To:	Utah DWQ, ULWQS Science Panel
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Date:	2021-09-30
Subject:	Bioavailability Memo for Utah Lake C, N, and P Study

1.0 INTRODUCTION

The purpose of this memo is to characterize the bioavailability of phosphorus (P) and nitrogen (N) in lakes and apply this evaluation to the stocks of P and N in Utah Lake. This analysis will identify which components of elemental stocks are actively cycled and which are inaccessible due to chemical form or binding. The results of this task will help to identify the stocks and fluxes of algal-accessible nutrients, which can inform prioritization of management activities to target the most effective measures for reducing phytoplankton growth.

2.0 IN-LAKE P BIOAVAILABILITY

The form of P taken up and used by biota is phosphate (PO_4^{3-}), also known as orthophosphate. Phytoplankton have evolved to be efficient at taking up phosphate in the water column, and this efficient uptake combined with other chemical binding processes result in very low concentrations of phosphate in most freshwater environments (Dodds and Whiles 2011). Although phosphate is the preferred form of P for biological uptake, phytoplankton also excrete phosphatase enzymes to access phosphate that is bound to other compounds as well. Thus, bioavailable stocks of P are made up of both phosphate and additional forms of P that can be cleaved by phosphatase.

Bioavailability of P in lakes is dependent on several biogeochemical factors, namely those that drive the precipitation and dissolution of P to and from bioavailable forms. A common paradigm in seasonally stratified lakes is the precipitation and dissolution of phosphate with iron. Under oxic conditions, phosphate precipitates with ferric iron, becoming non-bioavailable. Under anoxic conditions in the hypolimnion, iron is reduced to ferrous iron and dissociates from phosphate, which is then available for biotic uptake (Dodds and Whiles 2011). Utah Lake does not exhibit seasonal stratification due to its large area to depth ratio, but this mechanism may occur under transient stratification if anoxic conditions are reached or at the sediment-water interface where sediment oxygen demand may create an anoxic layer. A second mechanism for phosphate precipitation is the formation of calcium phosphate, also known as apatite (Dodds and Whiles 2011). Apatite formation can enhance the internal P sink in lakes, and calcite precipitation and P sedimentation can thus be closely related (Dittrich and Koschel 2002). Given the high concentrations of calcium, high pH, high alkalinity, and high primary productivity in Utah Lake, this process is expected to be a main driver of the conversion of bioavailable to bound P.

2.1 WATER COLUMN P

Total dissolved P (TDP) in the water column contains both bioavailable and non-bioavailable forms. Phosphate concentrations in lake surface waters are typically very low and often below detection. Therefore, most bioavailable dissolved P is contained in other forms, including dissolved inorganic P (analytically equivalent to dissolved reactive P or soluble reactive P [SRP]) which is fully bioavailable, and dissolved condensed phosphates and dissolved organic P, some of which can be converted to reactive forms and considered bioavailable

(Sonzogni et al. 1982). Several studies have quantified multiple forms of water column P in Utah Lake. Li et al. (2020) found that phosphate concentrations (0.00-0.07 mg/L) were one to two orders of magnitude lower than total P (TP) concentrations in the water column (0.27-1.04 mg/L). Collins (2019) quantified water column SRP and TP, with mean concentrations ranging from 0.016-0.025 mg/L for SRP and 0.077-0.189 mg/L for TP. Goel et al (2020) measued SRP and TDP in both the main basin and Provo Bay. Concentrations of both SRP and TDP were higher in Provo Bay (0.22-0.28 mg/L SRP and 0.028-0.51 mg/L TDP) than in the main basin (0.02-0.04 mg/L SRP and 0.05-0.10 mg/L TDP). In combination, these studies indicate that water column P in Utah Lake is made up of variable proportions of particulate and dissolved P, and that bioavailable P makes up a small fraction of the dissolved forms. Provo Bay generally has higher concentrations of dissolved P than the main basin, and bioavailable P makes up a larger proportion of dissolved P than in the main basin.

2.2 PARTICULATE AND SEDIMENT P

Particulate P in the water column is made up of organic materials (phytoplankton, other organisms, detritus), precipitates, and sediment-bound P. Phytoplankton are an important stock of P that participate in the active cycling of bioavailable P through uptake and excretion. Particulate organic P are typically not considered a permanent P sink, although particulate organic P that settles to the sediments can be stored and are subject to burial. Precipitated P settles out of the water column and becomes part of the sediment P stock unless chemical conditions become suitable for dissolution. Sediment-bound P may be introduced to the water column via sediment resuspension or external sediment loading from inflows.

