usually ranges from 0.01 to 0.1 % of the total soil phosphorus. Total soil phosphorus is measured in research using special lab techniques. Soil test extractants (e.g., Mehlich III) dissolve only a fraction of the total phosphorus into the chemical solution. This extractable phosphorus is related to the total quantity of phosphorus in a soil. Extractable phosphorus represents a total of the soluble fraction, a large portion of the readily available fraction, and some of the slowly available fraction. Soils may have a total phosphorus of 200 lbs/acre but could have only 20 lbs/acre P showing in a soil test. On the other hand, a phosphorus rich soil may have 2000 lbs of total phosphorus and 400 lbs P from a soil test. These differences represent differences in soil parent material, past fertilization, and solubility of phosphorus compounds found in a particular soil.

The research at Auburn University indicated that the amount of soluble phosphorus was very well related to soil test extractable phosphorus. Their research also indicated that as a monocalcium source (common in fertilizer) and poultry litter were added, the soluble phosphorus and soil test phosphorus increased with applied phosphorus rates. This is probably related to the earlier mentioned fact that soil test extractants measure all of the soluble, a significant portion of the readily soluble, and some of the slowly soluble fractions. Also, much of the added phosphorus in fertilizer will remain more soluble until combined with other elements to become more insoluble, or sorbed unto the hydroxy compounds of iron, manganese and aluminum.

The amount recommended by the US EPA that should not be exceeded for surface water bodies is 1 ppm (1 mg P/liter). If a soil has 1000 lbs/acre of total phosphorus and 0.1 % is soluble, then 1 lb phosphorus/acre may be in the soluble form. If the same soil has only 0.01 % soluble, then 0.1 lb phosphorus/acre may be in the soluble form. Assuming that 6 inches of this soil contains 25 % water by volume, then 1 acre would have 154,175 liters of water. If the soluble phosphorus is 1 lb/acre, then the concentration of soluble phosphorus could be 2.9 ppm, and if the soluble phosphorus is 0.1 lb/acre, the soluble phosphorus concentration in the soil water could be 0.29 ppm. With 400 lbs/acre of total phosphorus and the same relationships, the concentration of soluble phosphorus would be about 1.2 ppm and 0.12 ppm, respectively, for two solubility percentages. A key point of this discussion is that whatever level of phosphorus exists in solution, each soil has a specific set of interacting factors that will strive to maintain a concentration level between the previously mentioned ranges. Replenishment will result when phosphorus is removed by plant uptake, leached downward in the soil, or removed in surface runoff.

#### Potential removal in surface runoff

Precipitation as rainfall contains almost no phosphorus. Much of the rainfall infiltrates into the soil during the early part of a rainfall event. This infiltrating water can carry phosphorus to lower depths as described earlier. In this process the infiltrating water replaces soil solution. The tendency is for the soil to replenish the phosphorus in the infiltrating water through its normal mechanisms.

As rainfall events continue, the surface becomes more saturated and infiltration slows. This creates more opportunities for water to move over the surface and leave the land as surface runoff. Some studies have indicated that surface runoff tends to be very reactive with the surface 2 inches of soil. This suggests that soluble and some of the readily soluble phosphorus from the top 2 inches of soil can leave through surface runoff leaving the land. This happens through the

tendency of the soil to replenish phosphorus in the runoff water.

One must keep in mind that there is a lot of variability in soils even in short distances across a landscape, particularly as it relates to the soils' ability to either release phosphorus or to adsorb phosphorus. It appears that water low in phosphorus will tend to be a sink for soluble or readily soluble soil phosphorus (soil P ====> water). This removes phosphorus from the land area. On the other hand, runoff water that is relatively high in phosphorus, can have phosphorus removed from the water by being adsorbed to soil particles (water P ====> soil). The direction of this process is determined by the relative concentration of the water moving over a land area to the concentration of soluble and/or readily soluble phosphorus in the surface depth reacting with the moving water, and the soils' ability to either release or sorb soluble phosphorus. Studies have indicated that early runoff water leaving the land often contains a high level of soluble phosphorus from the soil solution existing at the time runoff started. Levels of phosphorus in later runoff appear to be more related to the replenishment ability of the soil usually resulting in lower phosphorus concentrations.

The water soluble phosphorus in animal manure has a high potential to move with surface water. When the animal manure remains on the soil surface and does not have sufficient time to react with soil before a significant rainfall event, the soluble phosphorus can move with the water. With intensive rainfall on sloping land, some of the animal manure consisting of either insoluble precipitates or organic particles can be carried in the rapidly moving water.



