



Brigham Young University
BYU ScholarsArchive

Theses and Dissertations

2020-08-10

Dynamics of Internal Phosphorus Cycling in a Highly Eutrophic, Shallow, Fresh Water Lake in Utah Lake State Park, Utah, USA

Sheena Marie Smithson

Follow this and additional works at: <https://scholarsarchive.byu.edu/etd>

 Part of the Physical Sciences and Mathematics Commons

Dynamics of Internal Phosphorus Cycling in a Highly Eutrophic,
Shallow, Fresh Water Lake in Utah Lake State Park, Utah, USA

Sheena M. Smithson

A thesis submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of

Master of Science

Gregory T. Carling, Chair
Barry R. Bickmore
Stephen T. Nelson
Zachary Aanderud

Department of Geological Sciences

Brigham Young University

Copyright © 2020 Sheena M. Smithson

All Rights Reserved

ABSTRACT

Dynamics of Internal Phosphorus Cycling in a Highly Eutrophic, Shallow, Fresh Water Lake in Utah Lake State Park, Utah, USA

Sheena M. Smithson
Department of Geological Sciences, BYU
Master of Science

Eutrophication is an increasing global concern as human effluent saturates lakes with an over abundance of nutrients. Phosphorus, generally being the limiting nutrient, is often the most impactful, allowing cyanobacteria populations to grow out of control leading to harmful blooms that can produce cyanotoxins, anoxic lake conditions, and mass fish kills. Utah Lake, a shallow highly eutrophic fresh water lake located in central Utah Valley, has experienced these harmful algal blooms for the last several years.

The internal phosphorus cycle is a significant driver in Utah Lake's eutrophication, as the sediments act as both a sink and a source for phosphorus. Most of the phosphorus originates from external sources, gets captured by the sediment, and then through several physiochemical and biological process, gets released back into the surface water as a self sustaining eutrophication system.

To determine the effects of the different physiochemical processes that drive the internal phosphorus system, we incubated 72 total sediment cores taken from two locations, chosen to best represent the lake's chemical and spatial variability, under aerobic, anaerobic, pH=9.5 and pH=7 conditions with various P concentrations (ambient, 0.5X, 2X, 4X) taking water samples at 0, 12, 24, and 72 hours. Dissolved oxygen (DO), pH, soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), and other major ions were measured for each sample. The highest P sediment release occurred under aerobic conditions, while the highest P sediment uptake occurred under anaerobic conditions. While pH did appear to have a mild effect on P flux, our study showed the lake has a remarkably stable bicarbonate buffer system making it unlikely that pH would contribute significantly under natural settings. Under all conditions the 2X and 4X cores experienced the highest P uptake, but final elevated P concentrations were still higher than initial ambient concentrations, indicating a probable delayed recovery time after external reductions occur.

Keywords: eutrophication, internal phosphorus cycle, aerobic, anaerobic, soluble reactive phosphorus, bicarbonate buffer system

TABLE OF CONTENTS

TITLE PAGE	i
ABSTRACT.....	ii
TABLE OF CONTENTS.....	iii
LIST OF FIGURES	v
LIST OF TABLES.....	vi
1. Introduction.....	1
2. Methods.....	2
2.1 Study Area	2
2.2 Background Chemical Analysis.....	3
2.2.1 Sample Collection.....	3
2.2.2 Sediment and Water Analysis.....	4
2.3 Sediment-Water Nutrient Interaction Experiments	5
2.3.1 Core Collection	5
2.3.2 Experimental Set-up.....	6
2.3.3 Aerobic and Anaerobic Experiments	6
2.3.4 pH Experiments	7
2.4 Data Analysis.....	8
3. Results.....	8
3.1 Background Chemical Analysis.....	8
3.1.2 Sediment and Water Chemical Analysis.....	9
3.2 Sediment-Water Nutrient Interaction Experiment Results	10
3.2.1 Phosphorus Dynamics Under Aerobic Conditions	10
3.2.3 Phosphorus Dynamics Under pH=9.5 and pH=7 Conditions	12
3.3 Relative Change of Major Ions with Phosphorus	13
4. Discussion	14
4.1 Spatial Variability of Phosphorus in Utah Lake	14
4.2 Phosphorus Dynamics Under Different Environmental Conditions.....	15
4.3 Phosphorus Flux.....	16
5. Conclusions.....	17
References.....	19

Figures.....	24
Tables	34

LIST OF FIGURES

Figure 1: Utah Lake map. Site Location.....	24
Figure 2: Model of incubated core.....	25
Figure 3: XRD results.....	26
Figure 4: Total Phosphorus by Total Digestion.....	27
Figure 5: TDP in surface and pore water measured by ICP-OES.....	28
Figure 6: Dissolved Phosphate in surface water measured by IC.....	29
Figure 7: Eh-pH diagrams.....	29
Figure 8: Solubility diagram for Calcite	30
Figure 9: The change over time and trend of change of TDP for pH = 9.5, aerobic, and anaerobic conditions.....	31
Figure 10: The change over time of SRP	32
Figure 11: The change over time and trend of TDP for pH = 7	33

LIST OF TABLES

Table 1: Calcium sink concurrent with P sink in anaerobic and alkaline conditions	34
Table 2: Flux calculations for P	35

1. Introduction

Excessive nutrient loading into freshwater lakes has caused increased eutrophication, and led to substantial phosphorus (P) storage in lake sediments. This enrichment of P in lake sediments has contributed to a rise in harmful algal blooms (HABs) (Correll, 1990). Some of these algal blooms contain harmful cyanobacteria. Cyanobacteria can produce toxins that have adverse effects on humans and animals (Christoffersen and Kaas, 2000). This has led to a growing public concern over lake eutrophication.

In an effort to mitigate eutrophication, limitations on external P-loading from waste water treatment plants (WWTPs) have been proposed. However, there have been several instances in which reductions in external P loading have had little to no decrease in total P throughout lakes (Kapanen 2012). This is because, in most lakes, sediments act as both a sink and source for P (Bostrom et al. 1988). While the P bound in sediments is not readily bioavailable (Lai and Lam 2008), certain sediment and water physiochemical properties cause a gradual release of P at the sediment-water interface (Richardson, 1985). This allows for an excessive production of algae and cyanobacteria. The high reproduction and respiration rates of these autotrophic organisms, if left unchecked, can lead to anoxic conditions. Lake anoxia promotes the release of more sediment bound P which further enriches the lake and reinforces eutrophication (Correll, 1999).

Several mechanisms contribute to the internal release of P at the sediment-water interface. Physical mechanisms such as re-suspension of sediment (i.e. wave action, boat propellers, or bottom dwelling fish) can be a significant driver of internal P release in shallow lakes (Søndergaard et al. 2013). The various chemical mechanisms that can drive internal P release are temperature, dissolved oxygen (DO), and pH level (Moore et al. 1998). Biological mechanisms,

such as bacteria that can produce organic acids able to dissolve mineral phosphate, can contribute to internal P release as well (Jansson et al. 1988). Because of these internal P release mechanisms, the delayed lake recovery could take between 10-15 years (Jeppesen et al. 2005).

Utah Lake is among the eutrophic lakes whose sediment chemistry provides for a strong internal P cycle. To understand what environmental conditions drive the internal P cycle, we first completed a comprehensive chemical analysis of the lake, followed by sediment core incubation experiments that measured the effects of time, dissolved oxygen (DO), and pH on P release. It is necessary to understand how each of these parameters influence P release before an effective remediation strategy can be developed for the lake.

2. Methods

2.1 Study Area

Utah Lake is a shallow, freshwater eutrophic lake located in north-central Utah Valley (Figure 1). It is the largest natural freshwater lake in Utah, with a surface area of ~375 square kilometers. Utah Lake has an average depth of 2.7-3 meters, with Provo Bay being the shallowest region (PSOMAS, 2007). Three mountain ranges surround the valley, the Wasatch Range to the east, the Traverse Range to the north, and the Lake Mountains to the west.

Snowmelt from the Wasatch and Uinta mountain ranges is the primary water source for Utah Lake. The Spanish Fork, Provo, and American Fork Rivers provide most of Utah Lakes water inflow, with an average inflow of 888.1 million cubic meters/year (Hooton 1989). Evaporation accounts for 42 percent of the lakes outflow (486.6 million cubic meters/year). The only outlet for the lake, Jordan River, flows into the south end of the Great Salt Lake and contributes, on average, 426.6 million cubic meters/year of outflow (Hooton 1989).

Between the mountains and the lake is the expanding Utah County metropolitan area. Utah County has a population of more than 600,000 as of 2017, and is continually experiencing rapid population growth with an estimated 2.4% increase per year (US Census Bureau, 2019). The highly urbanized county contributes a vast amount of anthropogenic nutrient sources into the lake. Located on the east side of the lake are inlets to seven waste water treatment plants (WWTPs), three of which are located around Provo Bay. The lake serves as a popular boating and fishing destination for many, as well as an irrigation source for farms along the southern end.

