# CHAPTER 2.0
# NUTRIENTS IN AQUATIC SYSTEMS AND RELATIONSHIP TO DRINKING WATER QUALITY

Phosphorus and nitrogen are the key nutrients that control primary productivity in many water bodies, especially when other factors, such as light, temperature, turbidity, and other micronutrients are not limiting. The limiting nutrient in a particular water body is the nutrient that is present in the lowest level relative to the cellular needs of the algae. For the purpose of this report, we focus only on nitrogen and phosphorus as nutrients of interest, although, depending on the overall water quality, other elements may become limiting for algal growth. For algal biomass, theoretical nitrogen requirements are about 7.2 times the phosphorus requirements on a weight basis (this is termed the Redfield ratio). If total nitrogen in the water is more than 7 times the total phosphorus, then phosphorus will be in low supply and limit algal growth. If the nitrogen is less than 7 times the phosphorus, then nitrogen will be limiting. However, the Redfield ratio is only a starting point for evaluation of limiting nutrients: the actual nutrient stoichiometry of algae varies somewhat between species, and more importantly with nutrient supply due to processes such as luxury consumption, which is the excess uptake and storage of nutrients when they are abundant to provide a temporary cellular supply for later deficiencies.

Depending on the water body, either nitrogen or phosphorus can be the limiting element for algal growth. As a general rule, lakes and reservoirs are found to be phosphorus limited more often than nitrogen limited, so efforts to control nutrient-related productivity are often focused on phosphorus alone. However, some lakes/reservoirs are nitrogen limited, and many are approximately balanced with nitrogen-to-phosphorus ratios close to 7. In addition, the N/P ratio often varies seasonally due to variations in external loads, internal loads from the sediments, and other internal biogeochemical cycling processes within water bodies that deplete or augment one nutrient relative to the other (e.g., phosphorus coprecipitation and adsorption on calcium carbonate, nitrogen fixation from the atmosphere by blue-green algae). Therefore, the limiting nutrient may change seasonally throughout the year, or from one year to another. Small streams are typically not nutrient limited because nutrients are efficiently retained and recycled, although larger streams may exhibit nutrient limitation, with nitrogen often being more important as a limiting element (e.g., Welch et al. 1989).

## 2.1 Impacts of Increased Phosphorus and Nitrogen on Surface Water Bodies

Phosphorus and nitrogen are vital for biological growth and, if other factors such as light, turbidity, other micronutrients, are not limiting, their levels have a major effect on the functioning of aquatic ecosystems. In general, phosphorus and nitrogen are vital for ecosystem functioning, and in their absence, there can be no aquatic life. Most designated used of water bodies, especially recreational and wildlife uses, depend on there being a certain level of nutrients (which may vary by location). However, a significant concern in surface waters over the past few decades is the process of eutrophication, which refers to increased primary productivity and associated impacts as a result of human-induced increases in nutrient supply over natural levels. The most conspicuous effect of increasing levels of nitrogen and phosphorus is an increase in biomass production, typically algae and macrophytes (Wetzel, 2001). The death and decay of this biomass typically creates an oxygen demand in sediments that lowers dissolved oxygen levels in the water column. Low oxygen levels adversely impact all other species in the water body, especially invertebrates and fish. The increased sediment oxygen demand may also be responsible for sulfate reduction and production of odorous substances such as hydrogen sulfide. Changing turbidity as a result of eutrophic conditions changes the balance of benthic and planktonic productivity and may also be associated with more subtle changes, such as shifts in the abundance of plants and wildlife species in water bodies.

Overall, increased primary production as a result of nutrients has the potential to impair a wide variety of beneficial uses of surface water, including recreational, wildlife, fishery, and drinking water uses. The last of these, the focus of this conceptual model, is discussed in more detail below. The USEPA has prepared guidelines for developing nutrient criteria for streams (USEPA, 2000a), and lakes/reservoirs (USEPA, 2000b) with the eventual goal of having nutrient standards for water bodies.

