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A Review of Phosphorous and Nitrogen in Groundwater and Lakes

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Introduction

Lakes are crucially important for water supply, food production, recreation, and climate regulation. During the last century, increasing pressure on lake ecosystem function and services have been exerted by climate change, intensified agriculture, and urbanization. Rising air temperature and nutrient loadings directly affect lake physical, chemical, and ecological properties. Increased phosphorus (P) and nitrogen (N) loading from agricultural and urban landscapes, along with meteorological drivers, leads to the degradation of lake water quality by way of eutrophication (Markelov et al. 2019; Thompson 2019; Gelbrecht et al. 2005). Eutrophication is a problem that has plagued water bodies since the industrial era. Despite the knowledge of this phenomenon for over 40 years, it still remains a highly complex issue. Cultural eutrophication is the enrichment of nutrients ensuing from human activities that results in excess growth of algae in downstream water bodies (Meinikmann et al. 2016). The excess growth of algae can cause large daily changes in the amount of dissolved oxygen in the water. Low concentrations of dissolved oxygen can stress or kill sensitive species living in the water (Domagalski and Johnson 2012). This leads to a shift from macrophyte-dominated aquatic ecosystems characterized by diverse biota to algae-dominated systems with low diversity. Eutrophication also results in decreased water clarity and poor drinking water (e.g. taste, odor, toxicity). Bloom-forming algal species may be toxic or inedible (e.g. cyanobacteria) (Lombardo 2006; Smith and Schindler 2009). Aquatic systems that are specifically at risk to eutrophication and in turn decreased biodiversity include phytoplankton-dominated small streams, periphyton-dominated small and large streams and lakes, mesotrophic lakes, stratified deep lakes, mesotrophic or oligotropic polymictic lakes, and shallow lakes with high macrophyte coverage (Newton and Jarrell 1999).

The oversupply of P and N, key limiting nutrients, is considered the most relevant factor driving lake eutrophication. P is of particular concern, as concentrations of dissolved P as low as 10 parts per billion (ppb) can cause eutrophic and hyper-eutrophic conditions (Sharpley et al. 2000). Therefore, in a lake experiencing eutrophic conditions it is important to analyze P and N inputs (point and non-point sources), transport to the lake, and cycling within the lake (Schindler 2012).

Nutrient Input

Action against cultural eutrophication has been primarily aimed at reducing the transport of nutrients to the lake, with a focus on point-sources and surface water flow. However, with the elimination of most point-source pollutants (e.g. wastewater treatment plants and factories; Orderud and Vogt 2013), the main contribution now comes from diffuse sources of N and P from surface (overland flow or wind and water erosion) and subsurface transport paths. Research has shown that the most significant non-point source is the agricultural application of fertilizer and manure, which can lead to P and N leaching into reservoirs within the hydrologic cycle. Other non-point sources include urban land-use and septic systems. It is important to identify non-point sources through geochemical tracing in order to prevent future harm to aquatic ecosystems.

Nutrient Transport

Due to a multitude of reasons, (e.g. difficulty of quantification, believed to be less important to lake-water budgets, belief that P is strongly adsorbed by soils and assimilated by plants and thus not transported by groundwater) groundwater flow has long been ignored as a significant contributor of nutrients to lakes (Meinikmann et al. 2016; Holman et al. 2018). However, groundwater often plays a larger role in lake-chemical budgets (i.e. a higher percent of overall nutrient input by mechanism) than in lake-water budgets (i.e. percent of water input by mechanism: precipitation, tributary input, runoff, or groundwater). In recent studies, the percent of groundwater P transport ranges from 0.5 to 91% of total P loading to the lake, with an average of 41.5% (Meinikmann et al. 2015). The importance of groundwater to the lake nutrient budget depends on the volume of groundwater exchange and the concentrations of nutrients associated with that exchange (Meinikmann et al. 2016). More research is needed to fully understand groundwater's role in nutrient transport. Subsurface flow is dominated by mechanisms in the unsaturated and saturated zones (e.g. saturation levels, Fe redox cycle, anoxia, denitrification). Vadose water travelling toward the water table ends up either as near-surface flow (fast lateral transport to receiving waters) or as groundwater flow (slower lateral transport component). Groundwater travelling through aquifers is an important input path for nutrients to lakes, as water is constantly exchanged between lakes and aquifers (Winter 1999; Meinikmann et al. 2016). A growing interest in and importance of the connection between groundwater and surface water is due to the increase of global use of less easily attainable water resources that have higher economic, social, and environmental costs. Future scientists and practitioners dealing with surface water eutrophication are urged to take into account the potential for groundwater as a significant source of external P (Meinikmann et al. 2015).

Internal Nutrient Cycling

Internal nutrient recycling from sediments plays a key role in the biogeochemical cycling and biological productivity of lakes. Lakes have been found to accumulate legacy P and experience its mobilization from the sediment after decades of external P loading. This is of particular concern due to continued water quality deterioration despite measures to reduce external P loads. Therefore, a better understanding of nutrient cycles within lake systems is necessary to maintain and restore healthy lake ecosystems (Marelov et al. 2019).

As the global climate changes, higher water temperatures, droughts, and longer hydraulic residence times are expected to worsen lake water quality and algal blooms in the future (Mosley 2015; Visser et al. 2016). These effects are also expected to worsen with increasing global population (Meinikmann et al. 2016). In addition, lakes, particularly seasonally ice-covered lakes, are warming and experiencing significant impacts on their water-column processes with decreasing ice cover duration. Models predict that with every degree of air temperature increase, the duration of lake ice shortens by about 21 days, greatly altering water-column processes (Gebre et al. 2014; Markelov et al. 2019). The decreased ice cover leads to prolonged wind exposure, further mixing the water column. While this mixing tends to shorten the length of low-oxygen periods, algal blooms will last longer due to increased P cycling up from the sediment (Markelov et al. 2019; Thompson 2019). The continued use of P and N fertilizer in agricultural practices, which contributes large amounts of nutrients to water systems through diffuse transport and nutrient leaching, will only worsen with the increased pressure of food supply for a growing global population without a halt of P and N fertilizer (Meinikmann et al. 2013). It is becoming increasingly essential to study the influence of groundwater and internal nutrient cycling of P and N as climate change, global population growth, and cultural eutrophication exert increasing pressure on the health of water bodies across the globe.

Groundwater-Lake Interaction

Groundwater-lake interaction and lacustrine groundwater discharge (LGD) have long been ignored in the study of lake and river systems, particularly their importance in nutrient import. However, groundwater can be more influential in the lake-nutrient budget (found to contribute up to 89% of total lake P input; Meinikmann et al. 2016) than the lake-water budget (average groundwater percentage of lake-water budget from 108 lakes equals 35.3%; Meinikmann et al. 2016), and is likely the cause, coupled with internal nutrient cycling, for persistent P and N input in eutrophic systems despite reduced P and N application in nearby agricultural systems. Therefore, better understanding of the interaction between groundwater and lakes, including LGD, exfiltration rates, spatial exfiltration, biogeochemical processes, and infiltration are essential to decreasing eutrophication in the world's waterbodies.

Groundwater-lake interaction is driven by factors such as the hydraulic gradient between groundwater and the lake surface, the hydraulic conductivity of the saturated sediments (*ksat*), the degree of anisotropy, and climatic settings. The hydraulic gradient drives the direction and intensity of the interactions while the hydraulic conductivity controls the actual flow velocities of saturated sediments (i.e. exchange rates between the sediments). The degree of anisotropy is the ratio of *ksat* in horizontal to vertical directions, which plays an important role regarding flow velocities (Winter 1999).

LGD exerts a control over nutrient fluxes depending on the length of the flow path and the groundwater flow velocity. Both of these controls have important impacts on the residence time and the opportunity for chemical processes between groundwater and the aquifer matrix (i.e. contact time). Groundwater flow rates determine the magnitude of land-derived nutrient transport. In addition, the redox (oxidation- reduction, i.e. aerobic vs. anaerobic) conditions in the subsurface strongly affect transformation processes and mobility of P and N. Due to these controls, the position of the lake within the regional hydrologic flow system is very important for groundwater and nutrient fluxes, along with localized LGD interactions and rates (Meinikmann et al. 2016).

It can be difficult to accurately measure the exchange rates of groundwater and lake water due to the size of the lakes and area of the exchange. Accurately scaling measurements up to the full lake is also difficult due to differences in exchange rates throughout the lake. LGD is expected to primarily take place close to the shoreline with an exponential decrease of exchange rates with increasing distance from the shore. This creates an upward bending of groundwater flow lines, pointing towards the breaking point of the water table and the lake surface (Fig. 1; Winter 1999). Exchange rates are limited farther from the shore due to the deposition of fine organic matter of low hydraulic conductivity. This organic matter clogs and inhibits groundwater exfiltration in the deeper parts of the lakes (Fig. 1; Krabbenhoft et al. 1990). However, if the bedrock and surficial geology beneath and adjacent to the lake is not homogenous, this trend could be altered (see P and N Groundwater Movement sections).

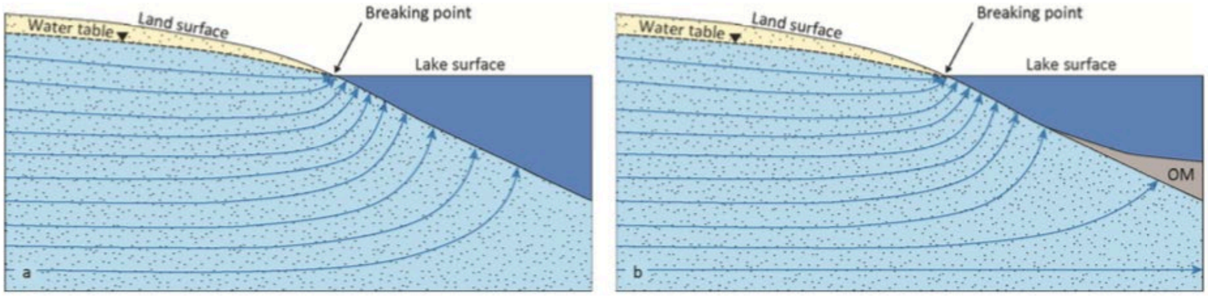

Figure 1. Focusing of groundwater flow (blue arrows) under exfiltrating conditions without (a) and with (b) an organic matter layer (OM). Source: Winter et al. (1998).

