Revisiting Internal P-Cycling in Shallow Lakes: A Detailed Perspective

Relating to Utah Lake

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WASATCH FRONT WATER QUALITY COUNCIL

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Phosphorus as a nutrient: Phosphorus is an essential part of life and an integral part of biological molecules ATP, ADP, and DNA, which sustain life. Phosphorus, represented as P, is a necessary part of our diet; we consume it in all our foods. Phosphorus is a vital plant element and an essential nutrient in plant growth. Phosphorus is very reactive and is not found in its elemental form (P). In nature, Phosphorus exists in the form of phosphates, in which case Phosphorus reacts with metals (like Aluminum, Magnesium, Iron Calcium, and many more) to form metal phosphates. Oxides of phosphorus form phosphoric acid when it reacts with water. Phosphoric acid is a polyprotic acid (3 H atoms). Phosphorus can enter surface water systems through various sources, including urban stormwater and agricultural runoffs, atmospheric deposition, and point discharges such as municipal wastewater treatment plants. These P inputs to surface water bodies such as lakes result in P accumulation in sediments through various bio-geochemical activities. Many of these biogeochemical activities are pH- and bacteria-mediated, causing the P to get exchanged between sediments and the overlying water constantly. Phosphorus is distributed in an aquatic ecosystem in several forms, such as organic Phosphorus, water-soluble inorganic Phosphorus, or water-insoluble inorganic Phosphorus. Hence, management and mitigation efforts should consider all sources and types while estimating the phosphorus loading in any surface water body.

P plays a vital role in the water quality due to its low stoichiometry (lower concentrations can cause problems) requirements. In addition to exogenous P sources, P within the freshwater lake ecosystem can undergo continuous dissociation (breaking down of P minerals)-adsorption (sorbed into pores of porous surfaces of minerals) equilibrium in the water-sediment interface through a series of physical and biochemical reactions including adsorption, desorption, precipitation, and ion-exchange (Cai et al., 2023). Primary production (e.g., algae and cyanobacterial growth) depends on external P sources (e.g., atmospheric deposition, stormwater discharges, point sources, and agricultural runoffs). However, internal turnover and phosphorus release from particulate (insoluble form of P such as in dead biomass) P in the water column (through hydrolysis) and labile P from surface sediments also contribute significantly.

P in sediments: For a broader understanding, P in aquatic ecosystems can be divided into two forms: inorganic P (IP), which primarily includes exchangeable P; P associated with Al, Fe, and Mn oxides and hydroxides; and Ca-bound P, and Organic P compounds, which were previously considered part of the refractory P pool because of analytical limitations and the complexity of their composition, have recently received increased attention. Organic-P comprises nucleic acids, phospholipids, inositol phosphates, sugar phosphates, and condensed P. Organic-P plays a vital role in aquatic P cycling. When IP is utilized by aquatic plants in water, the transformation of Or-P to IP in sediments becomes an essential means of P provision supporting phytoplankton growth. Around 90% of the Phosphorus accumulates in the sediments and can be released into underlying water due to various factors such as microbes, anoxic conditions, redox environments, temperature, pH, and organic matter. (Yin et al., 2023). Phosphorus in lake sediments is found in different forms. Some fraction of Phosphorus is bound to the sediments, while others are mobile. Inorganic Phosphorus is readily soluble in the form of orthophosphate anion. This orthophosphate is found in sediments as a part of minerals or as precipitated phosphate salts such as $Ca_5(PO_4)_3(OH)$, $FePO_4$, AlPO4, and $Ca_3(PO_4)_2$. Often, phosphates are fixed as adsorbed anions on the surface or the interior of various metal oxides and hydroxides, constituting the sediment particles (especially those of Fe, Mn, and Al). Phosphorus can also be absorbed by sedimentary organic matter or exist in the form of organic phosphate esters.