## 2.2 Effect of Phosphorus and Nitrogen on Drinking Water Supplies

In general, elevated levels of nutrients increase the risk for greater organic carbon fixation through photosynthesis (of phytoplankton, macrophytes, and benthic algae), although other factors, noted above, may also be limiting. Increased photosynthesis results in a greater supply of organic carbon both during the live and senescing stages of plant matter. As discussed in the organic carbon conceptual model report (Tetra Tech, 2006), elevated organic carbon negatively impacts drinking water supply because it may results in the creation of harmful byproducts during chlorination, if the organic matter is not removed through prior treatment steps. High algae levels in source water are also an adverse impact because they can clog filters and reduce the efficiency of filtration during water treatment. Higher algal production creates the risk of stimulating the growth of algal species, specifically some species of blue-green algae that are associated with the production of compounds such as geosmin and 2-methylisoborneol (MIB) that impart objectionable odors and tastes to waters, even at very low concentrations. Other species of blue green algae, in particular *Anabaena flos-aquae*, *Microcystis aeruginosa*, and *Aphanizomenon flos-aquae*, which could grow under higher nutrient levels, produce neurotoxins that can affect humans, fish, and wildlife. Higher nutrient levels increase the risk of producing these compounds at levels that are objectionable or harmful. Finally, nitrate and nitrite, significant components of total nitrogen in natural waters, have been linked to methemoglobinemia (blue-baby) syndrome in human infants at high levels. Current drinking water standards are of 10 mg/l of nitrate-nitrogen and 1 mg/l of nitrite-nitrogen (EPA, 1986).

Unlike other designated uses of waters (specifically those related recreation and wildlife), it appears that there is no lower threshold for nutrient concentrations for drinking water uses, i.e., extremely low values will not adversely impact drinking water quality. However, very low values of nutrients could adversely affect recreational and wildlife uses. Any efforts to manage nutrient levels in water bodies must balance the ecosystem needs against drinking water needs.

In the San Joaquin River and the Delta, existing data show that the nutrient concentrations are high enough to classify these waters as eutrophic water bodies. The San Joaquin River exhibits symptoms of eutrophic conditions, notably low dissolved oxygen concentrations that impairs migration of cold and warm freshwater species (Jassby, 2005). However, despite high nutrient concentrations, primary production in the Delta is fairly low (Jassby et al., 2002), indicating evidence of other limitations such as light limitation by high suspended solids. However, the water that is pumped out from the Delta and transported in aqueducts, or stored in reservoirs for future use, may not have this crucial limitation, and relatively high levels of primary productivity, with the associated impacts discussed above, such as algal blooms and low dissolved oxygen levels in deeper waters, can result. Methods to control algal growth in conveyance systems, such as the addition of copper sulfate, may create problems elsewhere, such as high copper concentrations in water treatment sludge.

## 2.3 PHOSPHORUS CYCLE IN LAKES, RESERVOIRS, AND STREAMS

Phosphorus is the key variable most commonly used to characterize the trophic status of lakes and reservoirs. Phosphorus is present in both dissolved and particulate forms. The particulate forms include organic phosphorus incorporated in living plankton, organic phosphorus in dead organic matter, inorganic mineral phosphorus in suspended sediments, phosphate adsorbed to inorganic particles and colloids such as clays and precipitated carbonates and hydroxides, phosphate adsorbed to organic particles and colloids, and phosphate coprecipitated with chemicals such as iron and calcium. The dissolved forms include dissolved organic phosphorus (DOP), orthophosphate, and polyphosphates. The organic forms of phosphorus can be separated into two functional fractions. The labile fraction cycles rapidly, with particulate organic phosphorus quickly being converted to soluble low-molecular-weight compounds. The refractory fraction of the colloidal and dissolved organic phosphorus cycles more slowly, regenerating orthophosphate at a much lower rate. Figure 2-1 illustrates the phosphorus cycle.

