Utah Lake Sediment–Water Nutrient Interactions

Ramesh Goel[1], Greg Carling[2], Hanyan Li[1], Sheena Smithson[2]

[1]Civil & Environmental Engineering, University of Utah, Salt Lake City, Utah 84121

[2]Geological Sciences, Brigham Young University, Provo, UT 84602

Final Report

UTAH DEPARTMENT of ENVIRONMENTAL QUALITY

February 19, 2020
First Revision Submitted: May 19, 2020
Final Revision Submitted May 27, 2020

Executive Summary

This report presents findings from laboratory experiments where sediment cores from Utah Lake were subjected to P spiking under different environmental conditions. The objectives of this project were to: (1) understand the role of aerobic/anaerobic conditions in nutrient (including N and P) release or retention from sediments over a range of P concentrations; (2) understand the role of water column pH (pH = 7 and 9.5) in nutrient release or retention; and (3) quantify the sediment oxygen demand in Utah Lake sediments under ambient conditions. Sediment cores were collected from two sites in Utah Lake (Provo Bay and State Park Buoy, each with a different trophic status) and incubated with filtered lake water at room temperature in the dark to avoid any interferences due to primary productivity. In addition to evaluating sediment dynamics under ambient P concentrations, P concentrations in the water column were adjusted to the equivalent of 0.5X, 2X and 4X of the ambient total dissolved P concentration to simulate varying conditions of nutrient loading from point 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 of the bioavailable P in the water column is not necessarily sourced from consumer-mediated nutrient cycling or anaerobic sediment release of P-rich porewaters. The highest P release was observed under aerobic_0.5X conditions (20.40$\pm$16.42 mg/m^2/d) and the greatest P loss was observed under anaerobic_4X conditions (-51.84$\pm$8.30 mg/m^2/d). However, the anaerobic experiments were confounded by a concomitant increase in the pH to nearly 10, probably due to CO_2 stripping by bubbling pure N_2 gas and resulting in the loss of the buffering capacity of the system. Although a pH of 10 is realistic for Utah Lake, especially in Provo Bay, having both high pH and anaerobic conditions is probably not realistic. A significant loss of Ca from the water column was also observed under anaerobic/high pH conditions, suggesting the potential formation of calcium carbonate mineral species (i.e., calcite) that may have scavenged P either by sorption or co-precipitation. The pH experiments also proved difficult because the water tended to quickly return to the ambient pH of ~8.5, regardless of the addition of acid or base, likely due to the natural buffering capacity in the sediments. Nevertheless, **the Buoy site showed higher ambient P concentrations when the pH was maintained at neutral (pH = 7, 0.09 - 0.53 mg/L) compared to the condition when the pH was kept in the alkaline range (pH = 9.5, 0.02-0.13 mg/L).** For the Buoy site, the flux rates were in the range of -17.28$\pm$3.60 to 14.64$\pm$6.69 mg/m^2/d at neutral pH and -4.56$\pm$1.81 to 2.83$\pm$1.99 mg/m^2/d at high pH. The flux data for the Buoy site suggest the tendency of Utah Lake sediments to release Ca-bound P

when the pH decreases from its natural state. Because of the difficulty in maintaining the adjusted pH to 7, the experiment was not conducted for the Provo Bay site cores based on the suggestion by the Science Panel.

As for the N species, ammonium-N and nitrate-N were present at concentrations of 0.015-0.658 mg/L, and from below detection limit to 0.239 mg/L, respectively, while nitrite-N was non-detectable in most samples. A significant variation of ambient concentrations was only observed for ammonium-N. Generally, the Provo Bay site had higher ambient ammonium-N concentrations (0.015 - 0.658 mg N/L) relative to the Buoy site (0.015 - 0.266 mg N/L). Aerobic conditions generally resulted in a higher ammonium loss (-33.36$\pm$23.04 to -7.44$\pm$3.00 mg/m^2/d) relative to the anaerobic conditions (-9.12$\pm$1.50 to 0.11$\pm$0.41 mg/m^2/d). The loss of ammonium-N under aerobic conditions likely is not related to autotrophic nitrification given the high pH of water. Rather, it was related to the loss of free ammonia under high pH conditions and/or chemical precipitation of ammonium-N with other minerals, although the occurrence of some nitrification could not be ruled out.

Sediment oxygen demand (SOD) was evaluated at the two sites using in-situ opaque chambers to ensure that there was no primary productivity inside the SOD chambers during actual measurements. The raw results, when normalized to temperature, were calculated as -0.052 g/m^2/day at the Provo Bay site (T=55.5^{o}F and pH=8.98) and -2.965 g/m^2/day at the Buoy site (T=58.7^{o}F and pH=8.42). Relatively lower SOD at the Provo Bay site was unexpected given that the site is richer in organic matter and thus was attributed to malfunctioning of data sondes.

Overall, the results suggest that Utah Lake sediments are active in terms of nutrient release and uptake depending upon the P concentrations, redox conditions, and pH in the water column. Further experiments may be necessary to maintain the ambient pH under anaerobic conditions and to maintain neutral or alkaline pH in the experiments over time. Further, the experiments were only run for 72 hours, while these processes likely take longer than 72 hours to reach equilibrium in Utah Lake.

1. Introduction

The Utah Division of Water Quality (UDWQ) recently initiated Phase 2 of the Utah Lake Water Quality Study (ULWQS) to evaluate the effect of excess nutrients on the lake's recreational, aquatic life, and agricultural designated uses and to develop site-specific nitrogen (N) and phosphorus (P) water quality criteria to protect these uses. Understanding the cycling of nutrients in Utah Lake will help describe the current state of the lake with respect to nutrients and ecology. Sediments are an important component of nutrient cycling within the lake. Available reports and initial information on sediment oxygen demand (SOD) and nutrient release from sediments in Utah Lake provide some insight into sediment P characteristics and fluxes but stop short of describing the mechanisms of nutrient release or of converting bulk measurements into mobile or bioavailable fractions. Based on these past research efforts and the need to better understand the fate of P in the water column under different environmental conditions, the UDWQ issued a request for proposals (RFP) in the summer of 2019, which included the following questions:

1. What is the role of anoxia in nutrient releases and sediment dynamics over a range of P concentrations?
2. What is the role of pH in water column-sediment interactions and nutrient releases? How do P concentrations change over a range of water column pH?
3. What is the sediment oxygen demand of, and nutrient release from, sediments in Utah Lake under current conditions?

To address these questions, we collected sediment cores and water from two sites in Utah Lake and measured changes in nutrient concentrations in incubation experiments under the following conditions:

1. Aerobic conditions at ambient, 0.5x, 2x, and 4x ambient P concentrations.
2. Anaerobic conditions at ambient, 0.5x, 2x, and 4x ambient P concentrations.
3. Aerobic conditions with a pH of 7 at ambient, 0.5x, 2x, and 4x ambient P concentrations.
4. Aerobic conditions with a pH of 9.5 at ambient, 0.5x, 2x, and 4x ambient P concentrations.

Additionally, SOD was measured in situ at the two sites.

2. Methods

Note: Please refer to the SOP (provided in the appendix) for details on field and laboratory methods. The SOP was approved by the UDWQ and Science Panel. Here we provide a summary of the methods.

2.1 Site selection

The RFP suggested studying two sites in Utah Lake. After discussion with UDWQ and the Utah Lake Water Quality Study Science Panel, the two sites selected for sediment core collection were in the middle of Provo Bay and near the State Park Buoy. The Provo Bay site is representative of the shallow, hypereutrophic bay on the east side of Utah Lake. The Buoy site is representative of the relatively deep, eutrophic open water of the lake. The sites and coordinates are shown in **Figure 1**.

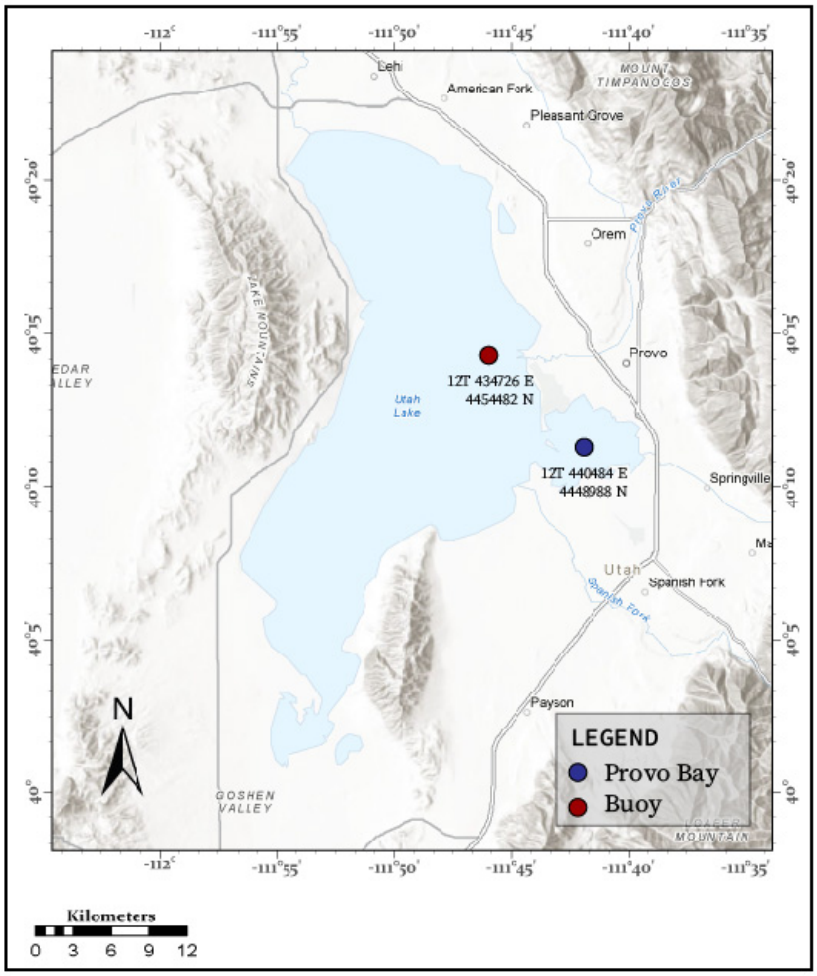


Figure 1. Map of sampling sites in Utah Lake.

2.2 Sediment core collection

A total of 72 sediment cores were collected over six trips to Utah Lake using boats from UDWQ and BYU at separate occasions. **Table 1** lists the dates of core collection and the experimental conditions tested with each set of cores. During each trip to the lake, we collected 12 sediment

cores from one of the sites and processed them immediately upon returning to lab. Each sediment core was collected with about 10 cm of sediment and 30 cm of overlying water to maintain appropriate physicochemical conditions. The cores were collected using a percussion corer. A drilling platform attached to a pontoon boat was used to support the sediment corer and make the process more efficient when the cores were collected using BYU boat. No such platform was used when collecting cores using UDWQ boat. The cores were capped, covered, and stored upright in a cooler on ice to prevent sediment disturbance and limit microbial activity.

We also collected 2 gallons of surface water during each collection trip to be used as replacement water for spiking the water column in the cores. Field parameters (pH, dissolved oxygen, specific conductance, temperature) were measured in situ at the time of water collection using a YSI Quatro multiparameter probe, which was calibrated each field day. As suggested by the Science Panel, the initial overlying water was siphoned out of each core in the lab and carefully replaced with 590 mL of lake water (~30 cm height), that was filtered (0.45 µm nylon) to remove plankton and adjusted to desired P concentrations and geochemical conditions.

Table 1. Sediment core collection details.

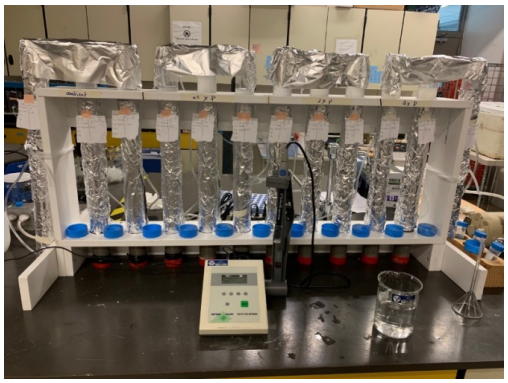
Site 1: State Park site near DWQ buoy		
Date	**# of cores**	**Experiment**
August 14th, 2019	12	Neutral pH
September 12th, 2019	12	Aerobic and anaerobic experiments
September 26th, 2019	12+2 (prepared for low pH detect)	pH=9.5
October 1st, 2019	3 chambers (1 control +2 experiment)	Sediment oxygen demand
Site 2: Provo Bay		
Date	**# of cores**	**Experiment**
September 4th, 2019	12	Aerobic and anaerobic experiments
September 17th, 2019	11(1 fewer for control)	pH=9.5
September 27th, 2019	12(experiment not conducted)	Neutral pH
October 3rd and 14th , 2019	3 chambers (1 control +2 experiment)	Sediment oxygen demand

2.3 P spiking experiments under aerobic and anaerobic conditions

To investigate P dynamics under aerobic and anaerobic conditions, we conducted experiments on the sediment cores across a range of water column P concentrations. Cores were wrapped in aluminum foil to maintain dark conditions and mounted on a stand (**Figure 2**). All experiments were conducted in the dark to eliminate the effects of primary productivity and changes in pH due to photosynthesis. The overlying water was gently drained and was replenished withfiltered lake water at ambient conditions or spiked with different concentrations of ortho-P in the form of KH_2PO_4 to achieve 0.5X, 2X and 4X total dissolved P

(TDP) relative to ambient TDP concentrations. The ambient TDP concentrations were based on historical data measured using ICP-OES in Summer 2018 provided by BYU. Each treatment was conducted in triplicate. A stock P solution of 10 mg P/L using KH_2PO_4 with 99.9% purity (Fisher Chemicals, Fair Lawn, NJ) was prepared to spike as needed. For the dilution of lake water to 0.5X, a major ion solution was prepared to simulate the natural conditions. To maintain aerobic conditions (~7.5 mg/L DO), air was purged intermittently through the water column using an aeration stone placed 5 cm above the sediment-water interface. The pH and DO in the water column were measured during sample collection (t=0, 12, 24, and 72 hours). Both pH and DO meters were calibrated before their usage. For DO, we used a HACH luminescent DO probe that measures DO to the accuracy of 0.1 mg/L. The pH meter was calibrated using pH standard solutions of 4, 7 and 10.

At each sampling time, 40 mL of water was collected from the water column in each core and filtered using a 0.45 µm nylon syringe filter. With samples taken at 12, 24 and 72 hours, the total sampling volume was approximately 120 mL. Water loss was compensated with the initial replacement lake water to maintain a constant water level. The t=0 sample was collected from the spike water rather than from the water column of sediment cores. Water samples were analyzed for ammonium-N, nitrate-N, nitrite-N, soluble reactive phosphorus (SRP), and TDP.



The same cores used for aerobic experiments were also used for anaerobic experiments. For anaerobic incubation experiments, first, the overlying water from top of each core was removed and replaced with a fresh batch of filtered lake water. To achieve initial anaerobic conditions, a sodium sulfite solution containing a trace amount of cobalt chloride (as a catalyst) was added to quickly remove oxygen by the following reaction:

Figure 2. Lab setup showing sediment cores.

$$2Na_2SO_3+O_2 = 2Na_2SO_4$$

Based on the above equation, to remove 7 mg/L O_2 from 590 mL of water, 55 mg/L Na_2SO_3 was added to the water prior to placing it in each core. Hence, no residual sulfide was present to cause any effect on system pH. Anaerobic conditions were maintained by purging with pure N_2 gas. A small flow of N_2 gas was maintained constantly to prevent aeration at the air-water interface at the top of the water column. A high flow rate was maintained when taking water samples. Gas flows were regulated using an electronic timer and a solenoid valve. Water

samples from the anaerobic cores were collected and analyzed in a similar fashion as the aerobic experiments.

2.4 P spiking experiments at pH=9.5 and pH=7

To understand P dynamics in response to changing pH conditions, we conducted experiments on the sediment cores across a range of water column P concentrations at pH=7 and pH=9.5. The mounting of sediment cores and preparation of P stock solutions followed the same procedures detailed in section 2.3 for aerobic and anaerobic experiments. Sediment core incubations were kept under aerobic conditions using the same strategy described earlier for the aerobic experiments. Filtered lake water was adjusted to pH= 9.5 using 1 N NaOH prior to gently pouring into each of the sediment cores. During the experiments, NaOH was intermittently added to each core because the pH quickly returned to ambient values of ~8.5. Sediment core incubation at pH =7 was conducted by adjusting the pH with 1 M (H_2SO_4) to filtered lake water prior to adding to water to the sediment cores at the beginning of experiment. After adding water to the sediment, we observed an increase in pH over time. Once mixing and aeration started, the pH returned to the initial value of ~8.5. The high pH experiment was conducted at both sites, while the low pH experiment was conducted only at the Buoy site. (The cores were collected at the Provo Bay site for low pH experiments but based on difficulty maintaining low pH and conversations with the Science Panel, the experiments were not completed).

2.5 Nutrient flux calculations

To better understand the flux between sediment and the water column, nutrient flux (TDP, SRP, and ammonium-N) was calculated with the following equation:

$$\text{Nutrient flux (mg/m}^2\text{/d)} = \frac{dCe}{dt} \times \frac{V}{A} \times 1000 \text{ mg/g} \times 24 \text{ hr/d}$$

Where, dC_e = change in nutrient concentrations in the water column (mg/L= g/m^3)

$\frac{dCe}{dt}$ = change in nutrient concentrations over time (g/m^3/hr)

V = volume of overlying water in the core (m^3)

A = sediment surface area in the core (0. 00785 m^2).

The area was not used in the calculation because the volumetric flux rate (e.g mass/Volume/time) was directly divided by the water column depth in the sediment cores to obtain nutrient fluxes.