As stated earlier, Phosphorus in sediment can widely be categorized as Organic Phosphate(oP) or Inorganic Phosphate(IP). Inorganic-P mainly contains Phosphate bound to Fe, Mn, or Ca as salts, along with metal hydroxides such as NaOH-P, which tend to be sinks for dissolved Phosphate. Phosphorus is generally released into water in anoxic conditions, such as those formed during the degradation of dead Cyanobacterial biomass (Ding et al., 2016). Meanwhile, organic-P, which had been primarily considered Refractory Phosphorus until the early 21st century, is mainly found as either Orthophosphate esters or biological compounds such as Nucleic acids and Polyphosphate chains, which can be scavenged by Cyanobacteria using enzymatic methods to release iP (Li et al., 2019). Organic P plays a vital role in aquatic *P* cycling. When IP is utilized by aquatic plants in water, the transformation of Or-P to IP in sediments becomes an essential means of *P* provision supporting phytoplankton growth (Ni et al., 2019). Agricultural and industrial inputs could also contribute to P bound to Fe, Al, and Mn oxides, hydroxides (NaOH-P), and organic *P (Long et al., 2023).* As a rule of thumb, Phosphorus present in sediments can be categorized in fixed or nonlabile pool (unavailable immediately), active or labile P pool (consists of adsorbed, secondary P minerals and organic P that mineralizes quickly), and readily available P (comprised of inorganic phosphates and a small portion of organic P). During the peak or declining stages of algal blooms, organic-P could be one of the significant forms of P depositing into lake sediments. For example, Wang et al. (2024) recorded that the sediment organic P contents decreased significantly at the early and last stages of the HABs outbreak and increased at the peak of the HABs outbreak and during the HABs decline.

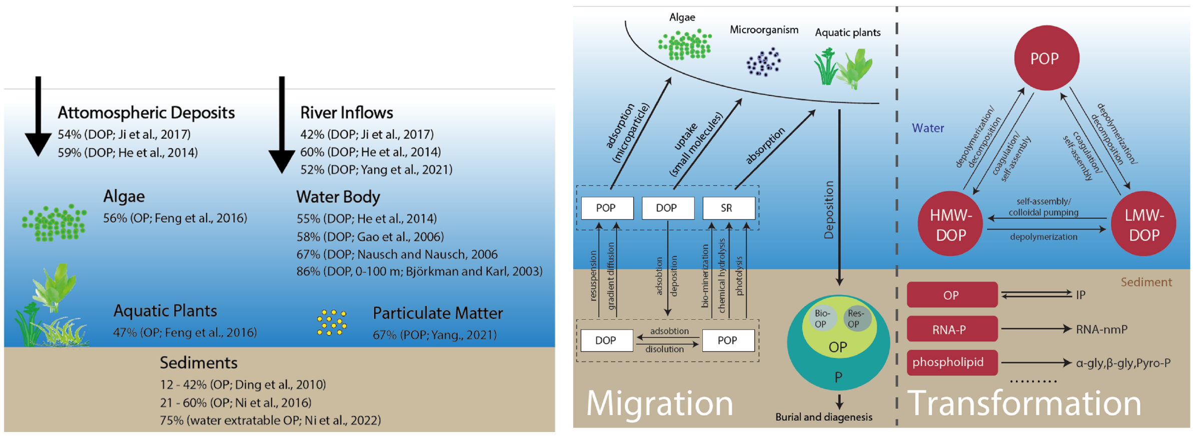

Figure 1: Left Panel: Typical contributions of OP in total P in river inflow, water bodies, macrophytes, phytoplankton, particulate matter, atmospheric deposits, and sediments from aquatic ecosystems, respectively, according to different published literature. **Right Panel**: Major paths of migration (left side) and transformation (right side) of OP in sediments (Source Ni et al., 2022). In the figure, DOP: Dissolved organic P, OP: Organic P, POP: Particulate organic P. LMW: Low molecular weight, HMW: High molecular weight.