In the past several years, Utah lake has been closed to recreation or put under an advisory due to HABs. The HABs pose risk to businesses that depend on the lake, animals for whom the lake is a vital water source, and the lake's own ecosystem. In response, the Utah Division of Water Quality has initiated the Utah Lake Water Quality Study (ULWQS) to develop a comprehensive understanding of the lakes water and sediment chemistry, nutrient cycling, and the effect of excess nutrients from human effluent. The results from this study will be used to develop criteria and legislation to further regulate the amount of external P loading into the lake.

2.2 Background Chemical Analysis

To acquire a comprehensive chemical understanding of Utah Lake, we sampled and analyzed surface water, sediment, and pore water from twelve sites, chosen to best represent spatial and temporal variability across the lake (Figure 1). Sample collection occurred three times in (July-2018, August-2018, and October-2018). A complete chemical analysis of the lake allowed us to choose the locations and the parameters best suited for our sediment core experiments.

2.2.1 Sample Collection

At each of the twelve sampling sites across Utah Lake, we collected the first 12 cm of sediment using a stainless-steel core catcher and stored them in a 3.8 liter Ziploc bag. We stored the

surface water samples collected at each site in a 1 L container. All samples were kept cool and dark to limit microbial activity until transported back to the lab. We measured water temperature, barometric pressure, DO, pH, and ORP in-situ at each sample location using a YSI multi-meter water probe.

Upon returning to the lab we filtered and prepped surface and pore water samples for analysis by ion chromatography (IC) and inductively coupled plasma – optical emission spectrometry (ICP-OES). Samples prepped for ICP-OES were acidified to 2% HNO₃. Water and sediment samples were stored at 4°C until analysis.

2.2.2 Sediment and Water Analysis

Surface and pore water samples were analyzed by ICP-OES and IC to determine total dissolved phosphorus (TDP) content. Total phosphorus (TP) in sediments was measured by total digestion with EPA method 3052. Major element concentrations of lake sediments was determined by X-ray fluorescence (XRF). X-ray diffraction (XRD) was used to determine the mineralogy of sediments. Geochemist Workbench was used to create Eh-pH and solubility diagrams to analyze the change of mineral precipitation relative to P.

Water samples were prepped for ICP-OES by a 2% HNO₃ acidification. To prepare for sediment analysis, all 36 sediment samples were dried for 3 days at 60°C. Dried sediments were then powdered with a ceramic mortar and pestle. Organic matter and carbonate content were measured by combustion at 550°C and then at 1000°C respectively for 6 fh in a Lindberg Blue M muffle furnace. For XRF analysis preparation, the calcined powder was dissolved into homogenous glass disks using a Katanax K1 Prime. The prepared glass disks were analyzed for major element oxide concentrations (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O,

and P₂O₅) using a Rigaku ZSX Primus II XRF spectrometer. The dried (non-calcined) powdered samples were analyzed with a Rigaku MiniFlex 600 XRD to determine mineralogy. Rietveld analysis was conducted using the Rigaku PDXL2 to estimate mineral abundances from patterns obtained using a Rigaku MiniFlex 600 and Cu radiation. TP in sediments was also evaluated by total digestion (EPA method 3050).

2.3 Sediment-Water Nutrient Interaction Experiments

To understand the internal mechanisms behind nutrient cycling in Utah Lake, we performed in-lab experiments using complete sediment cores taken from two locations in Utah Lake (Figure 1). Under controlled conditions we measured the role that time, DO, and pH play in the release and capture of nutrients at the sediment-water interface.

2.3.1 Core Collection

Sediment cores were collected from a DWQ site in the middle of Provo Bay, and from a site in the open water of the lake near the Utah Lake State Park water quality buoy (Figure 1). There were a total of 72 sediment cores collected over 6 collection trips, 3 of which were to the Provo Bay location, and 3 to the Buoy location. 12 sediment cores were taken during each collection trip.

A percussion corer was used to collect sediment cores in 5 cm diameter, 50 cm long plexiglass tubes. Each Sediment core was collected with ~10 cm of sediment and ~30 cm of over-lying water (Figure 2). Each core was capped, taped, covered, and stored upright in a cooler to prevent sediment disturbance and microbial activity. We also collected 2 gallons of surface water at the coring site for each collection trip to be used as replacement water for each experiment.

2.3.2 Experimental Set-up

To measure the effect of each parameter on P release in Utah lake, we used twelve sediment cores taken from the Buoy location, and twelve taken from the Provo Bay location with varying P concentrations (ambient, 0.5X, 2X, and 4X) under the effects of aerobic, anaerobic, high pH and low pH conditions.

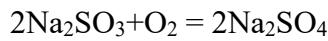
Each experiment followed the same procedure, except for the alteration of each measured variable. In each core, the initial overlaying water was syphoned out and replaced with water spiked at different P concentrations of 0 (control/ambient), 0.5X (by dilution using major ion water devoid of P), 2X, and 4X the ambient P concentration using a 1000 mg-P/L KH₂PO₄ stock solution in three sets of triplicated sediment cores. Each core was capped to prevent cross contamination by dust and other air particulates, wrapped in aluminum foil to prevent light exposure and limit microbial activity, and mounted on a wooden stand to prevent sediment disturbance.

2.3.3 Aerobic and Anaerobic Experiments

Experiments under aerobic conditions (7.5 mg/L DO) were maintained by purging air intermittently at 2 hour intervals through the water column using a small aeration stone placed in each core approximately 5-cm from the sediment-water interface. The 2 hour intervals were regulated with an electronic timer and a solenoid valve, this was to ensure the DO was maintained above 7.5 mg/L and that water conditions remain turbid. At t=0, 12, 24, and 72 hours, pH and DO measurements were taken and 50 mL of sample was extracted from each core using a disposable 50-mL plastic pipette, followed by immediate filtration (0.45 um nylon). Each sample was divided into four falcon tubes at 10-15 mL each and prepped for ICP-OES (2% HNO₃ acidification), IC, soluble reactive phosphorus (SRP), and Ammonium analysis. All

samples were stored at 4°C, except for the samples intended for SRP analysis which were frozen until analysis.

After the completion of the aerobic experiments, we subjected the same sediment cores to anaerobic conditions. The overlaying water from the aerobic experiments was syphoned out and replaced with surface water spiked to the appropriate P concentrations. To induce initial anaerobic conditions, we added 55 mg/L of a sodium sulfide solution containing trace amounts of cobalt chloride to remove oxygen.



Anaerobic conditions were maintained by continuous purging with pure nitrogen gas. The flowrate was kept high during sample collections and low in between. Water samples and pH and DO measurements were collected and analyzed using the same process detailed previously for the aerobic experiments.

2.3.4 pH Experiments

Using entirely new sediment cores, we measured the effects of high (9.5) and low (7) pH. The sediment cores were processed using the same procedure detailed in section 2.3.3 for aerobic and anaerobic experiments. The sediment cores were kept under aerobic conditions during incubation using the same strategy used for the aerobic experiments. Sediment core Incubation at high pH was conducted for both sampling locations, while incubation at low pH was only conducted for the Buoy site.

To achieve high pH conditions, 1 N NaOH solution was added to the filtered surface water before pouring into each core. Due to the lakes strong bicarbonate system and immense buffering capacity, NaOH had to be intermittently added to each column to maintain a pH of 9.5.

Low pH conditions were induced by adding 1 N H₂SO₄ solution to the filtered surface water of each core. Incubation at pH = 7 was maintained by intermittently adding the H₂SO₄ solution to each core. Water samples and pH and DO measurements were collected and analyzed using the same procedure detailed for the aerobic experiments.

2.4 Data Analysis

Nutrient flux (rate of sediment release or uptake) was calculated to observe P change as a product of water-sediment interactions. The equation used, per Hogsett et al. (2019), is as follows: flux values equal water column depth (d, m) times the slope of P concentration with changing time (dC/dt, g/m³ m³/d). The positive values indicate P release while the negative values indicate retention.

The change in nutrient concentrations during each sampling period was also measured. The following equation was used:

$$\text{Concentration change (mg/L)} = \text{final concentrations (mg/L)} - \text{initial concentrations (mg/L)}$$

For example, the concentrations change between 0 and 12 hours is calculated as final concentrations of 12 hour – initial concentrations of 0 hour.

3. Results

3.1 Background Chemical Analysis

Due to distinct differences in sediment chemistry and phosphorus concentrations between Provo Bay, Lindon Marina, and the rest of the lake, we have designated the Provo Bay and Lindon Marina samples as “east shore” and the rest of the lake as “open water” (Figure 1).