Lake-bottom sediments are rarely homogenous due to an array of factors. First, wave-induced erosion of sediments focused at the shoreline removes finer sediment and leaves behind coarser-grained sediments. Intense rainfall events can cause deposition of sediments focused at the shoreline brought in via overland flow. Changes in lake stage can cause lateral movement of the shoreline. Erosion and deposition of sediment can also occur due to seiche-induced, wind-induced, and wave-induced currents. There can be accumulation of biomass and/or woody debris from the adjacent upland and manipulation of near-shore sediments by physical (ice shove) or biological processes (plant roots, benthic invertebrates, freshwater mussels, crayfish, fish, and ducks). Finally, geologic heterogeneity and anthropogenic manipulations (shoreline alteration and/or stabilization) can cause heterogeneities in lake geology. Therefore, shore-line focused LGD is more likely than deep lake LGD (Fig. 1), however it does not tell the whole story. To get a fuller picture of LGD within specific lakes, full spatial research spanning the entire lake is necessary (Meinikmann et al. 2016).

While lake bottoms are notoriously heterogeneous, anthropogenic systems can also cause alterations in seepage between groundwater and the lake. The withdrawal of groundwater for private or municipal water supply or the addition of water associated with septic leachate can affect typical seepage patterns. The same is true of bank filtration, which is when large wells are intentionally placed near lakes to induce flow from the lakes to the well to meet water supply demands (Fig. 2). Along with the alteration of LGD flow patterns, the movement of contaminants from the adjacent river or lake to the water supply wells is a growing concern (Meinikmann et al. 2016).

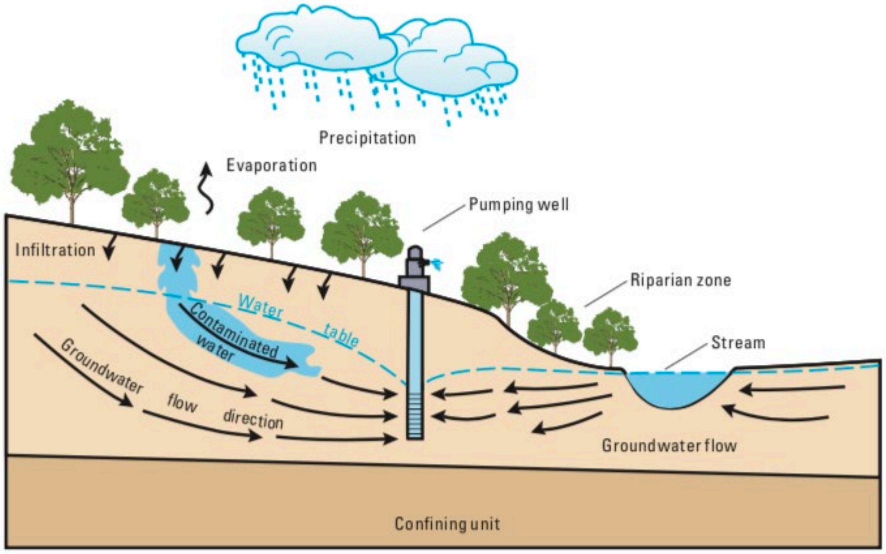

Figure 2. Schematic of a groundwater-flow system in an agricultural setting. In this example, infiltration of water from either precipitation or irrigation can transport P or other chemicals to the unsaturated zone and aquifer. Source: Domagslski and Johnson 2012.

Biogeochemical reactions along the flow path through the aquifer often alter the groundwater composition, especially as groundwater approaches the sediment-water interface (SWI). These variations can occur over relatively short distances within the same stratigraphic horizon and at the same depth (Frape and Patterson 1981). Temperature, pressure, and chemical concentrations can change substantially as water flows across the SWI. Spatial and temporal heterogeneity in biogeochemical conditions may be due to variations in sediment organic matter. This affects sediment microbial activity and therefore biogeochemical processes (Kilroy and Coxon 2005; Meinikmann et al. 2016). A high level of organic matter at the SWI may favor mineralization that alters the redox conditions and releases nutrients. Reducing conditions cause dissolution of redox-sensitive species (e.g. release of sorbed P, more information in Iron Redox Cycle P section; Meinikmann et al. 2016). A large amount of organic matter can also encourage biological activity and promote sorption and desorption reactions (Frape and Patterson 1981). Heterogeneities of groundwater composition can also be caused by varying hydraulic conductivities. Water in zones of low hydraulic conductivity are susceptible to reducing conditions (i.e. anoxia) that favor release of P. Several authors found that while P varied spatially, there was very little temporal variability in P loading by LGD (Hagerthey and Kerfood 1998).

Topography can also play a role in increased biogeochemical reactivity in groundwater approaching the SWI. The thin unsaturated zone above the aquifer can cause high metabolic activity in floodplain aquifers. Additionally, plant cover on land surface might deliver large amounts of fresh, easily degradable organic matter. The decay of this material consumes oxygen, reducing the subsequent delivery of oxygen from the shallow water table as diffusion is several magnitudes slower in the water-filled pores than in air-filled pores. Proximity to surface water can also play a role in contamination factors. In close proximity of surface waters, water tables are usually low. Therefore, near-shore groundwater is especially prone to contaminations (Fig. 2). The thickness of the vadose zone (i.e. the saturated zone), coupled with its adsorption and retention capacities, decreases with decreasing distance to the shoreline. Furthermore, the closer a contamination source is to surface water, the less time and flow path length is available for decomposition or retention of pollutants during passage towards the saturated zone (Meinikmann et al. 2015). Typically, groundwater quality is considered to be more stable than surface water primarily due to greater residence times (Kilroy and Coxon 2005; Meinikmann et al. 2016).

Transport processes from the lake into the sediment can contribute to P retention within the soil. They consist of diffusion, bioturbation, bioirrigation, and plant seepage. Diffusion, the downward transport of compounds due to concentration gradients or temporal fluctuation of water levels, can cause an alternation of exfiltration (groundwater to lake) and infiltration (lake to groundwater). Bioturbation and bioirrigation can help transport porewater and particulate material into deeper sediment layers. Finally plant seepage interactions, particularly in shallow near-shore margins of lakes, can precipitate and retain a large percent of iron in the LGD due to oxygen release from their roots. For example, *Littorella uniflora* (freshwater aquatic plant; "Shoreweed") was found to be an efficient binding agent of phosphate to the iron in sediment and was an important factor in the immobilization of P in the sediment (Christensen et al. 1997).

Phosphorus

Lake eutrophication is often attributed to P inputs from overland flow, however, more recently, groundwater has been proven to be able to carry significant amounts of dissolved P. Given that P is non-hazardous to human health, it is not regularly monitored in drinking water or groundwater (Meinikmann et al. 2015). For this and a multitude of other reasons (see Introduction), P concentrations, particularly in groundwater, have not been highly researched in relation to lakes and rivers.

Background P concentration

Background P concentrations in groundwater are usually quite low (~10 µg PO_4-P/l, i.e. 10 ppb P), especially in areas without anthropogenic impact. Meinikmann et al. (2016) found that groundwater borne P loads vary from 0.74 to 2900 mg PO_4-P m^{-2}/year. However, P concentrations can increase appreciably above natural groundwater conditions, especially with anthropogenic inputs (Meinikmann et al. 2015). Potentially mobile P (generally orthophosphate) is adsorbed in the soil or sediment matrix in the vadose (i.e. saturated) zone. Due to this phenomenon, unaffected (by anthropogenic sources) groundwater was considered to be a low source of nutrient transport by Edwards and Withers (2007). However, background P concentrations depend highly on the bedrock geology. For example, bedrock containing large amounts of apatite could have a higher background P concentration in its groundwater (along with increased uranium concentrations; Banning and Rude 2015). Wetlands, moors, and bogs also tend to have higher P concentrations in their groundwater due to decreased water outflow without an equal increased attenuation of P. This results in higher nutrient concentrated groundwater outflow (Meinikmann et al. 2016; Zhang et al. 2012). Ecosystems are of highest vulnerability to P input during the period of maximum primary productivity which typically occurs during late summer months (Holman et al. 2008 & 2010). Phosphorus has low solubility and shows high sorption and precipitation potentials to particulate or dissolved organic matter and other mostly inorganic matter, causing most P to be bound into crystal structures or onto surfaces of solids in soils and sediments. It is only transported at the surface via erosion of soil particles by wind and water and is largely immobile in the subsurface without saturation (Meinikmann et al. 2016). The high reactivity of the SWI complicates quantification of groundwater-borne P loads to a lake, making it difficult to differentiate internal and external P loads to surface water.

Anthropogenic P input

With the knowledge of P wastewater influence, most P point sources (e.g. sewage discharge) have been largely eradicated in the US (Orderud and Vogt 2013). However, P still affects bodies of water and rivers, indicating that non-point sources have a critical ecological relevance (Meinikmann et al. 2015), yet they have proven difficult to track. Agriculture is claimed to be the largest source of diffuse/non-point source P influence in freshwater systems (Domagalski and Johnson 2012; Heathwaite et al. 2005; Orderud and Vogt 2013; Withers and Haygarth 2007). Figure 3 indicates that agriculture (manure and fertilizer application) accounts for 72% of anthropogenic P loadings, while wastewater treatment plants now only account for 5% of anthropogenic P loadings (Gianessi and Peskin 1984). Intense agriculture, particularly in lowland areas, has resulted in an accumulation of P in soils, imposing the risk of elevated P losses with subsurface flow (Meinikmann et al. 2016).

Water and wind erosion are traditionally regarded as main routes of P transport from terrestrial to aquatic systems. P mobility is controlled by factors such as vegetation cover, cultivation, tillage, and precipitation. Manure and fertilizer should usually result in only small amounts of dissolved P draining into the aquifer when applied judiciously. In this case, soil adsorption properties and high biological uptake rates prevent excessive mobility of P (Meinikmann et al. 2016). However, according to Spiteri et al. (2007), groundwater P concentrations have increased worldwide as a result of the agricultural application of manure and synthetic fertilizer, indicating that excessive amounts are being applied on agricultural fields. For decades, P has been applied in excess of crop requirements leading to a well-documented P accumulation in many soils and a consequently increased risk of P transport to groundwater (Heckrath et al. 1995). Other potential sources of agricultural groundwater contamination include animal slurry lagoons (dairy, beef, and pig farms) and manure heaps (Gooddy 2002; Harper 1992; Holman et al. 2008 & 2010; Withers et al. 1998). Agricultural soils that receive large inputs of P can become saturated with P. Once saturated with phosphate, considerable time is required for noticeable depletion. McCollum (1991) found that 8 to 10 years of corn cropping without further P additions were necessary to reduce soil test P in agricultural soils. Excess P can also be found in urban areas, as P originates from infiltration of precipitation in unsealed urban areas and infiltration of road and roof runoff through storm water infiltration facilities, along with hazardous waste sites. Leaking pipes can also contribute to excess P in waterways and/or groundwater around urban areas (Meinikmann et al. 2016).