P Release from sediments: P release from sediments can last an extended period to the overlying water (Long et al., 2023; Yin et al., 2022). Internal loading is a complex process resulting from various physical, chemical, and biological processes. A few processes by which Phosphorus is released from the sediments are desorption, ligand exchange mechanisms, dissolution of precipitates, mineralization processes, release from living cells, and autolysis of cells. These P-release mechanisms may be balanced by opposing retention mechanisms like sorption, precipitation, assimilation, complexation, sedimentation, and burial of cyanobacteria. Internal P loading is a net process that requires P release to be greater than P retention. If P retention is greater than P release, burial of P within sediments occurs, and the internal loading flux is negative. Internal P cycling can sustain eutrophication for an extended period. P release from sediments is one of the most critical factors determining P concentrations in the overlying water column. The bulk of P deposited in sediments can be recycled into the water column, thereby impacting the status of lakes for years even after the reduction of external input of P. Numerous studies have determined that eutrophication in lakes cannot be mitigated by solely reducing exogenous P input because internal nutrient loads and pollutants from sediments may continue to contribute to eutrophication in the water column. Sediment is both the central P pool and source in lake systems and affects water quality due to the endogenous release of P even though the external P is restored. Internal P recycling mechanisms are complex and numerous, controlled by various physical and biogeochemical processes. The most active top layer of sediments is 10-30 cm, where active physical and biogeochemical reactions occur (Wang et al., 2023).

Among physical factors, Wind-induced waves are generally regarded as the most critical factor that can result in sediment resuspension in large and shallow lakes, particularly under solid wind, forcing the loosely bound P to be released into the overlying sediments. In anaerobic and anoxic environments, the complexes formed by ferrous iron with Phosphate are less stable, leading to P release in ambient water. Sulfate-reducing bacteria could form sulfide from sulfate. This in-situ formed sulfide could react with Phosphorus to precipitate. The vertical distribution of organic and inorganic P in sediments is controlled by molecular diffusion, burial, and deposition of particulate P. In shallow lakes, these processes are further complicated by sediment resuspension.

Bacteria-mediated processes can cause the recycling of P between the sediments and the overlying water column. Certain bacterial express enzymes can hydrolyze particulate P to dissolve one and make it bioavailable. Other microorganisms can accumulate ortho-P in the form of poly-P in oxygen-rich conditions. The same organisms can then release the poly-P back into the water column without oxygen. Nitrogen loading could also result in P release from sediments. For example, ammonium nitrogen concentration greater than ten mg/L has been shown to simulate alkaline phosphatase (an enzyme responsible for hydrolyzing organic P to inorganic P) activity, resulting in P release from sediments. Alkaline phosphatase is an enzyme bacteria/cyanobacteria could express during P crises.

Similarly, nitrate could have a dual effect on the P dynamic, in which case high nitrate concentrations exceeding 5-10 mg/L can inhibit sediment P release by improving the redox potential while promoting the P release by increasing the phytoplankton biomass simultaneously. Excess ammonia nitrogen inputs to the Lake could also cause P release from the sediments, perhaps due to the stoichiometric imbalance in the N:P ratio. For example, Ma et al. noticed that the sediment P release in shallow ponds increased when total nitrogen (added as ammonium chloride) exceeded 10-25 mg N/L. Inorganic phosphate solubilizing and organic solubilizing bacteria could also cause P release from sediments depending upon the organic carbon contents of sediments. Wang et al. (2023b) noticed that the concentrations of soluble reactive Phosphorus (SRP) in the water column and EPC_0 in sediments decreased with aggravated eutrophication. There was a significant negative correlation between the SRP concentrations and eutrophication parameters such as chlorophyll a (Chl-a), total phosphorus (TP), and algal biomass ($P < 0.001$). In addition, SRP concentrations were significantly affected by EPC_0 ($P < 0.001$), while EPC_0 was significantly affected by the content of cyanobacterial organic matter (COM) in sediments ($P < 0.001$). With their findings, Wang et al., 2023b further concluded that COM can alter the phosphorus release characteristics of sediments, including the phosphorus adsorption parameters of sediment (PAPS) and the phosphorus release rate of sediment (PRRS), thereby stabilizing SRP concentrations at lower levels and rapidly replenishing them when depleted by phytoplankton, which in turn benefits cyanobacteria due to their low SRP adaptation strategies.