Loading (kg/d) = area (km^2)* nutrient flux ($mg/m^2/d$)

2.6 Sediment Oxygen Demand (SOD)

For the SOD test, a control (water only) and two testing SOD chambers were installed at the sediment-water interface at each site. The control chamber was closed at the bottom and measured DO consumption in the water column only. The testing chambers were open at the bottom and measured DO consumption due to activities in the water column and sediments. Chambers were made opaque to prevent any phytoplankton photosynthesis. The data sonde in each chamber made measurements of DO during the two-hour experimental period every 5 min for Provo Bay to 15 min for Buoy (we directly used the calibrated sonde from UDWQ). A professional scuba diver was used for installing SOD chambers in-situ. The depth of each site at the time of experimentation was recorded. The top section of each SOD chamber consisted of a lid that contained the pump, plumbing, water sampling tube, water quality probe connection, and attachments for ropes used to lift the SOD chamber out of the sediments and water. A submersible pump was mounted on each chamber to internally circulate the water inside the SOD chamber at a predetermined flow rate of 11 L/min. The control SOD chamber had a working volume of 44 liters and the testing SOD chambers a working volume of 38 liters. This discrepancy in volumes is a result of the additional space provided in the control chamber due to closed bottom, which causes it to lose almost 1.5" of vertical length into the sediments. The construction and design of these chambers is based on SOD chambers used by Georgia EPA Sediment Oxygen Demand (507) AF.R4.

The SOD rate for each chamber were calculated based on the following equations:

$$SOD = 1.44 \left(\frac{V}{A}\right)(b\text{-}bc)$$

Where, SOD = sediment oxygen demand ($g/m^2/day$)

V = volume of testing and control chambers

A = sediment area within the chamber (0.16 m^2)

b = slope of oxygen depletion curve (mg/L/min)

bc = slope of the water column (mg/L/min)

WC = 1440*bc

WC = water column depletion ($g/m^3/day$)

bc = slope of the water column (mg/L/min)

Measured SOD was corrected to 20 °C using the standard Van't Hoff equation:

$$SOD_{20} = \frac{SOD}{1.065^{(T-20)}}$$

Where SOD_{20} is the rate at 20 °C, and T is in degrees Celsius.

For calculating SOD, the DO data (Y-axis) was plotted as a function of time (x-axis). For the Buoy site, the DO data for the sediment testing chamber was very consistent and enabled a good trend (e.g., consistent decrease over time). Hence, initial slope of the DO-time curve was considered for the Buoy site. However, for the Provo Bay site, the DO trend was initially consistent with a sharp decrease towards the end. To confirm this sharp decrease and to obtain more consistent results, we again visited the Provo Bay site with a scuba diver for a second time.

2.7 Analytical methods

The instrument, detection limit, and methods used for the water chemistry analyses are detailed in **Table 2**. For QA/QC, standards for major/minor ions, nitrite/nitrate and low concentrations of ammonium-N spike were prepared for ICP-OES, IC and HACH ammonium kit measurements. New calibration curves with $R^2 > 0.99$ were used for ICP-OES, IC and SRP measurements. Ammonium-N concentrations were obtained by the barcode reading on the Hach spectrophotometer DR 5000. The accuracy of HACH spectrophotometer for ammonium-N was the concentration of spiked standards. While preparing standards, autoclaved and acid wash glassware were used. The standards for SRP were 0, 0.02, 0.04, 0.06, 0.08, and 0.1 ppm P. Stock P solution was prepared by dissolving anhydrous KH_2PO_4 in Milli-Q water. The calibration curve and reagents were made fresh for each run on a 96-well spectrophotometer for SRP and the same spectrophotometer was used for all samples.

Table 2. Data analysis-analytical instruments and their detection limits.

Parameters	Instrument	Detection limit	Methods
P, Ca, K, Mg, Si, Fe, Pb…	Thermo Fisher iCAP 7400 Duo ICP-OES	Depend on major and minor ions	EPA method 200.7
SRP	Spectrophotometer for 96 well plate	0.001 mg/L	Modified Murphy and Riley, 1962.
Ammonium-N	Hach spectrophotometer Dr5000	0.015 mg/L NH_3-N	Hach ammonia TNT 830 Salicylate based ammonia chemistry
Nitrate-N, Nitrite-N	Metrohm 883 Basic IC plus	Depend on calibration curve, 0.1 mg/L in this case	EPA method 300.0 Determination of Inorganic anions by IC

2.8 Data analysis

The change in nutrient concentrations in the water column during each sampling interval was calculated as the concentration difference between the time steps. For example, the concentration change between 12 and 24 hours was calculated as the concentration at t = 24 hours minus the concentration at t = 12 hours. The differences among samples of varying

treatment groups were compared using a one way-ANOVA with R v3.4.0 (R Development Core team, 2013). The resulting nutrient concentration changes throughout 0-72 hour tests were compared for the different spike concentrations (ambient, 0.5X, 2X and 4X) or environmental conditions (aerobic, anaerobic, pH =9.5 and pH = 7). The 'R Stats Package' in R and Tukey multiple pairwise-comparison were applied to compare at a 95% confidence level. The nutrient flux rate (i.e., nutrient release or loss) from sediments to the water column was calculated to reflect the amount of nutrient change due to water-sediment interactions.

3. RESULTS AND DISCUSSION

3.1 Aerobic and anaerobic spiking experiments under ambient conditions

3.1.1 P dynamics under aerobic conditions

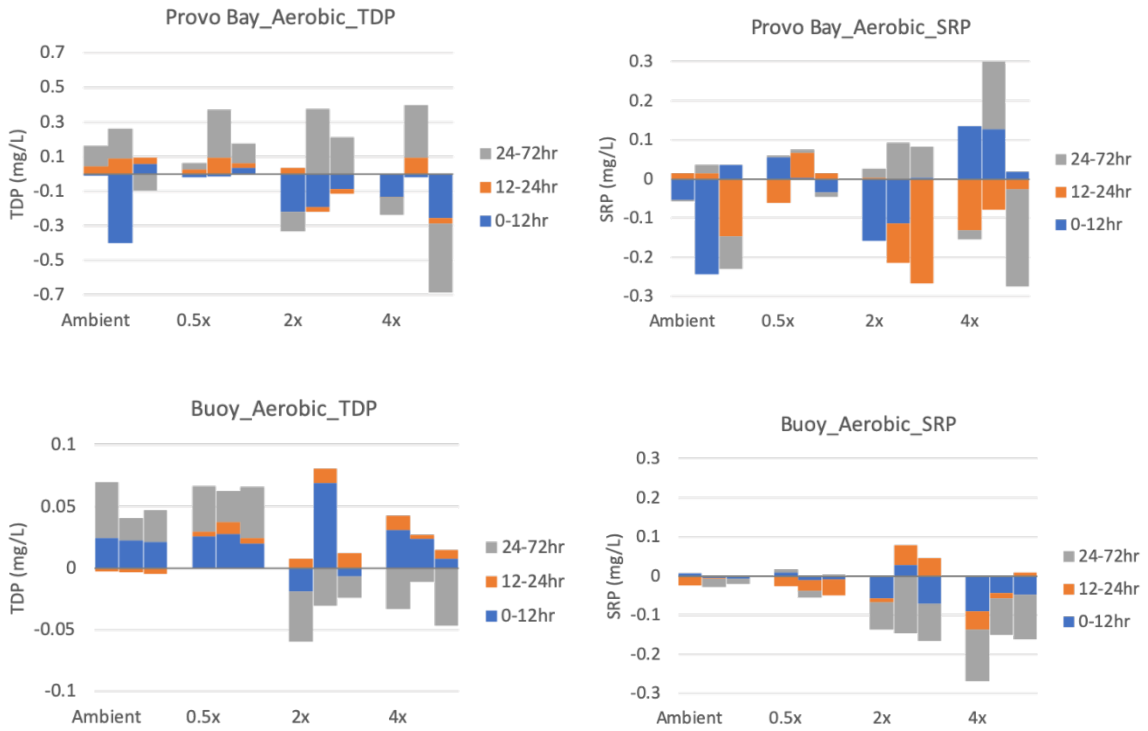


Figure 3. Relative change in TDP and SRP concentrations between sampling periods (0-12hr, 12-24hr and 24-72 hr) in the water column under aerobic conditions.

Under aerobic conditions, both the Provo Bay and Buoy sites showed similar trends in P concentrations, with the only notable difference being the overall higher initial TDP and SRP concentrations in Provo Bay (**Figure 3**). DO in the water column was maintained at about 7.5 mg/L. The water column pH in cores from the Buoy site remained at about 8.6 during the experiment, while the pH in cores from the Provo Bay site fluctuated between 8.53 and 8.82. Increasing P concentrations were mostly observed in the ambient and 0.5X spiked cores, with 0.5X spiked cores showing the highest increase in P concentrations in the water column over

time. In contrast to the ambient and 0.5X cores, P concentrations tended to decease over time in the 2X and 4X spiked cores, with the greatest decrease in P concentrations observed in the 4X cores. For the Provo Bay site, TDP concentrations (triplicate measurements) increased from 0.40-0.51 mg/L to 0.38-0.56 mg/L in the control core (no spiking) and 0.40-0.53 mg/L to 0.48-0.88 mg/L in the 0.5X spiked core from 0 to 72 hours.

In contrast, decreasing trends in TDP were observed in some sediment cores in the 2X and 4X spiked experiments (**Figure 3**). Specifically, TDP changed from 0.77-1.14 mg/L to 0.48-1.30 mg/L in 2X spiked cores and from 1.24-1.48 mg/L to 0.80-1.64 mg/L in 4X spiked cores after 72 hours for Provo Bay. Despite the decrease in TDP over time in the 2X and 4X cores, final concentrations (0.48-1.30 mg/L for 2X and 0.80-1.64 mg/L for 4X) were still higher than initial ambient concentrations (0.40-0.53 mg/L), indicating that the added P in the water column was not completely taken up by the sediments at the Provo Bay site. Similar trends were observed at the Buoy site.

Generally, the variations of SRP also showed a tendency to decrease in the 2X and 4X spiked cores, but at smaller amounts compared with TDP for both sites (**Figure 3**). The change of water column P concentrations was probably due to an exchange between particulate and soluble phases as well as between the water and surface sediments (Jenkins, 2005). In summary, the water column P concentrations (both SRP and TDP) increased in cores maintained at ambient and 0.5X spiked cores and decreased in 2x and 4x spiked cores. Oxygen level is one of the most important factors affecting the process of P sorption and desorption from sediments and, release or uptake of P by polyophosphate accumulating organisms (Nguyen and Maeda, 2016). Higher spiked P concentrations (e.g. 2x and 4x) caused negative flux of P to the sediments under aerobic conditions because of possible high sorption capacity of sediments due to retaining P to a mono-layer of iron salt (Hupfer and Lewandowski, 2008). However, this hypothesis needs further validation. P release in ambient and 0.5X spiked cores under aerobic conditions is intriguing and warrants further investigation.

3.1.2 P dynamics under anaerobic conditions

Under anaerobic conditions, P concentrations decreased in the water column in nearly all cores from both the Provo Bay and Buoy sites over the 72-hour experiments (**Figure 4**). In general, P concentrations decreased more in anaerobic conditions relative to aerobic conditions. Similar to aerobic conditions, a greater P decrease occurred in the 2X and 4X cores at both sites, for TDP and SRP. However, there was a confounding factor because over the 72-hour anaerobic experiments as the water column pH increased from initial values of 8.5 to 10. This was unexpected because the changing redox conditions should not cause a change in the pH. A possible reason for the increase in pH is that the continuous bubbling with N_2 gas to maintain oxygen free conditions purged dissolved CO_2 from the water column, thus altering the bicarbonate buffering system. In future experiments, the pH problem may be solved by purging with N_2 gas mixture containing 0.5% CO_2 and 999.5% [illegible] It is also possible that microbial activity under anaerobic conditions may have changed the pH.

Generally, soluble P is released under anaerobic conditions (Bates & Neafus, 1980) when Fe(III) reduction occurs under anaerobic conditions at the sediment-water interface, after which the P bound to Fe(III) oxides is released into pore water (Moore and Reddy, 1994) and/or polyphosphate accumulating organisms (PAOs) release their intracellular poly-P into bulk solution (Hirota et al., 2010). Another mechanism for P release under anaerobic conditions could be due to the release of sorbed P on oxyhydroxides present in the water column (Bostrom et al., 1998). Typically, P is released under anaerobic conditions, because of the gain of previously Fe^{3+} or the decomposition of organic matter (Baggie et al., 2005; Shen et al., 2013). However, in our anaerobic cores we observed the opposite, e.g. P decreased in the water column resulting in negative flux towards underlying sediments. The decrease in P concentrations in the cores may have been linked to calcite scavenging of P from the water column. As evidence of calcite precipitation, we observed decreasing Ca^{2+} concentrations over time in cores from both sites. Calcite may have scavenged P as a co-precipitate or by sorption. Precipitation of calcite mostly occurs under alkaline conditions in which pH ranges from 8.7 to 9.5 (Stocks-Fischer et al., 1999). The P loss observed in our anaerobic experiments could be caused by the increased pH or anaerobic conditions, which allowed P to be absorbed onto precipitated $CaSO_4$, $Ca(OH)_2$, and $CaCO_3$ compounds.

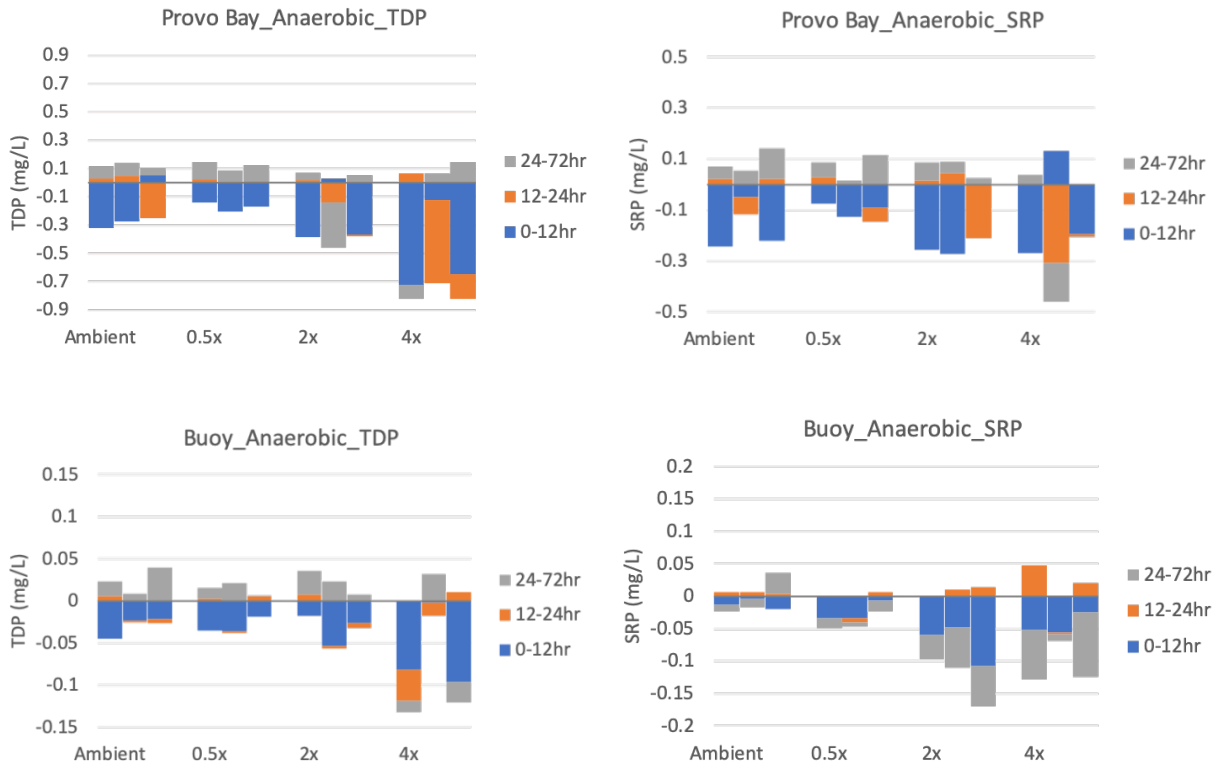


Figure 4. The change in TDP and SRP concentrations in the water column under anaerobic conditions.

3.1.3 P dynamics at neutral and alkaline pH

Under neutral (pH=7) and alkaline (pH=9.5) conditions, P concentrations in the water column increased or remained the same for the ambient and 0.5X cores and P concentrations decreased in the 2X and 4X cores. At the Provo Bay site, TDP and SRP concentrations behaved similarly throughout the pH=7 and pH=10 experiments for all treatments. At the Buoy site, TDP and SRP concentrations decreased over time, particularly in the 4x experiments. Similar to aerobic conditions, DO was maintained around 7.5 mg/L throughout the incubations during pH experiments. At both pH = 9.5 (high pH) and pH =7.0 (low pH), the buffering capacity of the sediment caused the pH to return to initial values of 8.6±0.2. Continuous addition of acid or base was required to maintain the targeted pH. As shown in the **Figure 5**, the trend of TDP is similar to SRP at both sites. Greater P release at lower water P concentrations was observed, while P loss from the water column was mostly observed at the 4X concentrations (**Figure 5**). As for the Buoy site, TDP concentrations were higher for the neutral pH (0.09 - 0.53 mg/L) relative to alkaline pH conditions (0.02-0.13 mg/L).