## **Phosphorus in Aquatic Environments**

## Why is phosphorus important?

Both phosphorus (P) and nitrogen (N) are essential nutrients for plants and animals that make up the aquatic food web. Since P is the nutrient most likely to be in short supply in most fresh waters, even a modest increase in P can, under the right conditions, set off a whole chain of events in a stream, many of them undesirable. These undesirable events include accelerated plant growth, algae blooms, low dissolved oxygen (when plants die and decay in water), and death of certain fish, invertebrates, and other aquatic animals.

There are many sources of P, both natural and as a result of human activity. These include soil and rocks, wastewater treatment plants, direct discharge of septage, runoff from fertilized areas, runoff from animal manure storage areas, disturbed land areas, drained wetlands, water treatment, and commercial cleaning preparations to name a few.

## Forms of phosphorus

Phosphorus has a complicated story in aquatic environments. Pure, elemental P is rare because it will chemically explode when exposed to oxygen in the atmosphere. In nature, P exists as part of a phosphate molecule (PO4). Phosphorus in aquatic systems occurs as organic phosphate and inorganic phosphate. Organic phosphate consists of a phosphate molecule associated with a carbon-based molecule, as in plant or animal tissue. Phosphate that is not associated with an organic molecule is regarded as inorganic phosphate. Inorganic P is the form required by plants. Animals may use either organic or inorganic phosphate. Both organic and inorganic P can either be dissolved in the water or suspended (attached to particles in the water column).

## The phosphorus cycle

Phosphorus cycles through various parts of the aquatic environment, changing forms as it cycles (See Figure 1). Aquatic plants take up dissolved inorganic P and convert it to organic P as it becomes part of their tissues. Animals can get the P they need by eating either aquatic plants, other animals, or decomposing plant and animal material.



Figure 1. P cycle in an aquatic environment.

As plants or animals excrete waste or die, the organic P they release sinks to the bottom of a water column, where bacterial decomposition converts the material back to inorganic P that may be dissolved or attached to other particles. This inorganic P gets back into the water column when the bottom sediments are stirred by animals, human activity, chemical reactions, or water currents. This P can then be taken up by plants and the cycles begins again.

In a stream system, the P cycle tends to move P downstream as the current carries decomposing plant and animal tissue and dissolved P. The P becomes stationary only when it is taken up by plants, is bound to particles that settle to the bottom, or is bound to sediment particles at the bottom.

In the field of water quality chemistry, P is described using several terms. Some terms are chemistry based (referring to chemically based compounds), and others are methods-based (they describe what is measured by a particular method). The term "orthophosphate" is chemistry-based and refers to the phosphate molecule all by itself. This form of P is closely related to plant available P in water. "Reactive P" is a method-based term that describes what you are actually measuring when testing for orthophosphate. Because the lab procedure for reactive P is not quite perfect, the test result measures not only orthophosphate but a small fraction of other forms. This form is important because the P measured in this test may be biologically available (bioavailable P) to many aquatic organisms in water. More complex inorganic phosphate compounds are referred to as "condensed phosphates" or "polyphosphates". These forms are more common to organic P forms. The method-based terms for these forms is "acid hydrolyzable".

### **Monitoring phosphorus**

Monitoring P levels in aquatic environments is challenging because it involves measuring very low concentrations – down to 0.01 mg/L or even lower. Even such very low concentrations of P can have a dramatic impact on streams. Less sensitive methods should be used only to identify serious problem areas.

While there are many tests for P, only four are likely to be performed with any regularity:

1. The **total orthophosphate** test is largely a measure of orthophosphate. As the sample is not filtered, this procedure measures both dissolved and suspended orthophosphate. The official EPA test uses ascorbic acid to develop a blue color following the addition of acid ammonium molybdate to the sample. The more intense the blue color, the higher the P concentration in the sample.

2. The **total P** test measures all the forms of P in the sample (orthophosphate, condensed phosphate, and organic phosphate). As the sample is not filtered, this procedure measures both dissolved and suspended phosphate. The sample is digested with heat and a strong acid converting all forms to orthophosphate. Then the ascorbic acid method is followed.

3. The **dissolved P** test measures that fraction of the total P which is in solution in the water. The sample is filtered, thus excluding any P attached to suspended particles. The sample is digested (some soluble P may be a part of soluble organic compounds) and analyzed with ascorbic acid and then acid ammonium molybdate is added.