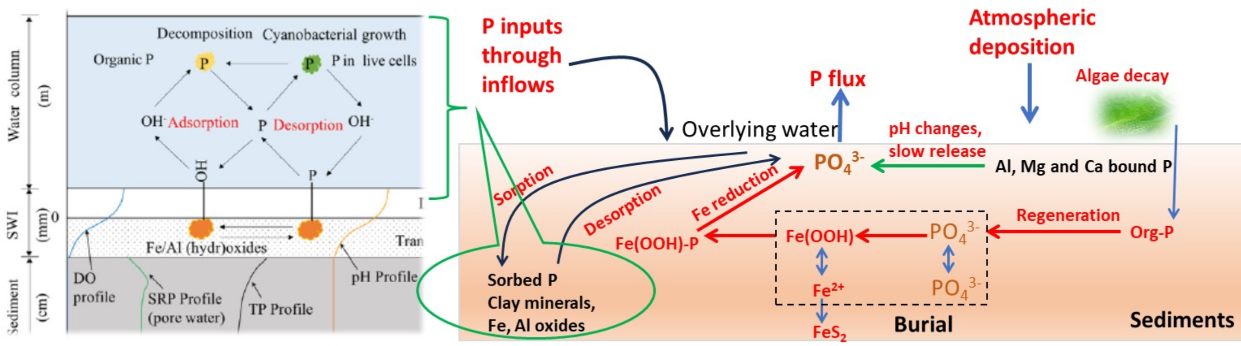

Figure 2: Important P retention and release mechanisms for P in sediments.

P release might occur under anaerobic conditions due to reducing conditions. For example, Spears et al., 2007 demonstrated that short-term, high-magnitude, redox-initiated P-release events occurred in late summer and winter due to anoxic sediment conditions in a shallow lake in Scotland. Spears et al., 2007 further demonstrated that lower magnitude long-term release conditions were maintained for most of the year, most likely due to organic P cycling and maintenance of high concentration gradients between the pore and bottom water P pools.

Loosely bound P to sediments can be quickly released in the water column during turnovers or lake turbulence. Iron and calcium-bound P could be extracted under basic and acidic conditions. This means that occasional alkaline conditions (much like in Utah Lake) will release iron-bound P into the water column, and a diminished pH would result in calcium-bound P being released in the water column. Phosphorus solubilizing and phosphorus mineralizing bacteria present in sediments could also contribute to the P release, the contribution of which needs to be addressed in lake management. The inorganic P released from the sediments due to the remineralization from organic P in sediments could be redistributed in sediments through precipitation and adsorption.

Several reports have mentioned the retention of Phosphate in lakes, even after significant efforts to curb the external supply of nutrients. Lake Mugglesee, a shallow freshwater lake in Germany, exhibited high Total Phosphate levels (TP) till six years after a 50% reduction in external Phosphate and Nitrate loadings, despite a drastic decrease in Total Nitrate (TN) levels in the same period, implicating sediment Phosphorus as a potential supplier (Kohler et al., 2005). A study in Lake Rotorua in New Zealand described the rate of release of Soluble Reactive Phosphate (SRP) from lake sediments, implicating it as a more significant source of Phosphorus than external loadings in anoxic conditions, such as those formed during blooms. Likewise, a study by Yin et al., 2022 estimated that nearly 256 tons of total P and 217 tons of soluble reactive P over six months in Lake Taihu could be released from sediments.

Not all P present in sediments is labile. The amount of P released from sediments mainly depends on the contents of sedimentary P compounds, which can vary significantly in chemical form, mobility, and bioavailability. **As shown in Figure 2** earlier, P can accumulate with organic matter (OM) or Fe-(oxy)hydroxides in the sediment under aerobic conditions. During early diagenesis and remineralization of OM, Fe-(hydroxy)oxides can release soluble P into interstitial water. Phosphate can form complexes with Fe oxide and exists as iron-bound P (Fe–P). In the anaerobic scenario, ferric iron (Fe^{3+}) could be reduced to ferrous iron (Fe^{2+}), resulting in the Fe–P dissolution as PO_4^{3-} into the water. This release can increase the P load, potentially exacerbating the eutrophication of the overlying water (Alam et al., 2020).

In summary, based on the extensive literature available, it could be concluded that it is less likely that exogenous control of P results in any immediate relief in eutrophication. For alkaline lakes such as Utah Lake, careful consideration of contributing factors to cause accumulation and release of P in and from sediments is needed. Although previous studies solely focused on Utah Lake have concluded that sediments control P cycling in this alkaline Lake, a holistic mechanistic understanding accounting for all contributing factors is still missing. Studies such as diffusion gradient measurements supplemented with P speciation and in-situ chamber installation have the potential to provide more helpful information.