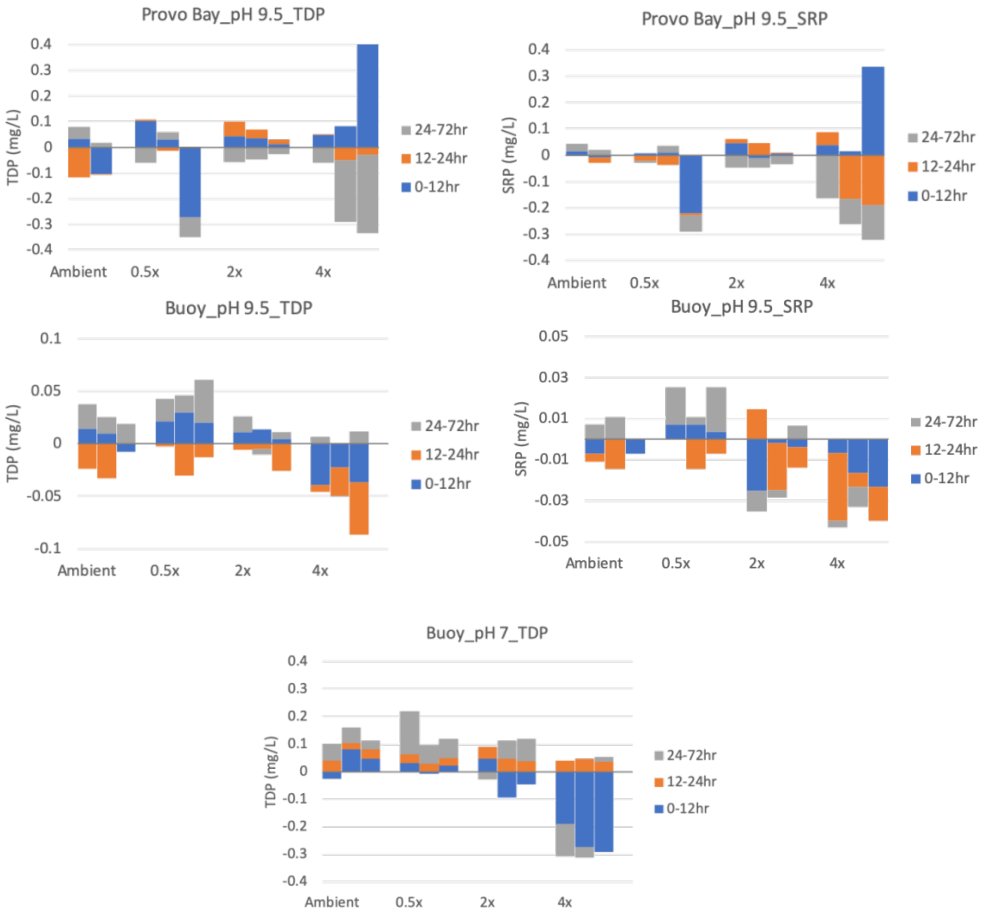


Figure 5. The TDP and SRP change at pH = 9.5 and pH =7.

A previous study found that the variation of pH can change the particle aggregation/cohesion behavior by altering their surface charge properties (Illés and Tombácz, 2006). At neutral to high pH (7- 9), P release from the sediment is inhibited by a layer of $Fe(OH)_3$ protective film at the surface of Fe-P complexes (Li et al., 2013). While the reduction of Fe(III) to Fe(II) that enhanced P release from sediment occurs more strongly under low redox potential and low pH (5.5) and/or anaerobic conditions (Moore and Reddy, 1994), the Fe phosphate precipitation or adsorption of P by Fe oxides or hydroxides could result in low P solubility in the lake. These discussions are consistent with our results that there was a tendency to release P when pH was decreased (Gomez et al., 1999). As the ambient lake water is deficient in Fe compared to Ca, the hypothesis could be that the formation of calcium-phosphate precipitation or adsorption of P by calcite species results in low P solubility in the lake. Formation of these compounds requires neutral to high pH, while the solubility of the complex is determined by the pH, alkalinity, and reacting compounds.

3.1.4 Summary of P concentrations in different experiments

In summary, throughout the 72-hour experiments, TDP concentrations were higher for aerobic (0.05 - 1.64 mg/L) than the anaerobic conditions (0.03 - 0.94 mg/L). The Provo Bay site generally had higher TDP concentrations (0.07-1.64 mg/L) than the Buoy site (0.03 - 0.35 mg/L) perhaps due to direct point and non-point discharges and higher productivity. At the Buoy site, the treatment with low pH generally had higher ambient TDP concentrations (0.09-0.53 mg/L) than the higher pH (0.02-0.13 mg/L). This is probably due to the redox change that causes the particle aggregations, making P easily released from the compounds (Illés and Tombácz, 2006). Similarly, the Provo Bay site had relatively higher SRP (0.02-0.53) than the Buoy site (0-0.39 mg/L). Under all conditions, SRP accounted for an average 40% and a median 38% of TDP. This would imply that nutrient cycling associated with other forms of P (such organic P and polyphosphate) could be major sources of TDP to the water column. While the SRP or inorganic P is mostly taken up and assimilated by primary producers in water, the transformation of TDP to SRP could be one of the supplementary ways for providing P for phytoplankton growth (Feng et al., 2018; Li et al., 2019). Nevertheless, the degradation of organic P derived from sediment and phytoplankton debris in lakes releases SRP through biomineralization and chemical decomposition (Huo et al., 2011; Bastamia et al., 2018).

Table 3. Concentrations of TDP and SRP initially present in lake water and after 72 hours of equilibrating in dark after spiking with different concentration of soluble ortho-P.

Site	Groups	Initial lake ambient TDP (mg/L)	TDP concentrations-72hour (mg/L)	Initial lake ambient SRP (mg/L)	SRP concentrations-72hour (mg/L)
Provo_aerobic	0.5x	0.40-0.51	0.48-0.88	0.22-0.26	0.10-0.22
	Ambient		0.38-0.56		0.04-0.17
	2x		0.48-1.30		0.13-0.31
	4x		0.80-1.64		0.08-0.50
Provo_anaerobic	0.5x	0.38-0.41	0.18-0.25	0.25-0.28	0.05-0.16
	Ambient		0.21-0.25		0.09-0.22
	2x		0.17-0.21		0.12-0.14
	4x		0.18-0.29		0.04-0.10
Buoy_aerobic	0.5x	0.05-0.06	0.12-0.14	0.03	0-0.02
	Ambient		0.09-0.12		0.08
	2x		0.14-0.20		0.02-0.04
	4x		0.29-0.32		0.11-0.15
Buoy_anaerobic	0.5x	0.06-0.10	0.06	0.02-0.04	0.01
	Ambient		0.04-0.08		0.01-0.04
	2x		0.10-0.17		0-0.1
	4x		0.09-0.22		0.03-0.05
Provo_high pH	0.5x	0.16-0.19	0.11-0.13	0.05-0.08	0-0.03
	Ambient		0.10-0.12		0.05-0.10
	2x		0.18-0.21		0.05-0.07
	4x		0.17-0.30		0-0.08
Buoy_high pH	0.5x	0.06-0.07	0.04-0.07	0.01-0.02	0-0.03
	Ambient		0.05-0.08		0.01
	2x		0.04-0.06		0.01-0.02
	4x		0.06-0.07		0.01

P concentrations in the ambient and 0.5X cores tended to increase over time while the concentrations of 2X and 4X cores tended to decrease. The spiked TDP concentrations (2X and 4X) typically did not decrease below initial pre-spiked concentrations (**Table 3**). This may have implications for different conditions of exogenous loading or dilution (0.5X, 2X or 4X of ambient P concentrations after loading) and the response of sediment to varying initial conditions as to release or hold P. The decrease of lake ambient P concentrations may enhance P release from the sediment, while the input of more P may potentially bind to sediments to reach equilibrium. Different from TDP, SRP concentrations after 72 hours decreased to or below the initial lake water concentrations. It is further emphasized that studying SRP alone may not be adequate to reveal the P dynamics in the lake and predict its effects on lake eutrophication.

Endogenous inputs of nutrients from point and non-point source discharges are important in lake nutrient management but internal cycling of nutrients also plays a role in supporting

surface water eutrophication. P loads from exogenous sources have a significant influence on dissolved P concentrations in streams and sediment-water column dynamics (Ekka et al., 2006). In terms of implications for loadings from wastewater treatment plants (WWTPs), the improvement of Utah Lake water quality may be delayed in response to decreased external loading and ambient concentrations because of internal recycling of P (Hogsett et al., 2019; Randall et al., 2019). Since our experiments were only run for 72 hours, they may not reflect the long-term equilibrium values for Utah Lake but they do suggest the direction that P concentrations would move under changing P loads. The 0.5X ambient concentrations generally enhanced P release compared to that of the ambient conditions. Previous studies also found that it may take nearly 10-15 years to reach a new equilibrium after exogenous nutrient reduction (Jeppesen et al., 2005). Also, with increased loadings, Utah Lake may act as a self-cleaning system to remove P from the water column by mineral precipitation with calcite (Brimhall & Merritt, 1981; Hogsett et al., 2019; Randall et al., 2019). However, it may not reduce spiked concentrations to the initial levels, as the high loads (2X and 4X of ambient water) resulted in P loss but relatively high ambient P concentrations remained under aerobic conditions after 72 hours (**Table 4**). For example, under aerobic conditions for Provo Bay, the final (72 hours concentration) for ambient, 0.5X, 2X and 4X were 0.38-0.56, 0.48-0.88, 0.48-1.29, and 0.80-1.64 mg/L respectively, while the initial lake P concentrations were in the range of 0.40-0.51 mg/L. For the buoy site, under aerobic conditions, the final (72 hour) concentration for ambient, 0.5X, 2X and 4X were 0.09-0.12, 0.12-0.14, 0.14-0.20, and 0.27-0.32 mg/L respectively, while the initial lake P concentrations were in the range of 0.05-0.06 mg/L.

3.1.5 Relative change of calcium and phosphorus concentrations and other major ions in the water column under all treatments

To further investigate the role of calcium-binding of P, calcium and P concentrations in the water column were compared for each treatment (**Table 4**). Calcium loss occurred mostly under anaerobic (-49.04 to -14.14 mg/L) or high pH (-32.29 to 14.54 mg/L) conditions for both sites, followed by low pH of the buoy site and aerobic conditions. The greater calcium precipitation under anaerobic conditions could be due to higher pH in the experiment or microbial-mediated activities. For example, denitrification activities could occur under anaerobic conditions, increasing the pH by consuming H^+ and producing CO_2, which favored carbonate precipitation (Zhu & Dittrich, 2016). Although not a part of this project, we have observed significant denitrification activities in Utah Lake sediments in our separate efforts. In addition, anaerobic oxidation of methane could potentially favor the precipitation of calcium carbonate, while the aerobic oxidation of methane causes more dissolution of calcite by increasing acidity (Reeburgh, 2007). This could be one of the reasons as why there was observed loss of P and calcium under anaerobic conditions. Under neutral pH conditions, water under no spiked

condition tends to show a greater release of P from the sediment than under neutral or the high pH for the buoy site (**Table 4**). This could be a result of P speciation in combination with metal oxides or hydroxides and their solubility was affected by pH (Van Nguyen & Maeda, 2016). However, the calcium P loss was also mostly observed under adjusted pH rather than the normal conditions (**Table 4**). The lowered pH generally caused less calcium loss with less precipitation and more possibility of Ca-P dissolution (Huang et al., 2005). Under all conditions, the amount of P release or loss is not comparable to the loss of calcium. There could be a larger amount of calcite species precipitation than Ca-P precipitation or attachment to the surface of minerals based on the water column Ca:P concentration ratios. The formation of calcite species reduces the free Ca^{2+} concentration, thereby reducing P precipitation. However, with the large amount of Ca^{2+} in the alkaline lake, the reduction effect is negligible.

Table 4. The relative change (between 0 and 72 hours) of calcium and phosphorus concentrations in the water column (units of concentrations are mg/L).

Treat-ment	Category	Provo_ aerobic	Provo_ anaerobic	Buoy_ aerobic	Buoy_ anaerobic	Provo_ high pH	Buoy_ high pH	Buoy_ low pH
0.5X	**P**	0.192	-0.050	0.065	-0.017	-0.0848	0.0345	0.1420
	Ca	2.08	-36.42	0.98	-28.69	-22.91	-18.36	-5.38
Ambient	**P**	0.005	-0.692	0.049	-0.008	-0.0624	0.0056	0.1157
	Ca	-6.08	-49.04	1.12	-14.14	14.54	-24.39	-12.08
2X	**P**	-0.014	-0.161	-0.004	-0.076	0.0232	0.0031	0.0516
	Ca	-6.61	-45.08	0.65	-8.60	-19.33	-13.16	-10.62
4X	**P**	-0.180	-0.354	-0.002	-0.014	-0.0461	-0.055	-0.257
	Ca	-2.81	-47.35	0.16	-10.72	-32.29	-26.53	-8.18

Note: The positive values represent release and negative values represent loss.

In addition to the nitrogen and phosphorus ions, other major ions in the lake water column play important roles like undergoing complexation and precipitation reactions include Al^{3+}, Ca^{2+} and Mg^{2+}. The complex formed by aluminum (Al) and inorganic phosphate can present a significant portion of both the dissolved and particulate Al pool under certain conditions. Briefly, the observations suggest that the Al-P complexation is pH-dependent and appears to predominate around pH= 6 (Dickson, 1980; Nalewajko and O'Mahony, 1988). The Al-P complex can be soluble or insoluble: two soluble forms are $AlH_2PO_4^{+2}$ (log K ~ 3) and $AlHPO_4^{+}$ (log K ~ 7), however the insoluble form of the $AlPO_4$ complex is more well-known. Moreover, inorganic phosphate can also absorb onto the aluminum oxides and hydroxides, which has been extensively applied to both water treatment and lake management as a means of controlling excess dissolved P (Davis and Hem, 1989). As for the toxicity of Al to algae, it is most toxic under

slightly acidic conditions and the toxicity could be reduced by forming compounds with organic matter, etc. in the lake (Gensemer & Playle, 1999).

Compared with Al, most alkaline lakes are $CaCO_3$-dominated systems, such as Utah Lake. Ca-P complexes can be formed in the surface sediment of the lake and eventually transformed to crystalline apatite (Stumm and Leckie 1971). The formation of complex, $Ca_3(HCO_3)_3PO_4$, in $CaCO_3$-H_3PO_4-H_2O systems mostly takes two reacting compounds of $CaCO_3$ and H_3PO_4 into consideration. The solubility of the complex is determined by the pH, alkalinity, and reacting compounds. It appeared that the Ca-bound pool of phosphorus in sediments requires lower pH (pH =3) to break down (Gao, 2012). Similar to calcium, magnesium is another ion that can form complexes with phosphates in lake sediments, such as compounds composed of calcium, magnesium and ammonium phosphates (e.g. struvite – $(NH)_4Mg[PO_4]\times 6H_2O$).

3.1.6 SRP and TDP flux to/from sediment under all treatments

Figure 6 shows SRP and TDP fluxes from and to sediments calculated from measured P concentrations. These fluxes could be termed gross P fluxes as these were estimated over a few days. In general, more negative fluxes were observed for SRP (**Table 6**, **Figure 6 A,B**) compared with TDP (**Table5**, **Figure 6 C,D**). Specifically, the positive fluxes for SRP were observed for Provo_aerobic_0.5X (0.96$\pm$5.40mg/m^2/d), Buoy_anaerobic_ambient (0.24$\pm$2.31 mg/m^2/d), Provo_pH=9.5_ambient (2.02$\pm$3.26 mg/m^2/d) and Buoy_pH=9.5_0.5X (1.25$\pm$1.58mg/m^2/d). The negative fluxes were recorded at 2X or 4X treatment similar to the TDP fluxes. The most negative flux was detected at Provo_anaerobic_4X (-21.84$\pm$14.76 mg/m^2/d). Compared to TDP fluxes, there could be some other forms of P release from sediment during the experimental period. Negative fluxes of SRP under high pH conditions could be due to precipitation of calcite in which case SRP tend to either coprecipitate with and/or sorb to the surface of calcite.

Significant differences in P release/retention were detected at different spike concentrations (ambient, 0.5X, 2X and 4X) or environmental conditions (aerobic, anaerobic, pH =9.5 and pH = 7) ($p<0.05$, ANOVA). P flux and net loads from/to the sediment were also calculated (**Table 4**). The methods used for nutrient flux, per Hogsett et al., 2019, where flux values equal to the depth of water column (d, m) times the slope of P concentration with changing time ($\frac{dC}{dt}$, $\mathrm{g/m^3/d}$). The positive values indicate P release while the negative values indicate retention. One-way ANOVA was applied to compare P concentrations at different treatments (initial concentrations or environmental conditions). The F ratios and other parameters for each comparison were calculated using in-house R-coding.

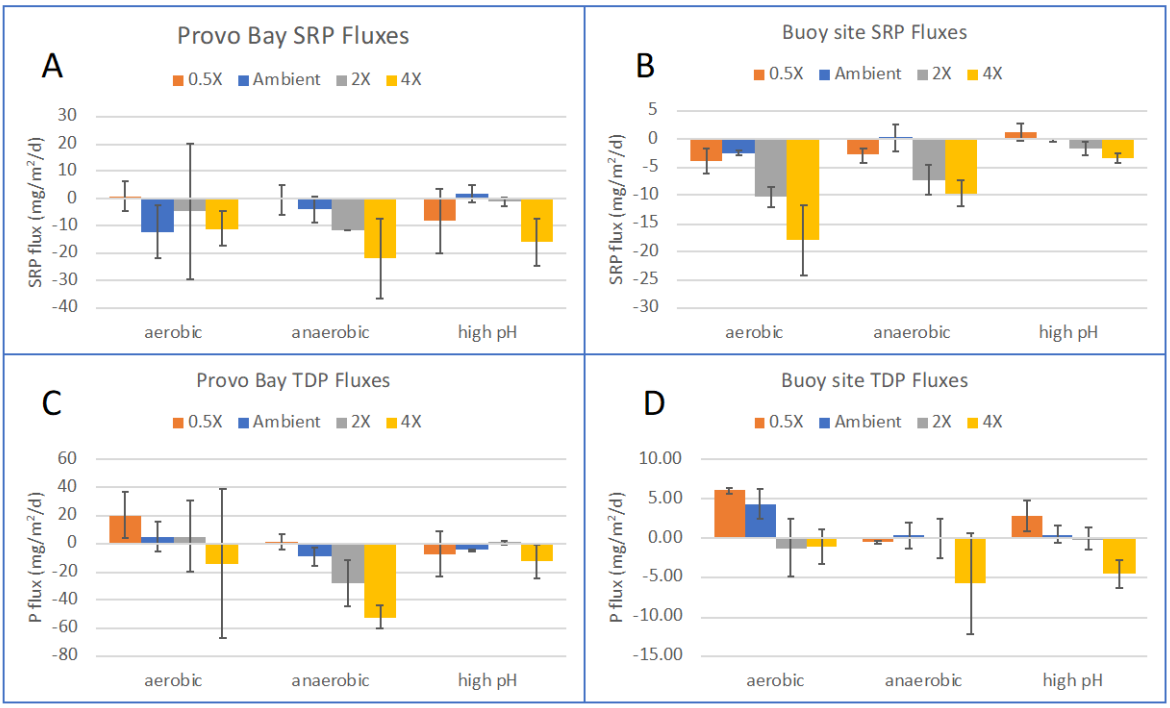


Figure 6. SRP and TDP fluxes under different conditions at two sites.