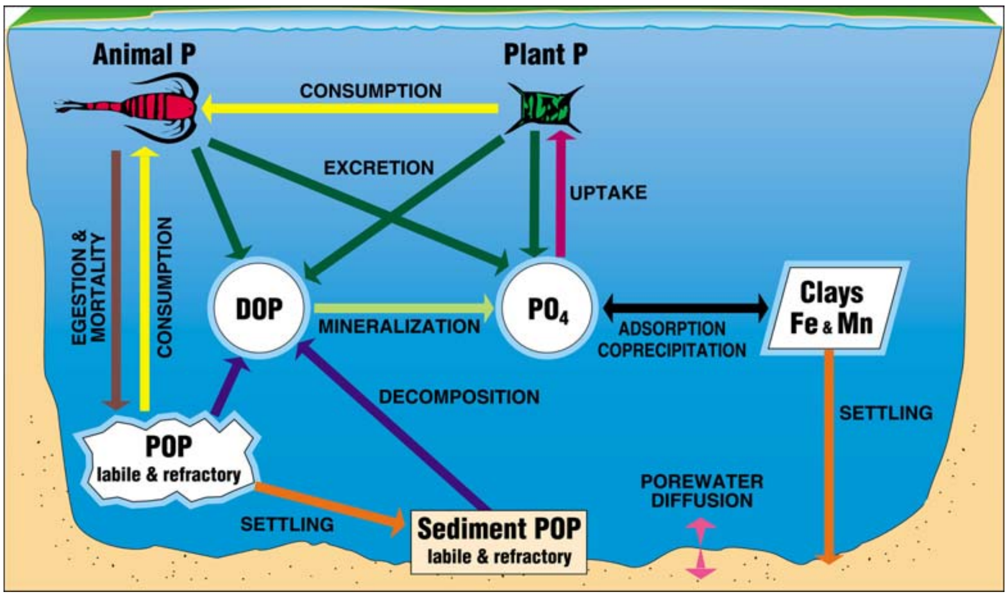


**Figure 2-1. Phosphorus cycle in aquatic ecosystems.**

Dissolved phosphorus may be reported as total dissolved phosphorus, total phosphate, orthophosphate, and dissolved organic phosphorus. Care must be taken in interpreting monitoring data to determine if a reported total phosphorus value represents both dissolved and particulate forms (unfiltered sample), or only total dissolved forms (filtered sample). Confusion is also common in interpreting phosphate data, since it may not be clear if it represents only orthophosphate, or orthophosphate plus polyphosphates. The latter should be reported as total dissolved phosphates.

Dissolved orthophosphate, sometimes reported as soluble reactive phosphorus, is the only form that is generally considered to be available for algal and plant uptake. Although this is the primary bioavailable form, total phosphorus, including all dissolved and particulate forms, is a better determinant of lake and reservoir productivity. This is because most of the phosphorus is tied up in plankton and organic particles during periods of high productivity. Often more than 95% of the total phosphorus is incorporated in organisms, especially algae (Wetzel, 2001). Any orthophosphate released by excretions, decomposition of organic matter, and mineralization of dissolved organic phosphorus is immediately taken up by phytoplankton. Phosphorus uptake and turnover rates are extremely fast, on the order of 5 to 100 minutes, during summer periods of high productivity (Wetzel, 2001). Therefore, the dissolved orthophosphate concentrations in the water column are often very low in highly productive systems. Phosphorus uptake and turnover rates are much slower during the winter due to the colder temperatures and lower light intensities. Uptake rates and optimum phosphate concentrations for growth vary among algal species, so seasonal changes in phosphate influence the structure and seasonal succession of phytoplankton communities.

Phosphorus concentrations and distributions between phosphorus forms vary both spatially and seasonally and can change rapidly due to both biogeochemical cycling processes and seasonal variations in phosphorus loading. The major cycling processes include algal and plant assimilation of orthophosphate, decomposition of organic detritus, mineralization of DOP, DOP and phosphate excretions by aquatic organisms, phosphate adsorption/desorption to suspended particulates and sediments, coprecipitation of phosphate, sediment release, macrophyte release, and sedimentation of plankton and other particulate forms of phosphorus. The external load sources include inflowing rivers and streams, direct runoff from the surrounding watershed, groundwater inflows, atmospheric deposition, and waste discharges. The phosphorus loads from the watershed depend on the phosphorus contents of the soils and parent rock material, vegetation characteristics including surface detritus and organic content of the soils, the amounts of animal wastes present, and human activities in the watershed such as fertilization and detergent use.