4. Insoluble P is calculated by subtracting the dissolved P result from the total P result.

All of the above tests have one thing in common, they depend on measuring orthophosphate in the final solution. This orthophosphate either exists in solution or the sample has other forms that were converted to orthophosphate by digestion.

## EUTROPHICATION and PHOSPHORUS CYCLING IN A SHALLOW WATER BODY

**Eutrophication** is the process by which a rich flow of nutrients into a body of water, especially a lake or pond, causes excessive growth of aquatic plants, particularly algae. The premise of many articles on theories of phosphorus as a limiting nutrient were developed from observation and analysis of deep lakes. The majority of lakes, ponds and other waters of prime concern are shallow, and different mechanisms of nutrient balance appear to be in operation.

In any water body, the balance of nutrients, principally nitrogen and phosphorus, is a function of inflow from the surrounding watershed, outflow to a stream, denitrification to the atmosphere, and phosphorus settling as organic or precipitated material to the bottom of the water body. Compared to a deep lake, a shallow lake has considerable denitrification to the atmosphere (a function of area/volume), and major recycling of phosphorus between bottom sediments, growing plants, and the water. Thus, there is a major difference between the nitrogen/phosphorus ratio between the two sizes of systems.

An understanding of the ratio and recycling differences between the two lake size systems has come from the lack of success in attempts at restoring shallow lakes modeled on methods tested on deep lakes. Studies of these failures led to the hypothesis that in a eutrophied lake (dominated by algae), reeds, pondweeds, lilies, and other large plants cannot survive. But these plants are essential for survival of zooplankton (which graze on the algae) as they provide a refuge from zooplankton-eating fish. Without these plants, fish will eat almost all the zooplankton and algae growth will remain unchecked.

A second factor in shallow lake ecology is that the activity of bottom-feeding fish and other animal life stirs up the sediment in search of food. In doing so, phosphorus is re-suspended into the water column which serves as an additional source of nutrients for growth and regrowth of algae. Boat propellers may create similar effects.

The two states of a lake, a) clear water with larger plants, and b) algal eutrophication, are essentially stable and self-sustaining. These two states can, however, be "switched," not only by limiting one or more of the nutrients (nitrogen and phosphorus) but also by the removal and replacement of plant and fish species (biomanipulation). This has been successful in Great Britain. A dammed lake became eutrophied after the brown trout were naturally replaced by common carp and other bottom feeding fish. Blooms of potentially toxic blue-green algae appeared, and warning notices on this recreational lake had to be posted. The carp had acted as a "switch" to permanently change the state of the lake. The lake was drained to remove the existing fish and restocked with non-bottom feeding fish. The lake is now recovering and is much clearer than it has been in decades.



## Factors Affecting the Response of Aquatic Systems to Nutrients

The response of a waterbody to changes in nutrient loading depends on many factors. The essential factors are those that affect algal and plant abundance, and biomass accumulation, such as availability of nutrients, light, substrate for attached plants, time for growth, temperature, grazing pressure, and physical suitability. Each essential factor may be controlled by additional factors and processes.

For this discussion on nutrients, particularly N and P, you may want to review Appendix A and Appendix B related to aquatic systems. These transformations are displayed as nutrient cycles.

## **Dominant plant forms**

Growth of aquatic vegetation is desirable in most systems to support the aquatic food chain. However, overabundance of plants disrupts the normal processes and often leads to degradation of the entire system. The three basic forms of aquatic plants are phytoplankton, periphyton, and macrophytes. Each form has requirements for growth and different implications for aquatic management.

**Phytoplankton** are microscopic algae suspended in the vertical water column. Their form may be single cell, filaments, or colonies of cells. Most have limited mobility in water, and thus, are carried with flowing water. They must take up nutrients directly from the water. Some cyanobacteria (also called blue-green algae) can use atmospheric N gas as a source of N. Some cyanobacteria have gas vacuoles that allow them to float on the water surface which promotes surface scum formation.

**Periphyton** are a community of organisms, often dominated by algae, but also include other bacteria, fungi, protozoa, and other microbes, that grow attached to a solid surface. These organisms often attach to a stable surface, such as rocks, woody debris, and plants. The two main types of periphyton associated algae are either filamentous or nonfilamentous. Filamentous algae are composed of many cells linked together forming long strands. Nonfilamentous algae grow as single cells or colonies attached to bottom surfaces. Nonfilamentous periphyton communities are generally dominated by diatoms.