The flux results were consistent with the dynamics of water column P concentrations throughout the 72-hour experiments, as the P loss was greater in the 2X and 4X spiked cores relative to the ambient (e.g. no spike) or 0.5X spiked cores. Also, the release was detected more at aerobic and neutral pH, while retention was dominant at anaerobic or high pH. Provo Bay generally had higher release/loss flux (-51.84±8.30 to 20.40±16.42 mg/m^2/d) than the buoy site (-5.76±6.40 to 6.00±0.42 mg/m^2/d), partly due to the differences in initial ambient P concentrations and eutrophication status (Herrmann et al., 2009; Hou et al.,2013). The highest release and loss were observed at Provo_aerobic_0.5X (20.40±16.42 mg/m^2/d) and Provo_anaerobic_4X (-51.84±8.30 mg/m^2/d), respectively. There was generally greater P loss under anaerobic conditions (-51.84±8.30 to 1.44±5.44 mg/m^2/d) relative to aerobic conditions (-13.92±52.84to 20.40±16.42 mg/m^2/d). Sediment had higher potential to release P at lower pH; the Buoy site has the highest release at 0.5X_low pH followed by aerobic, high pH and anaerobic conditions with the same initial conditions (0.5X). P release from sediments was more significant at 0.5X concentrations (-7.25±16.24 to 20.40±16.42 mg/m^2/d) than under any other condition. Under all conditions, net loss of P to sediments occurred at 4X P concentrations. Anaerobic P release could be associated with iron reduction and/or P release by PAOs. As for the total P load from/to the lake, higher flux estimates are still well within the realm of organic matter decay or exude from phytoplankton/bacteria in the water column.

Table 5. TDP flux to/from sediment and corresponding loads.

Site	Groups	Rate $g/m^3/hr$	R square	TDP flux $(mg/m^2/d)$	Load (Kg/day)
Provo aerobic	0.5x	0.028	0.381	20.40±16.42	7842±6313
	Ambient	0.0007	0.0248	5.04±10.38	1937±3992
	2x	0.0008	0.0087	5.52±25.32	2122±9732
	4x	-0.0019	0.0649	-13.92±52.84	-5351±20311
Provo anaerobic	0.5x	0.0002	0.0077	1.44±5.44	554±2090
	Ambient	-0.0013	0.0837	-9.12±6.49	-3506±2496
	2x	-0.0038	0.263	-27.84±16.46	-10702±6325
	4x	-0.0072	0.3744	-51.84±8.30	-19927±3192
Buoy aerobic	0.5x	0.0008	0.7599	6.00±0.42	2306±923
	Ambient	0.0006	0.7332	4.32±1.90	1661±732
	2x	-0.0002	0.035	-1.2±3.62	-461±138
	4x	-0.0002	0.0493	-1.08±2.25	-415±864
Buoy anaerobic	0.5x	-0.00007	0.0228	-0.50±0.19	-194±73
	Ambient	0.00005	0.0057	0.34±1.59	129±610
	2x	-0.000007	5.00E-05	0.00±2.49	0±959
	4x	-0.0008	0.1191	-5.76±6.40	-2214±2460
Provo high pH	0.5x	-0.001	0.0803	-7.25±16.24	-2768±6243
	Ambient	-0.0007	0.1679	-4.68±0.51	-1799±196
	2x	0.0001	0.0156	0.84±1.21	323±465
	4x	-0.0018	0.1487	-12.72±11.88	-4890±4567
Buoy high pH	0.5x	0.0004	0.4436	2.83±1.99	1089±764
	Ambient	7.00E-05	0.0205	0.48±1.10	185±423
	2x	-3.00E-07	6.00E-07	-0.05±1.44	-18±554
	4x	-0.0006	0.4108	-4.56±1.81	-1753±697
Buoy low pH	0.5x	0.002	0.7687	14.64±6.69	5628±2572
	Ambient	0.0015	0.7319	11.04±2.31	4244±890

	2x	0.0009	0.3065	6.48±2.60	2491±998
	4x	-0.0024	0.3296	-17.28±3.60	-6642±1384

Note: The average water column depth (d) is 0.3m. Rate is calculated from the slope of concentration and time best fit curve.

Tables 5 and 6 show TDP and SRP fluxes, respectively. These two tables also present estimated TDP and SRP loads in kg/day calculated based on fluxes plotted in **Figure 6**. For example, for the Provo site under_aerobic and ambient conditions with a positive rate of 0.0007 g/m^3/hr, the total P flux released from sediments will be equal to= (0.0007 g/m^3/hr - 0) x 0.3m x1000mg/g x $\frac{24hr}{1d}$ = 5.04 mg/m^2/d, the lake area is 384.4 km^2

Load = 5.04 mg/m^2/d * 384.4km^2 = 1937 kg/d. The estimated TDP loads as a result of either flux from sediments (e.g. gain in water column) or to the sediments (e.g. loss to sediments) are presented in **Table 5**.

Table 6. SRP flux to/from sediment.

Site	Groups	Rate g/m^3/hr	R square	SRP flux (mg/m^2/d)	Load (Kg/day)
Provo aerobic	0.5x	0.0002	0.013	0.96±5.40	369±2077
	Ambient	-0.0016	0.2642	-12.00±9.72	-4613±3737
	2x	-0.0015	0.1594	-4.56±24.94	-1753±9589
	4x	-0.0006	0.0299	-10.8±6.24	-4152±2397
Provo anaerobic	0.5x	-6.00E-05	0.001	-0.48±5.50	-185±2114
	Ambient	-0.0005	0.0226	-3.84±4.68	-1476±1801
	2x	-0.0016	0.1546	-11.52±0.00	-4428±1944
	4x	-0.003	0.2712	-21.84±14.76	-8395±5674
Buoy aerobic	0.5x	-0.0005	0.5321	-3.84±2.20	-1476±846
	Ambient	-0.0003	0.6897	-2.40±0.42	-923±160
	2x	-0.0015	0.6154	-10.32±1.81	-3967±697
	4x	-0.0025	0.8113	-18.00±6.24	-6919±2397
Buoy anaerobic	0.5x	-0.0004	0.5655	-2.88±1.25	-1107±479
	Ambient	2.00E-05	0.0023	0.24±2.31	92±890
	2x	-0.0013	0.3384	-7.20±2.60	-2768±998
	4x	-0.001	0.5615	-9.60±2.31	-3690±890
Provo high pH	0.5x	-0.0011	0.1732	-7.99±11.82	-3072±4545
	Ambient	0.0003	0.2739	2.02±3.26	775±1253
	2x	-0.0001	0.0348	-1.10±1.58	-424±607
	4x	-0.0022	0.3295	-15.84±8.76	-6089±3367
Buoy high pH	0.5x	0.0002	0.3277	1.25±1.58	480±607
	Ambient	-4.00E-05	0.0461	-0.25±0.28	-95±107
	2x	-0.0002	0.2917	-1.63±1.16	-627±447
	4x	-0.0005	0.6003	-3.36±0.83	-1292±320

Note: The water column depth (d) is 0.3m. Rate is calculated from the slope of concentration and time best fit curve.

3.1.7 Equilibrium phosphorus concentrations

To determine sediment—water equilibrium P concentrations (sediment—EPC_0) for Utah Lake, we compared the TDP concentrations in our aerobic cores at t=72 hours and the change in TDP concentration from 0 to 72 hrs. A traditional sediment—EPC_0 calculation requires measuring the amount of P sorbed to sediments after a batch experiment and comparing sorbed P to aqueous P concentrations at the end of the experiment (e.g., Haggard et al., 2004). In our case, however, we did not measure the P concentrations (sorbed P) in sediment for any of the cores. Instead, we assume that the change in TDP concentrations in the water column over 72 hours is a result of loss/gain of P to/from the sediments. If TDP concentrations decreased in the water column we assume that the sediments gained an equal amount of P and vice versa. For the sediment-EPC_0 calculations, we used data from the aerobic cores because these are the most representative of lake conditions. The average TDP concentrations (and change in concentrations) were calculated for the 0.5x, ambient, 2x, and 4x experiments. Since these concentrations cover the range of sediment P gain loss (the 0.5x and ambient cores gained P from the sediments while the 2x and 4x cores lost P to the sediment), the point at which there is no net change in TDP concentrations in the water column over 72 hours represents the sediment—EPC_0 concentration. We used average concentrations (each data point represents three measurements) from Provo Bay and Buoy sites to calculate sediment-EPC_0 for these distinct locations within Utah Lake. However, these two locations are not necessarily representative of the entire lake system. Another caveat is that P in the cores may not have reached equilibrium over a 72 hour experiment.

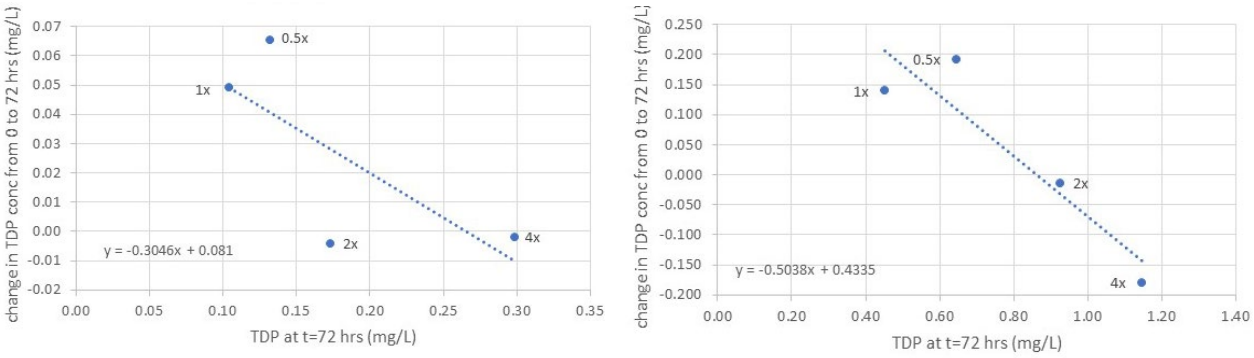


Figure 7. Left panel for For the Buoy site and right panel for Provo Bay: TDP concentrations in aerobic cores at t=72 hours and the change in TDP concentration from 0 to 72 hrs. The sediment—EPC_0 is the value "x" for which y=0, or the concentration at which TDP would not change over a 72 hour experiment. For Buoy site, sediment—EPC_0 = 0.27 mg/L and for Provo site, sediment—EPC_0 = 0.86 mg/L.

Our results are shown in **Figure 7** for the Buoy and Provo Bay sites. The sediment EPC_0 was 0.27 mg/L for the Buoy site and 0.86 mg/L for the Provo Bay site. The different EPC_0 values may be caused by different mineralogy and sediment types at each site. Provo Bay sediment contains less carbonate minerals and more silicate minerals relative to the main lake, which makes it less able to sorb P from the water column and allows the water column concentrations to be higher.

4. Nitrogen dynamics

4.1 The dynamics of N species and ammonium flux

Ammonium-N, nitrite-N and nitrate-N were presented at concentrations of 0.001-0.658 mg/L, 0-0.048 mg/L, and 0-0.239 mg/L, while nitrite-N was undetectable most of the time. A significant change in ambient concentrations was only observed for ammonium-N. One-way ANOVA was used to compare the differences among different treatments. No significant difference in ammonium-N concentration was found among samples with different orthophosphate concentrations (e.g., the concentrations treatment for Provo_aerobic). Under all P concentrations tested, there were significant differences among treatment groups (<0.05, ANOVA). Specifically, average ammonium-N concentrations throughout the 72-hour period were higher under aerobic conditions (0.07 - 0.24 mg N/L) than that under anaerobic conditions (0.03-0.09 mg N/L). For pH changes, the average ammonium-N concentrations throughout the 72-hour period were also higher for Provo Bay (0.06-0.21 mg N/L) than that for the Buoy site (0.05-0.08 mg N/L), likely due to different mineralogy compositions. No significant difference was found for nitrate-N concentration changes. Nitrate-N concentrations mostly remain in the range of 0.124-0.156 mg N/L as detected.

Ammonium flux was also calculated under different conditions following the same methods as phosphorus (**Table 7 and figure 8**). Generally, ammonium loss (negative values) was observed for most of the locations with different treatments. Provo Bay was a higher loss of ammonium (-33.36±23.04 to -0.96±13.61 mg/m^2/d) than the buoy site (-12.96±5.04 to 0.11±0.41 mg/m^2/d). Aerobic and high pH conditions generally result in a greater loss of ammonium (-33.36±23.04 to --3.6±5.04 mg/m^2/d) than the anaerobic conditions (-9.12±1.50 to 0.11±0.41 mg/m^2/d). Even with similar high pH, the ammonium loss under anaerobic condition is not comparable to aerobic condition. Similar to ANOVA analysis, no significant difference of ammonium loss was observed among treatments with different initial P concentrations.

Table 7. Ammonium flux to/from sediment.

Site	Groups	K value	R square	Ammonium-N flux ($mg/m^2/d$)	Load (Kg/day)
Provo_aerobic	0.5x	-0.0012	0.1027	-8.40±6.53	-3229±2511
	Ambient	-0.0024	0.1346	-17.28±9.90	-6642±3805
	2x	-0.0014	0.5333	-9.84±3.40	-3782±1308
	4x	-0.0042	0.3455	-33.36±23.04	-12824±8858
Provo_anaerobic	0.5x	-0.0006	0.1561	-4.08±0.42	-1568±160
	Ambient	-0.0012	0.3266	-9.12±1.50	-3506±576
	2x	-0.0009	0.3541	-6.24±5.82	-2399±2237
	4x	-0.0001	0.0026	-0.96±13.61	-369±5232
Buoy_aerobic	0.5x	-0.0013	0.4608	-9.12±5.45	-3506±576
	Ambient	-0.0014	0.6298	-9.84±1.66	-3782±639
	2x	-0.0018	0.4926	-12.96±5.04	-4982±1937
	4x	-0.001	0.2355	-7.44±3.00	-2860±1152
Buoy_anaerobic	0.5x	-0.0002	0.3140	0.11±0.41	-738±320
	Ambient	2.00E-05	0.0019	-1.92±0.83	42±159
	2x	-0.0001	0.1013	1.03±1.62	-397±623
	4x	-0.0002	0.1980	-1.34±0.87	-517±334
Provo_high pH	0.5x	-0.0032	0.2135	-22.56±22.42	-8672±8617
	Ambient	-0.0052	0.5338	-23.40±15.78	-8995±6067
	2x	-0.0008	0.1494	-6.00±5.11	-2306±1964
	4x	-0.0037	0.2607	-26.40±18.08	-10148±6949
Buoy_high pH	0.5x	-0.0008	0.3199	-5.28±3.69	-2030±1420
	Ambient	-0.0007	0.2720	-4.80±2.91	-1845±1119
	2x	-0.0013	0.2005	-9.36±6.87	-3598±2640
	4x	-0.0005	0.2000	-3.6±5.04	-1384±1937

Note: The water column depth (d) is 0.3m. K is the slope of ammonium-N concentrations along with time. R square measures how close the slope fits values.

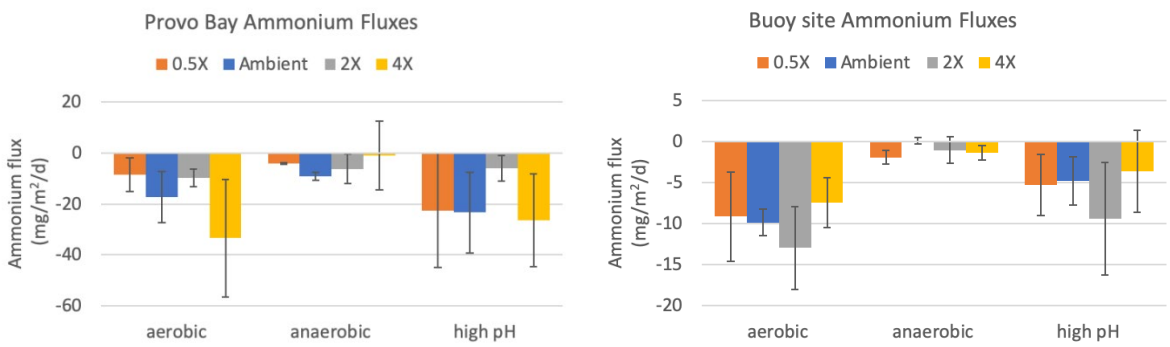


Figure 8. Ammonium-N fluxes under different tested conditions at two sites.