Total phosphorus can range from <5 ug/l in very unproductive lakes to >100 ug/l in very eutrophic lakes, although the usual range is between 10 and 50 ug/l in uncontaminated systems (Wetzel, 2001). Typical average total phosphorus concentrations for different trophic categories are 8 ug/l in oligotrophic lakes, 27 ug/l in mesotrophic lakes, and 84 ug/l in eutrophic lakes (Vollenweider, 1979; Wetzel, 2001). The 1986 EPA Water Quality Criteria recommend a maximum total phosphorus concentration of 25 ug/l in lakes to prevent eutrophication problems, and maximum concentrations of 50 ug/l in streams that enter lakes. Although inflow phosphorus concentrations drop in lakes due to phytoplankton uptake and settling, they may not drop 50 percent unless the residence is very long. This is particularly true if internal loads from sediments and macrophytes are important. Therefore, the 50 ug/l recommendation for inflowing streams may not adequately protect lakes. It is anticipated that, in coming years, new phosphorus criteria will be developed that vary by region and implement recent USEPA guidelines on nutrient criteria (USEPA 2000a, 2000b).

The dynamics of phosphorus limitation in flowing water bodies, such as streams and aqueducts, is not as straightforward as that for lake environments. Unlike lake and reservoir environments where phosphorus is often bound and tightly cycled within the biota, stream environments are open and therefore continually receive phosphorus from upstream, groundwater, or runoff. Current also helps reduce limitation by reducing diffusion barriers. Under natural conditions, much of the phosphorus delivered to streams is bound in organic forms (e.g., in leaves, woody debris, invertebrates, etc.) and is then transferred between and among the different trophic levels within the lotic ecosystem. The role of macroinvertebrates in this transformation process is very important. Ward (1989) states that invertebrates may act as temporal mediators; their feeding activities result in a more constant supply of detritus to downstream communities by reducing the buildup of benthic detritus below levels subject to episodic transport during high flow events.

When human-derived sources of phosphorus are delivered to a stream, such as wastewater and stormwater runoff, the ratio of dissolved phosphorus immediately available to algae may be high relative to particulate forms of phosphorus such as those attached to soil particles (Robinson et al. 1992). However, the discharged phosphorus cycles rapidly between abiotic and biotic phases, and after some distance of transport from the discharge point, the bioavailability of the newly introduced phosphorus may be no different from that previously in the stream.

## 2.4 NITROGEN CYCLE IN LAKES, RESERVOIRS, AND STREAMS

Nitrogen occurs in numerous dissolved and particulate forms. The particulate forms include organic nitrogen incorporated in living plankton, organic nitrogen in dead organic matter, and ammonia adsorbed to inorganic particles and colloids. The dissolved forms include dissolved organic nitrogen, ammonia, nitrite, nitrate, and dissolved molecular nitrogen gas ($N_2$). The organic forms of nitrogen include many compounds such as amino acids, ammines, nucleotides, proteins, and humic compounds (Wetzel, 2001). The nitrogen cycle is illustrated in Figure 2-2.