3.1.2 Sediment and Water Chemical Analysis

Sediment mineralogy, as determined through XRD, consists mostly of calcite, quartz, and dolomite. The mineralogy of the Lindon Marina and open water samples is very similar, while the mineralogy of the Provo Bay samples differed slightly in calcite and quartz content (Figure 3 A-C). Calcite was the dominate mineral in the Open Water and Lindon Marina samples averaging a mass percent of 77% and 85% respectively. The dominant mineral in the Provo Bay samples was quartz (51.6% average mass percent), with calcite having an average mass percent of 42% and dolomite averaging 6.6%. The quartz and dolomite mass percent averages for the open water and Lindon Marina samples were 14.4% quartz and 8.3% dolomite, and 12.1% quartz and 2.5% dolomite, respectively.

Major element concentrations of lake sediments, as measured by XRF, show that the sediment is dominated by SiO₂ and CaO. Just as the XRD results showed a distinction between the open water and Lindon Marina sediments and the Provo Bay sediments, the same distinction is seen in the XRF results (Figure 3 D-F). In the Open Water and Lindon Marina samples, the sediment samples are primarily composed of CaO (\approx 51% CaO and \approx 34% SiO₂), whereas in the Provo Bay samples, the sediment contains more SiO₂ than CaO (\approx 29% CaO and \approx 56% SiO₂).

For TP by total digestion, the east shore samples show a higher concentration with a maximum value of 1109 ppm. The distinction between TP measured by digestion in the open water and the east shore sediment samples is less prominent. However, the east shore samples have a greater variation in TP than the open water samples (Figure 4).

TDP is consistently higher in the east shore than in the open water samples (Figure 5). TDP measured in pore water for the East Shore samples had an average TDP of 0.66 mg/L and an average TDP of 0.34 mg/L for Open Water samples. TDP in surface water, as determined by

ICP-OES, is also higher in the East Shore samples (average \approx 0.22 mg/L) than in the Open Water samples (average \approx 0.038 mg/L). No data is available for surface water TDP by IC because it fell below the detection limit for the Open Water and East Shore samples.

The solubility and Eh-pH diagrams created through Geochemist workbench (Figure 7 and 8 respectively) show the conditions required to get the precipitation or dissolution of minerals bound with P and the speciation at which they occur. The Eh-pH diagram in Figure 7B shows the high speciation of P with Ca under the lake's natural pH of \sim 8.5, and the solubility diagram (Figure 8) represents the pH and concentrations at which Ca^{2+} will precipitate out of the water column. As the pH increases towards 10 the precipitation of Calcite increases significantly, likely binding with P, pulling them from the water column and trapping both in the sediments.

3.2 Sediment-Water Nutrient Interaction Experiment Results

The effects of aerobic, anaerobic, high pH and low pH conditions were measured using intact sediment cores taken from two locations in Utah lake designated as "Provo Bay" and "Buoy" (Figure 1).

3.2.1 Phosphorus Dynamics Under Aerobic Conditions

Under aerobic conditions, both the Provo Bay and Buoy sites showed similar trends of P release or retention, with the only notable difference being the overall higher initial TDP and SRP concentrations in Provo Bay. Though overall SRP concentrations were higher for Provo Bay, it accounted for 21% less of the TDP on average than at the Buoy site (49%).

During aerobic incubation, DO was maintained at approximately 7.5 mg/L, and pH 8.5 ± 0.2 . The ambient and 0.5X cores experienced the highest P release from sediments, with the 0.5X cores showing the highest increase in TDP concentrations over time. In contrast, TDP

concentrations tended to decrease over time in the 2X and 4X spiked cores, with the greatest P uptake seen in the 4X cores.

For the Provo Bay site, TDP concentrations increased from 0.40-0.51 mg/L to 0.38-0.56 mg/L in the water column under ambient conditions, and from 0.40-0.53 mg/L to 0.48-0.88 mg/L in the 0.5X cores from 0-72 hours. Conversely, TDP concentrations were found to decrease over time in the 2X cores, from 0.71-1.14 mg/L to 0.48-1.30 mg/L, and 4X cores, from 1.24-1.48 mg/L to 0.80-1.64 mg/L. Despite the decrease of TDP over time in the 2X and 4X cores, final concentrations (0.48-1.30 mg/L and 0.80-1.64 mg/L respectively) were still higher than initial ambient concentrations (0.40-0.53 mg/L), indicating that the increased TDP in the water column was not completely lost to the sediments of the Provo Bay site (Figure 9A-B) (p value = 0.0055)

For the Buoy site, the ambient and 0.5X cores follow a similar trend in TDP release over time with concentrations increasing from 0.05-0.06 mg/L to 0.09-0.12 mg/L and from 0.05-0.08 mg/L to 0.12-0.14 mg/L respectively. Unlike Provo Bay, the Buoy 2X and 4X cores experienced the highest TDP release between 12-24 hours, with TDP concentrations returning close to initial (0 hour) values by 72 hours (Figure 9G-H).

Generally, SRP also observed a tendency to decrease at 2X and 4X spiked, but at smaller quantities than TDP (Figure 10B) for the Buoy site. Figures 9 and 10 provides an overview of the relative changes in TDP and SRP concentrations.

3.2.2 Phosphorus Dynamics Under Anaerobic Conditions

Under anaerobic conditions, TDP concentrations decreased in the water column in cores from both the Provo Bay and Buoy sites over 72 hours (Figures 9C-D & 9I-J). SRP trended similarly to TDP, decreasing over time with the 2X and 4X generally experiencing a more substantial loss

(Figures 10C-D). A considerable decrease in Ca^{2+} , as well as a steady increase in pH (from 8.5 to 10) was observed to occur in every core over the 72-hour anaerobic incubation period (Table 1).

For the Provo Bay site, a significant loss of TDP occurred in nearly all cores (Figures 9C-D).

The 0.5X cores experienced the least amount of TDP loss with concentrations decreasing from 0.21-0.30 mg/L to 0.18-0.25 mg/L, compared to the average 0.40 mg/L P loss in all other cores (p value = 4.59244E-05). For the Buoy site, the cores experienced a similar, though less substantial, decrease in TDP (Figure 9I-J). Concentrations decreased from 0.06-0.1 mg/L to 0.05-0.08 mg/L in the ambient cores, and from 0.07-0.08 mg/L to 0.06 mg/L in the 0.5X cores. The 2X and 4X cores experienced a slightly larger TDP decrease over time, from 0.20-0.32 mg/L to 0.09-0.22 mg/L, and from 0.13-0.16 mg/L to 0.10-0.17 mg/L respectively.

3.2.3 Phosphorus Dynamics Under pH=9.5 and pH=7 Conditions

During incubation at both pH=9.5 and pH=7, DO was maintained around 7.5 mg/L. At both pH = 9.5 and pH = 7.0, the lake's buffering system decreased (when adjusted to high pH) or increased (when adjusted to low pH) pH towards the initial values of 8.5 ± 0.2 . Continuous addition of acid or base was required to maintain the targeted pH.

At the Buoy site, the cores under pH=7 incubation had overall higher TDP concentrations (0.09 - 0.53 mg/L) relative to those under pH=9.5 incubation (0.02-0.13 mg/L) (3.62842E-18). Similar trends, however, were observed for both in which TDP concentrations increased in the ambient and 0.5X cores, remained relatively consistent in the 2X cores, and decreased in the 4X cores over time (Figures 9K-L & 11A-B). SRP concentrations trended similarly to TDP concentrations (Figure 10F).

For the Provo Bay site, only pH=9.5 incubation was conducted. TDP and SRP concentrations trended similarly over time, remaining relatively consistent throughout the experiment (Figures 9E-F & 10E). The 4X cores experienced a brief TDP increase between 12-24 hrs (0.36-0.53), before returning to initial concentrations.

3.3 Relative Change of Major Ions with Phosphorus

To investigate the dynamic of some major ions relative to P in the water column, their concentrations were compared for each treatment. Generally, the concentration of dissolved Mg²⁺ observed a slight hike in the 0.5X cores under all conditions. The increased concentration of Mg²⁺, however, is not comparable to any trend in TDP change. Calcium tends to experience the most significant change over time, with sediment uptake occurring under the anaerobic (-49.04 to -14.14 mg/L) and pH=9.5 (-32.29 to -14.54 mg/L) conditions for both sites. The decrease in dissolved Ca²⁺ trends with decrease in TDP under the same conditions (Table 1).