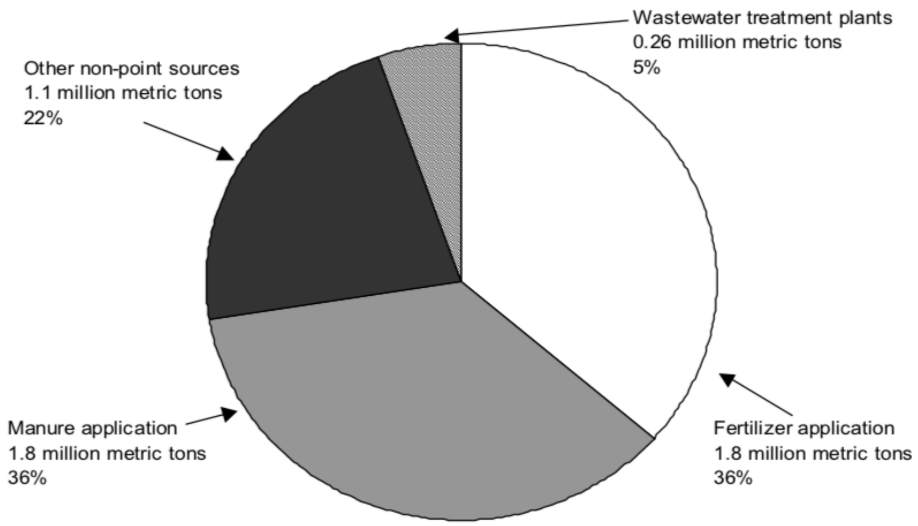

Figure 3. Chart of the 1984 nationwide loading estimates of anthropogenic phosphorus to the environment. Source: Gianessi and Peskin (1984).

Forms of Phosphorus

Phosphorus is naturally and synthetically found in several different forms. These forms include, but are not limited to: total P, dissolved inorganic P, dissolved organic P, particulate inorganic P, and particulate organic P (TP, DIP, DOP, PIP, POP respectively). Total P (TP) is the sum of all phosphorus found in water. This form is unfiltered and typically preserved with pH <2 H_2SO_4. P is then separated into dissolved vs particulate and organic vs inorganic. Dissolved P is categorized as filtered P < 0.45 μm while particulate P is > 0.45 μm and associated with particles retained on the filter membrane during filtration (Lombardo 2006; Sims et al. 1998). Colloidal P falls into both categories, with particles between 1nm and 1 μm. Inorganic P derives from fertilizers and urban runoff and is not preserved with acid when sampling. Organic P is formed primarily through biological processes and is generally derived from animal and human waste (manure, animal slurry, urban wastewater, septic leachate). However, organic P can be mineralized to inorganic P in water once favorable conditions (e.g. temperature; ~37°C; Whitton et al. 1991) are approached, along with during the course of transport. Organic forms of P are also potentially available to organisms in aquatic ecosystems (Whitton et al. 1991; Toor et al. 2003). Organic P may pose a greater threat to freshwater ecosystems, perhaps equal to the threat posed to these ecosystems by inorganic P (Toor et al. 2003).

Dissolved inorganic P (DIP) primarily occurs as orthophosphate (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}). Orthophosphates can either be dissolved or particulate, however they are most often discussed in their dissolved form. In its dissolved form in lakes, this P is highly bioavailable to algae (i.e. supports rapid algal growth and reproduction) and is most commonly attributed to eutrophication (Domagalski and Johnson 2012). Therefore, orthophosphate is the filterable, soluble, inorganic, bioavailable fraction of P (Murphy 2007). In waters with a pH close to 7, the soluble forms of P that are most abundant are $H_2PO_4^-$ and HPO_4^{2-}. The different forms of P can enhance the solubility of orthophosphate or limit adsorption reactions (Lombardo 2006). Soluble reactive P (SRP) is lab measured DIP. DIP is reactive, which refers to its response to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample. Since DIP is measured based on its reactive property, when measured in a lab it is referred to as SRP. SRP is often equated with free orthophosphate, however, it can also include sorbed orthophosphate (Baldwin 1998). Haygarth et al. (1995) determined that SRP analysis must happen within 24-48 hours and samples must be stored at 4° C in the dark in order to record a precise measurement. Condensed phosphates, such as pyrophosphate ($P_2O_7^{4-}$) and ($P_3O_{10}^{5-}$) are primarily derived from laundry detergents, automatic dishwasher detergent, and other cleansers. These condensed phosphates slowly convert to orthophosphate. If these forms are present in Vermont lakes they would be legacy contaminants given that P laundry detergents were banned in the state in the 1970s, and automatic dishwasher detergent was banned in 2010 in Vermont as well as seventeen other states (Cohen and Keiser 2017; Domagalski and Johnson 2012).

Although orthophosphate has the potential to be moderately soluble in water, it can bind or adsorb onto soil particles, defined as particulate inorganic P (PIP; >0.45 µm; Domagalski and Johnson 2012). Particulate P may be bioavailable as well due to algae release of alkaline phosphatase (i.e. an enzyme capable of cleaving orthophosphate from the organic particles). However, particulate P is generally assumed to not be transportable via groundwater.

Finally, organic P is incorporated with organic compounds such as phospholipids, sugars, and nucleotides. All of these different types of P can be complex or associated with dissolved cations and organic species present in wastewater, soil solutions or groundwater. Hence, organic P is categorized as dissolved organic P (DOP) or particulate organic P (POP; Domagalski and Johnson 2012).

Geochemical Conditions

Phosphorus geochemical conditions are governed primarily by precipitation and adsorption. Precipitation, the formation of a three-dimensional solid phase arrangement of molecules from the solution phase (Doner and Grossi 2002), is sustainable only if the supply of cations (usually iron as Fe^{2+} or Fe^{3+}) necessary to complete the reaction is also sustainable. Adsorption, or the formation of a two-dimensional structure (i.e. PO_4^{3-} on the surface of the mineral rather than within the mineral itself), occurs in both rapid and slow reactions and is also dependent on the supply of cations necessary to complete the reaction. An initial rapid uptake occurs when phosphate is initially exposed to soil, followed by a slower development of crystalline phosphate minerals within the adsorbent. The initial rapid adsorption may slow down over time as sorption sites are depleted, as the amount of orthophosphate that can be adsorbed is limited to the amount of total surface area of the oxides or clays in a soil (Domagalski and Johnson 2012; Lombardo 2006). Studies show that phosphate adsorption takes place via specific adsorption, that is the formation of a bond between phosphate and a specific site on the adsorbing solid phase, which binds much more strongly than the alternative hydrophobic or electrostatic adsorption (Sposito 1989). Fast surface sorption of the dominant forms of phosphate ($HPO_4^{2-}$to $H_2PO_4^-$) occur by anion exchange onto positively charged mineral surfaces under near-neutral pH conditions in the subsurface such as Al-containing, Mn(IV)-containing, and Fe(III)-containing oxides and (oxy)hydroxides (Ptacek 1998; Spiteri et al. 2007; Wilhelm et al. 1994; Domagalski and Johnson 2012; Ptacek et al. 1994; Foussard et al. 1995; Lombardo 2006), and solid organic carbon (Harman et al. 1996). Phosphate can also adsorb on clay surfaces by complexing with calcium (calcite ($CaCO_3$) surfaces), despite calcite having a negative charge under slightly-basic to basic pH conditions (White 1982).

The pH of soil or sediments exerts a strong control on the solubility of phosphate minerals, on the adsorption of phosphate onto mineral surfaces, and on the speciation of the Al, Ca, and Fe commonly contained in phosphate minerals. A decrease in pH causes transformation from PO_4^{3-} to HPO_4^{2-} to $H_2PO_4^-$ to H_3PO_4 as the dominant phosphate species. It also causes an increase in the positive surface charge of Fe and Al (hydr)oxides, and therefore an increase in the affinity that these surfaces have for phosphate adsorption. An increase in Al^{3+} concentrations in solution, an increase in Fe^{3+} and Fe^{2+} concentrations, and an increase in Ca^{2+} concentrations due to the increase in calcite solubility at lower values of pH can also be observed (Lombardo 2006).

Iron Redox Cycle

The P concentrations and movement found in soil solutions or groundwater are closely tied to the iron (Fe) redox cycle, which basically involves changes in aerobic-anaerobic conditions. Phosphate can be retained in the soil under oxic conditions in the form of ferric phosphate, inhibiting its movement to surrounding water bodies (Fig. 4). The Fe redox cycle in conjunction with P works as such: when ferrous iron (Fe^{2+}) diffuses to the oxidized side of the redox interface (near the soil or sediment surface; with oxygen present) it can sorb or precipitate phosphate when oxidizing to ferric iron (Fig. 5).

$$Fe^{2+}\ (aq) + H_3PO_4\ (\text{orthophosphate}) \rightarrow FePO_4\ (\text{ferric phosphate}) + 3H^+ + e^-$$

$$\text{simplified reaction: } Fe^{2+} + PO_4^{3-} \rightarrow FePO_4 + e^-$$

Then, when ferric iron (Fe^{3+}) compounds are reduced (lack of oxygen present), they may release occluded phosphate and ferrous iron to the soil solution.

$$FePO_4\ (\text{ferric phosphate}) + 3H^+ + e^- \rightarrow Fe^{2+}\ (aq) + H_3PO_4\ (\text{orthophosphate})$$

$$\text{simplified reaction: } FePO_4\ (Fe^{3+}) + e^- \rightarrow Fe^{2+} + PO_4^{3-}$$

The oxidation reaction is only effective if the overlying water (flood, lake etc.) remains oxic or the concentration of phosphate remains below the capacity of Fe to reprecipitate. This is because oxygen is necessary for the electron transfer occurring as ferrous iron oxidizes to ferric iron and loses an electron. Therefore, if flood water becomes anoxic or the concentration of phosphate exceeds saturation with respect to Fe precipitation, phosphate will be released from the soil by way of the reduction reaction (Young and Ross 2001).

Above and below the SWI interface the dynamics of P cycling are completely different. Young and Ross (2001) found that phosphate concentrations in anoxic sediments were correlated with total Fe oxides and the degree of P saturation (DPS). This is due to the reduction of Fe oxides that occurs, resulting in a solubilization of sorbed P, which is then released into solution. Conversely, above the SWI, P could be removed from solution through co-precipitation with or sorption on freshly precipitated Fe oxides (Young and Ross 2001). The Fe redox cycle can restrict the movement of phosphate after soil reduction when it sorbs or precipitates with ferric iron. The redox potential at the SWI in shallow lakes and wetlands is a crucial variable with respect to internal P cycling (Moore and Reddy 1994).