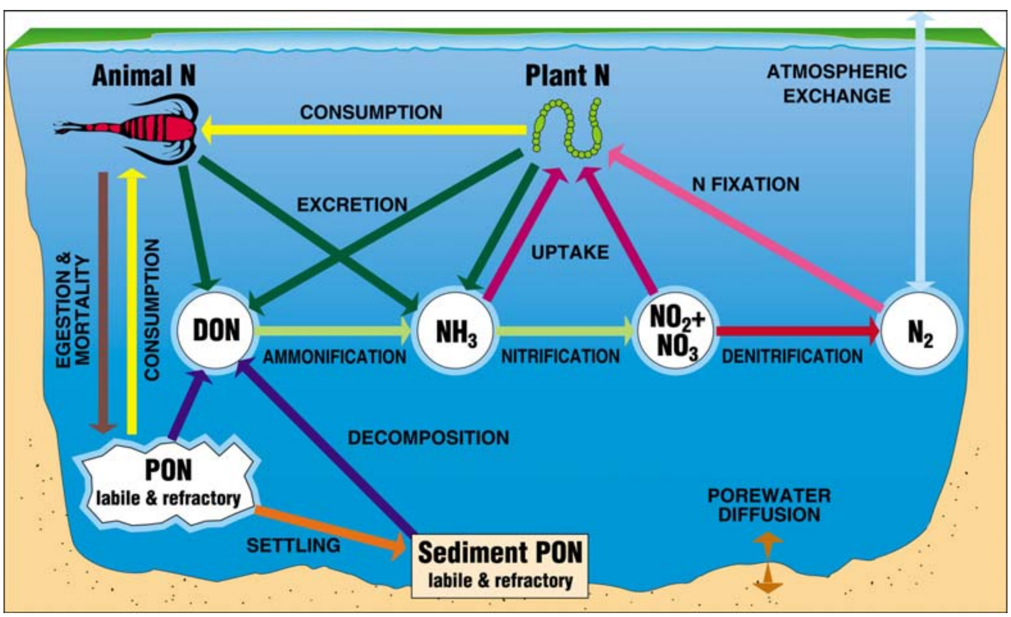


**Figure 2-2. Nitrogen cycle in aquatic ecosystems.**

Dissolved nitrogen may be reported as total dissolved nitrogen, total nitrogen, ammonia, nitrite, nitrate, nitrate plus nitrite, total Kjeldahl nitrogen (TKN), and dissolved organic nitrogen (DON). TKN represents organic nitrogen plus ammonia nitrogen. Care must be taken in interpreting monitoring data to determine if a reported total nitrogen or TKN value represents both dissolved and particulate forms (unfiltered sample), or only dissolved forms (filtered sample).

Nitrogen concentrations and distributions between nitrogen forms vary both spatially and seasonally and can change rapidly due to both biogeochemical cycling processes and seasonal variations in nitrogen loading. The major cycling processes include algal and plant assimilation of nitrate and ammonia, decomposition of organic detritus, deamination and ammonification, nitrification, denitrification, nitrogen fixation by blue-green algae and bacteria, DON and ammonia excretions by aquatic organisms, ammonia adsorption/desorption to suspended inorganic particulates and sediments, sediment decomposition and release, macrophyte decomposition and release, sedimentation of plankton and other particulate forms of nitrogen, and gaseous exchange with the atmosphere.

Nitrate and ammonia, the major dissolved inorganic forms of nitrogen, are the only forms that are available for algal and plant uptake. Most algae preferentially uptake ammonia over nitrate since more energy must be expended to reduce nitrate to ammonia before it can be biologically assimilated. Therefore, uptake and photosynthesis rates are higher for ammonia than nitrate at the same concentrations. However, very high ammonia concentrations can have a toxic effect and inhibit photosynthetic uptake, particularly at high pH. Under these conditions, nitrate uptake rates may exceed ammonia uptake rates.

The main source of ammonia in lakes and rivers is the decomposition of organic matter (proteins, other organic compounds) by heterotrophic bacteria. Aquatic animals also excrete ammonia, but this source is small relative to decomposition. Intermediate dissolved organic nitrogen compounds are also released, but they do not accumulate to high levels because deamination and ammonification by bacteria is rapid (Wetzel, 2001). However, some of the dissolved organic nitrogen compounds are more resistant to bacterial degradation than others.

Nitrate and nitrite are generated through nitrification of ammonia. In aerobic waters, bacterial nitrification oxidizes ammonia to nitrate in a two-stage reaction in which ammonia is first oxidized to nitrite, and then nitrite is oxidized to nitrate. Nitrite oxidation is very fast, so nitrite levels in lakes and rivers are usually very low unless the waterbody is very nutrient enriched. Nitrate is the dominant oxidized form in lakes and rivers. Highest nitrite concentrations are typically found in areas where there is a transition from aerobic to anaerobic conditions, such as the metalimnion or upper hypolimnion of lakes, or the sediment interstitial waters near the lower boundary of the oxidized microzone. These represent areas that have low enough oxygen levels to slow down the nitrification reactions, but still high enough to prevent significant denitrification reactions. In addition to nitrification as a nitrate source, nitrate is also often the dominant dissolved nitrogen form in external loads from surface waters, groundwater, and the atmosphere. The riparian zone, through which groundwater and surface runoff enters streams, plays a very important role in the nitrogen cycle as both aerobic and anaerobic conditions are usually present. Green and Kauffmann (1989) indicate that riparian zones are important for denitrification.