3.4 Phosphorus Flux from Sediment Under Different Conditions

The different environmental conditions (aerobic, anaerobic, pH=7 and pH=9.5) and spiked concentrations (ambient, 0.5X, 2X, and 4X) showed to have a significant effect on P release/retention in the sediments. Using the nutrient flux method per Hogsett et al., P flux to/from the sediment was calculated (Table 2). Phosphorus flux trended consistent with the dynamics of ambient TDP concentrations. Phosphorus uptake was observed in the 2X and 4X cores, and P release was observed in the ambient and 0.5X cores. Cores under aerobic and pH=7 conditions experienced the highest P release, while the highest P retention occurred in the cores under anaerobic and pH=9.5 conditions.

Provo Bay experienced a higher release/uptake flux (-51.84 to 201.6 mg/m²/d) than the buoy site (-5.76 to 5.76 mg/m²/d) (p value = 1.2739E-18). The highest release flux occurred in the Provo Bay aerobic 0.5X cores (201.6 mg/m²/d), and the highest uptake flux occurred in the Provo Bay anaerobic 4X cores (-51.84 mg/m²/d). Anaerobic conditions provided for significantly more P uptake (-51.84 to 1.44 mg/m²/d) than the aerobic conditions (-13.68 to 201.6 mg/m²/d) (p value = 5.22507E-10). Cores incubated under pH=7 conditions demonstrated a high P release potential, with the highest release observed in the Buoy pH=7 0.5X core. Across all experiments, P release was most significant in the 0.5X cores (-7.2 to 201.6 mg/m²/d) and P uptake was most significant in the 4X cores (p value = 4.95065E-12).

4. Discussion

4.1 Spatial Variability of Phosphorus in Utah Lake

The highest concentrations of TP were generally measured in Provo Bay. A likely cause for the heightened TP in this area is that Provo Bay receives more external P loading than anywhere else in the lake. Two wastewater treatment plants (WWTP) have effluent inlets on the east side, and the south side is dominated by several miles of agricultural land. The site with the second highest on average TDP concentrations, near Lindon Marina, also neighbors a WWTP inlet.

In addition to having an overall higher concentration of TP, Provo Bay also exhibited the most dissimilarity in mineralogy. Utah Lake's overall mineralogy primarily consists of calcite, quartz, and dolomite. The dominant mineral in Provo Bay is quartz, compared calcite in the rest of the lake. While a strong correlation exists between areas with high TP and inlets for WWTPs, how far the P gets and how long it remains, is dependent on the dynamics of the sediment-water interface.

4.2 Phosphorus Dynamics Under Different Environmental Conditions

The cores taken from Provo Bay generally experienced the most dramatic P release/uptake flux under all conditions. This is likely due to the Buoy site generally having lower initial P concentrations. Despite having overall higher initial values, SRP accounted for 21% less of the TDP in Provo Bay than at the Buoy site. The probable cause of this is a more significant algal population in Provo Bay, as SRP primarily consists of inorganic orthophosphate, the form of P directly taken up by algae.

Under aerobic conditions, P tended to increase in the ambient and 0.5X cores, and decrease in the 2X and 4X cores for both sites from 0-72 hrs. Despite the decrease over time in the 2X and 4X cores, final concentrations were still higher than initial ambient concentrations, indicating that the increased TDP in the water column did not completely lost to the sediments. The change in TDP concentrations was probably due to a state of dynamic equilibrium between particulate and soluble phases of P, in which TDP increased or decreased in the water column until an equilibrium was met (Jenkins, 2005).

The most significant P uptake was observed in the cores subjected to anaerobic conditions. Both sites experienced a decrease in TDP over time for every core (ambient, 0.5X, 2X, and 4X). This was unexpected, however, because generally, soluble P is released under anaerobic conditions (Bates et al., 1980) as redox-sensitive Fe^{3+} - and Al^{3+} -bound P becomes subject to mobilization or dissolution (Lai and Lam 2008). The trend of TDP decrease coincides with a decrease in Ca^{2+} and an increase in pH over time. Under anaerobic conditions, pH steadily increased until reaching a maximum of 10. At such a high pH, dissolved Ca is able to precipitate out of the water column, likely binding with P along the way (Figures 7B and 8). Redox conditions from anaerobic conditions alone should not cause such a significant change in pH. A possible cause

could be that the continuous purging of N₂ gas (used to maintain anaerobic conditions) in a closed system removed dissolved CO₂ from the water column, thus altering the bicarbonate buffering system. In future experiments, this issue may be solved by purging with a combination N₂ gas containing 5% CO₂.

Cores subjected to pH=7 and pH-9.5 conditions tended to increase or decrease pH back towards the lakes natural state (pH = 8.5). To maintain the desired pH conditions, a continuous addition of acid or base was required throughout the experiment. This can be attributed to the lakes strong bicarbonate buffer system. The cores incubated under pH=7 experienced a greater P release than those incubated under pH=9.5 conditions, as well as a more significant P release than observed for the aerobic conditions at the same site. This is likely the result of P speciated metal oxides or hydroxides becoming more soluble with decreased pH (Nguyen et al., 2016). Both pH=7 and pH=9.5 incubations, followed a similar trend where TDP increased in ambient and 0.5X cores, remained stable in 2X cores, and decreased in 4X cores. Similar to anaerobic incubation, Ca experienced sediment uptake under pH=9.5 conditions. It is likely due to the pH only being 9.5 that Ca and P uptake was less substantial, as the possibility of Ca-P dissolution was higher, than under anaerobic conditions.

4.3 Phosphorus Flux

P flux was consistent with the trends of measured concentrations under all conditions. Generally, the ambient and 0.5X cores experienced the highest P release, and the 2X and 4X cores experienced the highest P uptake. The more substantial P release and uptake that occurred in the Provo Bay compared to the Buoy cores can likely be attributed to Provo Bay's higher initial ambient concentrations. The measured concentration and calculated flux data show agreement in the sediments response to release or hold P based on the initial P concentrations in the water

column. Lower P concentrated water encourages the release of previously sediment bound P, and higher P concentrated water encourages sediment uptake of previously dissolved P. However, despite the sediments tendency to decrease surface water P concentrations at higher initial values, the overall P concentration remains higher than that observed under ambient conditions.

Given these observations, it is likely that Utah Lake will experience a delayed recovery response to decreased external P loading, as the sediments release previously bound P in an attempt to equilibrate with the surface water. The lake's overall P flux will likely increase following reduced loading. Previous studies suggest a delayed recovery time could be within 10-15 years after nutrient reduction (Jeppesen et al., 2005).

5. Conclusions

Understanding Utah Lakes internal P cycle is essential to formulate a remediation strategy that most effectively reduces lake eutrophication. The mobility and transformation of P determines the lake's rate of internal nutrient loading, and gives insight into the time of recovery that can be expected once external nutrient loading is reduced. Our sediment core incubation experiments suggest that while increasing P in the water column promotes increased P uptake into the sediments, the overall P concentrations remained higher than under ambient conditions. This indicates that a delayed recovery time can be expected in the lake after external P loading is reduced, as P release from sediments is increased in an attempt to reach equilibrium. The effects of pH and DO were shown to have an effect on the P flux. However, our study shows the lake to have a remarkably stable bicarbonate buffer system making it unlikely that pH would be able to naturally fluctuate significantly enough to be a contributing factor. More experiments on the effect of DO should be done in order to more substantially measure its effect on P-cycling.

Overall, a reduction of external P loading will be beneficial in reducing eutrophication in Utah Lake, though a delayed recovery time should be expected as legacy P depletes.

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.
- 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 Tolland, 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.
- Gao, Y., Cornwell, J.C., Stoecker, D.K., and Owens, M.S. (2012). Effects of cyanobacterial-driven pH increase on sediment nutrient 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, O₂ and loading influence. *Water Res.*, 33(10), 2437–2447, 1999.

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

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 sediments with different ratios of iron-bound P to calcium-bound P. *Chemical Speciation & Bioavailability*, 17(2), 55-61.

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 from 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.

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.

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 N₂O 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.