The pH at the sediment-water interface (SWI) plays a significant role in P release and sink at this interface. The pH can change from nearly neutral in the subsurface to alkaline at the interface. As a result, cyanobacterial blooms can pump a large amount of P from sediments through the ligand exchange processes of hydroxyl ions with increased pH to sustain blooms (Spears et al., 2014; Zheng et al., 2023).

Utah Lake literature review: Utah Lake, the largest freshwater lake in the State of Utah, is in north-central Utah near Orem and Provo. Utah Lake has a surface area of roughly 380 km2 (145 sq mile) and a storage capacity shy of a million acre-feet (902,400 ac-ft). It is a shallow lake with an average depth of approximately 9-10 feet during normal reservoir operating conditions. Utah Lake is generally known as an alkaline Lake with pH touching in the upper 8's at some places in summer. As a part of the Great Salt Lake watershed, Utah Lake is a habitat for 10 million migratory birds that fuel up or nest here annually. Approximately 75% of the invasive carp and phragmites have been removed, and harmful algal blooms are declining in most of the Lake. Utah Lake only experiences occasional blooms, usually only over a portion of the Lake. Utah Lake was ranked in the lowest category of algal bloom severity and persistence by a nationwide satellite study this year—cleaner than many lakes and reservoirs in Utah. The high rate of evaporation causes the constant formation of calcite, which scrubs nutrients from the water or makes them difficult for the algae to use (Abbott et al., 2022)

Utah Lake Sediments and associated P contents: Although the Lake sediment mineralogy varies, according to a study by Hogsett and Goel in 2013, Utah Lake sediments mainly consist of carbonates, with silica oxide minerals being the second largest component in sediments. The calcerous nature of sediments in Utah Lake suggests that the sediments can scavenge water column P in the form of calcium phosphates and other physical processes such as sorption to calcium, iron, and aluminum minerals.