Particulate P comprises inorganic and organic forms, and the inorganic forms are divided into nonapatite inorganic P (NAIP) and apatite inorganic P (AIP). Iron and aluminum oxides and minerals as well as calcium minerals are classified as AIP and are generally non-bioavailable, whereas a large fraction of NAIP is bioavailable (Sonzogni et al. 1982). Chemical forms of particulate P are often characterized by their reactivity or extractability with specific compounds. Bioavailable forms of sediment P include water soluble P, readily desorbed P that is extracted via a neutral salt solution, and NaOH-extractable P. These forms of P are highly positively correlated with total sediment P, though their relative and absolute magnitudes may vary greatly even in lakes with large P stocks (Zhou et al. 2001). NaOH-extractable P is used as a proxy for NAIP, generally constituting 70% of NAIP (Sonzogni et al. 1982). Therefore, SRP and NAIP (i.e., NaOH-extractable P) make up the potentially bioavailable P pool. The capacity for potentially bioavailable P to be taken up is dependent on its proximity to phytoplankton, which for sediment P is dependent on the rates of sediment resuspension and diffusion out of the sediment.

Dapeng et al. (2011) highlighted the impacts of sediment resuspension on sediment P bioavailability and water column P concentrations. In general, sediment resuspension induces several biogeochemical changes that impact the forms and amount of sediment P. Increased oxygen exposure encourages the conversion of amorphous iron oxides to crystalline iron oxides. The exposure of water column P to sediment particles also promotes the role of clays, humic acids, metal oxides, hydroxides, and calcite as P sorbents and reactants, inducing a redistribution of sediment P forms. In total, resuspension generally promotes the transformation of mobile P to inert P, reducing the bioavailability of the P pool. In the experiments conducted, sediment resuspension resulted in removal of water column SRP due to increased contact with reactants and sorbents, and sediment bioavailability was lower than under static conditions. Thus, in Utah Lake, we might expect reductions in water column TDP and reductions in bioavailable sediment P as a result of frequent resuspension, resulting in enhanced P storage and burial.

Randall et al. (2019) evaluated the forms of sediment P in Utah Lake. The majority of sediment P was associated with AIP fractions that are non-bioavailable, including 49.1% associated with iron and manganese oxides and 38.5% associated with calcium phosphate minerals (and a likely small amount of organic P). The remaining 12.4% of sediment P as associated with loosely bound, exchangeable, and refractory P. Exchangeable P, extracted by NaOH, was considered the bioavailable fraction and made up 4.5-6.8% of total sediment P. In sum, these results indicate that only approximately 1/20 of sediment P is bioavailable in Utah Lake, with the remainder

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associated with non-bioavailable forms that may constitute a permanent P sink if requisite chemical conditions are maintained.

3.0 IN-LAKE N BIOAVAILABILITY

Dissolved inorganic N (DIN), comprised of ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-), is considered the most bioavailable pool of N for phytoplankton growth. The form of N taken up by cells as part of assimilatory N uptake is NH_4^+ (in chemical equilibrium with ammonia [NH_3] depending on pH). Thus, NH_4^+ is the chemical form that is energetically most favorable for uptake by phytoplankton. However, NH_4^+ concentrations tend to be low in the water column of most lakes, so phytoplankton rely on other forms of N as well. NO_3^- and NO_2^- are converted to NH_4^+ by the nitrate reductase enzyme, so these forms are considered bioavailable for phytoplankton uptake albeit at a greater energetic cost than NH_4^+. Dissolved organic N (DON) is made up of both bioavailable and non-bioavailable forms of N, and forms can become biologically available through decomposition by microbial activity or through enzyme activity by phytoplankton. Urea ($CO(NH_2)_2$) is an example of a bioavailable DON compound, which has an intermediate energetic assimilation cost between NH_4^+ and NO_3^-. In the absence of a consistently available pool of bioavailable N, the phytoplankton community may favor the dominance of taxa that have the ability to fix N from dissolved atmospheric N (N_2). N fixation requires the nitrogenase enzyme and is the most energetically expensive process by which to assimilate N. However, under seasonal or consistent N limitation of phytoplankton growth, N fixation can be a competitively advantageous pathway. Several cyanobacterial taxa are N fixers that can both assimilate bioavailable N as well as fix N when those compounds are scarce.

Note: this memo does not address dissimilatory pathways of N uptake and transformation, including denitrification, dissimilatory nitrate reduction to ammonia (DNRA), nitrification, and anammox.