Figures

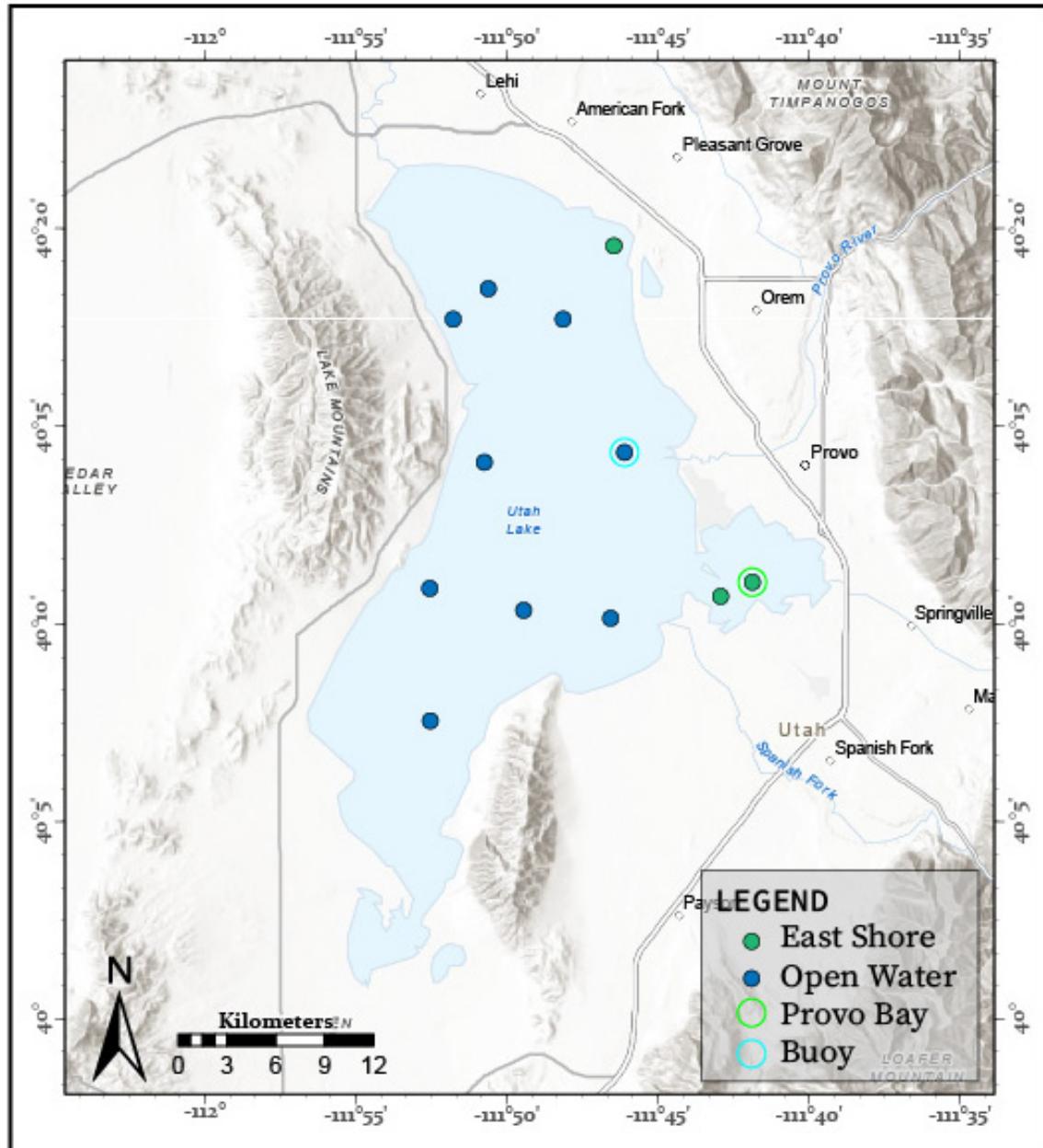


Figure 1: Utah Lake map. Site Location Solid circles represent sample locations for the background chemical analysis. Open circles represent the collection sites for the sediment cores used in the incubation experiments. Green represents “East Shore” which includes Provo Bay and Lindon Marina. Blue represents “Buoy” which includes the rest of the lake.

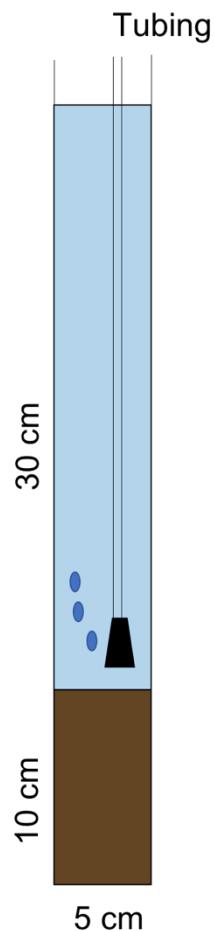


Figure 2: Model of incubated core. Each core had approximately 10 cm of sediment and 30 cm of water. Tubing for oxygen (aerobic) or nitrogen (anaerobic) was connected to an aeration stone and placed right above the sediment water interface to maintain desired oxygen and turbidity conditions.

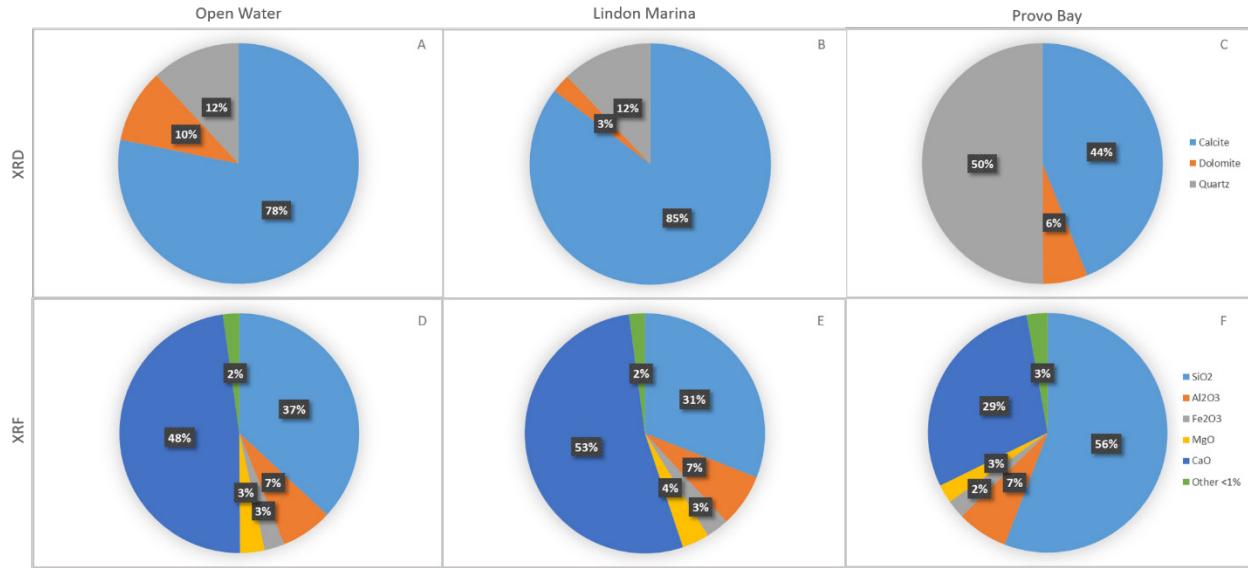


Figure 3: XRD results are presented in A-C and XRF results are presented in D-F for Open Water, Lindon Marina, and Provo Bay respectively. Open Water and Lindon Marina samples exhibit higher amounts of Ca composition than Provo Bay samples which is Si dominant.

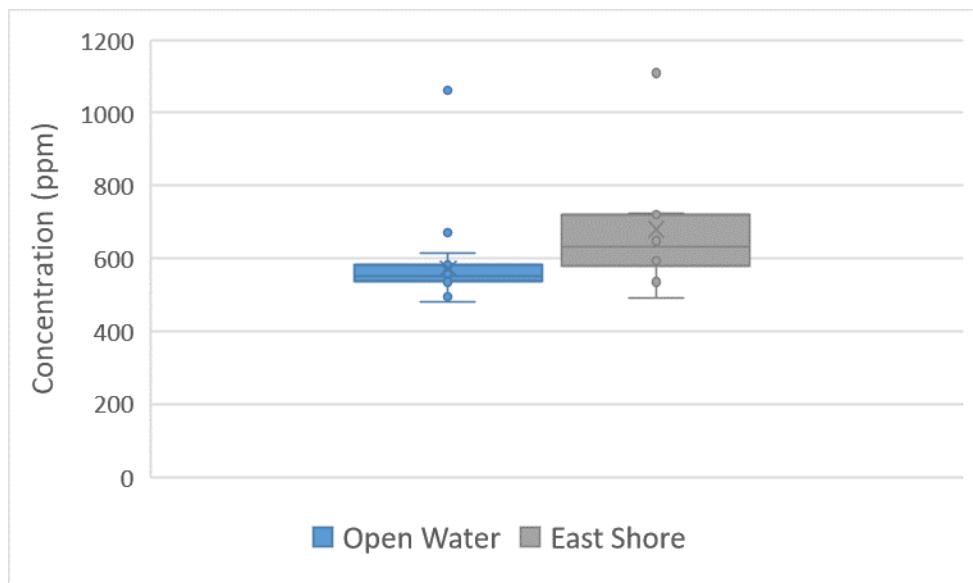


Figure 4: Total Phosphorus by Total Digestion. East Shore (Lindon Marina + Provo Bay) has higher amounts of sediment bound phosphorus than measured in the Open Water sediment samples (rest of lake).