**Macrophytes** are any plant large enough to be visible without magnification. More commonly, macrophyte refers to plants that have roots, stems, and leaves, although in some areas mosses and liverworts are important macrophytes. These plants may be rooted in the sediment or free-floating. Rooted macrophytes obtain nutrients through their roots and translocate the nutrients to other parts of the plant. These rooted plants depend largely on sediment for nutrients.

**Plant Relationships.** The physical and chemical environments of the aquatic systems strongly affects which types of plant dominate. Deep, turbid water does not support periphyton because light cannot penetrate to the bottom, but could support phytoplankton because they would spend part of their time in a lighted zone. Rivers without sufficient residence time (rather rapid flow) do not support phytoplankton as these organisms are swept away before any substantial population can develop and expand. Rapidly flowing streams and rivers are thus usually free of algae masses.

The kinds of plants that dominate influence the systems' biological and chemical characteristics. In favorable conditions phytoplankton populations can increase rapidly and may cause an algal bloom. These blooms are identified as green coloration of the water or development of a surface scum when the algae are buoyant. If the bloom is large or when it dies, dissolved

oxygen is rapidly depleted during decay of the organisms. Some algal blooms produce toxins that can kill livestock and fish.

Macrophytes can move P out of the sediment and, through dieback and decomposition, release soluble N and P into the water column where it is available for phytoplankton. Macrophyte beds also stabilize sediment and reduce resuspension of sediment (and associated P) by wind-induced water turbulence. In some aquatic systems, phytoplankton create sufficient turbidity that prevents good macrophyte establishment because of limiting light. In this case, sufficiently reducing nutrient concentrations in the water column to control phytoplankton may lead to increased macrophyte abundance. This condition can create a whole set of different impairments.

## Water Residence Time

Residence time is measured by dividing the waterbody volume by the flow rate out of the waterbody. For example, if a lake has a volume of 200 acre-ft with outlet flow rate of 30 cu ft/sec, water residence time is 290,400 seconds [(200 ac-ft x 43,560 cu ft/ac-ft) / (30 cu ft/sec)] or 3.4 days. For a stream, residence is usually the travel time for a specific stream reach with some common characteristic, such as land use, gradient, or substrate. Generally, the slower the water flow or the more complex the stream (e.g., lots of woody debris or curving channels), the longer the residence time. For an estuary, residence time is volume divided by net water loss/day. In total, lakes will trap nutrients more efficiently than rivers, and P retention through either sorption or precipitation is proportional to residence time. Residence times change seasonally as outlet flows or volumes change.

Residence time of the water system determines whether phytoplankton populations have time to establish and accumulate. Phytoplankton are swept out of the water system before populations can increase (i.e., population growth cannot overcome losses) when residence time is too short. Thus, phytoplankton populations in such waterbodies will remain low. In some cases, where the water is nutrient enriched, an increasing population may cause downstream problems.

## Water Temperature

Most algae grow more rapidly at higher temperatures. Within a range of 32 to 77 degrees F, temperature increases of 18 degrees F typically double growth rate. Therefore, the plant response to nutrient inputs during winter is less pronounced or visible than during summer months. Blue-green algae tolerate higher temperatures than most other algae forms.

Another important factor is that oxygen solubility (DO) in water decreases with increasing temperature. Solubility in fresh water at 68 degrees F is 9.1 mg/L but at 86 degrees F the solubility decreases to 7.5 mg/L.

Controlling stream water temperatures may be a feasible algal control strategy to reduce adverse effects of nutrients when shade can be increased along banks. Water temperature often rises because of warmer water inputs from above or by having direct sunlight on the water. Shade from riparian vegetation and decreasing the width-to-depth ratio of a stream (encourages faster flow) are the primary strategies for lowering water temperature in many streams. Shading is often not a practical method of lowering temperatures in lakes, reservoirs, ponds, and wide rivers.

#### Sunlight

Both algae and macrophytes rely on sunlight for photosynthesis and growth. In most cases plant growth rates are a function of sunlight intensity up to a maximum, provided nutrient supplies

and temperature are favorable. Sunlight can be attenuated in several ways in aquatic systems.