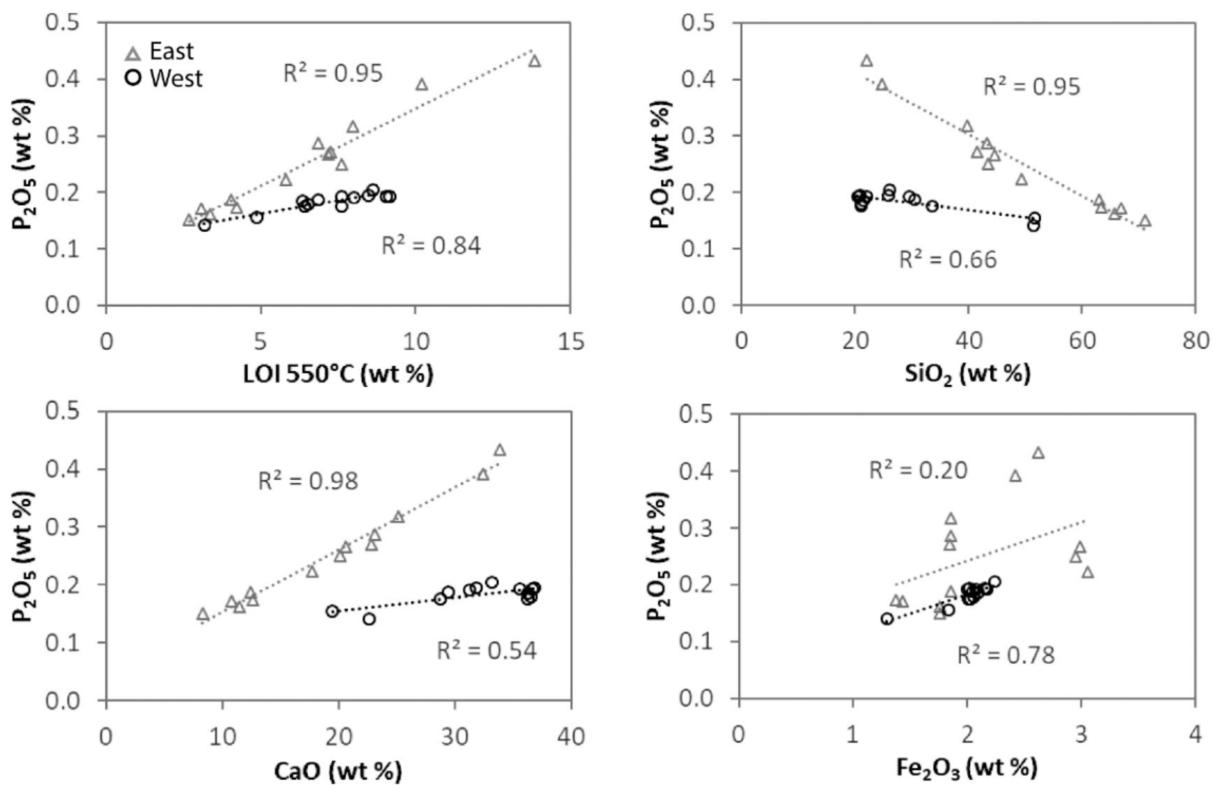

Figure 3: Correlations between sediment P2O5 and other minerals in Utah Lake (Source: Randall et al., 2019).

There are potentially more snails, clams, and mussels in Utah Lake sediments than any other freshwater lake in the Western United States. Although these creatures contribute to the water purification process in the Lake, their movement in sediments could disturb sediments and cause loosely bound P to release. Because Utah Lake is a shallow lake, wind action easily stores the Lake for turnovers, causing sediments to resuspend and deliver loosely bound P to the water column. A study by Randall et al. (2019), which collected several sediment samples from various locations in Utah Lake, concluded that total P concentrations in Utah Lake sediments ranged from 280 to 1710 mg/kg. Randall et al. (2019) also concluded that lake sediments P (in the form of P_2O_5) were positively correlated with CaO abundance and inversely with SiO_2. Positive correlations were also recorded between P_2O_5 and ferric iron contents of sediments (figure 3). Additionally, Randall et al., 2019 estimated that sediment P in Utah Lake was primarily bound to oxidized Fe/Mn compounds (BD fraction) and Calcium phosphorus. These results mostly agree with those obtained by Hogsett and Goel (2013), who also conducted P fractionation and found similar P speciation in Utah Lake sediments at several sites.

Table 1: Utah Lake sediment phosphorus speciation (Source Hogsett and Goel, 2013).

Sediment Phosphorus (mg P/kg dry mass)							
Sample #	loosely bound P	Fe & Mn bound P	P from minerals and Al oxides	Ca bound P	residual P	total P (sum)	% Ca bound
1	253	439	148	778	150	1767	44
2	12	15	0	234	22	282	83
3	135	309	116	888	226	1674	53
4	0	63	332	319	0	715	45
5	81	157	83	692	120	1132	61
6	17	138	31	509	71	766	66
7	15	133	21	119	1	289	41
8	59	202	41	274	362	937	29
9	33	142	14	605	18	811	75
10	26	69	10	541	22	669	81
11	90	159	71	549	19	888	62
12	31	110	15	897	135	1188	76

These results are in agreement with those obtained by Xu et al., 2021, albeit for a different freshwater eutrophic lake, West Lake in China, where these researchers recorded an average total P content between 397.36 and 2578.90 mg/kg, and the average content was 1391.20 mg/kg. A similar study by Abu-Hmeidan et al., 2018 on Utah Lake sediments concluded that concentrations in historic geologic sediments were not statistically different from lake sediments. A detailed statistical analysis incorporating sediment P speciation results from 84 Lake sediment samples concluded that internal natural phosphorous loadings could be significant, and the impaired state may be relatively insensitive to external anthropogenic loadings. Randall et al., 2019 also concluded that shallow lake eutrophication may be a function of P in legacy sediments that contribute to observed HABs in specific locations of shallow lakes. In a laboratory study conducted by Goel et al. (2020) with sediment cores collected from two sites in Utah Lake, the P concentrations in the overlying water in the column were adjusted to 0.5x, 2x, and 4x of the ambient dissolved P concentrations to simulate varying conditions of P loading from various sources. The experiments showed that P release from sediments mainly occurred at ambient and 0.5X concentrations, with increasing P concentrations in the water column over time, while at the 4X level, P concentrations in the water column tended to decrease over time. P release was more prevalent under aerobic conditions relative to anaerobic conditions. This demonstrates that the non-calcium bound P would be released from the sediment to the water column if P concentrations in the water column decreased or remained the same. The data also suggest that some bioavailable P in the water column is not necessarily sourced from consumer-mediated nutrient cycling or anaerobic sediment release of P-rich porewaters. Taggart et al. (2024) conducted a P mass balance based on historical data. They concluded that P concentrations in Utah Lake have remained stable over time. They further concluded that P's fate in Utah Lake is decided by its sorption to sediments and other suspended solids. Taggart et al., 2024 concluded that P concentrations in the Utah Lake water column are unlikely to change under external loadings and that the external P load reduction may not cause any P changes in the water column.