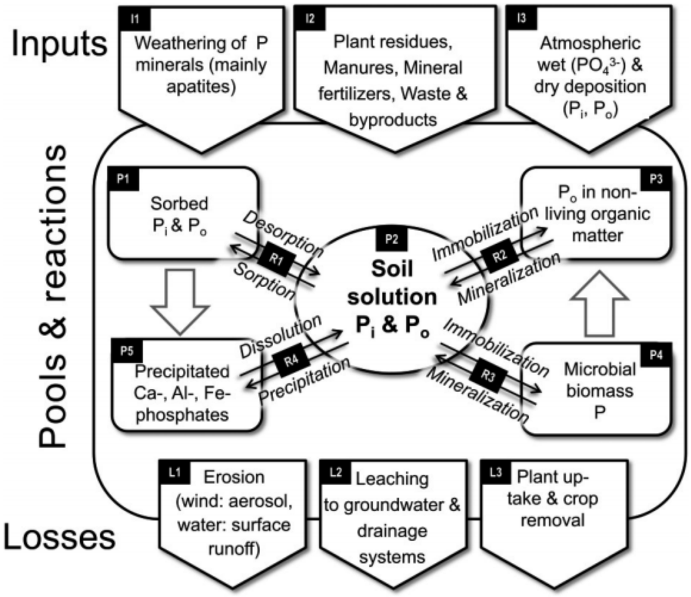

Figure 4. Schematic presentation of the soil phosphorus (P) cycle. The names in the black boxes (I = Inputs, P = Pools, R = Reaction, and L = Losses) indicate which methods are suitable to characterize the respective part of the P cycle. Source: Kruse et al. (2015).

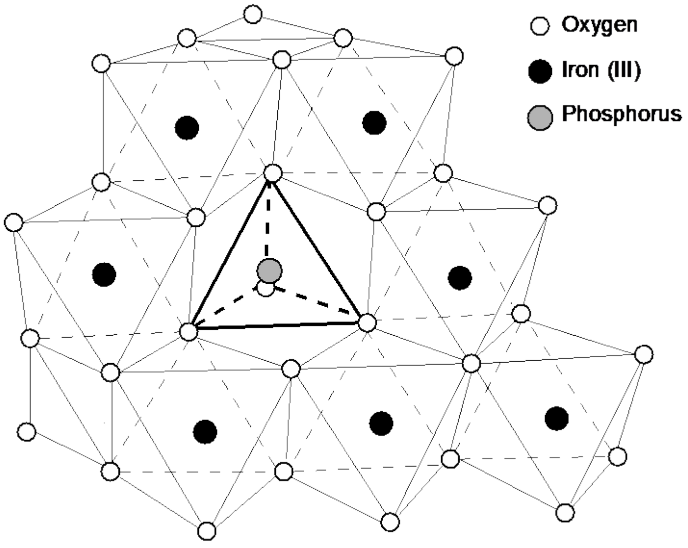

Figure 5. Molecular model of ferric phosphate. Tetrahedral PO_4 fits into the hexagonally-arranged FeOOH lattice and is released in reducing conditions as ferric iron is reduced to ferrous iron. Source: Ryan (2019).

Movement in Groundwater/Surface Water

P transport occurs as particulate or dissolved P in overland flow, channelized surface runoff, drainage, or groundwater flow (Meinikmann et al. 2016). Little attention has been paid to groundwater transfer of P due to the long-held belief that phosphate readily sorbs in the unsaturated zone, in the saturated zone, or precipitates with other groundwater constituents (Holman et al. 2008 & 2010). It has long been understood that adsorption and mineralization can immobilize P and limit its movement within or below the root zone, however, new understanding of the migration of P in groundwater is developing (Domagalski and Johnson 2012). Analyses of long-term data sets have demonstrated that P does migrate in groundwater, raising concerns that P-containing groundwater may accelerate eutrophication of receiving water bodies (McCobb et al. 2003; Stollenwerk 1996; Walter et al. 1995). Meinikmann et al. (2015) and Ommen et al. (2012) determined that groundwater can drive P concentrations and eutrophication in water bodies by finding that LGD accounted for 50%-85% of overall external P loading, which thus fueled the eutrophication of lakes.

The intensity and proximity of the contamination both have strong controls over the amount of P that will be discharged into a lake. With increased intensity and proximity to the lake, nutrient retention can be inhibited within the vadose zone and aquifer, allowing significant P loads to be discharged into the lake (Meinikmann et al. 2015). Physical and chemical characteristics of the soils and sediments, and several variable environmental factors such as soil-water redox potential, water depth, temperature, and turbulence, also control P concentrations in groundwater, lakes, and streams (Sallade and Sims 1997a). In flooding areas that are adjoined to bodies of water (i.e. streams or lakes), soluble P could reach sensitive water bodies and exacerbate water quality problems further (Young and Ross 2001).

Saturation of Sorption Sites

The intensity of transport depends on site conditions like the P retention capacity of soils or sediments and the slope of the land surface or water table (Meinikmann et al. 2015). Soils only have a limited capacity to store P, so when the sorption sites on the mineral surfaces become saturated with orthophosphate or other ions, any additional orthophosphate will remain in solution and move more freely as a dissolved phase in water. Therefore, when a soil nears or reaches saturation, dissolved P can be transported to deeper portions of the unsaturated zone and into the underlying aquifer as soil water moves downward. This dissolved orthophosphate can also be exfiltrated into the overlying water or transported to a nearby waterbody. Typically, extremely high P loads are necessary to exhaust this sorption capacity given that most soils have high P sorption capacity under oxic conditions (Vanek 1993). However, under prolonged high nutrient loading (e.g. agricultural fertilizer use, manure as fertilizer, build-up of nutrients on impervious cover), phosphate can be mobile, indicating a problem with excess (typically anthropogenic) P input (Domagalski and Johnson 2012; Meinikmann et al. 2016).

Vadose zone

In the vadose zone, P is typically immobilized provided that sediments have not reached saturation with respect to sorption of P. The amount of P that aquifer sediments can adsorb is related to the amount of Fe oxides present, the pH, the total amount of P present, the amount of dissolved oxygen in water, other ions in solution, and saturation levels. The most important control on the levels of phosphate dissolved in water is the amount of Fe oxide (emphasizing the importance of the Fe redox cycle as described in the previous section). When P concentrations in an aquifer are low, the oxide surfaces are most likely under-saturated and can adsorb more.

Conversely, when P concentrations are higher in groundwater, the oxide surfaces may be saturated or approaching saturation (Domagalski and Johnson 2012). Sorption capacity is low in soils with low amounts of clay minerals, calcium and metals. Decreased P sorption capacities are correlated with a loss of calcium during soil genesis (Meinikmann et al. 2016).

Phreatic zone

In the phreatic (saturated) zone, P mobilization typically relies on the Fe redox cycle (described in depth in the Iron Redox Cycle section above). Reducing conditions lead to decreased P sorption capacity, in turn enhancing the transport of phosphate with groundwater in sub-oxic conditions compared to oxic conditions (McCobb et al. 2003). Under anaerobic conditions phosphate immobilization is less efficient than under oxic conditions, relying on the precipitation of mineral phases such as hydroxyapatite or vivianite. Due to high sorption potential, P migration in the phreatic zone is slower than water flow and conservative water components (e.g. Na, Cl) by a factor of 5 to 100 (Lamontagne 2002; Robertson 2008; Meinikmann et al. 2016).

Sediment-water interface

Depending on the soil P status, Fe availability, and soil-water redox, interfaces (e.g. SWI) may act as a barrier to the mobilization of solubilized phosphate to floodwater, thus influencing exfiltration and infiltration rates (Domagalski and Johnson 2012). A fraction of particulate inorganic and organic P settles at the SWI where P is cycled through biochemical processes leading to the return of dissolved P to the hypolimnion (dense, bottom layer of water) or to burial in the sediments. The fate of this deposited P is highly variable as it depends on many different physical, biological, and geochemical properties and processes of the sedimentary reservoir (Fig. 6; Markelov et al. 2019). This previously immobilized and accumulated P at the SWI can be released through exfiltration with changes of environmental conditions including processes consuming oxygen, which lead to anoxic conditions and the resulting reduction of ferric iron to ferrous iron and release of phosphate. Markelov et al. (2019) indicated that about one third of P deposited at the SWI is sorbed to ferric Fe (oxy)hydroxides and the remaining consists of particulate organic P. Upon reductive dissolution of the Fe oxides and microbial degradation of the particulate organic P, on average 60% of the deposited P is returned as orthophosphate to the overlying water, while 40% remains trapped in the Fe redox cycle or precipitates as apatite. The release of P from the sediment is usually smaller than the amount of P deposited with previously settled sediment. In lakes that are in a steady state with respect to P, the sediment is a net sink for P on an annual basis. This adsorbed phosphate can form legacy P reservoirs in aquifer soils and bottom sediments. After substantial changes occur in the lake or its catchment, especially after load reduction, the sediment might function for a limited time or as long as decades, as a net P source and could supply P input into a lake for decades or centuries (Hupfer and Lewandowski 2008; Meinikmann et al. 2016; Markelov et al. 2019). Markelov et al. (2019) found that P recycling within the lake-sediment system supported P levels 20 years after P input was halted. The previous loading of 200 years provided a long-term source of P to the water column, stored as ferric phosphate. P exchanges between sediments and overlying water varies significantly along a single year, however sediments become a more pronounced source of P to the water column during the growing season (mid-late summer; Markelov et al. 2019). One solution to this legacy P recycling problem that has been implemented at some lakes is to increase oxygenation during the growing season through aerator compressors at the deepest sections of the lake, maintaining an oxic environment and fostering adsorption of P to ferric iron in the form of ferric phosphate (see Treatment practices and P removal strategies section; DEC 2019).