4.2 The absolute concentrations of ammonium under different treatments

Under aerobic conditions, ammonium was mostly released before 24 hours. Generally, Provo Bay has higher surrounding ammonium-N concentrations (0.015 - 0.658 mg N/L) than the Buoy site (0.015 - 0.266 mg N/L) (**Figure 9**). However, significant loss of ammonium was observed between 24 and 72 hours. In contrast to aerobic conditions, a continuous ambient ammonium concentration decrease was observed under anaerobic conditions. In general, ammonium was lost from the system, likely due to ammonia volatilization under high pH (8.5 to 10) that probably also affected nitrifying bacterial activities (EPA, 2002). Although under aerobic condition, higher DO levels could activate nitrifying bacteria, leading to high rates of biological ammonia oxidation and coupled nitrification–denitrification (Palmer et al., 2009). In such cases, P spiking in the water column may have caused any potential N limitations but this should not have affected the plankton dynamics because experiments were conducted in the dark. While under anaerobic conditions, ammonium release could be triggered due to anaerobic fermentation from nitrogen-rich sediments to the overlying water (Zhang et al., 2019). However, a loss of ammonium was still observed under anaerobic conditions, which could be caused by ammonia volatilization under alkaline conditions. Under increased pH, un-ionized ammonia and associated toxicity increased. The increased pH and toxicity may inhibit bacterial activities and cause more ammonia volatilization, which explains the high ammonium loss under high pH (Kadam & Boone, 1996; Venterea et al., 2015). Some other recent discovered pathways, such as ammonia-oxidation by archaea (He *et al.,* 2018), anammox (Yang et al., 2017) and dissimilatory nitrate reduction to ammonium (DNRA) (Nizzoli et al., 2010) have been discovered in lake sediments, resulting in increasing or decreasing ambient ammonium concentrations. Similar to P release, the release of ammonium is also correlated with trophic status with higher ambient concentrations observed at Provo Bay (Herrmann et al., 2009).

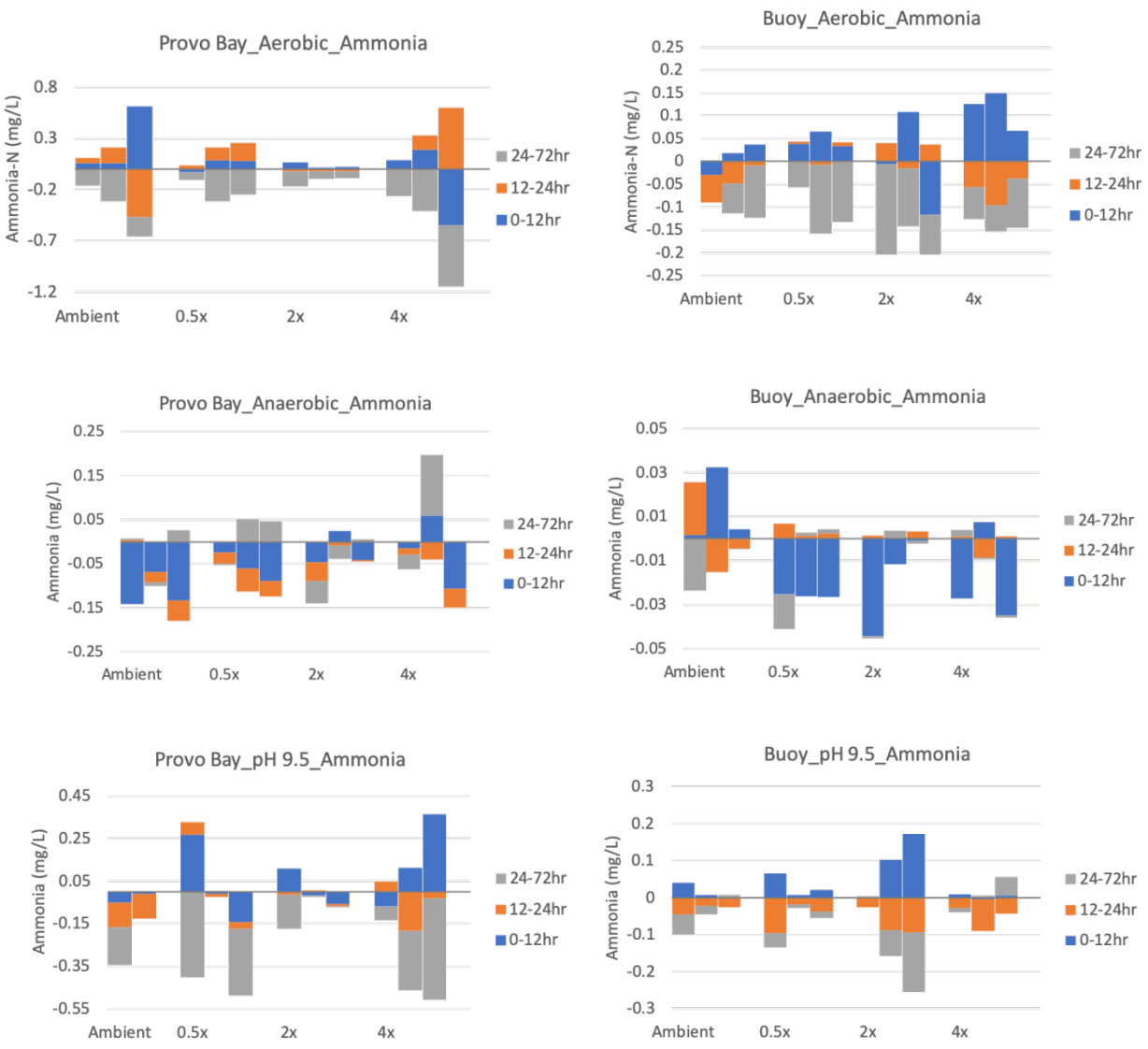


Figure 9. The changes of ammonium under different conditions.

To have an estimated percentage ammonium loss from our study, **Table 8** was listed at varying pH based on 20 ℃ ambient temperature. At the same temperature, the percentage of free ammonia increases along with pH increase. The highest percentage of free ammonium at pH =10 is 79.83%. From **Table 8**, we can conclude that the ammonium loss was higher in our study at some conditions (e.g., Provo_aerobic, pH =8.5) than the percentage of unionized form estimated in the **Table 8**. This may indicate ammonium loss through other previously discussed pathways or continuous air stripping. Table 9 presents percentages of ammonium-N which have stripped off to the atmosphere as free ammonia-N during different treatments.

Table 8. Percentages of free ammonia.

pH	8.0	8.4	8.8	9.2	9.6	10.0
Percent	3.81	9.04	19.98	38.55	61.17	79.83

Temperature was at 20 °C for percentage of unionized-ammonia (Emerson et al., 1975).

Table 9. Percentage of ammonium-N removed under different conditions.

Treatment	0.5X	Ambient	2X	4X
Provo_ aerobic	96.525	97.092	96.174	97.441
Provo_ anaerobic	70.864	91.879	69.723	90.775
Buoy_ aerobic	88.013	73.795	81.248	47.144
Buoy_ anaerobic	55.856	-34.417	28.566	38.618
Provo_ high pH	80.671	90.932	69.375	90.062

5. Sediment oxygen demand

Sediment oxygen demand (SOD) is the rate at which dissolved oxygen is removed from the overlying water column in the bed sediments (Hatcher, 1986). SOD is often the cause of low dissolved oxygen concentrations in lakes and streams (Doyle and Lynch, 2003). Several factors determining SOD values include temperature, water column dissolved oxygen concentrations, sediment organic matter content, sediment grain size, flow rate, sediment disturbance and toxic substances, analytical techniques (Medine et al., 1980; Krantzberg, 1994). SOD chambers were installed in Utah Lake by a professional scuba diver **(Figure 10)**. SOD values were calculated for each site as the difference between experimental and control chambers (Hogsett & Goel, 2013). To have a standard comparison among different SOD values, SOD at different conditions were temperature corrected to 20 degrees Celsius using a standard Van't Hoff equation. The resulting water column oxygen depletion estimates were -1.584 g/m^3/day and -0.432 g/m^3/day for the Provo Bay and Buoy sites respectively **(Table 10)**. The SOD values were calculated as -0.052 g/m^2/day and -2.96 g/m^2/day for the Provo Bay and Buoy sites respectively. The SOD value for the Buoy site was similar to a previous study, which reported SOD values in the range of -4.61 to -0.90 g/m^2/day from eight sites across Utah Lake (Hogsett et al., 2019). In contrast, SOD for the Provo Bay site was much lower as compared to previously reported SOD values. The SOD calculation for Provo Bay was based on one SOD chamber because the data

SONDE for the other chamber did not work properly. We revisited the Provo site and installed one control and two SOD chambers again. Unfortunately, all three data SONDES did not work this time because SONDES were mistakenly switched off when we obtained them from the UDWQ. In calculating SOD for the Provo Bay and Buoy sites, we only considered the part of DO-time curve with gradual slope changes (**Figure 9**).

Table 10. SOD measurement by considering initial slope change.

Date	Chamber	pH	Temp (F)	Parameters (SOD or WC)	Corrected SOD (20°C)
Site: Provo Bay					
Oct 3rd, 2019	Water ($g/m^3/day$)	8.98	55.5	-1.584	
	Sediment ($g/m^2/day$)	8.98	55.5	-0.034	-0.052
Site: State Park site near DWQ buoy					
Oct 1st, 2019	Water ($g/m^3/day$)	8.42	58.7	-0.432	
	Sediment ($g/m^2/day$)	8.42	58.7	-2.018	-2.965

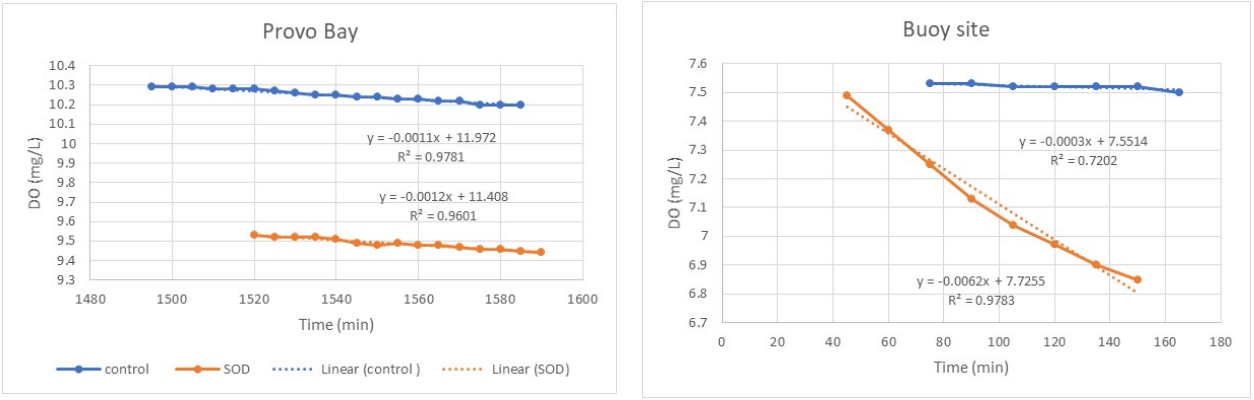


Figure 10. DO versus time for the Provo Bay and Buoy sites site with gradual slope change.

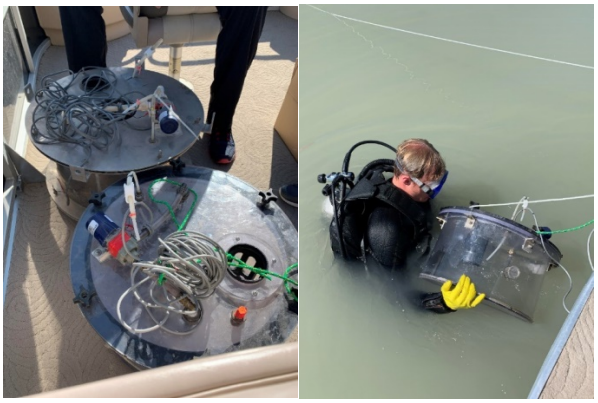


Figure 11. SOD chambers and installation in the field**.**

7. Future perspectives

As sediments responded significantly to different initial P concentrations, the effects of endogenous loading can be better predicted. The mineral composition of surface sediment can be further studied to correlate with the P retention/release under different environmental conditions. Furthermore, field studies can be conducted to detect the anaerobic or aerobic conditions at different layers of sediment, as sediment responded quite differently to these situations. Temperature/seasons and algal blooms may also have effects on sediment nutrient release; for example; blooms could block sunlight and cause endogenous decay of benthic algal biomass and cause nutrient release. Heavy algal blooms could also shift ecosystem nutrient status in terms of nitrogen and/or phosphorus limitation, thus creating nutrient gradients resulting in nutrient fluxes from sediments. pH changes due to algal blooms could also drive nutrient fluxes from or to sediments. In this regard, we make the following possible recommendations for future improvements and data gaps.

1. Conduct anaerobic experiments by purging with nitrogen gas with 0.5% CO_2 to maintain ambient pH in the water column.
2. Run light versus dark experiments.
3. Run experiments for longer than 72 hours to investigate long-term equilibrium.
4. Conduct other analysis such as X-ray diffraction (XRD) and XPS to reveal the minerology of potential precipitates/complexes formed during experiments at the sediment-water column interface.
5. Include a complete mass balance approach for both nutrients, e.g. nitrogen and phosphorus in which case studying bacterial mineralization of P (from mineral phosphates to orthophosphate by bacterial enzymes) and bacteria mediated fate of N (e.g. fixation, denitrification) become important.

6. Study the sources and fate of organic P and its mineralization to SRP.

8. Conclusions

Distribution and transformation of nutrients in large shallow lakes has raised great concern as it may enhance internal nutrient loadings to the system. Being a naturally alkaline lake, Utah Lake was previously reported to remove excess P by mineral precipitation. However, the incubation of sediment cores in dark with varying initial P concentrations suggest that the lake may not remove all additional P when it is above a tolerant limit (2X and 4X of initial concentrations). In contrast, 0.5X initial P concentrations in the water column prompted an increase in P concentrations in some cases over time as P was released from the sediment released. Together with P, concentrations of other ions (e.g., ammonium and calcium) were also observed to change significantly. Additionally, varying of physical parameters (e.g., DO and pH conditions) did affect the overall chemistry of the ecosystem, whereas the lake's strong buffer system can maintain a relatively stable state in natural conditions. Overall, the improvement of Utah Lake water quality may be delayed in response to decreased external loading and ambient concentrations based on these 3-day experiments, although longer duration experiments would help make this conclusion stronger. Results acquired from this study could help with explaining similar phenomenon in other freshwater lakes, as well as decision-making for environmental agencies.

9. Acknowledgements

Special thanks to DWQ's support and sampling team for lending us their boat and assisting with core collection. We also thank the BYU Civil and Environmental Engineering Department for providing access to their boat during the initial trips to the lake. Dave Tingey and Kevin Rey at BYU helped design the coring devices and setup the lab experiments. We greatly appreciate the valuable guidance and advice given by the Utah Lake Science Panel members throughout the entire project.

7.0 References

Baggie, I., Rowell, D. L., Robinson, J. S., & Warren, G. P. (2005). Decomposition and phosphorus release from organic residues as affected by residue quality and added inorganic phosphorus. *Agroforestry Systems*, *63*(2), 125-131.

Bates, M. H., & Neafus, N. J. E. (1980). Phosphorus release from sediments from lake Carl Blackwell, Oklahoma. *Water research*, 14(10), 1477-1481.

Bastami, K. D., Neyestani, M. R., Raeisi, H., Shafeian, E., Baniamam, M., Shirzadi, A., ... & Shahrokhi, B. (2018). Bioavailability and geochemical speciation of phosphorus in surface sediments of the Southern Caspian Sea. *Marine pollution bulletin*, *126*, 51-57.

Boström, B., Andersen, J.M., Fleischer, S., Jansson, M., (1998). Exchange of phosphorus across the sediment–water interface. Hydrobiologia 170, 229–244.

Brimhall, W.H., and Merritt, L.B. (1981). Geology of Utah Lake: Implications for resource management. Utah Lake Monograph, volume 5.

Davis, J. A. and Hem, A. R. (1989). The surface chemistry of aluminum oxides and hydroxides. In: The Environmental Chemistry of Aluminum, pp. 185–219. (Sposito, G., Ed.) Boca Raton, FL, CRC Press.

Dickson, W. (1980). Properties of acidified waters. In: Proceedings of the International Conference on Ecological Impacts of Acid Precipitation, pp. 75–83. (Drablos, D. and Tollan, A., Eds.) Oslo, Norway, SNSF Project.

Doyle, Micelis C., and Dennis D. Lynch. Sediment Oxygen Demand in Lake Ewauna and the Klamath River, Oregon, June 2003.(2005). US Department of the Interior, US Geological Survey.

Ekka, S. A., et al. (2006). Dissolved phosphorus concentrations and sediment interactions in effluent–dominated Ozark streams. *ecological engineering* 26.4: 375-391.

Emerson, K., Russo, R. C., Lund, R. E., & Thurston, R. V. (1975). Aqueous ammonia equilibrium calculations: effect of pH and temperature. *Journal of the Fisheries Board of Canada*, *32*(12), 2379-2383.

EPA. (2002). Nitrification. U.S. Environmental Protection Agency Office of Ground Water and Drinking Water Standards and Risk Management Division 1200 Pennsylvania Ave., NW Washington DC 20004. Prepared by AWWA With assistance from Economic and Engineering Services, Inc.

Feng, W., Wu, F., He, Z., Song, F., Zhu, Y., Giesy, J. P., ... & Sun, F. (2018). Simulated bioavailability of phosphorus from aquatic macrophytes and phytoplankton by aqueous suspension and incubation with alkaline phosphatase. *Science of the Total Environment*, *616*, 1431-1439.

Gao, Y., Cornwell, J.C., Stoecker, D.K., and Owens, M.S. (2012). Effects of cyanobacterial-driven pH increase on sediment nu- trient fluxes and coupled nitrification-denitrification in a shallow fresh water estuary. *Biogeosciences* 9, 2697.

Gensemer, R. W., & Playle, R. C. (1999). The bioavailability and toxicity of aluminum in aquatic environments. *Critical reviews in environmental science and technology*, *29*(4), 315-450.

Gomez E, Durillon C, Rofes G, Picot B. (1999). Phosphate adsorption and release from sediments of brackish lagoons: pH, O_2 and loading influence. *Water Res.*, 33(10), 2437–2447, 1999.

Harris, G.P. (1986). Phytoplankton Ecology: Structure, Function and Fluctuation; Springer: Berlin, Germany.

E. Haggard, B., A. Ekka, S., D. Matlock, M. & Chaubey, I.: 2004, 'PHOSPHATE EQUILIBRIUM BETWEEN STREAM SEDIMENTS AND WATER: POTENTIAL EFFECT OF CHEMICAL AMENDMENTS', Transactions of the ASAE 47, 1113-1118.