P inputs to the Lake: According to a Utah Division of Water Quality study, 77 % of the Phosphorus coming to Utah Lake came from wastewater treatment plants. However, this study did not extensively measure stormwater inputs of P, which could also significantly contribute to the total P inputs to the Lake. Additionally, this study did not consider the atmospheric deposition of nutrients to the Lale. Disturbances in sediments caused by natural habitats such as carp, other invasive fish, and numerous misuses could result in massive amounts of P release into the overlying water column. However, these instantaneous P releases due to sediment disturbances are not well quantified in Utah Lake. As indicated earlier for other shallow lakes, wind disturbances and turnovers in shallow lakes are common mechanisms of sediment disturbances resulting in P and other nutrient release into the water column. It is estimated that Phosphorus in the inflows to the Lake is 300 tons/year, with 80 % of this coming from wastewater treatment plants. Point sources are easy to quantify regarding P discharges because of the concrete monitoring data available, with most WWTPs discharging to Utah Lake. However, the contribution of air deposition and urban stormwater inputs are more difficult to quantify and perhaps significantly underestimated in the aforementioned estimate because of the lack of scientific data. A document published by the Wasatch Front Water Quality Council claimed that nearly 32 to 150 tons of Phosphorus per year can enter Utah Lake through the aerial path. Based on the available data and reports, it can be concluded that the contributions of stormwater, groundwater, and aerial deposition are less understood and that the P inputs from point sources have been significantly overestimated in terms of their contribution to the total P input to the lakes. Additionally, recently completed or current projects under construction at WWTP will reduce WWTP P into the Lake by about 75%, thus minimizing their impact as future P sources.

Future perspective: Utah Lake is a complex ecosystem, and this complexity is further exacerbated due to the lack of convincing data related to urban stormwater contributions to P in the Lake, the absence of data about the mechanisms of P sedimentation and retention in sediments, bacteria mediated enzymatic P release from sediments and a lack of scientific consensus on atmospheric deposition of P. Among many potential future target investigations, one possible way could be conducting a sediment study to determine the oxygen isotopic composition of Phosphate in addition to P fractionation. Such a study could shed light on sources of P in sediments. Additionally, using EPA methods, different extraction methods should be compared first to determine total P and P fractionation in sediments. The post-treatment procedures after digestion, which influence the effects of insoluble particles and adsorption/precipitation of Phosphorus in TP analysis, are quite different in the EPA methods 365.1, 365.2, 365.3 (USEPA, 1982) and the Standard Method (SM) 4500 (APHA-AWWA-WEF, 1998). The USEPA method 365.2 requires neutralizing and filtering the digestates before TP analysis.

In contrast, EPA method 365.1 requires cooling the digestates, and EPA method 365.3 requires cooling and filtering the digestates before TP analysis. In comparison, SM4500 requires neutralizing and mixing the digestates before TP analysis. Bacteria-mediated P release needs special attention. Bacteria residing in sediments could contribute to P dynamics between sediments and the overlying water column in two ways: (1) by accumulating and releasing P in the presence of readily biodegradable organic carbon and (2) by hydrolyzing organic P to inorganic P through their alkaline phosphatase activity. Experimentally, the P sorption and P saturation indexes should be established for lake sediments to accurately estimate the potential of P sinks and P release from lake sediments. Additionally, treating the whole Lake as a batch or semi-batch reactor and conducting mass balance would not be appropriate because the composition of lake sediments varies (Calcite versus silica). Hence, the Lake should be compartmentalized based on the bathymetry and sediment composition for modeling purposes or P mass balance.

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