Seasonal Changes and Stratification

Dissolved oxygen (DO) and temperature play important roles in the productivity and health of lakes. In the summer, lakes with sufficient depth (greater than 25 ft., i.e. 8 m) become stratified into three distinct layers of distinct temperatures (Fig. 6). These layers include the epilimnion (warm water, well oxygenated), the metalimnion (thermocline layer, i.e. stratum of rapidly changing temperature), and the hypolimnion (cold, high or low oxygen levels). Physical and chemical changes within these layers influence the cycling of nutrients and other elements within the lake. High levels of DO produced in the warm and well-lit waters of the epilimnion by plant photosynthesis are prevented from reaching the cold dark hypolimnion waters by the thermocline during summer stratification. Therefore, the hypolimnion only contains DO acquired in the spring from lake mixing. According to a stoichiometric equation, due to mineralization processes, O_2 decreases and SRP increases steadily in the hypolimnion of a lake during stratification. This causes the ratio $(dSRP/dt)(dO_2/dt)$ to be equal to -0.007 mg P/mg O_2 (Gachter and Mares 1985). An anoxic environment can then be created after bacteria use the DO supply to decompose dead plant and animal organic matter from the epilimnion. With increased supply of organic matter from the epilimnion and a small volume of water in the hypolimnion, the more rapid the oxygen depletion in the hypolimnion will occur. Highly productive eutrophic lakes with small hypolimnetic volumes can lose their DO in a matter of a few weeks after spring overturn ends and summer stratification begins. The water chemistry of bottom sediments then changes with decreased DO concentrations. As discussed earlier in this section, anoxic/reducing conditions can cause the release of sorbed P to Fe from the sediments to the water column. Consequently, P can reach extremely high levels in the hypolimnion of productive eutrophic and hypereutrophic lakes. During major summer storms or at fall overturn, this excess P can be mixed into the surface waters to produce or contribute to algal blooms (Michigan Clean Water Corps 2008).

With each summer storm, eutrophic lakes of moderate depth (25 to 35 ft. [7-11 m] maximum depth) can destratify after stratification and experience loss of hypolimnion DO. So much P can be brought to surface water during these temporary stratifications and destratifications that the primary source of P for the lake is not from the watershed but from the lake itself in the form of internal loading or recycling. This summer stratification can create a positive feedback loop where algal blooms decrease DO and result in increased death of aquatic biota (i.e. fish, marine mammals, birds), increasing the amount of organic matter raining down on the hypolimnion, increasing the decomposition by bacteria and in turn decreasing DO supply. This will result in the release of P sorbed to Fe, feeding the algal blooms further with mixing events and worsening the state of the lake. This pattern may be interrupted by hilly terrain protecting the lake from strong wind forces preventing complete water circulation or strong prevailing winds preventing original stratification. Groundwater inflow could also reduce DO concentrations itself by being a stronger influence than lake productivity and biological decomposition (Michigan Clean Water Corps 2008). The use of an aerator compressor (sends oxygen to the deepest points of the lake where legacy P is preferentially stored) can keep P sorbed to Fe and in turn prevent the release of P to the hypolimnion. P will then be unable to reach the surface waters where algae could have used this P to increase algal bloom spread. Due to the stratification of lakes with moderate depth (25 to 35 ft maximum depth), seasonality and temperature could be the reason for algal bloom presence concentrated in the summer and fall, coupled with the high primary productivity of the summer (Holman et al. 2008 & 2010).

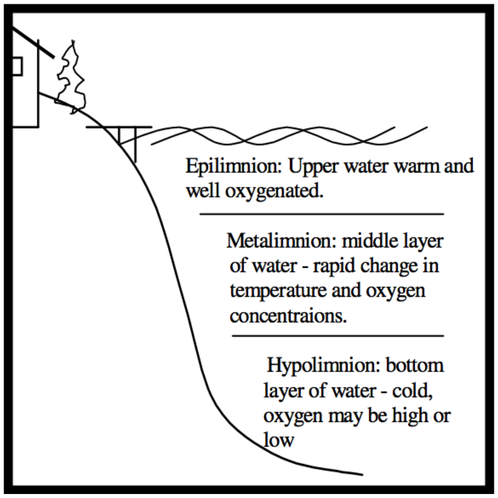

Figure 6. Lakes over 25 feet deep are divided into three layers during the summer. Source: Michigan Clean Water Corps (2008).

Exfiltration

Exfiltrating groundwater can be an important process that transfers P from porewater into the water body, however exfiltration rates vary spatially in a lake system. Highest porewater P concentrations typically occur in the deepest areas of the lake where thick layers of fine sediments have accumulated over millennia. Low hydraulic conductivity of these sediments essentially seals the lake bottom and inhibits exfiltration (Fig. 1). Conversely, exfiltration is usually focused at near-shore areas where sediment is commonly sandy and porewater P concentrations are typically small. Despite this mismatch between zones of high groundwater exfiltration and zones with high porewater P concentrations, groundwater exfiltration into lakes can be considered as a mechanism fueling the internal P cycle by increasing P flux from the lake sediments to the overlying water (Meinikmann et al. 2016; Shaw and Prepas 1990).

pH

Another factor to be considered in P movement and sorption is pH. Below-neutral pH (less than 7) is necessary for Fe oxides to adsorb and retain orthophosphate (Domagalski and Johnson 2012). Detenbeck and Brezonik (1991) found that in most systems, as pH increases sorption of phosphate decreases, and surface charge becomes more negative. This increase of pH causes a decrease in the positive surface charge of Fe and Al (hydr)oxides, and therefore a decrease in the affinity that these surfaces have for adsorption of phosphate anions. In general, soils and aquifers having pH values higher than 7 will become saturated in orthophosphate faster than more acidic soils and aquifers due to decreased available sorption sites. Therefore, when pH >7, P concentration at saturation will be higher as there are fewer available sorption sites and more free P (see P Geochemical Conditions).

Internal vs External P

After taking into consideration many soil-P processes including uptake of nutrients by macrophytes, delivery of P immobilized in the aerobic surface layer, and a potential diffusive P flux from the sediment and from the overlying water, Meinikmann et al. (2016) suggested that the border between groundwater-borne P and internal P should be set at about 50 to 100 cm sediment depth. However, the best way to differentiate P is to sample along the subsurface flow path to observe the concentration changes of groundwater with distance from the SWI, which would lead to an understanding of P mobilization processes, and advective and diffusive transport processes. Due to the difficulty of differentiating between internal and external P, the resulting estimates of P loads from LGD may include P released from sediments in some cases (Meinikmann et al. 2016).

Floodwater

An important aspect of surface water is flooding, which tends to flush contaminants into waterways, leading to remobilization and deposition downgradient. Additionally, the high volume of water flowing over a short time period causes increased P transport due to the lack of time available for P to adsorb to the aquifer media (Pang et al. 2016). Research has shown that P can be more readily transported in floods not only due to P accumulation on the surface of soils, but also from phosphate-saturated soils. Flood water also has the potential to transport not only dissolved P, but also P particles like colloidal P (see the next section: Potential for Colloidal P Transport in Subsurface Flow). Young and Ross (2001) found that phosphate-saturated soils act as sources of phosphate to overlying water and surrounding watersheds due to the Fe redox cycle and availability of DO. As an area is flooded, oxygen is added to the system, causing oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}), which leads to formation of solid ferric phosphate ($FePO_4$) and fixes the formerly free phosphate. Therefore, soils with lower phosphate and higher-organic matter concentrations display lower release of this phosphate to floodwater, as sorption sites are more readily available and oxidation causes the sorption of phosphate to iron hydroxides. In contrast, soils containing higher P concentrations and lower organic matter show more variability in release to porewater and greater release of phosphate to floodwater (Young and Ross 2001). This process is indicated in a study by Young and Ross (2001) which found rust-colored precipitates forming at or near the soil-water boundaries of soil microcosms in their flooding experiments. Anoxic floodwaters can result in the mobilization of phosphate from porewater to floodwater as reducing conditions release sorbed phosphate into the floodwater (Moore and Reddy 1994). Young and Ross (2001) also found a negative correlation between floodwater phosphate and porewater phosphate and Fe(II); when floodwater phosphate decreased rapidly, porewater phosphate and Fe(II) increased rapidly. This is further evidence of the effect the Fe redox cycle has on the release and retention of phosphate to and from porewater and floodwater. However, the oxidation of Fe(II) at the SWI did not completely stop the mobilization of phosphate from porewater to floodwater. Therefore, soils subject to over-fertilization and subsequent high extractable phosphorus have the potential to cause the release of large quantities of phosphate in a flood. In addition, it is statistically unlikely that this excess P would contribute to significantly greater crop yields in those fields (Jokela et al. 1998; Magdoff et al. 1999).

Potential for Colloidal P Transport via Subsurface Flow

The particle-facilitated transport of highly sorbing chemicals such as P requires further investigation. Colloidal P is largely not researched and poorly understood, particularly as a component of P transfer in runoff (Zhang et al. 2016). However, colloidal P may also act not only as a contaminant source of P, but also as a mechanism of P transport (Zang et al. 2011). P may be transported in dissolved (< 0.45 μm), colloidal (1 nm to 1 μm), and particulate (> 0.45 μm) forms (Sims et al. 1998). These P forms are arbitrary, as there exists no natural cut off between these P forms, and the colloidal size range spans the arbitrary 0.45 μm divide. This makes it difficult to fully understand the modes of P transfer from land to water. A few researchers have started to analyze the potential for colloidal P transfer, as it could have higher importance than previously understood (Heathwaite et al. 2005).

There are many types of colloids in subsurface media, such as metal oxides, clay minerals, bio-colloids (viruses, bacteria, and protozoa), and natural organic matter, which can lead to colloidal P sorbed to e.g. goethite, kaolinite and *E. coli* respectively. Significant variability exists among colloids for their influence on P attenuation and transport due to their different physicochemical properties (Pang et al. 2016). P displays an affinity for binding to colloids, especially Fe and Al oxides and aluminosilicate minerals (Brennan et al. 1994; Zhang 2008; Zang et al. 2011). Colloids and related fine particles have large specific surface area and thus enhanced adsorption characteristics, which is important to P transfer (Newman et al. 1994; Beckett and Chittleborough 1994). In a study on the effect of dissolved and colloidal P on P cycling in calcareous forest soils, Wang et al. (2020) found that colloids aren't locally generated, like SRP, instead they originate from the overlying organic soil horizons. Ca^{2+} can contribute to colloid formation by bridging organic matter. Colloid formation is also influenced by climate, vegetation, and soil characteristics (Wang et al. 2020).

While colloidal transport has been observed in surface runoff, less evidence and investigation has gone into subsurface colloidal P flow. However, Wang et al. (2020) found that while SRP wasn't detected in deeper mineral soil horizons (due to effective retention by Ca minerals), colloidal P was still present in deeper soil layers and therefore of significance for potential P vertical transfer. In the De Jonge et al. (2004) study, about 75% of the leached P was transported in a particle-facilitated manner. Field tracer experiments have shown that colloidal particles can be transported relatively rapidly in subsurface pathways compared with solutes (Becker et al. 1999; Cumbie and McKay 1999; Heathwaite et al. 2005). Therefore, some studies have found the potential for colloidal P transport in subsurface flow. Subsurface transport of colloidal P depends on soil properties (e.g. pore size, soil structure, fractures, flow paths), colloidal properties (e.g. size, shape, and surface chemistry), and rainfall (e.g. intensity, temporal distribution, duration of no-rain period prior to storm even/contaminant build-up) (Liu et al. 2013; Zhang et al. 2016).