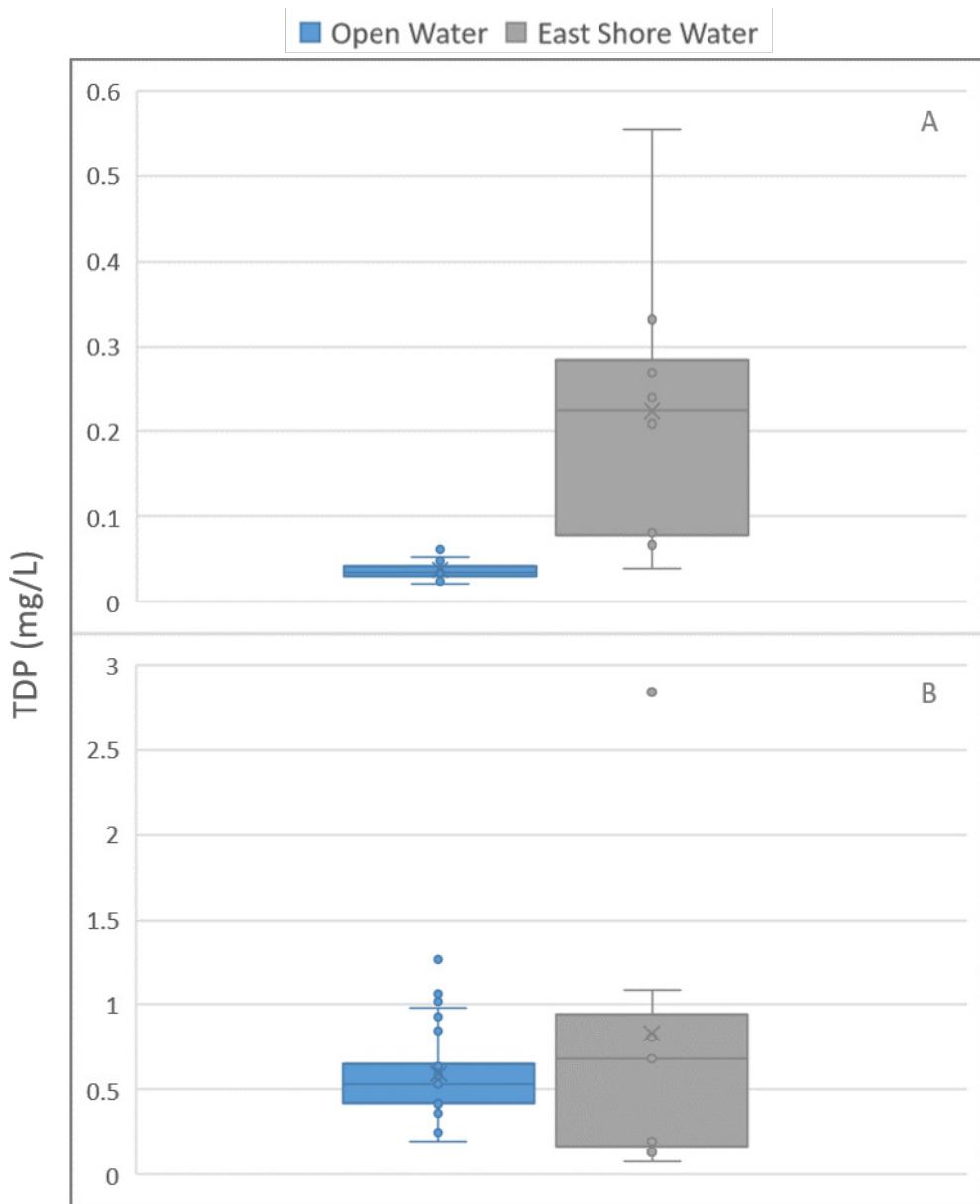


Figure 5: TDP in surface and pore water measured by ICP-OES. Surface Water measurements are represented in box plot A and pore water measurements are represented in box plot B. Both surface (A) and pore (B) water have higher TDP in the East Shore water samples (Lindon Marina + Provo Bay) than in the Open Water samples (rest of the lake).

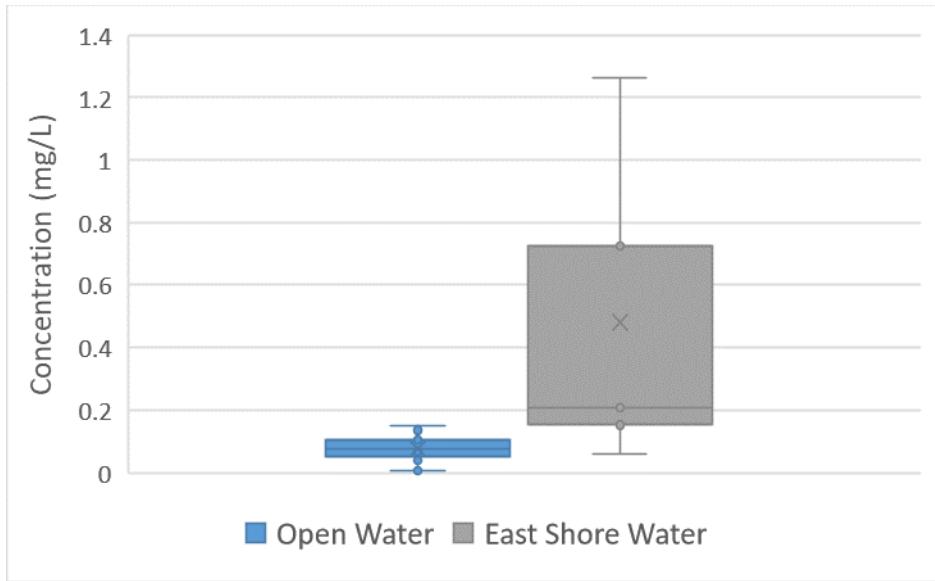


Figure 6: Dissolved Phosphate in surface water measured by IC. Surface water levels of dissolved phosphate are substantially higher in the East Shore Water (Provo Bay + Lindon Marina) than in the Open Water samples (rest of the lake).

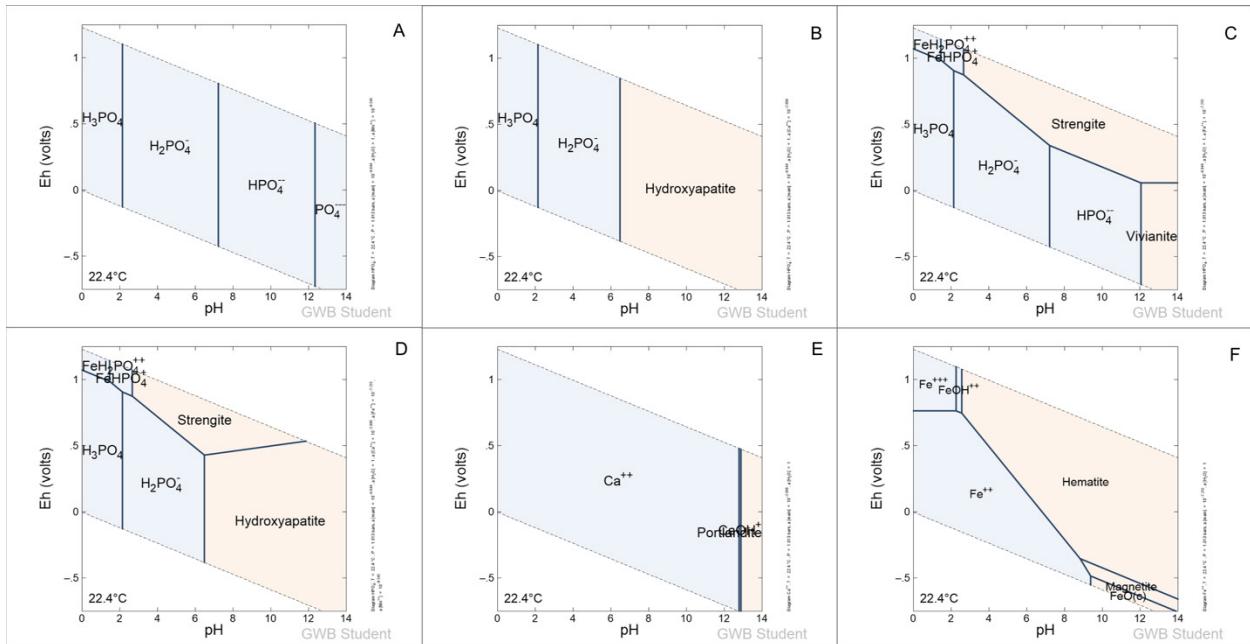


Figure 7: Eh-pH diagrams for P (A), P + Ca^{2+} (B), P + Fe^{2+} (C), P + Ca^{2+} + Fe^{2+} (D), Ca^{2+} (E), and Fe^{2+} (F). These diagrams provide a basis for the Eh-pH conditions required for speciation of common P binding minerals in Utah lake. Ca^{2+} has the strongest P speciation under the lake's natural pH of ~ 8.5 .