Hatcher, K. (1986). Introduction to Part 3: Sediment Oxygen Demand Measurement. In: Sediment Oxygen Demand: Processes, Modeling, and Measurement, Kathryn Hatcher (Editor). Institute of Natural Resources, University of Georgia, Athens, Georgia, pp. 301-305.

He, Hui, et al. (2018). Ammonia-oxidizing Archaea and Bacteria differentially contribute to ammonia oxidation in sediments from adjacent waters of Rushan Bay, China. *Frontiers in microbiology* 9: 116.

Herrmann, Martina, Aaron M. Saunders, and Andreas Schramm. (2009). Effect of lake trophic status and rooted macrophytes on community composition and abundance of ammonia-oxidizing prokaryotes in freshwater sediments. *Appl. Environ. Microbiol.* 75.10: 3127-3136.

Hirota, R., Kuroda, A., Kato, J., & Ohtake, H. (2010). Bacterial phosphate metabolism and its application to phosphorus recovery and industrial bioprocesses. *Journal of bioscience and bioengineering*, *109*(5), 423-432.

Hogsett, M., Li, H. and Goel, R. (2019). The role of internal nutrient cycling in a Freshwater shallow alkaline lake. *Environmental Engineering Science*. *36*(5), 551-563.

Hogsett, M. and Goel, R. (2013). Dissolved Oxygen Dynamics at the Sediment–Water Column Interface in an Urbanized Stream. *Environmental Engineering Science*. 30(10): 594-605.

Hogsett, (2015). Water Quality and Sediment Biogeochemistry in the Urban Jordan River, UT. A dissertation submitted to the University of Utah to fulfill the degree of Doctor of Philosophy.

Hou, D., He, J., Lü, C., Sun, Y., Zhang, F., & Otgonbayar, K. (2013). Effects of environmental factors on nutrients release at sediment-water interface and assessment of trophic status for a typical shallow lake, Northwest China. *The Scientific World Journal*, *2013*.

Huang, Q., Wang, Z., Wang, C., Wang, S., & Jin, X. (2005). Phosphorus release in response to pH variation in the lake sedimentswith different ratios of iron-bound P to calcium-bound P. *Chemical Speciation & Bioavailability*, *17*(2), 55-61.

Huo, S., Zan, F., Xi, B., Li, Q., & Zhang, J. (2011). Phosphorus fractionation in different trophic sediments of lakes from different regions, China. *Journal of Environmental Monitoring*, *13*(4), 1088-1095.

Hupfer M, Lewandowski J: (2008) Oxygen controls the phosphorus release from lake sediment – a long-lasting paradigm in limnology. Int. Rev. Hydrobiol., 93(4–5), 415–432.

Illés E, Tombácz E. (2006). The effect of humic acid adsorption on pH-dependent surface charging and aggregation of magnetite nanoparticles. *Journal of Colloid and Interface Science*. 295(1):115–123.

Jenkins, C. H. (2005). *Nutrient flux assessment in the Port waterways*. Environment Protection Authority.

Jeppesen E, Søndergaard M, Jensen JP, Havens KE, Anneville O, Carvalho L, et al. (2005). Lake responses to reduced nutrient loading–an analysis of contemporary long-term data from 35 case studies. *Freshwater Biology.* 50(10):1747–71.

Kadam, P C, and D R Boone. (1996). Influence of pH on Ammonia Accumulation and Toxicity in Halophilic, Methylotrophic Methanogens. *Applied and environmental microbiology* vol. 62,12 :4486-92.

Krantzberg, G. (1994). Spatial and Temporal Variability in Metal Bioavailability and Toxicity of Sediment form Hamilton Harbour, Lake Ontario. *Environmental Toxicology and Chemistry*. 13(10): 1685-1698.

Li H, Liu L, Li M, Zhang X. (2013). Effects of pH, Temperature, Dissolved Oxygen, and Flow Rate on Phosphorus Release Processes at the Sediment and Water Interface in Storm Sewer. *J Anal Methods Chem.* 104316.

Li, X., Guo, M., Duan, X., Zhao, J., Hua, Y., Zhou, Y., ... & Dionysiou, D. D. (2019). Distribution of organic phosphorus species in sediment profiles of shallow lakes and its effect on photo-release of phosphate during sediment resuspension. *Environment international*, *130*, 104916.

Loewenthal, R. E. Marais G. v. R. (1976). Carbonate Chemistry of Aquatic Systems: Theory and Application. *Ann Arbor Science, Ann Arbor, MI*.

Matisoff et al., (2016). Internal loading of phosphorus in western Lake Erie. Journal of Great Lake Research; 42: 775-788.

Medine, A., D.B. Porcella, and D.V. Adams. (1980). Heavy-Metal and Nutrient Effects on Sediment Oxygen Demand in Three-Phase Aquatic Microcosms. Microcosms in Ecological Research. Technical Information Center, U.S. Department of Energy, Washington, D.C. (USA), 52: 279-303.

Moore PA, Reddy KR. (1994). Role of Eh and pH on phosphorus geochemistry in sediments of Lake Okeechobee, *Florida. J. Environ. Qual*., 23(5), 955–964.

Nalewajko, C. and O'Mahony, M. A. (1988). Effects of acid pH shock on phosphate concentrations and microbial uptake in an acidifying and a circumneutral lake. *Can. J. Fish. Aquat. Sci.*45, 254–260.

Nizzoli, Daniele, et al. (2010). Effect of organic enrichment and thermal regime on denitrification and dissimilatory nitrate reduction to ammonium (DNRA) in hypolimnetic sediments of two lowland lakes. *Water research* 44.9: 2715-2724.

Nguyen, H. V and Maeda, M. (2016). Effects of pH and oxygen on phosphorus release from Agricultural Drainage Ditch sediment in reclaimed land, Kasaoka Bay, Japan. Journal of Water and Environmental Technology; 14(4): 228-235.

Obenour, D.R., Gronewold, A.D., Stow, C.A., Scavia, D. (2014). Using a Bayesian hierarchical model to improve Lake Erie cyanobacteria bloom forecasts. *Water Resour. Res*. 50, 7847–7860.

Palmer, Huckleberry, Marc Beutel, and Seyoum Gebremariam. (2009). High rates of ammonia removal in experimental oxygen-activated nitrification wetland mesocosms. *Journal of Environmental Engineering* 135.10: 972-979.

PSOMAS, and SWCA. (2007). Utah Lake TMDL: Pollutant loading assessment and designated beneficial use impairment assessment. Prepared for the Utah Division of Water Quality. Salt Lake City, UT.

R Development Core Team. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. (2013). ISBN 3-900051-07-0. http://www.R-project.org.

Randall, M.C., Carling, G.T., Dastrup, D.B., Miller, T., Nelson, S.T., Rey, K., Hansen, N., Bickmore, B.R., Aanderud, Z.T., (2019). Sediment potentially controls in-lake phosphorus cycling and harmful cyanobacteria in shallow, eutrophic Utah Lake. *PLOS ONE* 14: e0212238.

Reeburgh W. S. (2007). Oceanic methane biogeochemistry. *Chem. Rev*. 107, 486–513.10.1021/cr050362v.

Seitzinger, Sybil P. (1988). Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. *Limnology and Oceanography* 33.4part2: 702-724.

Shen, Z., Niu, J., Wang, X., Wang, H., & Zhao, X. (2013). *Distribution and transformation of nutrients in large-scale lakes and reservoirs: the Three Gorges Reservoir*. Springer Science & Business Media.

Stocks-Fischer, S., Galinat, J. K., & Bang, S. S. (1999). Microbiological precipitation of CaCO3. *Soil Biology and Biochemistry*, *31*(11), 1563-1571.

UDWQ. (2016). Utah Lake, Jordan River, Canals Algal Bloom 2016.Retrieved from https://deq.utah.gov/water-quality/utah-lake-jordan-river-canals-algal-bloom-2016.

Van Nguyen, Huy, and Morihiro Maeda. (2016). Effects of pH and oxygen on phosphorus release from agricultural drainage ditch sediment in reclaimed land, Kasaoka Bay, Japan. *Journal of Water and Environment Technology* 14.4: 228-235.

Venterea, Rodney T., et al. (2015). Ammonium sorption and ammonia inhibition of nitrite-oxidizing bacteria explain contrasting soil N_2O production. *Scientific reports* 5: 12153.

Yang, Yuyin, et al. (2017). Temporal and spatial dynamics of sediment anaerobic ammonium oxidation (anammox) bacteria in freshwater lakes. *Microbial ecology* 73.2: 285-295.

Zhang, Yaping, Xiaohong Ruan, and Wenli Shi. (2019). Changes in the nitrogen biogeochemical cycle in sediments of an urban river under different dissolved oxygen levels. *Water Supply* 19.4: 1271-1278.

Zhu, T., & Dittrich, M. (2016). Carbonate Precipitation through Microbial Activities in Natural Environment, and Their Potential in Biotechnology: A Review. *Frontiers in bioengineering and biotechnology*, *4*, 4.

Appendix A- SOPs

Utah Lake Sediment–Water Nutrient Interactions
Detailed Experimental and Quality Assurance Plans

Prepared by
Dr. Ramesh Goel, Professor, University of Utah
Dr. Greg Carling, Associate Professor, Brigham Young University
Graduate Students

Submitted
August 8, 2019

1.0 Project rationale and objectives

1.1 Rationale: The Utah Division of Water Quality (DWQ) recently initiated Phase 2 of the Utah Lake Water Quality Study (ULWQS) to evaluate the effect of excess nutrients on the lake's recreational, aquatic life, and agricultural designated uses and to develop site-specific nitrogen and phosphorus water quality criteria to protect these uses. Understanding the cycling of nutrients within Utah Lake will help describe the current state of the lake with respect to nutrients and ecology, and sediments are an important component of the nutrient cycling within the lake. Available reports and initial information on sediment oxygen demand (SOD) and nutrient release from sediments in Utah Lake provide some insight into sediment phosphorus characteristics and fluxes but stop short of converting bulk measurements into mobile or bioavailable fractions.

1.2 Study Objectives: The overall objective of this collaborative project is to; (1) understand the role of anoxia in nutrient release and sediment dynamics over a range of phosphorus concentrations, (2) understand the role of pH in water column–sediment interactions and nutrient releases and how does the equilibrium phosphorus concentration change over a range of water column pH and, (3) estimate the sediment oxygen demand and nutrient release from sediments under current conditions. Although nitrogen species will be measured during these experiments, the current RFA does not suggest calculating nitrogen fluxes or determining the fate of nitrogen species during these experiments. Four different tasks will complement these aforementioned objectives identified by the Science Panel in the recently released RFP.

3.0 Experimental Plan (SAPs)

Task 1. Develop sampling and analysis plan (SAP) (Drs. Goel and Carling and graduate students)

Sub task 1.1: ***Project kick off meeting***: Pending approval and then contract signing of this project, we will immediately conduct an in-person meeting among us including the PI (Dr. Goel), the Co-PI (Dr. Carling) and potential graduate and undergraduate students. The purpose of this meeting will be to discuss project milestones, assign duties in terms of SOPs and QAPP writing. We will also discuss about the lab infrastructure in each key personnel's lab and the overall time frame of experiments. Minutes of the meeting will be recorded and stored electronically.

Sub task 1.2: ***Develop sampling and analysis plan (SAP):*** We will follow a similar strategy that we have followed for our EPA and current UDWQ funded projects. In summary, we plan to submit all necessary QAPP and SAP documents to the Science Panel before the beginning of any field work. We will access the available QAPP and SAP documents related to water quality sampling and sediment work available at the UDWQ website as reference material (https://deq.utah.gov/water-quality/quality-assurance-and-quality-control-program-monitoring-water-quality). ***UDWQ's vision is that QAPP is meant to be an umbrella document***

outlining the minimum QA/QC requirements for environmental data collection. As a team, we share DWQ's vision about QAPP and SAP importance and will adhere to these standards while coordinating with the Science Panel and UDWQ. In developing QAPP and SAP documents, we will coordinate with UDWQ through in person meetings and phone calls. After such meetings, a first draft of QAPP and SAP will be submitted to UDWQ for their input. Once the documents are finalized, they will be submitted to the Science Panel for their comments and approval. The format of SAP will follow the style suggested by the Science Panel in the sediment RFP document. We will also refer to SAP documents for common water quality parameters that are available at

https://deq.utah.gov/water-quality/quality-assurance-and-quality-control-program-monitoring-water-quality. We expect to finish a first draft of SAPs and QAPP plans by August 8, 2019 to be shared with UDWQ and Science Panel members for their further comments. While preparing these documents, we will incorporate all the excellent comments provided by UDWQ and the Science Panel on the overall workplan and responses to our list of questions.

Final Deliverables of task 1: (I) Finalized milestones, (II) written QAPP and SOPs.

Task 2. Collect sediment cores from Utah Lake (Both labs)

Sub-task 2.1: Coordination with UDWQ and BYU for sediment core collection: This task will be jointly completed by Drs. Goel and Carling. Graduate students working directly on this project are also expected to help with sediment core collection. We will use a percussion corer to collect sediment cores from two sites specified in the project. We expect to collect our first set of cores on August 12th, 2019.

Sub-task 2.2: Collecting sediment cores: Sediment cores will be collected from one site in the middle of Provo Bay (DWQ monitoring site with UTM coordinates: 12T 440484 E 4448988 N) and one site in the open water of Utah Lake near the Utah Lake State Park water quality buoy. We will use the BYU pontoon boat to access sites. We will tow a smaller pontoon raft behind the boat that will be used as the drilling platform. The drilling platform will enable us to efficiently collect and extract cores, using a winch if necessary. We will use a percussion corer to collect sediment cores in plexiglass tubes that are 5 cm in diameter by 50 cm long. Each sediment core will be 10-20 cm long with at least 30 cm of overlying water. After collection, the cores will be placed upright in a cooler with ice. The cooler is designed with a rack to secure the cores. The samples will be kept cold and in the dark until returning to the lab. We will collect 12 cores per sampling day, with three sampling days to collect 36 cores at each site. The Co-PI Carling has successfully collected dozens of similar cores with overlying water from multiple sites across Utah Lake using a percussion corer.

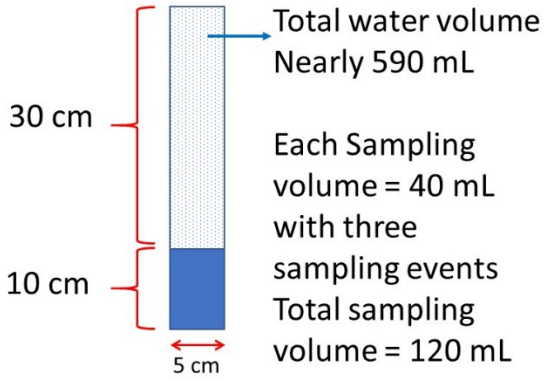


Figure 1: Sediment core with overlying lake water. Based on the given height and diameter of the core, the overlying water volume is calculated. With samples taken at 0, 12-, 24- and

72 hours, the total sampling volume is approximately 120 mL. The t=0 sample will be directly collected from separate container.

As suggested by the Science Panel members, we expect to collect approximately 10 cm (~4 inches) sediment core with 30 cm overlying lake water on the top thus enabling 1:3 sediment to water column ratio.

Table 1 provides details of cores and experiments. A total of 36 cores (39 if SOD conducted in the lab) will be collected per site. Our strategy is to sample the first site and finish all related experiments before sampling the second site. This strategy will allow us to avoid storing the sediment cores for an extended period of time. Nevertheless, we will make sure that both sites are sampled within a time span with no more than a $\pm 5^0$F change in ambient water temperature difference over days of sampling. In the lab, the cores will be stored in the dark at 4^0C walk-in refrigerator until further processing. If conducted ex-situ, sediment oxygen demand (SOD) experiments will be conducted immediately after returning to the lab.

Table 1: Details of cores that will be collected per site for two sites

Parameter/s and experiments	Rationale
Set 1: Sediment core P spiking in the water column under aerobic conditions, no spiking (control), 0.5, 2 and 4 times the ambient P concentration. (**12 cores**)	To determine the fate of dissolved P present in the overlying water column when the water column is in constant contact with sediments. Different concentration ranges reflect low, medium and high end of spiking.
Set 1 continuation: Sediment core P spiking in the water column under aerobic conditions, no spiking (control), 0.5, 2 and 4 times the ambient P concentration and then create anaerobic conditions after an equilibrium has been established under previous aerobic conditions. (Same 12 cores from ambient aerobic spiking experiments)	To determine the fate of dissolved P present in the overlying water column when the water column is in constant contact with sediments under oxygen free conditions. This experiment is a continuation from the previous set of experiments under aerobic conditions.
Set 2: Sediment core P spiking in the water column under aerobic conditions at a pH of 7.0, no spiking (control), 0.5, 2 and 4 times the ambient P concentration. (**12 cores**)	To determine the fate of dissolved P present in the overlying water column when the water column is in constant contact with sediments at neutral pH. Different concentration ranges reflect low, medium and high end of spiking.
Set 3: Sediment core P spiking in the water column under aerobic conditions at a pH of 9.5, no spiking (control), 0.5, 2 and 4 times the ambient P concentration. (**12 cores**)	To determine the fate of dissolved P present in the overlying water column when the water column is in constant contact with sediments at a slightly alkaline pH. Different concentration ranges reflect low, medium and

	high end of spiking.

The following table shows the sequences and potential dates for our sediment core collection. As recommended by some of the Science Panel members, this sampling strategy will allow us to quickly process the cores with limited storage time. Of course, this will require us to revisit the field sites multiple times but this will ensure maximum quality control.