Influence of Soil Properties

Soil properties appear to exert the strongest control over colloidal transport due to pore space, soil structure, and soil particle size. De Jonge et al. (2004) found that soil structure controlled to a large extent the leaching of particles and particle-bound P. The mass of leached particles was positively correlated to the macropore flow velocity, implying that colloidal P transport would be greatest in soils or sediments with high permeability (high hydraulic conductivity, the *K* variable in Darcy's Law). Leaching of P from soils was therefore associated with mobile colloids through preferential flow paths, which could range from sandy layers in unconsolidated sediments or fractures in bedrock. The potential for colloidal P transport is greatest where flow is fastest. Colloids, however, also can act to slow P transport in some cases; for example, by increasing attenuation caused by the presence of colloids (goethite, kaolinite, Fe or Al hydroxides, and *E. coli*) that are immobile and sorb P, which even limits its potential to migrate in solution. Pang et al. (2016) found that colloid-assisted P attenuation and colloid-enhanced retardation was most significant in the presence of fine porous media (silts and clays) and Fe-containing colloids at low flow rates but was least significant in the presence of coarse gravels and *E. coli* bacteria at high flow rates. Colloids in interflow transport through soil macropores and mesopores are more likely to be retained on soil matrix or pore walls by being physically captured by the soil pore throats or diffused into the soil matrix, resulting in much lower concentrations in the interflow (Zhang et al. 2016). Contaminants can adsorb to immobile colloids that deposit in porous media, therefore being retained in small pores and reducing their subsurface transport. Conversely, contaminants adsorbed to mobile colloids can be transported through large pores, enhancing their transport velocity (Walshe et al. 2010). Thus, it appears that sandy to gravelly soils with E Coli are likely to foster greatest colloidal P transport by groundwater flow to a lake.

Colloidal Properties

Colloidal properties such as size, shape, and surface area can impact their transport through soils, however, the size of colloids that are preferentially transported depends greatly on soil properties. Zhang et al. (2016) found that colloidal particles with sizes <10 μm dominated the surface runoff (accounted for >80% of the total suspended particles) while in the subsurface lateral interflow and fracture flow, the particle size distribution shifted towards larger average diameters. Larger particles were transported via subsurface flow because <10 μm colloids were more likely to diffuse into the pores of the soil matrix or rock fracture surfaces during their transport in the subsurface (Mohanty et al. 2015a). In contrast, large particles can be trapped by settling quickly by gravity, by particle sedimentation, and by surface vegetation, therefore being less likely to migrate (Zhang et al. 2016).

Rainfall

Colloid transport can occur rapidly over long distances via both surface runoff and subsurface flows with rainfall. Rainfall intensity governs colloid dispersion or detachment in surface and subsurface flow, as well as the transport of colloids by hydrodynamic forces. Rainfall intensity also dominates the release and transport of colloids (Zhang et al. 2016). In the upper Yangtze River, peak colloid concentration reached 188 ppm in subsurface bedrock aquifer flow during heavy storms (Zhang et al. 2015). However, colloid concentrations in subsurface flows post rainfall events is 1-2 orders of magnitude lower than surface runoff (Zhang et al. 2016). This implies that intense precipitation or rapid snowmelt could cause pulses of colloidal P transport to lakes.

Air-Water Interface

Zhang et al. (2016) proposes that the dominant mechanism responsible for an early peak of colloid discharge before saturation in fractures above the water table is the moving air-water interface (AWI). They suggest that gaseous phases (often trapped air bubbles) in partially saturated porous media can promote colloid mobilization and attachment to the AWI due to the greater surface tension at the AWI relative to that at the liquid-solid interface. Therefore, when an infiltrating water front arrives at the AWI, adsorbed colloids are mobilized (Zhang et al. 2016).

The Influence of P Accumulation Over Time

Mobile particles must be present in sufficiently large quantities for colloid-facilitated transport to be a significant mechanism of P transfer. Abundant P occurs in naturally P-rich soils, or in soils that receive animal manure and/or fertilizer, and P concentrations tend to build up in no-rain periods (longer than 48 hours; Zhang et al. 2016). Colloidal P transport can be enhanced in P-rich subsoil (i.e. with P saturation) with (1) a large flow of water, (2) after nitrate has been flushed from the soil profile and (3) when total solute concentrations are small. Accumulation of P in soils can increase the risk of colloid-facilitated leaching of P, as shown by their mobilization with drainage water or during rainfall events from agricultural soils (Heathwaite 2005; Siemens et al. 2004). The replenishment of the colloid source during a dry spell mainly depends on the slow diffusion of dispersed colloids from the bulk matrix toward pore surfaces. The longer the no-rain period lasts, the lower the soil capillary pressure is. A decrease in capillary pressure in the soil pores facilitates the collapse of the pore walls and thus the generation of colloids (Majdalani et al. 2008).

Fecal Colloids and P Transport

P transfer in association with fecal colloids could be a large source of mobilization to surface waters and subsurface flow from manure applications, dairy slurries, and septic tanks. P concentrations from these sources are very high, ranging from 3-40 ppm in septic tank effluent (Lowe et al. 2009) and 18-82 ppm in farm dairy effluent (Longhurst et al. 2000). McGechan et al. (2002) found that P attached to fecal colloidal particles is preferentially transported via soil macropores in subsurface pathways (Heathwaite et al. 2005). Mechtensimer et al. (2017) found that there is potential for P transport from septic systems located in areas with sandy soil and high groundwater tables. Pang et al. (2016) found that a setback distance of 49 m down-gradient from septic effluent discharge and 53 m down-gradient of a dairy effluent discharge was needed to allow sufficient reduction of inorganic P concentrations in groundwater to acceptable levels (5 ppb) in the receiving water. Similarly, Gray et al. (2015) and Close (1989) found that the impact of inorganic P discharge from septic tank effluent was limited to 38-44 m in groundwater. However, with subsurface saturation of dissolved organic carbon which would compete with anionic P for available sorption sites in the aquifer media, P transport could occur over much larger distances. Colloid transport is strongest when strongly-sorbing agrochemicals (anionic pesticides, P fertilizers) are applied immediately before rainfall events after long dry periods. (Zhang et al. 2016).

Organic P

Organic or nonreactive P is most likely associated with colloidal P transport. Organic P (e.g. as a component of humic or fulvic acid) has been found to be mobile in the soil profile (Frossard et al. 1989) and can represent a significant proportion of P present in leachate from grassland soils (Toor et al. 2003). Organic P may be mineralized to inorganic P (e.g. PO_4^{3-}) during the course of P transport to water bodies, therefore posing an equal threat to freshwater ecosystems as inorganic P transport. Mechtensimer et al. (2017) found that while dissolved orthophosphate was attenuated in septic system drainfields (gravel trench drainfields and drip dispersal systems), there is potential for P in organic and colloidal forms to leach and reach groundwater below septic systems. Concentrations of dissolved orthophosphate tend to decrease with depth of soil (due to sorption and microbial uptake), however, concentrations of other P forms (in this study: TP – DIP) increased with depth, suggesting that other P is more mobile or microbial transformations influenced P proportions in the drainfields. In addition, dissolved orthophosphate was attenuated in septic system drainfields (gravel trench drainfields and drip dispersal systems). These results indicate that unlike inorganic P forms, organic and colloidal forms of P can leach and reach groundwater below septic system drainfields (Mechtensimer et al. 2017). Additionally, organic and particulate P forms dominantly leach from soil to groundwater with dairy slurry seepage and manure application (Mechtensimer et al. 2017). Studies using inorganic P (potassium phosphate) injections found little to no colloidal-facilitated P transport (Gray et al. 2015; Fuchs et al. 2009). However, Pang et al. (2016) found that with injections of undiluted sewage and dairy shed effluent, P (associated with the effluent) was found to be transported in both dissolved and colloid-associated forms. Therefore, colloid-associated P is probably related to the type of P species and the amount and nature of the colloids in the effluent (Pang et al. 2016).

Nitrogen

Much like P, the natural global N cycle has been extensively altered by human activities, doubling the rate of N inputs into the terrestrial N cycle (Vitousek et al. 1997). Natural N inputs are caused by downward leaching of N from soil organic matter and in situ-release from organic matter in the aquifer. The main anthropogenic sources of N are commercial fertilizers, manure, sewage, atmospheric deposition, and contaminated land. From these sources, N is usually supplied in the form of nitrate, which can easily leach from the vadose zone into an aquifer or surface water body (Meinikmann et al. 2016). In the US, the amount of N entering the environment from the application of fertilizer increased 20-fold between 1945 and 2001, with about 20 million metric tons of N introduction in 1997 (Burow et al. 2010). Only 2 to 4% of N fertilizer is used in nonagricultural settings (e.g. city parks and residential lawns) (Burow et al. 2010; Ruddy et al. 2006). This augmentation of N inputs has increased leaching and runoff of this nutrient that threatens water quality, particularly in agricultural areas where elevated nitrate concentrations are common (Scalon et al. 2007). Higher N inputs can cause eutrophication (e.g. N-fixing algae), reduced biodiversity, polluted air, greenhouse gas emissions, and increased human health risks (Meinikmann et al. 2016). While the use of N in agriculture was important to increase food production to feed the growing world population, questions have been raised about its sustainability without causing further impairment of water resources (Eickhout et al. 2006). Due to nitrogen's hazardous health effects for humans, it has been more closely monitored and researched than P. However, N in groundwater has remained largely under-researched as a significant transporter of contaminants. Many surface water bodies receive significant groundwater discharge, which supplies more than 33% of the water used for public drinking-water supply in the US (Burrows et al. 2010). Therefore, excess N in groundwater can lead to ecological and public-health disturbances in receiving surface water, which emphasizes the need to more closely study N's processes in groundwater (Howarth et al. 1996; Puckett et al. 2008).

Geochemical Conditions

Nitrate occurs in the environment in several different redox states, including ammonium and dissolved organic N (DON). In oxic aquifers, ammonium is converted to nitrate by nitrification. Anaerobic ammonium oxidation provides a microbially mediated ammonium removal process under anoxic conditions, however ammonium is regenerated in the aquifer by the decomposition of sedimentary and dissolved organic N. Another source of ammonium is the dissimilatory nitrate reduction to ammonium (Meinikmann et al. 2016).

Dissolved organic N (DON) is a reduced N form, however relatively little is known about this form of N. It is known that large quantities might occur in groundwater and that N fertilizer may increase DON concentration in soils, particularly ones with low sorption capacities. DON is typically attributed to natural sources, however, in urban settings DON could be from wastewater or other anthropogenic sources due to its high concentration in close proximity to landfills and wastewater disposal sites (Meinikmann et al. 2016).