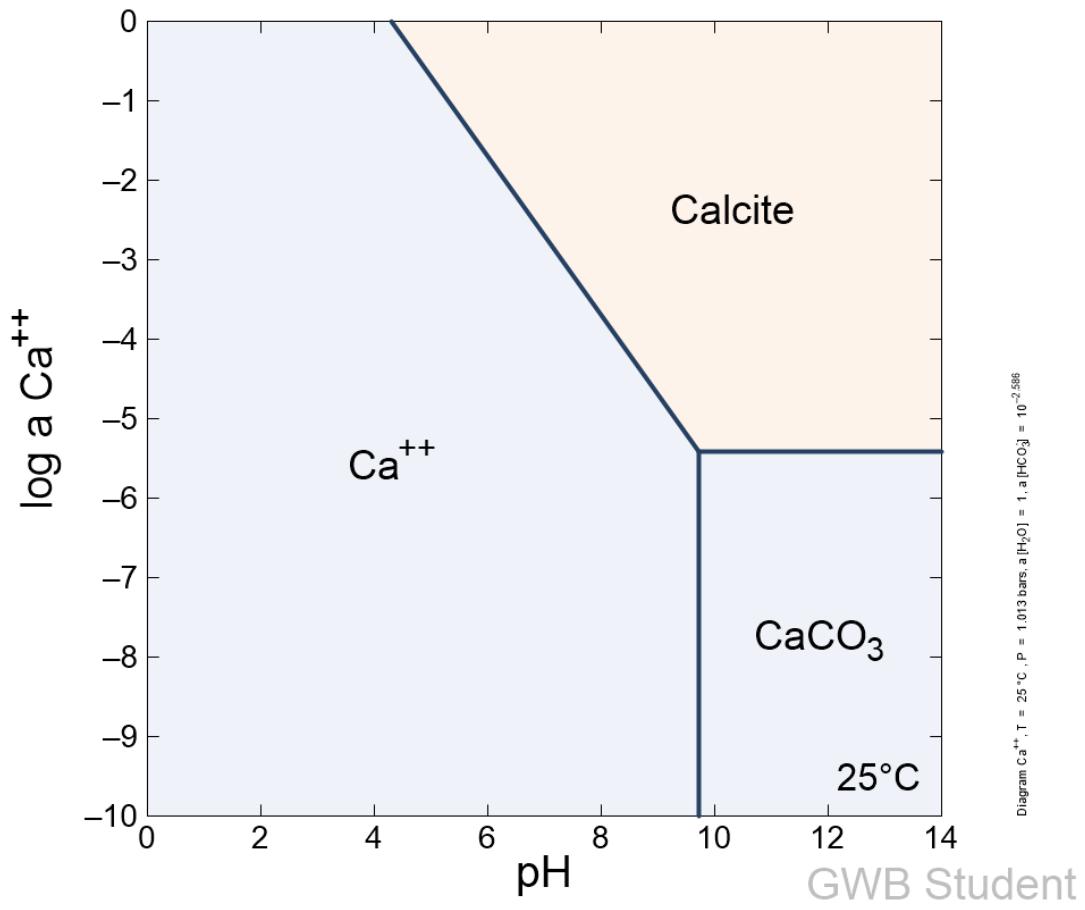


Figure 8: Solubility diagram for Calcite. As pH increases towards 10 from it's natural level of ~8.5, as it did in the anaerobic experiments, the precipitation of Calcite from the water column increases significantly.

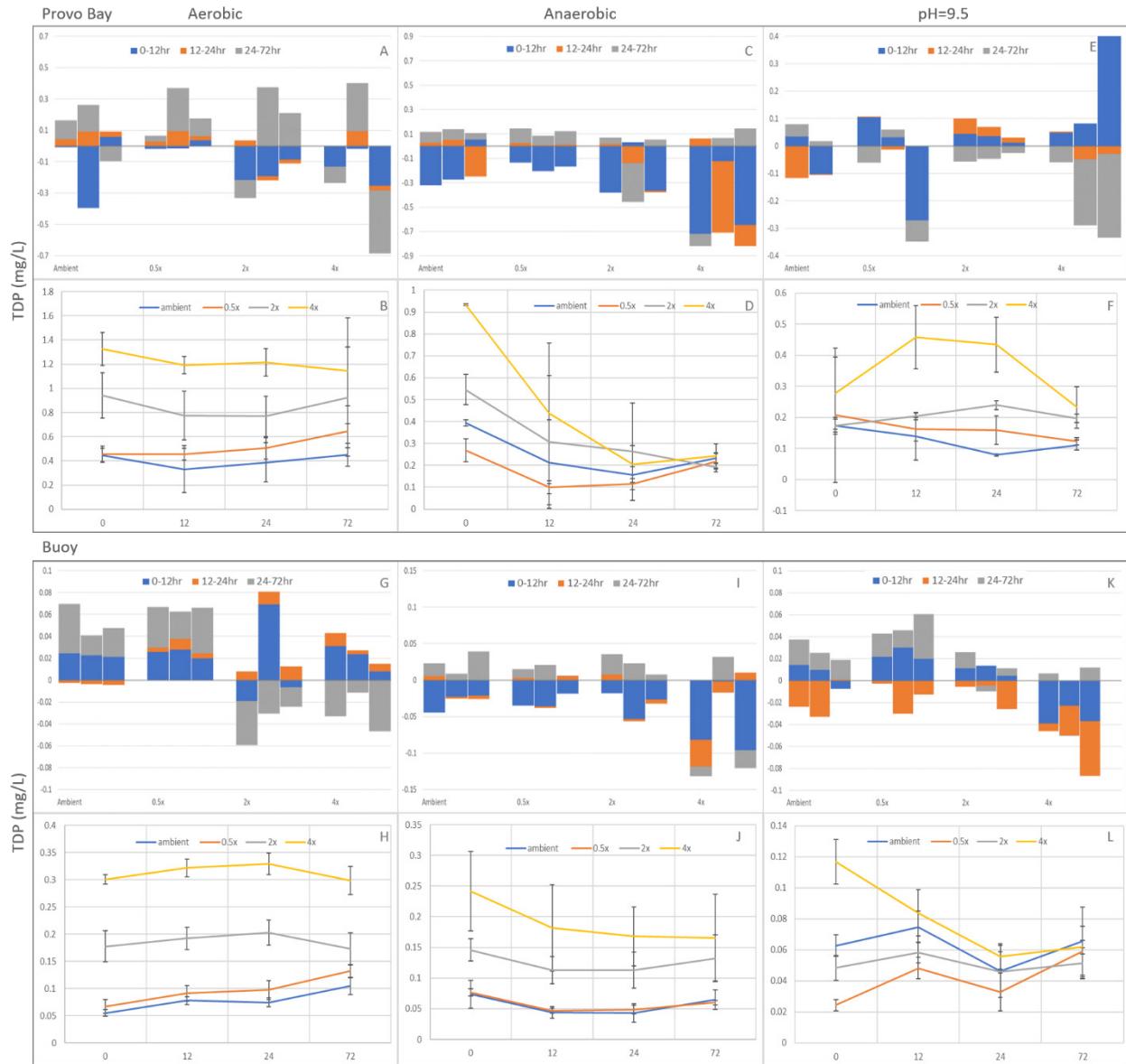


Figure 9: The change over time and trend of change of TDP was analyzed for each incubation condition (aerobic, anaerobic, pH=9.5) at each core collection site. For Provo Bay: A, C, and E represent the change over time of TDP under each incubation condition. B, D, and F represent their respective trends of change. For Buoy: TDP change over time is represented by G, I, and K, and their respective trends are represented in H, K, and L.