**Riparian vegetation** - Riparian vegetation shades near-bank areas. Narrow streams surrounded by mature trees may have full shaded areas for the entire day. Well-shaded streams have low amounts of periphyton due to light limitations, even with high nutrient concentrations.

**Suspended sediment** - Suspended soil and organic particles in the water column scatter light and thus decrease the depth of light penetration. As a result, plant growth depends on the depth of light penetration.

**Color** - In some systems drained by wetlands and forests, dissolved organic compounds, such as tannins, will affect the light intensity and depth of penetration due to interception by the colored compounds.

**Self-shading** - Sunlight penetrates less deeply into water as phytoplankton or macrophyte abundance increases. At some depth in the water column too little light is available to support plant growth and maintenance. Plants remaining below that critical depth too long will die and decompose.

## Water Depth

Water depth affects sensitivity of nutrient inputs. Particles in the water column scatter, reflect or absorb light. Light intensity decreases as depth increases below the water surface. The point at which available light is too low to support plant growth is called the <u>compensation point</u>. Depth to the compensation point depends on the light intensity at the water surface and the number of scattered particles in the water. The scattered particles may include suspended clays, organic detritus, and phytoplankton. Lake bottom or streambed areas that are below the compensation point do not support periphyton or macrophyte growth.

In shallow (<6 ft) water, efforts to reduce suspended sediment and phytoplankton greatly increases water transparency thus increasing light intensity on the bottom sediment. If the bottom sediment is high in nutrients, macrophytes and sometimes periphyton will establish and grow although the overlying water column is low in nutrients.

## Water Column Stratification

Less dense water stays on top of more dense water. Layers of water tend to form in the water column starting with the least dense layer at the surface with each lower layer getting progressively more dense. This layering is termed <u>stratification</u>. Layers deeper in the water column of lakes, large ponds or reservoirs do not mix with each other and chemical concentrations in one layer can be very different from those in another layer. Shallow water columns tend to have more mixing due to wind aided wave action or rapid water flow. In most freshwater systems, water temperature is the most important factor affecting water density. Water is most dense at 39 degrees F, and it is a poor heat conductor. Therefore, layers with different temperatures (and thus different densities) can become established and persist. In summer, warmer layers are on top of cooler layers and warming from sunlight tends to strengthen this layering. In winter, the temperature pattern may be reversed with the 39 degrees F water (most dense) on the bottom with the colder (less dense) water and ice layering or floating on top.

Stratification may be broken down (sometimes called turnover) either by turbulence or by temperature changes in the surface layer. Turbulence can result from water flow changes or from wind. In lakes with long, open stretches or with relatively shallow depth, strong wind-induced turbulence can break up stratification. In temperature climates like Kentucky, seasonal air

temperature changes cause the surface layer of lakes or ponds to either cool (in the fall) or warm (in the spring) to the same temperature as a lower layer. This results in a turnover of the water and a breakdown of stratification. In many areas a turnover occurs both in the spring and fall although not all lakes may follow this pattern.

Stratification has important implications for nutrient dynamics. Because the deeper cold water is isolated from the atmosphere, dissolved oxygen in this water may be entirely depleted by microbes decomposing organic matter in the water or in the bottom sediment. The resulting hypoxic (low oxygen) or anoxic (devoid of oxygen) conditions converts iron from ferric (oxidized) to ferrous (reduced), thus releasing P in the sediment. When stratification breaks down with turning, the water layers mix and the released P becomes available within the new surface water where increased light conditions are suitable for algal growth. With more favorable conditions rapid algal growth can result. However, oxygenation (through surface exposure or wave action) of the former anoxic water oxidizes the ferrous iron back to ferric iron, resulting in the precipitation and sedimentation of P. It is evident that a cycle of internal release, circulation, precipitation and sedimentation exists in many lakes.

## **Ground water**

Although we commonly think of a stream as being contained within its channel, there is considerable interchange between surface water and ground water. Some sections of a stream may have significant inflows of ground water while other sections may experience significant outflows to ground water. Much of this is dependent on soil texture of the stream bottom, stream banks or stream valley, prevailing ground water movement in a defined stream valley, and water additions or withdrawal in the stream valley. During low stream flow, ground water inflow is likely to maintain some level of base flow, and during higher flow, water will tend to move outward through the stream banks. Even where the net gain or loss of flow is not significant, a high degree of exchange occurs between the stream and either ground water or surface water. This exchange occurs readily in a zone just below and adjacent to the stream channel where a mixture of ground and stream water can be found.