In anaerobic waters and sediments, bacterial denitrification rapidly reduces nitrate and nitrite to nitrogen gas ($N_2$). Nitrate is used as a hydrogen acceptor during the oxidation of organic matter under anaerobic conditions. Some of the N2 produced during denitrification leaves the lake through outgassing, and some is fixed by blue-green algae and bacteria.

Particulate organic nitrogen in plankton and detritus is removed from the water column through sedimentation. Bacterial activity in the sediments decomposes the particulate organic nitrogen to release dissolved organic nitrogen and ammonia. Since most of the sediments are anaerobic, nitrification cannot occur, so ammonia levels increase in the sediment porewaters. Nitrification does occur in the oxidized microzone at the top of the sediments. Any nitrate or nitrite that diffuses into the anaerobic sediments from the water column or oxidized microzone is quickly denitrified to $N_2$. Ammonia sorbs to sediment particles under aerobic conditions in the oxidized microzone. Once the hypolimnion becomes anaerobic and the oxidized microzone disappears, the adsorptive capacity of the sediments diminishes, and sediment release of ammonia increases substantially.

Dissolved nitrogen gas ($N_2$) enters lakes and rivers through both atmospheric exchange and denitrification reactions. Both blue-green algae and bacteria can fix $N_2$, although nitrogen fixation by blue-green algae is usually greater than by bacteria. However, $N_2$ fixation requires more energy than assimilation of ammonia or nitrate, so blue-green algae typically fix nitrogen when ammonia and nitrate concentrations are low (Wetzel, 2001). Blue-green algae dominate the phytoplankton during periods when nitrate and ammonia are depleted by algal uptake because of their ability to fix nitrogen. Nitrogen fixed by bacteria in wetlands surrounding lakes or inflowing streams can also be a significant nitrogen source in some situations. In some cases, certain riparian plants, such as alder, can add nitrogen to riverine ecosystems by fixing atmospheric nitrogen.

Total nitrogen can range from 0.3 mg/l in very unproductive lakes to >2000 mg/l in very eutrophic lakes (Wetzel, 2001). Typical average total nitrogen concentrations for different trophic categories are 0.66 mg/l in oligotrophic lakes, 0.75 mg/l in mesotrophic lakes, and 1.9 mg/l in eutrophic lakes (Wetzel, 2001). It is anticipated that, in coming years, new nitrogen criteria will be developed that vary by region and implement recent USEPA guidelines on nutrient criteria (USEPA 2000a, 2000b).

In lakes, the seasonal dynamics of the nitrogen cycle along with the effects of stratification and dissolved oxygen profiles determine the temporal and spatial variations of the different nitrogen forms in the water column. However, the nitrogen speciation of major external load sources, and whether they enter the epilimnion or hypolimnion, can also play an important role, particularly if the external loads are high and the lake residence time is low.

As with phosphorus, the external nitrogen sources to lakes and rivers include inflowing rivers and streams, direct runoff from the surrounding watershed, groundwater inflows, atmospheric deposition, and waste discharges. In addition, nitrogen also enters lakes and rivers though atmospheric exchange and nitrogen fixation. The nitrogen loads from the watershed depend on the nitrogen contents of the soils and parent rock material, vegetation characteristics including surface detritus and organic content of the soils, the amounts of animal wastes present, and human activities in the watershed such as fertilization. Septic systems can also be significant sources since organic nitrogen and ammonia in the septic fields are oxidized to nitrate, which is highly mobile in soils. Therefore, it can enter lakes through shallow groundwater flows directly to the lake or through stream inflows from the watershed. In contrast, phosphate tends to be retained in soils by adsorption, so septic systems are not such a large phosphorus source unless they are situated close to receiving waters or are not operating properly. Atmospheric deposition is also more significant for nitrogen than for phosphorus in most areas due to contamination by combustion emission products.

The temporal dynamics of the nitrogen cycle make it more appropriate to use total nitrogen (dissolved and particulate), rather than only the bioavailable forms such as ammonia and nitrate, in identifying impacts on lakes and rivers. Ammonia and nitrate are typically very low and sometimes immeasurable during the peak growing season of highly productive lakes. Ammonia and nitrate are rapidly taken up by phytoplankton, so much of the nitrogen is bound in plankton and organic detritus. In rivers, Dodds, et al., (1997) report that total nitrogen concentrations were more indicative of the nitrogen form that is ultimately bioavailable for benthic algal growth (periphyton) than dissolved nitrogen.