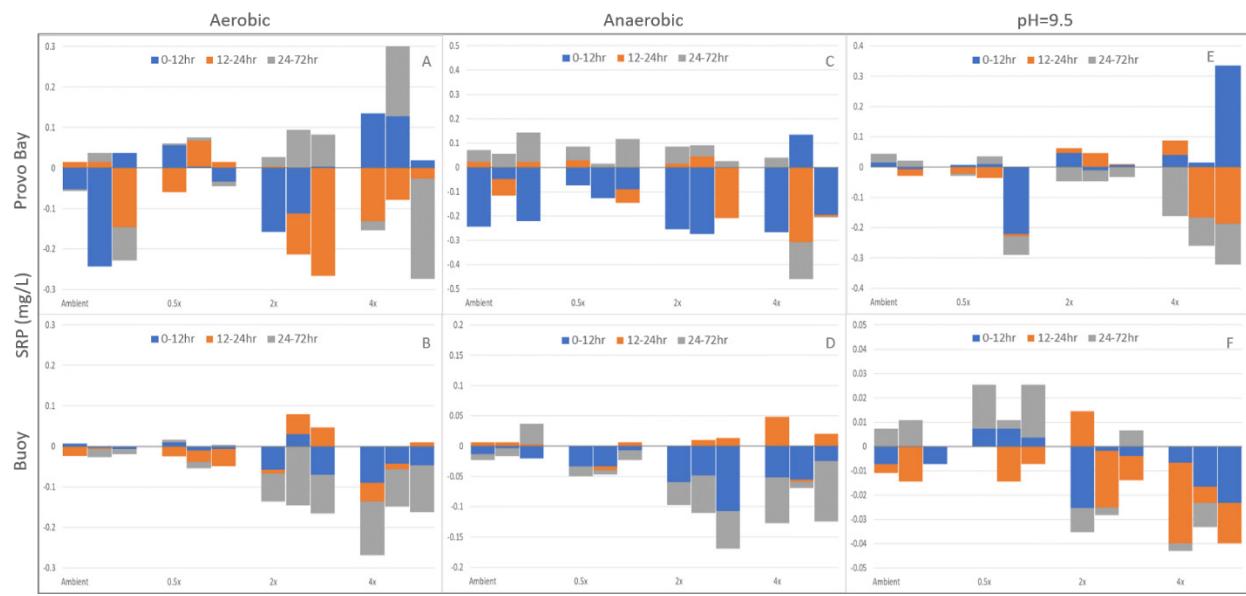


Figure 10: The change over time of SRP was analyzed for each incubation condition (aerobic, anaerobic, pH=9.5) at each core collection site. For Provo Bay: A, C, and E represent the change over time of SRP under each incubation condition. For Buoy: SRP change over time is represented by B, D, and F.

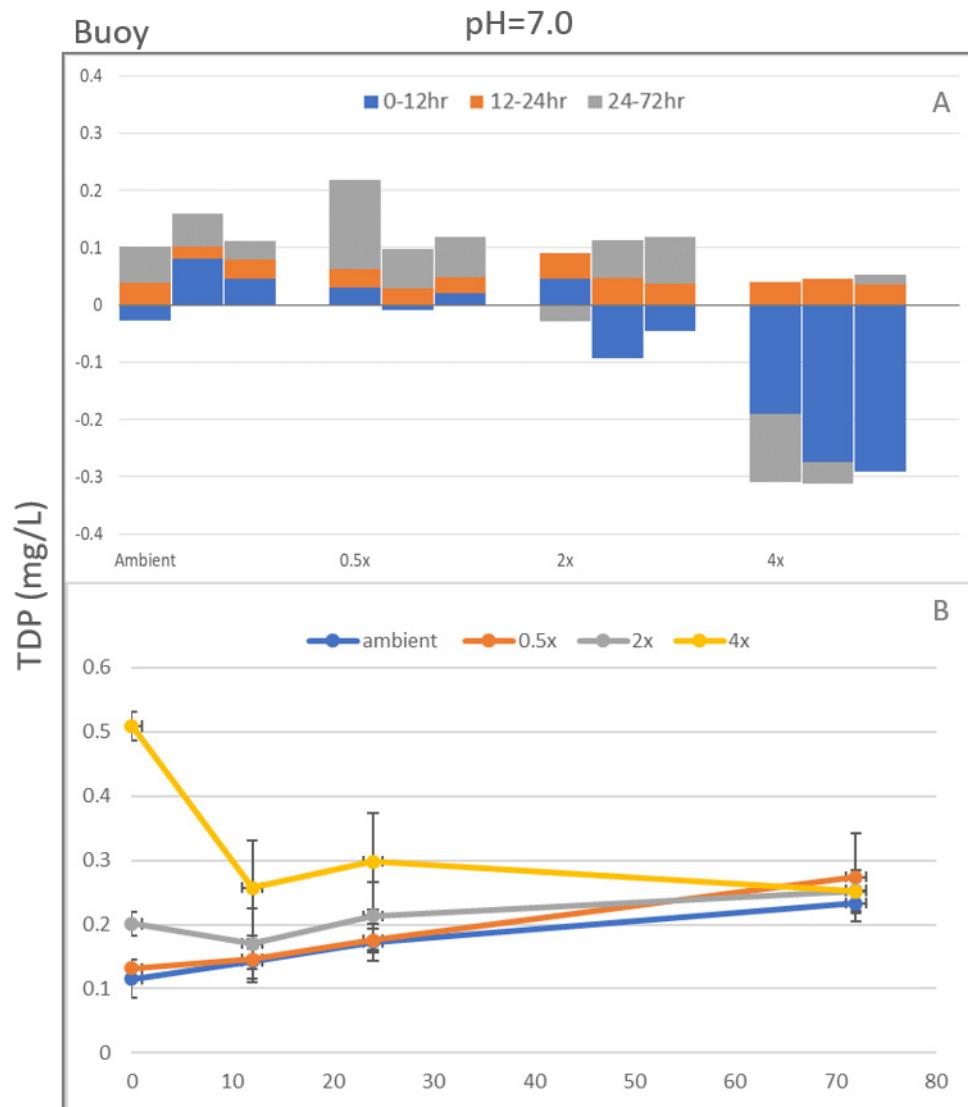


Figure 11: The change over time and trend of TDP for the $\text{pH}=7$ experiments at the Buoy core collection site are represented in A and B respectively.

Tables

Treatment	Category	Provo Bay	Buoy	Provo Bay	Buoy
		Anaerobic	Anaerobic	Alkaline	Alkaline
Ambient	P	-0.692	-0.008	-0.062	0.006
	Ca	-49.036	-14.137	14.538	-24.391
0.5X	P	-0.008	-0.017	-0.085	0.035
	Ca	-14.137	-28.693	-22.909	-18.357
2X	P	-0.008	-0.076	0.023	0.003
	Ca	-14.137	-8.600	-19.335	-13.156
4X	P	-0.008	-0.014	-0.046	-0.055
	Ca	-14.137	-10.723	-32.285	-26.532

Table 1: Calcium sink concurrent with P sink in anaerobic and alkaline conditions

Site	Grouping	k value	R^2	Nutrient Flux (mg/m^3/d)
Provo Bay Aerobic	Ambient	0.0007	0.0248	5.0400
	0.5X	0.0280	0.3810	201.6000
	2X	0.0008	0.0087	5.7600
	4X	-0.0019	0.0649	-13.6800
Provo Bay Anaerobic	Ambient	-0.0013	0.0837	-9.3600
	0.5X	0.0002	0.0077	1.4400
	2X	-0.0038	0.2630	-27.3600
	4X	-0.0072	0.3744	-51.8400
Buoy Aerobic	Ambient	0.0006	0.7332	4.3200
	0.5X	0.0008	0.7599	5.7600
	2X	-0.0002	0.0350	-1.4400
	4X	-0.0002	0.0493	-1.4400
Buoy Anaerobic	Ambient	0.0001	0.0057	0.3600
	0.5X	-0.0001	0.0228	-0.5040
	2X	0.0000	0.0001	-0.0504
	4X	-0.0008	0.1191	-5.7600
Provo Bay Alkaline	Ambient	-0.0007	0.1679	-5.0400
	0.5X	-0.0010	0.0803	-7.2000
	2X	0.0001	0.0156	0.7200
	4X	-0.0018	0.1487	-12.9600
Buoy Alkaline	Ambient	0.0001	0.0205	0.5040
	0.5X	0.0004	0.4436	2.8800
	2X	0.0000	0.0000	-0.0022
	4X	-0.0006	0.4108	-4.3200
Buoy Neutral pH	Ambient	0.0015	0.7319	10.8000
	0.5X	0.0020	0.7687	14.4000
	2X	0.0009	0.3065	6.4800
	4X	-0.0024	0.3296	-17.2800

Table 2: Flux calculations. Provo Bay generally experiences the highest levels of P flux. Anaerobic conditions resulted in the highest P sink fluxes.

ProQuest Number: 28810097

INFORMATION TO ALL USERS

The quality and completeness of this reproduction is dependent on the quality
and completeness of the copy made available to ProQuest.



Distributed by ProQuest LLC (2021).

Copyright of the Dissertation is held by the Author unless otherwise noted.

This work may be used in accordance with the terms of the Creative Commons license
or other rights statement, as indicated in the copyright statement or in the metadata
associated with this work. Unless otherwise specified in the copyright statement
or the metadata, all rights are reserved by the copyright holder.

This work is protected against unauthorized copying under Title 17,
United States Code and other applicable copyright laws.

Microform Edition where available © ProQuest LLC. No reproduction or digitization
of the Microform Edition is authorized without permission of ProQuest LLC.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 - 1346 USA