In areas where surface materials have been weathered from low P containing geologic material, unpolluted ground water generally contains <0.1 ug/L or ppb. Where high P containing geologic material has been weathered, unpolluted ground water may have 0.2 ppm P. Nitrogen in unpolluted ground water is <1 ppm. Natural enrichment from N is more rare.

Deeper ground water temperature is generally near the mean annual air temperature of a given location. As a result, ground water is usually cooler than surface water during summer months. Increasing the quantity of ground water input to a stream, or even into a small lake or reservoir, generally lowers its summer temperature, and may increase the likelihood of stratification.

## Forms of N and P Inputs

Nitrogen and P are carried into a waterbody in dissolved and particulate forms. In addition, the gaseous form of N dissolves into the water from the atmosphere. This N form can be used by blue-green algae to grow and reproduce.

Chemical analysis of water usually involves measuring both the dissolved and total concentrations of nutrients. Total concentrations are measured analytically after treating the sample with a strong acid to break down the compounds and particles into simple ionic forms.

**Dissolved forms.** Orthophosphate is the inorganic dissolved form of P. Results are often reported as soluble reactive P (SRP) because the analytical method is not perfect and thus may measure a small fraction of other P forms. Nitrate and ammonium, rarely nitrite, are the predominant dissolved forms of N. These forms can be taken up directly by plants and microbes, but in some cases, these ions must be further broken down before uptake can occur. Dissolved inorganic N and P are bioavailable to plant life in water.

**Particulate forms.** These are solid forms that can be divided into several general classes: <u>Organic material</u> - The N and P in organic particles are held in strong bonds that are generally broken down and released by microbial and enzymatic processes.

Low solubility inorganic particles - P can occur in particles as insoluble compounds of calcium, iron, manganese, aluminum or magnesium. Under conditions such as low dissolved oxygen or high pH, bioavailable P may be released from these compounds. Nitrogen rarely occurs in low solubility inorganic particles as either nitrate-nitrogen or ammonium nitrogen renders the compound readily soluble.

Sorbed or exchangeable forms-some P and ammonium-N are held on solid particle surfaces (especially clays) in forms that can move into the solution when concentration of the dissolved forms is reduced. These solid particles can be either sources of P (sorbed P ====> water P) or sinks (water P ====> sorbed P) depending on the dissolved concentration in the water. As an example, when the sorbed or exchangeable forms of N and P come in contact with rain water, the tendency is to release N and P into the rainwater until an equilibrium is reached because of the very low initial concentrations.

## **Stream bottoms**

Stream bottoms are characterized as being either soft or hard which affects their chemical stability and functions. Hard bottoms are usually made of bedrock, boulders, gravel or cobble stones that provide surfaces for attachment of organisms like algae. These hard materials are chemically stable. However, impurities in rock, such as clays, can remove or sorb P and ammonium N compounds. It has been observed that some P compounds may be attached to carbonate rocks due to their high calcium content.

Soft sediment bottoms are made up of clay, silt, sand and organic matter, or more often a mixture of these. Sand is the least chemically reactive, and does not stick together. Silt is more reactive and can retain or lose chemical compounds. Clays are very reactive and can have a large affect on water chemistry. The reactive compounds may remove P (water P ===> sorbed P) and some ammonium N from the water, depending on concentration levels and water pH. Iron phosphate compounds are likely to become soluble when dissolved oxygen concentrations become low.

Accumulated organic matter that is decomposing will release some or all of the N and P into the water. Decomposition rates will be higher at higher temperatures with sufficient dissolved oxygen in the water.

## Nutrient availability

All types of plants or organisms, whether they reside in water or grow on land, require N and P for their growth. Thus, N and P are two of several essential nutrients. Nitrogen is an essential part of amino acids that make up proteins, enzymes, nucleic acids and chlorophyll. Phosphorus is required for ATP, cell membranes, nucleic acids, seed phytate, and other energy storing compounds.

Growth is obviously inhibited when these nutrients are in short supply.

In some water systems, the "desired condition" requires low concentrations of N and P in a soluble or bioavailable condition. Most freshwater systems have P as the limiting nutrient. In water systems, algae and plants can obtain N and P from both the sediment and the water column. Also, when P is not limiting, algae such as the blue-greens get enough P from these sources and have the capability to fix N from the atmosphere. This adds bioavailable N to the water system. Concentrations of nutrients in the water column are often measured but in some instances they are not very useful without accompanying biological determinations.