## 2.5 MEASUREMENT OF NUTRIENTS

There are two ‘phases’ of nutrients that are commonly measured in water: soluble and particulate. Within each phase, particular chemical species are identified. In some instances, measurements of nutrient concentrations in biota, specifically algae and macrophytes, can also be performed, but these are typically not relevant for drinking water supply concerns. Figure 2-3 shows the various species of nitrogen and phosphorus that are present in water samples, some of which are measured analytically and some of which are estimated by difference. For nitrogen species, total ammonia includes both the ionized ($NH_4^+$) and unionized ($NH_3$) forms. Dissolved nitrite and nitrate are often combined, as the concentration of nitrite in natural waters is generally small. Dissolved organic nitrogen can be obtained from the difference between Kjeldahl nitrogen and total ammonia. Kjeldahl nitrogen combines both organic nitrogen and total ammonia. Adding Kjeldahl nitrogen to dissolved nitrite + nitrate yields total dissolved nitrogen. For phosphorus species, the commonly reported quantities are soluble reactive phosphorus, a measure of the most biologically available fraction, total dissolved phosphorus, and total phosphorus.

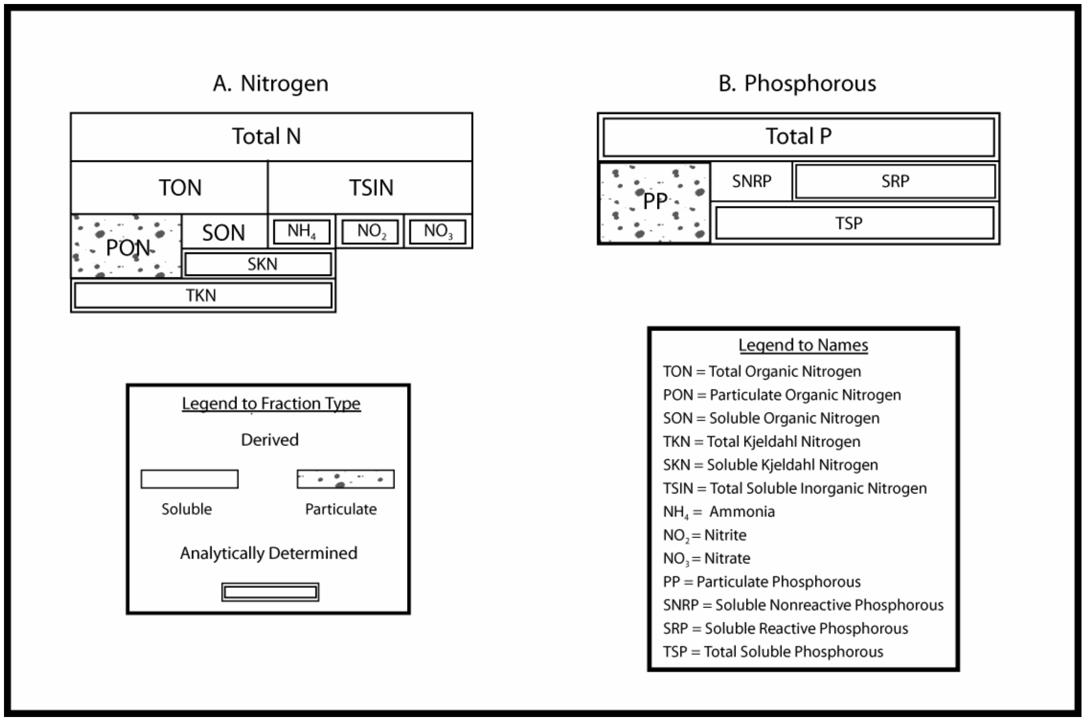


**Figure 2-3. Nutrient species found in water bodies. Some are analytically determined (indicated by double-lined boxes), and the others calculated by difference. The species identified in this Figure can be related to data presented in Chapters 3, 4, and 5. In particular, soluble reactive phosphorus is synonymous with orthophosphate.**