Site 1: State Park site near DWQ buoy		
Date	**# of cores**	**Experiment**
August 12th, 2019	12	Neutral pH
August 14th, 2019	12	pH=9.5
August 16, 2019	12	Aerobic and anaerobic experiments
Site 2: Provo Bay		
Date	**# of cores**	**Experiment**
August 19th, 2019	12	Neutral pH
August 21st, 2019	12	pH=9.5
August 23rd, 2019	12	Aerobic and anaerobic experiments

List of supplies for sub-task 2.2

1. Lake travel
    a. BYU motor boat
    b. Keys
    c. Full tank of gas
    d. Motor oil
    e. Anchors
    f. life jackets
2. Coring platform
    a. Pontoon raft modified for coring; will be towed behind the motor boat
    b. Pully mechanism and winch for extracting core from the lakebed (if necessary)
3. Sediment cores
    a. Percussion corer
    b. 4 extension poles
    c. Handle
    d. 40 plexiglass core sleeves
    e. 40 core catchers

    f. 80 caps
    g. Tape measure for measuring core length and lake depth
    h. Pole for measuring lake depth
    i. Electrical tape
    j. Aluminum foil
    k. Cooler with ice, retrofitted to hold sediment cores upright
4. Water sampling
    a. YSI Quattro multiparameter probe calibrated prior to each field day)
    b. 16 wide mouth 1-gallon jugs (2 gallons of water per 12 cores)
    c. Disposable gloves
    d. Cooler with ice to hold water samples
    e. Deionized water for rinsing
5. Miscellaneous
    a. GPS
    b. Field notebook with pencil
    c. Sharpie
    d. Lab tape
    e. Paper towels
    f. Wash cloths
6. Hand held camera to take field pictures
7. GPS device

Experimental steps for sub-task 2.2

1. Secure all equipment and sampling devices in the boat and drive to the sampling location. Anchor the motor boat and pontoon raft. Record GPS coordinates using a handheld GPS device.
2. Measure field parameters (temp, pH, conductivity, dissolved oxygen) at top and bottom of water column using YSI probe. Record measurements.
3. Collect 2 gallons of water (prior to sediment sampling, which would stir up the water column) and place in cooler.
4. Decontaminate the sampling apparatus and tools by rinsing with lake water. Perform decontamination process downstream of the boat.
5. Measure and record water depth to the nearest 10 cm with a pole and tape measure.
6. Assemble the core sampler and push it in the sediment to the depth required.
7. Pull out the corer out of the sediments. When the corer is relatively free from the surrounding sediment, pull the corer to the surface, detach the plexiglass tube containing the core, and cap the top and bottom of the core. Wrap electrical tape around the caps. Rinse the outside of the core with distilled water. Label core with a unique identifier using tape and Sharpie.
8. Wrap the core in aluminum foil and place it on the rack in a cooler.
9. Repeat steps 4 through 8 to collect more sediment cores, 12 cores per day.
10. Take photographs of water sampling and coring activities to document the field day.

Experimental quality control and assurance plan for core collection: The following quality controls will be exercised.

(1) For each core collection exercise, a fresh set of plexiglass tubes will be used. Each tube will be thoroughly rinsed in autoclaved deionized water and air dried. A clean plastic core catcher and new lids will be used with each tube.

(2) Upon collection, the sediment height is measured. Sediment height must be between 10-20 cm or the sediment is discarded. Further, if the core appears disturbed it is discarded.

(3) Each core is given a unique identifier.

(4) The core is immediately wrapped in aluminum foil, placed upright in a cooler, on ice and in the dark. The cooler contains a rack so the cores do not tip over during transport to the lab.

Deliverables of task 2: **(I) A short report on field experiences for sediment core collection, (2) field pictures**

Task 3. Perform sediment core experiments and laboratory analysis (All sub tasks under this task will be performed at the University of Utah).

Sub-task 3.1: Nutrient spike experiments under aerobic conditions**:** A set of 12 sediment cores will be used for this set of experiments. The cores with overlying Utah Lake water will be mounted on a PVC stand and wrapped in aluminum foil from the side. Two gallons of water is filtered using a vacuum filter and 0.45 µm filter paper, and filtered water is placed in separate 2 L bottles to adjust redox conditions and for phosphorus spiking. Ambient nutrient concentrations will be determined in the lake water samples. One strategy could be to use historical data collected by UDWQ for ambient nutrient concentrations and decide the spiking concentrations before the onset of sediment core collection. However, to ensure maximum accuracy, we would decide the spiking concentrations based on the measured ambient P concentration in lake water samples. Other water quality parameters such as temperature, pH, dissolved oxygen using a luminescent DO probe and turbidity will also be determined to ensure that they have not changed since the field measurements. After equilibrating at room temperature, the overlying water from nine out of twelve sediment cores will be taken out gently using a vacuum pump, leaving 1 cm of water above the sediment so it is not exposed directly to the atmosphere. Care will be taken as not to disturb sediments. Utah Lake water collected from the same site will be used to replace the overlying water after adjusting the total dissolved P (TDP) concentrations to 0.5X (by diluting with major ion water devoid of P), 2X and 4X the ambient P concentration using a 1000 mg-P/L KH_2PO_4 stock solution in three sets of sediment cores with each set consisted of triplicate cores. The unspiked set of sediment cores will serve as a control. The adjusted/spiked water is carefully added back to the sediment cores to limit disturbing the cores. To preserve water volume, time zero samples are collected from the 2 L bottles rather than from the cores. Immediately after adding water to sediment cores, a

small aeration stone will be placed in each sediment core column at approximately 5-cm from the sediment-water interface. The aeration stones will be connected to an aquarium aeration pump which will be regulated by an electronic timer. The core columns are capped to prevent evaporation and contamination by lab dust; the air tubing will enter the column via a small hole in the cap.

Once spiked, all sediment columns will be kept un-agitated in the dark wrapped in aluminum foil. Additionally, to maintain mixed and aerobic conditions and to overcome diffusion limitations between sediment and the water column for nutrient fluxes, column water will be aerated every 2-h using the electronic timer. Care will be taken as not disturb the sediments during the aeration. Water samples for water quality analysis at 12-, 24-, and 72-h will be withdrawn from each column using a disposable 50-mL plastic pipette and, will be filtered (0.45 µm) and transferred to a 50-mL falcon tube for further analysis. Fluxes of phosphorus, ammonium, nitrite and nitrate will be calculated based on the concentrations measured and the internal cross-sectional area of each column. This sub-task will be performed at the University of Utah under the direction of Drs. Ramesh Goel and Greg Carling. Please note that the Dr. Carling's graduate student (Sheena Smithson) will also be helping with these experiments.

List of supply for sub-task 3.1

1. PVC racks to hold cores
2. Freshly collected Utah Lake water
    a. Vacuum filtration unit with pump
    b. 0.45 µm filter paper (47 mm diameter)
    c. 32 2-L bottles for transferring filtered water
3. Peristaltic pumps for removing overlying water from core columns
4. Chemicals for spiking/adjusting samples
    a. Scientific grade KH_2PO_4 with 99.9. % purity
5. Tubing to carefully transfer filtered/spiked/adjusted water back into core columns
6. Major ion solution to match Utah Lake water for 0.5x P dilution
7. Core column measurements
    a. Luminescent DO probe
    b. Benchtop pH probe
    c. Turbidity meter with cuvettes or turbidity probe
8. Core column aeration

a. Aeration stones (one stone per core; 72 total)
b. Aquarium pumps (one pump per two cores)
c. Tubing from pump to column (100 ft total)

9. Core column water samples
    a. Syringes (1 per core)
    b. Syringe filters (0.45 µm nylon)
    c. 50 mL falcon tubes for sample collection
    d. HNO3 to acidify ICP-OES samples in separate vials from other non-acidified samples
10. Miscellaneous
    a. Disposable gloves
    b. Paper towels
    c. Weighing balance
    d. Tubes of different sizes
    e. Disposable pipettes
    f. Analytical pipette and pipette tips of varying volumes.
    g. Milli Q grade water
    h. Electronic timers
    i. 1-L glass cylinders, Erlenmeyer flasks and volumetric flasks
    j. Extension cords
11. Lab analyses
    a. Ion chromatograph (IC) with auto sampler
        i. IC tubes
        ii. Eluents for IC
    b. ICP-OES with autosampler
        i. ICP-OES tubes
    c. HACH spectrophotometer
        i. Ammonium HACH kits

ii. Total dissolved N

Experimental steps for sub-task 3.1

1. Take out the sediment cores from cooler and let them equilibrate at room temperature for 30 minutes.
2. After 30 minutes, gently extract the overlying water using a peristaltic or vacuum pump without disturbing the underlying sediments from all 12 columns, leaving 1 cm of water so the sediment is not exposed to the air.
3. Suspend aeration stones approximately 5 cm from the interface of sediment and water column and connect them with aquarium pump which in turn will be connected with a timer. The timer to initiate aeration cycle at every 2-h. Do not start the aeration.
4. Filter 2 gallons of lake water that was collected separately at the time of sediment core collection using vacuum filter. Put filtered water into separate 2 L bottles. Measure the ambient nutrient concentrations in the filtered lake water.
5. Fill in the first set of three columns with Utah Lake to obtain 1:3 sediment to water ratio. This set will serve as a control. Start the aeration.
6. Take a known volume of Utah Lake water in a separate clean container and dilute it to 0.5 X times using major ion solution (devoid of P). Mix it well and take sample to measure different water quality parameters.
7. Add this diluted water to the next set of three columns to enable 1:3 sediment to water ratio. Start the aeration.
8. Likewise, take a known volume of filtered Lake water and spike with the stock solution of KH_2PO_4 to obtain 2X times the ambient P concentration. Add this P spiked Utah Lake water to the top of the next set of three columns to enable 2X times P concentration. Start the aeration.
9. Repeat step 9 with the only difference that the spiked concentration of KH_2PO_4 will be higher to obtain 4X times the ambient P concentration. Start the aeration.
10. Analyze water samples collected from step 6 through 10 at time zero and analyze for different water quality parameters.
11. Obtain water samples from a location at approximately 5 cm from the sediment water column interface in each column at 12-, 24-, and 72 hours. Analyze for different water quality parameters after filtering using syringe filter. Acidify sample for ICP-OES to 2% v/v HNO3.
12. Record all the data and lab observation in the lab book. Take pictures of set-ups.
13. Proceed to task 3.2 after 72 hours.

Experimental quality control and assurance plan for sub-task 3.1: The following quality controls will be exercised.

1. All aeration stones will be thoroughly washed in acid water to clean them. Aeration stones will be supplemented with 0.2 µm filter paper to avoid any aerosols entering the column.
2. All sediment columns will be covered with aluminum foil to avoid any light exposure of water column.
3. For each sampling period and for each column, separate and fresh disposable pipettes will be used and will be sacrificed after their usage.
4. Fresh autoclaved falcon tubes will be used for sample collection.
5. Personnel working on this task will be required to wear fresh gloves during the setting up of experiments and during each sampling event.
6. Samples needed to measure soluble constituents will be filtered immediately using a 0.45 µm nylon syringe filter.

***Sub-task 3.2: Column experiments under anaerobic conditions*:** After the aerobic set of experiments have been completed, the sediment core columns used in aerobic experiments in sub-task 3.1 will be subjected to anaerobic conditions. The overlying water from the previous aerobic experiments will be replaced with fresh Utah Lake water. The aeration stones will be kept inside each column and will be connected with nitrogen cylinder. To create initial anaerobic conditions, a predetermined volume of a stock solution of sodium sulfide containing trace amount of cobalt chloride will be added to each column and nitrogen gas will be purged to mix the added sodium sulfite solution. Thereafter, the nitrogen purging trend will follow the similar trend which was maintained for aeration in sub-task 3.1, e.,g nitrogen purging at every two hours to mix the water column and overcome the diffusional limitations. All columns will be covered air tight with a stopper as not allow the atmospheric oxygen to diffuse in the water column. A vent will be kept in the stopper to release nitrogen pressure during nitrogen purging. Care will be taken as not disturb sediments during nitrogen purging. Water samples for water quality analysis at 12-, 24-, and 72-h will be withdrawn from each column using a disposable 50-mL plastic pipette, filtered with a syringe filter, and transferred to a 50-mL falcon tube for further analysis. Dissolved oxygen will be routinely measured using a luminescent DO probe routinely and, especially during sampling times to ensure strict oxygen free conditions. Fluxes of phosphorus, ammonium, nitrite and nitrate will be calculated based on the concentrations measured and the internal cross sectional area of each column. This sub-task will be performed at the University of Utah under the direction of Drs. Ramesh Goel and Greg Carling. Please note that the Dr. Carling's graduate student (Sheena Smithson) will also be helping with these experiments.

List of supply for sub-task 3.2

1. PVC racks to hold cores
2. Freshly collected Utah Lake water
    a. Vacuum filtration unit with pump
    b. 0.45 µm filter paper (47 mm diameter)
    c. 32 2-L bottles for transferring filtered water
3. Peristaltic pumps for removing overlying water from core columns
4. Chemicals for spiking/adjusting samples
    a. Scientific grade KH_2PO_4 with 99.9. % purity
    b. Scientific grade sodium sulfite with 99.9 % purity
    c. Cobalt chloride with 99.9 % purity
5. Tubing to carefully transfer filtered/spiked/adjusted water back into core columns
6. Major ion solution to match Utah Lake water for 0.5x P dilution
7. Core column measurements
    a. Luminescent DO probe
    b. Benchtop pH probe
    c. Turbidity meter with cuvettes or turbidity probe
8. Core column aeration
    a. Nitrogen cylinder fitted with regulator
    b. Four way channel to distribute nitrogen gas.
    c. Tubing from regulator to column
9. Core column water samples
    a. Syringes (1 per core)
    b. Syringe filters (0.45 µm nylon)
    c. 50 mL falcon tubes for sample collection
    d. HNO3 to acidify ICP-OES samples in separate vials from other non-acidified samples
10. Miscellaneous

a. Disposable gloves
b. Paper towels
c. Weighing balance
d. Tubes of different sizes
e. Disposable pipettes
f. Analytical pipette and pipette tips of varying volumes.
g. Milli Q grade water
h. Electronic timers
i. 1-L glass cylinders, Erlenmeyer flasks and volumetric flasks
j. Extension cords

11. Lab analyses
    a. Ion chromatograph (IC) with auto sampler
        i. IC tubes
        ii. Eluents for IC
    b. ICP-OES with autosampler
        i. ICP-OES tubes
    c. HACH spectrophotometer
        i. Ammonium HACH kits
        ii. Total dissolved N

Experimental steps for sub-task 3.2

1. Continuing from task 3.1, stop aeration and take out the overlying water using peristaltic or vacuum pump.
2. Disconnect aeration stone from aquarium pump and connect with Nitrogen cylinder.
3. In a separate container, add a predetermined volume of a stock solution of sodium sulfite supplemented with trace amount of cobalt chloride (catalyst).
4. Mix the water containing sodium sulfite and monitor drop in dissolved oxygen.
5. Spike water to 2x and 4x ambient phosphorus concentrations. Add synthetic lake water to make a 0.5x dilution.

6. Once the DO drops below instrument detection limit, obtain a homogenized water sample and analyze for proposed water quality parameters. This will constitute zero time sample.
7. Once the DO concentration falls below detection limit, fill in the sediment core columns with this oxygen free/spiked water simultaneously to the same height in sub-task 3.1.
8. Start nitrogen purging and close the top of each sediment core with an air tight stopper (having a small hole to release nitrogen pressure) to minimize air transfer from the atmosphere.
9. Monitor DO and pH periodically by opening the top stopper.
10. Collect water samples from a location at 5-cm from the bottom of the sediment in each column at 12-, 24-, and 72 hours. Acidify ICP-OES sample to 2% v/v HNO3.
11. Analyze water samples for proposed water quality parameters.

Experimental quality control and assurance plan for sub-task 3.2: The following quality controls will be exercised.

1. All aeration stones will be thoroughly washed in acid water to clean them before using them again.
2. All sediment columns will be covered with aluminum foil to avoid any light exposure of water column.
3. For each sampling and for each column, separate and fresh disposable pipettes will be used and will be sacrificed after their usage.
4. Fresh autoclaved falcon tubes will be used for sample collection.
5. Personnel working on this task will be required to wear fresh gloves during the setting up of experiments and during each sampling event.
6. Scientific grade nitrogen will be used during experiments.
7. Samples needed to measure soluble constituents will be filtered immediately using a 0.45 µm nylon syringe filter.
8. All chemical used will be have more than 99 % purity.

Sub-task 3.3: P spiking column experiments under ambient conditions (neutral pH): These experiments will follow a similar strategy detailed in sub-task 3.1 under aerobic conditions except that the pH of the Utah Lake water will be gently adjusted to 7 by adding 0.5 N H_2SO_4 before spiking with P stock solution. All other experimental conditions and sampling strategy will be similar to aerobic experiments detailed in sub-task 3.1. Twelve cores will be used for this set of experiments with triplicate measurements under ambient, 0.5x, 2x, and 4x lake water P concentrations. This sub-task will also be performed at U of Utah under the direction of Drs.

Greg Carling and Goel. All graduate students working on this project will participate in this experiment.

List of supply for sub-task 3.3

1. PVC racks to hold cores
2. Freshly collected Utah Lake water
    a. Vacuum filtration unit with pump
    b. 0.45 µm filter paper (47 mm diameter)
    c. 32 2-L bottles for transferring filtered water
3. Peristaltic pumps for removing overlying water from core columns
4. Chemicals for spiking/adjusting samples
    a. Scientific grade KH_2PO_4 with 99.9. % purity
    b. 0.5 N H_2SO_4 for adjusting pH
5. Tubing to carefully transfer filtered/spiked/adjusted water back into core columns
6. Major ion solution to match Utah Lake water for 0.5x P dilution
7. Core column measurements
    a. Luminescent DO probe
    b. Benchtop pH probe
    c. Turbidity meter with cuvettes or turbidity probe
8. Core column aeration
    a. Aeration stones (one stone per core; 72 total)
    b. Aquarium pumps (one pump per two cores)
    c. Tubing from pump to column (100 ft total)
9. Core column water samples
    a. Syringes (1 per core)
    b. Syringe filters (0.45 µm nylon)
    c. 50 mL falcon tubes for sample collection
    d. HNO3 to acidify ICP-OES samples in separate vials from other non-acidified samples

10. Miscellaneous
    a. Disposable gloves
    b. Paper towels
    c. Weighing balance
    d. Tubes of different sizes
    e. Disposable pipettes
    f. Analytical pipette and pipette tips of varying volumes.
    g. Milli Q grade water
    h. Electronic timers
    i. 1-L glass cylinders, Erlenmeyer flasks and volumetric flasks
    j. Extension cords
11. Lab analyses
    a. Ion chromatograph (IC) with auto sampler
        i. IC tubes
        ii. Eluents for IC
    b. ICP-OES with autosampler
        i. ICP-OES tubes
    c. HACH spectrophotometer
        i. Ammonium HACH kits
        ii. Total dissolved N

Experimental steps for sub-task 3.3

1. Take out the sediment cores from cooler and let them equilibrate at room temperature for 30 minutes.
2. After 30 minutes, gently extract the overlying water using a peristaltic or vacuum pump without disturbing the underlying sediments from all 12 columns, leaving 1 cm of water so the sediment is not exposed to the air.
3. Suspend aeration stones approximately 5 cm from the interface of sediment and water column and connect them with aquarium pump. Do not start the aeration.
4. Filter 2 gallons of lake water that was collected separately at the time of sediment core collection using vacuum filter. Put filtered water into separate 2 L bottles. Measure the

ambient nutrient concentrations in the filtered lake water. Adjust all water to pH =7 with 0.5 N H2SO4.