Reducing conditions/Anoxia/Denitrification

Several natural influences on nitrate concentrations make it difficult to link high nitrate concentrations in groundwater directly to overlying N inputs. These influences include complex unsaturated zone processes which influence N leaching to the water table (Green et al. 2008), and physical and chemical processes within the aquifer resulting in some areas being more vulnerable to nitrate contamination than others (McMahon and Chapelle 2008). Conditions favorable to low nitrate concentrations include geochemically reducing conditions and low N inputs. Reduced geochemical conditions promote attenuation of nitrate through denitrification (Meinikmann et al. 2016). This is an inverse relationship compared to the relationship of P to anoxia, in which P is released to groundwater with anoxia, while N is attenuated (i.e. permanently removed from the system).

Denitrification is an anaerobic microbial respiratory pathway in which nitrate is converted to N_2. In this N_2 gaseous phase, N is permanently removed from groundwater, therefore, denitrification is the predominant removal process for groundwater N. Denitrification requires anoxia and an electron donor, which can come from organic carbon, sulfide, or Fe^{2+} (Slomp and Van Cappellen 2004; Starr and Gillham 1993; Tesoriero et al. 2000). The highest rates are restricted to the upper layers of groundwater where DOC concentrations are the largest (Meinikmann et al. 2016).

Reduced conditions predominate in groundwater where there are large amounts of organic carbon (whether natural or anthropogenic) and where oxygen is depleted, such as along long groundwater flow paths or in low permeability, waterlogged soils. This corresponds to areas with shallow seasonal water tables, typically occurring in the eastern half of the US where the climate is humid and soils have a high organic content (Burow et al. 2010). Redox conditions seem to exert a stronger control on nitrate concentration than either N inputs or groundwater age (followed by non-point source N inputs), indicated in the Burow et al. (2010) study where nitrate concentrations were found to be highest in young, oxic groundwater regardless of N inputs (Fig. 7).

Oxia/Nitrification

Conditions favorable to high nitrate concentrations include oxic environments and high N input (Meinikmann et al. 2016). Oxic conditions tend to occur in the western half of the US where the climate is dry, soils have a low organic content, and irrigation pumps often increase the depth to water. There are also links between soil drainage characteristics and oxic geochemical conditions. Well-drained soils influence both the transport and attenuation factors that control nitrate concentrations in groundwater. Nitrate concentrations and the prevalence of oxia in wells generally increases as the percent of well-drained soils increases due to less denitrification occurring in these soils (Burow et al. 2010).

There exists a significant difference in nitrate concentrations among groundwater beneath agricultural land-use (highest median concentration), urban land-use (middle), and major aquifer wells (lowest) (Burow et al. 2010). Differences in sources typically cause characteristic isotopic signatures of groundwater particularly in the ratio of ^{15}N to ^{14}N (Meinikmann et al. 2016). However, as indicated above with anoxic conditions, other factors besides purely N input influence nitrate concentration in groundwater. This is indicated in some networks where Burow et al. (2010) found that high N input had low nitrate concentrations and vice versa. This study also found, using ^{3}H to determine groundwater age, that nitrate concentrations are higher in more recently recharged groundwater, i.e. younger groundwater, and shallow groundwater is younger than deep groundwater. Wells in northeastern US surficial and bedrock aquifers were shallower than wells in most of the other major aquifers studied and therefore might represent younger groundwater that has moved rapidly through the system. Young groundwater tends to be more oxic because dissolved oxygen may be progressively depleted along groundwater flow paths with time. The higher nitrate concentrations in younger oxic groundwater is therefore consistent with the geochemical conditions described above, as denitrification occurs in anoxic waters and removes N from the system, causing oxic groundwaters to contain higher N concentrations than anoxic water. This indicates the importance of redox conditions on nitrate concentrations (Burow et al. 2010).

Nitrate concentrations can also be linked to aquifer characteristics due to their relationship with the age of groundwater and the level of anoxia. Nitrate concentrations tend to be significantly higher in unconfined aquifers than confined aquifers (Borchardt et al. 2007). This has to do with groundwater age, as unconfined aquifers contained more young groundwater than confided aquifers (82% vs 56%) according to Burow et al. (2010). Confined aquifers are more protected from overlying land surface activities than are unconfined aquifers. Therefore, young affected water has longer travel times to reach these aquifers, increasing the likelihood that nitrate concentrations will be low when it reaches the aquifer. This is due to historically lower N input concentrations in the past as well as the increased opportunity for attenuation. Aquifer lithology and structure also correlate with groundwater velocity, affecting groundwater travel times and geochemical conditions. Aquifer lithologies that are associated with the highest nitrate concentrations may reflect the quicker speed at which groundwater and associated contaminants move through the system (Burow et al. 2010).

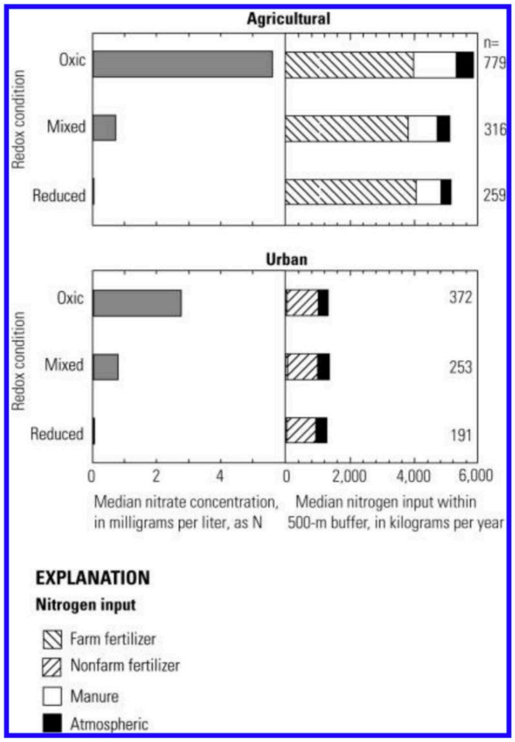

Figure 7. Median nitrate concentration and nitrogen input grouped by redox classification for agricultural and urban land use studies. Displays the importance of redox condition over that of N input. Source: Burow et al. 2010.

Movement in Groundwater

The environmental fate of N differs as it occurs in several different redox states each varying in mobility. Groundwater borne N loads vary greatly in different studies from 0.001 to 640 g m^{-2}/year. N more generally has high solubility and is transported relatively fast in the subsurface, especially in groundwater. However, a considerable portion of the N that enters a watershed is eventually immobilized (adsorption of ammonium and DON) or eliminated (denitrification of nitrate) (Meinikmann et al. 2016).

Oxic Conditions. Under oxic conditions, nitrate might exhibit a nearly conservative behavior and thus travel much faster than P, with minimal physical retention. Ammonium's mobility most closely matches that of phosphate, as sorption to clays and other cation exchangers causes ammonium retention. The contrasting behavior of nitrate and phosphate in oxic groundwater systems typically results in a strong increase of the dissolved N: P ratio along a groundwater flow path compared to the Redfield ratio of 16:1, particularly in contaminated systems (Meinikmann et al. 2016).

Reducing Conditions

At higher redox potentials (oxidizing conditions) N becomes nitrate and can be permanently leached from soils, while reducing conditions enhance P mobility as it is released from ferric iron, making it available to be transported downstream; Meinikmann et al. 2015). Most notably different from P is the ability of N to be permanently removed through the system by denitrification, in which nitrate is transformed to gaseous N_2 in reducing conditions (Meinikmann et al. 2016).

Fate at the Sediment-Water Interface

A large amount of nitrate undergoing transport in the subsurface of a catchment could be lost at the SWI as the water enters the lake, as biochemical turnover of N is common at the reactive aquifer-lake interface. The uppermost layer of the lake sediment contains freshly settled easily degradable organic matter, creating a reduced redox potential and potentially intense denitrification at the SWI (Meinikmann et al. 2016). Chen and Keeney (1974) showed that there is a decrease of nitrate and nitrite concentrations as groundwater approaches the SWI. Well chemistry does not provide a good indication of the composition of groundwater entering the lakes due to SWI interactions as well as the content of surrounding areas. For example, denitrification occurs as subsurface flow approaches some lakes because many are surrounded by areas with wet soils, fens, bogs, or low permeability silty sediments. These wet areas and high content of easily degradable organic matter provide circumstances favoring denitrification (Brock et al. 1982; Meinikmann et al. 2016).

Aquifer Characteristics

Aquifer heterogeneities (notably in fractured rock aquifers) could support nitrate exfiltration and alter nitrate concentrations. Nitrate concentrations are decreased in aquifers with poorly drained soils, greater depth to the groundwater table, artificial drainage systems, intervening layers of unfractured bedrock, a low rate of groundwater recharge, lithologic sources of DOC and sulfides, and anaerobic conditions in the aquifer (Meinikmann et al. 2016). The highest potential N concentrations occur in peat deposits, whose low hydraulic conductivity diverts groundwater flow around peat lenses and through surrounding sand and gravel deposits where faster flow and shorter contact time results in less potential for denitrification (Deviot et al. 2000).

Exfiltration Pattern

*T*he exfiltration pattern of N in groundwater closely resembles that of P concentrations. Lee (1977) found that groundwater with high nitrate concentrations seeped into a lake primarily within the first few meters of the shore, while groundwater deeper in the flow system had lower nitrate concentrations and appeared to enter the lake farther from the shore (Fig. 1). The vertical distribution of N concentration in horizontally flowing groundwater that discharges to a lake is rotated 90° and distributed across the lake bottom with distance from shore (Fellows and Brezonik 1981). The vertical groundwater chemical profile exhibits a pattern of alternating elevated ammonium concentrations and elevated nitrate concentrations across a lake bed with increasing distance from the shoreline, as studied by McCobb et al. (2003). However, as with P (see P Movement in Groundwater/Surface Water), many natural and anthropogenic processes can affect the pattern of exfiltration, highlighting the need for spatial exfiltration pattern sampling.

Quantifying LGD and LGD-derived nutrients

A few studies have tried to quantify groundwater borne P loads to lakes and rivers and evaluate the impact on their trophic state, however, it is difficult to quantify LGD-derived P loads (Ala-aho et al. 2013; Jarosiewicz and Witek 2014; McCobb et al. 2003; Ouyang 2012; Shaw et al. 1990). Below are several methods used to quantify LGD, determine the spatial distribution of LGD, and quantify LGD-derived nutrients.

Quantifying LGD loads and rates

A common way to quantify LGD loads is by using Darcy's Law. The hydraulic gradient, $\frac{\Delta h}{L}$, between the lake level and groundwater table is equivalent to the infiltrating or exfiltrating conditions. The absolute value of the hydraulic gradient is equivalent to the intensity of seepage. More information can be found on pages 5 and 6 in Meinikmann et al. (2016).