3.1 WATER COLUMN N

Several studies have measured water column N concentrations in Utah Lake, as compiled in the Utah Lake C, N, and P Data Compilation Spreadsheet (Tetra Tech 2021). Measured constituents were typically NH_4^+ and NO_3^-, with some studies measuring combined forms including DIN, total dissolved N (TDN), and total N (TN). All measured forms can be considered bioavailable with the exception of TDN and TN, which also include non-bioavailable forms. DON can be calculated as the difference between TDN and DIN. Concentrations of water column N are highly variable in Utah Lake, ranging over three orders of magnitude. There is evidence that N periodically limits primary productivity, and N fixation also occurs (see section 4).

3.2 SEDIMENT N

Unlike P, N does not sorb strongly to inorganic particulates. Thus, transfer of bioavailable N from the sediment to the water column is largely regulated by diffusion and advective mixing rather than sediment resuspension. Pools of sediment N may become bioavailable through microbial transformations of N, including decomposition, nitrification, and DNRA. Fluxes of N from sediment to water column in Utah Lake are largely made up of DIN and are generally positive (Hogsett et al. 2019, Goel et al. 2020)

4.0 RESULTS OF UTAH LAKE BIOASSAY STUDY

Aanderud et al. (2021) showed through bioassay experiments that supplies of bioavailable nutrients (DIN and SRP) were sufficiently low to limit primary productivity in Utah Lake. As displayed in the summary table from this study, phytoplankton tended to be limited by both N and P, whereas cyanobacteria had more variable responses to nutrient supplies. N fixation was also observed, suggesting an alternate pathway of N acquisition and a potential response to reduced bioavailable N supply in the water column. Dilution bioassays showed reduced

phytoplankton activity in response to reduced nutrients, further supporting the finding of dual nutrient limitation in Utah Lake.

Variable and Location	spring	early summer	summer	late summer	fall
Cyanobacteria nutrient limitation					
East	No limitation	No limitation	P	No limitation	No limitation
West	N+P	No limitation	N	No limitation	No limitation
Provo Bay	P	N+P	P	No limitation	No limitation
Total phytoplankton nutrient limitation					
East	No limitation	N+P	N+P	N+P	N+P
West	P	No limitation	N+P	N+P	N+P
Provo Bay	N+P	N	N	N+P	N

5.0 SOURCE WATER P BIOAVAILABILITY

In addition to water column and sediment P, the bioavailability of P in external nutrient loads is an important factor driving potentially bioavailable P stocks in Utah Lake. Preliminary analysis for the C, N, and P study indicates a variable proportion of tributary inflow P is in dissolved form, with higher proportions of TDP in sub-catchments containing wastewater treatment plants (65-97% in sub-catchments with WWTPs, 7-63% in sub-catchments without WWTPs). An additional source of P to Utah Lake is atmospheric deposition, and the subject of an in-progress study is to quantify total and bioavailable P loads from the atmosphere.

Literature estimates indicate the proportion of bioavailable P in lake inflows is controlled by both land use and hydrologic condition. Ellison and Brett (2006) found the percent of bioavailable particulate P was higher under baseflow conditions than stormflow conditions in the Lake Washington/Sammamish basin, although the total load of bioavailable particulate P was higher under stormflow conditions due to a higher TP load delivered during storm events. The percent of bioavailable particulate P was higher under baseflow in an urban catchment (73%) than in other land use-hydrologic condition combinations (17, 26, and 24% in forested, mixed, and agricultural catchments, respsectively). In the Great Lakes basin, Sonzogni et al. (1982) found that 50% or more of TP loading was non-bioavailable, with agricultural and urban TP loads being 20-30% bioavailable. Although the bioavailability of external P inputs to Utah Lake has not been quantified to date, we expect the degree of bioavailability to vary along both land use and hydrologic gradients, and these variables should be prioritized for future bioavailability quantification efforts.

Previous studies have found that wastewater treatment plant effluent is highly bioavailable, with proportions ranging from 45-98% of the TP pool (Gerdes and Kunst 1998) and 73-75% of the dissolved organic P pool (Qin et al. 2015). Discharge monitoring reports from WWTPs around Utah Lake follow a similar pattern of bioavailability, with an average 64-98% of the TP pool made up of orthophosphate.

6.0 SOURCE WATER N BIOAVAILABILITY

As with P, the bioavailability of N in external nutrient loads is an important factor driving potentially bioavailable N stocks in Utah Lake. Preliminary analysis for the C, N, and P study indicates a consistently high proportion of tributary inflow N is in dissolved form, with similar proportions across sub-catchments containing WWTPs and sub-catchments that do not (89-100% in sub-catchments with WWTPs, 83-100% in sub-catchments without WWTPs). It is unknown what proportion of TDN is made up of bioavailable forms vs. non-bioavailable forms. An additional external source of N is N fixation (Aanderud et al. 2021), from which bioavailable N may be recycled to the water column.

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7.0 REFERENCES

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