5. Fill in the first set of three columns with Utah Lake to obtain 1:3 sediment to water ratio. This set will serve as a control. Start the aeration.
6. Take a known volume of Utah Lake water in a separate clean container and dilute it to 0.5 X times using major ion solution (devoid of P). Adjust solution to pH=7 if needed. Mix it well and take sample to measure different water quality parameters.
7. Add this diluted and pH-adjusted water to the next set of three columns to enable 1:3 sediment to water ratio. Start the aeration.
8. Likewise, take a known volume of filtered Lake water and spike with the stock solution of KH_2PO_4 to obtain 2X times the ambient P concentration. Add this P spiked Utah Lake water to the top of the next set of three columns to enable 2X times P concentration. Start the aeration.
9. Repeat step 9 with the only difference that the spiked concentration of KH_2PO_4 will be higher to obtain 4X times the ambient P concentration. Start the aeration.
10. Analyze water samples collected from step 5 through 9 at time zero and analyze for different water quality parameters.
11. Obtain water samples from a location at approximately 5 cm from the sediment water column interface in each column at 12-, 24-, and 72 hours. Analyze for different water quality parameters after filtering using syringe filter. Acidify sample for ICP-OES to 2% v/v HNO3.
12. Record all the data and lab observation in the lab book. Take pictures of set-ups.

Experimental quality control and assurance plan for sub-task 3.3: The following quality controls will be exercised.

1. All aeration stones will be thoroughly washed in acid water to clean them before using them again.
2. All sediment columns will be covered with aluminum foil to avoid any light exposure of water column.
3. For each sampling and for each column, separate and fresh disposable pipettes will be used and will be sacrificed after their usage.
4. Fresh autoclaved falcon tubes will be used for sample collection.
5. Personnel working on this task will be required to wear fresh gloves during the setting up of experiments and during each sampling event.

6. Aeration stones will be supplemented with 0.2 µm filter paper to avoid any aerosols entering the column.
7. Samples needed to measure soluble constituents will be filtered immediately using a 0.45 µm nylon syringe filter.
8. Scientific grade nitrogen gas will be used.
9. All chemical used will be have more than 99 % purity.

Sub-task 3.4: P spiking column experiments under elevated pH condition (pH=9.5) (BYU): These experiments will follow a similar strategy and similar quality controls detailed in sub-task 3.3 under neutral pH conditions except that the pH of the overlying water column will be gently adjusted to 9.5 by adding 0.5 N NaOH. A small change will be employed in this set of experiments. Instead of adding the KH2PO4 stock solution into the Utah Lake water separately in a container, a predetermined volume (based on column overlying water volume) KH2PO4 will be added directly to the water column to accomplish 2X and 4X times the ambient P concentrations. All other experimental conditions and sampling strategy will be similar to neutral pH experiments detailed in sub-task 3.3. Twelve cores will be used for this set of experiments with triplicate measurements under ambient, 0.5x, 2x, and 4x lake water P concentrations.

Sub-task 3.5: Sediment oxygen demand determination (University of Utah): For shallow site with accessibility (for example Provo Bay), we will install SOD chamber in-situ using the methodology demonstrated by us in the past for the Utah Lake (Hogsett et al., 2019). For open water site, we will first try to go in the route of installing in-situ SOD chamber using a SCUBA diver. In case this does not work out, we will collect sediment cores in triplicate and determine SOD under laboratory scale controlled conditions. If conducted in the lab, care will be taken to inhibit any primary production by covering the sediment cores with dark cloth or aluminum foil. For in-situ determination, automated data Sonde borrowed from UDWQ will be installed for continuous monitoring of DO. For lab scale SOD measurements, digital luminescent DO probe will be used in the sediment column. The sediment column during SOD determination in the lab will be gently agitated to enhance DO mass transfer but not to the extent to disturb sediments. The duration of experiments will be 180 minutes as opposed to 90 minutes. Please refer to our previous publication (Hogsett et al., 2019) for details. For in-situ SOD measurements, three SOD chambers will be installed as detailed in Hogsett and Goel, 2016. Two chambers will be open at the bottom (testing chambers) and will measure oxygen consumption in sediments and the overlying water column due to various activities. The third chamber (control chamber) will be closed at the bottom to measure oxygen consumption in the water column only. The duration of installation will be 3 hours from mid-morning to early afternoon.

The top section of each SOD chamber will consist of a lid that contains the pump, plumbing, water sampling tube, water quality probe connection, and attachments for ropes used to lift

the SOD chamber out of the sediments and water. A submersible pump will be mounted on each chamber to internally circulate (if needed) the water inside the SOD chamber at a predetermined flow rate of 11 L/min. The Control SOD chamber will have a working volume of 44 liters and the Testing SOD chambers a working volume of 38 liters. This discrepancy in volumes is a result of the additional space provided in the Control chamber due to closed bottom which prohibits this control chamber to lose almost 1½“ of vertical length into the sediments. The construction and design of these chambers is based on SOD chambers used by Georgia EPA.

In case we cannot deploy in-situ chambers for deep site, similar experiments will be conducted using sediment cores. In this case, oxygen consumption in the overlying water column due to activities in the sediments and water column will be measured directly in cores in triplicate after a specified period of time (e.g 180 minutes). A second set of triplicate PVC tubes containing Utah Lake water to the same water depth as in the sediment cores will measure oxygen consumption in the water column. However, in this document, we are including SAP for SOD assuming that we will be able to conduct SOD in-situ. In case this does not happen, we will submit a revised SAP for lab scale SOD protocol.

List of supply for sub-task 3.5

1. 2 SOD chambers with open bottom and one control chamber with closed bottom
2. Three data SONDES borrowed from the UDWQ
3. Submersible pumps
4. Portable small battery
5. One big battery to charge small batteries.
6. Electric cables
7. A laptop with SONDE software installed.
8. Disposable gloves
9. Paper towel
10. Scuba diving gear
11. Scuba diver
12. Motor boat (UDWQ)
13. DI water to rinse probe
14. Aeration stones to calibrate probes

15. A desktop computer to download data.

Experimental steps for sub-task 3.5

1. Calibrate data SONDEs in the lab by merging them in oxygen saturated water.
2. Check the air tightness of each SOD chamber in the lab.
3. Rinse all three SOD chambers thoroughly with DI water.
4. Load all equipment into the boat and drive to the site.
5. Locate approximate the same locations used in sub-tasks 2.2 to collect sediment cores using GPS device**.**
6. Scuba diver gets into water and examine locates relatively flat surface of sediments at the site to install chambers.
7. The control chamber will be first placed in the upstream of the boat approximately 10 meters from the boat by gently lowering it toe sediments and filling it with lake water slowly while lowering it.
8. The control chamber with closed bottom will be allowed to sit on the bottom and the data SONDE will be inserted into the SONDE holder mounted at the top of the chamber.
9. Likewise the two testing chambers will also be placed on the sediments in the similar fashion.
10. After placing the testing chamber, the chamber lid will be manually pressed to ensure water tightness and to avoid any hydraulic connection between the water inside and the chamber and the lake water.
11. Start internal submersible pumps mounted on each chamber to internally circulate water inside each chamber.
12. Activated data SONDE.
13. Monitor the submersible pumps in between for their operation.
14. Continue this experiments for 180 minutes.
15. Stope the submersible pumps after 3 hours and remove the data SONDES.
16. Download the data from each SONDE and check the accuracy of the data.
17. Gently take out the SOD chambers one by one from the water and place them on the boat.
18. Drive back to the shore.

Experimental quality control and assurance plan for sub-tasks 3.5: The following quality controls will be exercised.

1. Care will be taken as not to allow any air bubble either during in-situ chamber installation or during lab scale column experiments.
2. Data SONDE/ DO probes will be fully calibrated prior to their use.
3. The bottom rim of each chamber will be fully pushed into sediments for the sediment chambers to ensure no exchange of water between the chamber and outside water column.

Deliverables of task 3: (I) Raw data arranged electronically from all sets of experiments, (II) report on challenges and learning experience.

Sub-task 3.6: Statistical analysis: We will use the R package to conduct all the statistical analysis. We will use t-tests for more direct tests and comparison between data sets. Significance levels (p values) will be reported to levels of 0.05, and 0.01. For small sample sizes, we will also report p values between 0.05 and 0.10. Two-tailed Pearson correlation analysis will be used to determine the correlations between different parameters between different treatments. Principal component analysis will be used to evaluate interdependency of different parameters.

Task 4: Prepare technical report: We will use a three tier reporting strategy. First, we will present results at in-person meetings with UDWQ personnel and the Science Panel to inform about project progress and to seek input on future research direction. Secondly, we will submit a synopsis of preliminary analysis within two weeks from the date of experiments in the form of interim reports. Lastly, we will submit draft and final project reports containing all analyzed data, project rationale, future recommendations. The final project report will also contain raw data in the appendix.

Data analysis will focus on the following questions; (**1**) What is the equilibrium total dissolved phosphate concentration in the water column under all scenarios tested, (**2**) what is the internal P recycling from sediments to the water column based on P released from sediments expressed as flux (mg P/m^2/hour) and loading (e.g., kg/day) and, (**3)** is there any anaerobic release and if yes, is it purely related to redox chemistry, primarily iron reduction or bacteria mediated or both. A detailed statistical analysis will be conducted (**see sub-task 3.6**) on different data sets to established correlations and interdependency. We will follow standard format for report preparation which we have been following for our EPA and UDWQ funded research projects.

Deliverables of task 4: (I) Final report with all results analyzed and future recommendations.

4.0 Approach for Science Panel Collaboration and Data Sharing

Our goal is to closely work with the Utah Lake Science Panel during the project period. We will accomplish this goal right from the beginning of the project. SAP and QAPP documents will be prepared in collaboration with the Science Panel by sharing the documents in the ULWQS Dropbox folder for their inputs and comments. Additionally, we will also attend Science Panel meetings as needed during the course of this project. Towards the middle of the project when we have finished field sediment core collection, we will request an Adobe Connect meeting with all Science Panel members to update them about the progress of the project and seek their inputs on pending lab work. **Please refer to each task for deliverables.**

The data management and data sharing are an integral part of this project and, the success of the scientific and engineering outcomes will depend upon a robust data sharing and data management plan. The new data generated by the project includes raw metadata from lab and literature review. The quality control and quality assurance plan for all the acquired data will be implemented according to US EPA established rules. Management of data will be accomplished on daily basis by maintaining proper lab notebooks and then managing the data electronically. Data will be made accessible to the Science Panel, UDWQ, other interested people, and the environmental community through presentations, interim reports, and peer reviewed publications. All the data including raw lab results, QA/QC results, final lab results, interpreted results, and any other associated data product will be shared with the Science Panel at the frequency stated in the RFP. We will also create a password protected online data repository to be shared with the Science Panel. All the collected data will be stored electronically with a weekly backup on an external hard drive. Proper statistical analyses will be conducted. Statistical analysis incorporating ANOVA and t-tests will be conducted to compare performance data between different experiments. The quality of sample measurements will be maintained by the daily use of standards and periodic analysis of blind standards. Our data dissemination plan will include presentations to local and national conferences, publishing in peer reviewed journals of international repute. No intellectual property is expected from this research.

5.0 SOPs and QAPP for water quality parameters

A. PROJECT/TASK ORGANIZATION

(a) Project team and responsibilities

Table 1 lists all personnel involved in the project.

Title	Name	Affiliation	Responsibilities	Contact
Project Manager	Dr. Ramesh Goel	University of Utah	Oversee and manage the whole project. He will also be responsible for project's QC plan	801-581-6110 (ram.goel@utah.edu)
Co-Project	Dr. Greg	BYU	Help with	greg.carling@byu.edu

Manager	Carling		sediment core collection, analytical parameter quality controls and data analysis	
Graduate student	Hanyan Li	University of Utah	Help with field and lab activities & data analysis	lihanyan7@gmail.com
Graduate student	TBD	University of Utah	Help with field and lab activities & data analysis	TBD
Graduate student	Sheena Smithson	BYU	Help with field and lab activities & data analysis	sheenamsmithson@gmail.com

(b) Quality assurance manager

The point of contact (Dr. Ramesh Goel) will be responsible for all quality control measures associated with the project activities, particularly with field and laboratory scale experiments and analytical measurements.

(c) Individual responsible for maintaining QA project plan

Dr. Ramesh Goel, project manager, and Dr. Greg Carling, CO-PI, will be responsible for maintaining the QA project plan. They will make sure that all project related activities are completed with milestones met and project reports are submitted as proposed.

(d) Parameters to be measured

The parameters include water quality and molecular microbiology. Table 3 lists these parameters and will be measured at all sites in impounded wetlands.

Table 3 lists different parameters which will be measured in different tasks.

Parameters-Tasks 3.1 -3.4- P spiking experiments	**Methodology**	**Parameters-Task 3.5- SOD measurement**	**Methodology**
pH	pH probe	pH	Data Sonde*
Dissolved oxygen	Luminescent DO probe	Dissolved oxygen	Data Sonde*
Dissolved Orthophosphate	Ion chromatography	SOD	SOD chamber detailed earlier
Soluble reactive P only if ortho P is below detection limits	Molybdenum blue method These samples are analyzed in Dr. Aaunderud's lab at BYU		

Nitrate	Ion chromatography		
Nitrite	Ion chromatography		
Ammonium	Low range HACH Kit		
Turbidity	Turbidity probe or meter		
Alkalinity**	Titration		
Total dissolved P, major cations, and metals	ICP-OES		

*Will be borrowed from DWQ and will be conducted with DWQ staff.

**Alkalinity will only be measured at 0 and 72 hours.

(e) Standard operating procedures

For Dissolved NH3-N, NO3-N, NO2-N, PO4-P sample collection and analysis and, sediment sample collection, we will employ protocols provided at UDWQ's water quality website.

(f) Instrument detection limits

Table 4 shows IC detection limits and precision, accuracy and recovery.

Table 4: Analytical QC limits and reporting ranges

Parameter	**Method**	**MRL* (mg/L)**	**Calibration range (mg/L)**	**Precision (%)**	**Accuracy (%)**	**Recovery (%)**
NH_3-N	TNTplus 830, Method 10205 (HACH)	0.05	0.05-10	±10	±10	±10
NO_3-N	Ion Chromatograph	0.05	0.05-10	±10	±10	±10
NO_2-N	Ion Chromatograph	0.05	0.05-10	±10	±10	±10
PO_4-P	Ion Chromatograph	0.02	0.02-5	±10	±10	±10
Total dissolved P and trace metals	ICP-OES	0.005	.001-1	±10	±10	±10

(g) Resource and time constraints

The data produced from this project will be disseminated through peer reviewed conferences, peer reviewed publications and most importantly through status and final reports to UDWQ. The uncertainty associated with sample collection could be the significant source of errors. This

uncertainty is mostly associated with spatial and temporal variations in constituent concentrations. The only way to minimize such variability is to sample frequently and at more locations. However, sometime this cannot be possible due to time and budgetary constraints. Uncertainty can also be introduced through sample handling, storage and laboratory analysis. In this project, we have designed a very practical and robust experimental plan with a solid quality assurance project plan to minimize the uncertainty associated with these sampling, handling and analysis for example. To ensure highest data accuracy, only assigned students will be doing field sampling and analysis and, everything will be recorded in the lab notebooks. This will eliminate data uncertainty that may come if sampling and analysis are done by different personnel at each sampling time. The project will sample 2-sites in Utah Lake. Hence, we expect the data generated to be very site specific. However, we also expect to generate a trend based on the produced data. Furthermore, even if the data generated will be site specific, conclusions drawn will lead us to apply some observations for other sites. These limitations will be reported in reports to UDWQ. The report will include future recommendations about how the uncertainties (if any) observed be minimized or overcomes in future.

(h) The responsibility of the project QA officer from QA in charge, training and method of training

The personnel working on this project will involve graduate students under the direct supervision of the project directors Drs. Ramesh Goel and Greg Carling. All personnel working on this project will receive prior training, both on laboratory as well as on field protocols such that the students working on the project can implement lab and field activities independent of the project Director. The training will include laboratory scale as well as field scale components. In the lab, students working on this project will be guided PI and the Co-PI during protocol development and testing. Personnel performing water sampling must be familiar with sampling techniques, safety procedures, proper handling, and record keeping. Samplers are responsible for attending refresher meetings held before the onset of each experiment to review procedures and techniques. Students will be trained well before the beginning of the sampling. For example, Ms. Hanyan Li is a senior PhD student and has been working on the Utal Lake water quality research for the past 3 years. She is well trained in field sampling, collection of sediment and water samples. Students will be required to document everything related to the project in their laboratory/field notebook. For laboratory related analysis work, students will be trained to run the required analytical machines (such as IC machine) independently with known standards prepared in the lab.

Appendix B- Raw Data- This will be uploaded in Ubox – an online repository.

Appendix C: Field Pictures: These were provided to the UDWQ. However, these will be uploaded in Ubox – an online repository.