Groundwater recharge calculations are another method for quantifying LGD volume. Over a long period of time, the amount of groundwater recharged in a lake catchment equals the amount of groundwater discharged to the lake. However, this method only produces one number for the whole lake and no spatial information, which has been found to be very important in calculating LGD rates (Meinikmann et al. 2016).

The only technique to directly measure LGD rates is with seepage meters, which collect exfiltrating water. The volume of exfiltrating water is collected in a bag within a cylindrical vessel deployed into the lake sediment. Seepage meters are typically handmade by the sampler. This method has been widely used and improved by Rosenberry and LaBaugh (2008). Seepage meters can also be used to quantify nutrient concentrations (Meinikmann et al. 2016).

Spatial determination of LGD loads and rates

*T*ypically, LGD volume fluxes (hydrological factor) and nutrient concentrations (biogeochemical factor) are determined separately and subsequently multiplied. However, both factors may be affected by spatial and temporal heterogeneities, impeding the empirical determination of representative values (see Groundwater-Lake Interaction section). Therefore, detailed spatial information on groundwater P concentrations could increase the accuracy of P load calculations and aid in the tracking of anthropogenic P inputs (Meinikmann et al. 2015). P loads are spatially consistent with LGD loads, therefore, LGD hot spots could be used to interpret groundwater flow directions to help identify contaminated sites, or to help in planning in situ-restoration measures. Meinikmann et al. (2013) determined that it might be insufficient to multiply the total annual LGD volume with the mean groundwater nutrient concentration to determine the absolute nutrient load. Seasonal temperature differences between groundwater and surface water can be used to determine point measurements and spatial measurements of LGD. In quantifying groundwater vs surface water flow, the use of distributed temperature sensing, airborne thermal infrared, or fiber-optic temperature sensing can help identify major water exfiltration zones (Lewandowski et al. 2013). The intensity of advective and conductive heat exchange across the groundwater-surface water interface is represented in vertical temperature distributions in the sediment. Significant differences between temperatures of groundwater and surface water typically occur during summer and winter seasons. The curvatures of temperature gradients in the sediment close to the interface represent the direct and intensity of vertical groundwater exchange. These profiles of lake sediment temperature can be applied to calculate the exchange rate using the heat-transport-equation, solved by adjusting the Darcy velocity (Meinikmann et al. 2013 & 2016). While typically temperature sensing is not quantitative, it is very detailed, allowing small scale variations of LGD to be detected. More information can be found on page 6 and Chapters 2.1 and 3.1 of Meinikmann et al. (2016) and page 203 of Meinikmann et al. (2013).

Quantifying nutrient LGD loads

Nutrient concentrations in LGD are best measured as closely to the SWI as possible due to modifying processes during their transport towards a lake. Specific LGD concentration sampling includes multi-level samplers, seepage meters (direct sampling of exfiltrating water), dialysis samplers (provide vertical concentration profiles with high spatial resolution), and piezometers (active sampling of porewater from 1 depth). More information on these sampling methods can be found on page 8 of Meinikmann et al. (2016).

Piezometers, placed along the shoreline where exfiltration occurs, collects SRP concentrations which can then be multiplied by LGD volume fluxes to determine SRP loads for single shore-line segments. Higher numbers of piezometers allow increased spatial resolution and increase the accuracy of P load determinations (Meinikmann et al. 2015). Values of P loading via LGD from literature range from 6 to about 2900 mg Pm^{-2}/yr (e.g. McCobb et al. 2003; Ommen et al. 2012; Shaw et al. 1990; Vanek 1991).

Meinikmann et al. (2015) performed an evaluation of external P loads using piezometers (described above), bulk samplers, agricultural drainage, storm water discharge, and water fowl numbers. Bulk samplers were installed to quantify P import by atmospheric deposition. Water fowl and different geese species stayed overnight at the lake studied, and therefore their numbers were counted and multiplied by their duration of stay and literature values for the P concentration of their excrements. Agricultural drainage was discharged into the lake through a ditch system. Therefore, this study took measurements of discharge and equipped two ditches with V-weirs and pressure sensors to record water levels. Storm water discharge was collected with an ultrasonic flow measurement device and analyzed for SRP and TP. The external P loads were then evaluated by mass balance using these two equations:

$$P_{load} = P_{sed} + P_{exp} + \Delta P_{lake}$$

P_{load} = external P loads
P_{sed} = P rentention in the lake sediment
P_{exp} = P export from the lake by surface and gw outflow
ΔP_{lake} = changes in P inventory of the lake water

$$Q_{out} = Q_{in} - E_{lake}$$

Q_{out} = surface and gw outflow from the lake
Q_{in} = water inflow to the lake (sum of all hydrological input paths)
E_{lake} = water loss from the lake surface by evaporation

Treatment practices and P removal strategies

There are possible solutions to reduce the amount of P contamination in water bodies. Reducing the P flow into the lake by half would decrease contribution of sediment to the lakes P levels by 20% in a decade. However, if P inputs were halted entirely, it would take up to 200 years to decrease its contribution by 50% due to attenuation and storage along the flow path. Therefore, the reduction of eutrophication and removal of excess P and N from lakes is only sustainable if internal and external measures are taken (Thompson 2019).

External measures include: a permeable reactive barrier close to the shoreline that could directly remove diffuse P from shallow groundwater before it enters the lake (Meinikmann et al. 2015), nitrate removal by denitrification (Meinikmann et al. 2016), vegetation growth (Meinikmann et al. 2013), and most importantly, the decrease of P and N rich fertilizer used on agricultural fields and/or septic sources near bodies of water. Effective nitrate removal by denitrification in riparian zones may produce redox conditions, which at the same time increases the release of soil-retained P. Generally, redox conditions favoring nitrate removal increase phosphate mobility and thus phosphate input by LGD (Meinikmann et al. 2016). Vegetation growth along the shoreline might cause a decrease of LGD due to the accumulation of fine sediments and thus lower hydraulic conductivity. In addition, emersed vegetation could result in the transpiration of subsurface water prior to its discharge into the lake. The use of shoreline stabilization could inhibit LGD, but decrease contaminants (Meinikmann et al. 2013). The most important step is to decrease the nutrient concentrations in anthropogenically affected groundwater, especially for aquifers located in the catchment of seepage lakes.

There exist a few internal removal measures for P, however, these are less researched and could be impacted by an array of processes and cause unintentional consequences. An Fe amendment could be used to sequester P in the sediments so that it is no longer biologically available for algae (Thompson 2019). There is a strong coupling of the early diagenetic cycle of P and Fe, therefore many studies have tried this method with Fe^{3+}, Al^{3+}, and Ca^{2+} phases, each of which have the potential to bind P and make it less mobile (Markelov et al. 2016). Markelov et al. (2016) found that the Fe amendments did decrease the internal P loading, leading to lower phytoplankton biomass. The efficiency depended on the existing Fe inventory in the sediments. Lower amounts of existing Fe will allow for more effective P sorption with the amendments. However, once the treatment was terminated, the lake's phytoplankton biomass returned to its pretreatment level within 15 years. Therefore, this internal measure must be met with an external decrease of P in order to be effective in the long term. An internal treatment practice being conducted at some lakes is the use of aerator compressors. The aerators supply compressed oxygen to the deepest sections of the lake where the most legacy P has accumulated in order to increase DO and oxic conditions, therefore keeping P sorbed and retained in the sediment (DEC 2019).

Major Takeaways:

- Excess input of limiting nutrients P and N cause eutrophication in downstream waterbodies, which leads to algal blooms, lake water anoxia, death of lake biota, reduced water clarity and quality, reduction of biodiversity, and toxicity to humans.

- Non-point sources and diffuse transport are now the main contributors of excess nutrients; from agricultural fields (fertilizer), septic systems, and urban land-use.

- Recent studies found that groundwater can transport P, particularly that an average of 41.5% of total P delivered to lakes is transported by groundwater, but it is important to recognize that this factor is highly variable depending on physical and biogeochemical factors outlined in this report.

- With consistent over-application of manure and synthetic fertilizer, soils can become saturated with P, which creates a long-lasting supply of P to groundwater that can take decades to start depleting.

- Complex groundwater-lake interactions (e.g. sediment homogeneity, hydraulic conductivity, biogeochemical reactions, topography, anthropogenic disruptions) can affect the amount of P and N being transported into the lake, and it is important to understand spatial and temporal variability of exfiltration, which can be measured with seepage meters (only way to directly measure LGD rates) and thermal imaging (can help determine contaminations sources and sites).

- P is naturally found in many different forms; dissolved inorganic P, which primarily occurs as orthophosphate (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}), is the most important when considering groundwater transport and eutrophication in its dissolved form due to its high bioavailability. Total P (TP) is most commonly measured as it includes all forms of P found in water.

- The Fe redox cycle can retain P in the soil during oxic conditions, while in anoxic conditions P can be released from ferric phosphate and be transported via groundwater.

- Several controls limit the transport of P in groundwater including: intensity and proximity of contamination, P saturation levels within sediments (increased P loading leads to increased P transport due to oversaturation), sediment-water interface (long-lasting supply of lake bottom legacy P), seasonal changes and stratification (transport of this legacy P to be bioavailable), exfiltration rates, pH, and floodwater (potential for increased transport of P to downstream waterbodies during floods).

- Soil properties exert the strongest control on colloidal P subsurface transport. In coarser grained soils, colloid facilitated transport of P is more likely to occur. Other controls include colloidal properties, rainfall, the air-water interface, and P build-up (i.e. saturation). Fecal colloids and inorganic P colloids could pose specific risk due to the transport of this form of P from manure or septic systems.

- The global N cycle has been extensively altered by human activities, specifically through the use of N-rich fertilizer from which nitrate can easily leach into aquifers, a specific concern due to the hazardous health effects that nitrate poses to humans.

- N concentrations are lowest in anoxic waters, where denitrification can permanently remove nitrate from groundwater. This relationship extends to the age of groundwater, due to the amount of time allowed for denitrification to occur. This is of particular importance because while transportable N decreases with anoxia, transportable P increases with anoxia.

- While N generally has high solubility, and is transported relatively fast in the subsurface, a considerable portion is immobilized (e.g. adsorption of ammonium and DON) or eliminated (e.g. denitrification of nitrate). N concentrations may decrease greatly at the SWI due to the high content of organic matter and high level of anoxia, therefore raising the potential for intense denitrification.

- Internal (e.g. Fe amendment, lake bottom aeration) and external (e.g. decrease fertilizer application, vegetation growth, permeable reactive barrier) treatment practices are necessary for a timely decrease in P and N loading.

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