## **Dissolved oxygen (DO)**

Dissolved oxygen gas in water supports microbes, fish, animals, and plants. At 68 degrees F, freshwater in equilibrium with the atmosphere can support 9.09 mg O<sub>2</sub>/L (9.09 ppm DO). This concentration is approximately 22,000 times lower than the atmosphere. Oxygen solubility decreases in water with an increase in temperature. Many organisms show affects of low oxygen when DO levels fall below 6 mg/L. That is why cold water in the winter often has a higher DO level than in summer. In summer, freshwater containing microbes, animals or fish must be moving to maintain sufficient oxygen levels. These organisms can eventually remove all of the DO from the water if oxygen is not replenished rapidly from the atmosphere. Oxygen is also added from photosynthesis of algae and some underwater plants during the day.

When organic matter containing sediment becomes anoxic (all DO is removed), P and undesirable organic acids are released into the water. Iron is easily reduced (ferric to ferrous) in water. Ferric phosphates are rather insoluble and thus remain as small particle precipitates in water. However, ferrous phosphates are quite soluble in water which increases the amount of soluble and bioavailable P. As the water is re-oxygenated to a satisfactory level, the ferrous iron is converted back to ferric iron which will recombine with soluble P to form new ferric phosphate precipitates removing soluble P from the water. During the time the soluble P was increased, a "flush" of algae growth is likely.

Anoxic conditions promote the formation of short-chain, highly volatile organic compounds that have various degrees of toxicity to plants and animals. They are easily detected by the odor given off from a water body.

## Appendix A

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Phosphorus cycle in aquatic ecosystems



Appendix **B** 

# Nitrogen cycle in aquatic ecosystems







The Environmental Problem with P in Surface Water
Eutrophication:

excessive growth of algae and oxygen depletion

Decrease in aesthetic quality
Increased costs for water treatment





























Forms of P in agricultural runoff			
NC study, piedmont soil, 20 tons/acre litter	Conventional Tillage	No-till	
Dissolved P (mg/L)	0.08	0.20	
Particulate P (mg/L)	5.81	1.20	

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Forms of P in agricultural runoff			
KY study, Maury silt loam, 90 lbs/acre P <sub>2</sub> O <sub>5</sub> , 5.2 inches simulated rain	Conventional Tillage	No-till	
Dissolved P (mg/L)	2.3	5.1	
Runoff Volume (in)	1.8	0.3	
Dissolved P loss (lbs/A)	0.63	0.28	





















## Temperature Affects on algae growth and dissolved oxygen

Increased Temperature.....

... increases algae growth

... decreases dissolved oxygen

Shade is good to offset these affects























































Precipitation reactions can explain P retention in soils at high P concentrations.

Common condition around fertilizer granules having high water solubility

Adsorption reaction of P in soil explains P retention at low P concentrations.

> Common condition at sites far away from watersoluble fertilizer granules or when fertilizers of low water solubility are added to soil







# **Common P soil tests**

Bray I Bray II Mehlich I Mehlich III Olsen

























# Critical Environmental P Concentrations

- 1.0 mg/L P (common for discharge from municipal water treatment plants)
- 1.0 mg/L dissolved P (proposed for ag runoff, USEPA, 1986)



## Soil Test P values found to correspond to 1 mg/L soluble P in runoff

State	Year	Test	Soil test, lbs/acre
Arkansas	1995	Mehlich III	230 to 450
Oklahoma	1995	Mehlich III	300 to 500
Arkansas	1996	Mehlich III	600
Alabama	1997	Mehlich I	600
Sharpley	1996	Bray I	160 to 1400
North Carolina	2000	Mehlich III	500 , 1400
Oklahoma Arkansas Alabama Sharpley North Carolina	1995 1996 1997 1996 1996 2000	Mehlich III Mehlich III Mehlich I Mehlich I Bray I Mehlich III	230 to 430 300 to 500 600 600 160 to 1400 500 , 1400



State P Threshold Values (Ibs/acre)					
Arkansas:	300	M3	Oklahoma:	260	М3
Delaware:	100	M1	Michigan:	150	B1
Idaho:	200	Olsen	Texas:	400	TA&M
Ohio:	300	B1	Wisconsin:	150	B1
P application limited above these Threshold Values					



Advantages & Disadvantages			
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P Threshold	easy & simple	Does not consider all factors	
P Index	Considers all factors	Not simple	
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