Sampling Analysis Plan for
Utah Lake Water Quality Study
Phosphorus Binding in Utah Lake

Joshua J. LeMonte[1*], Gregory T. Carling[1], Kevin Rey[1], Stephen T. Nelson[1]

[1]Department of Geological Sciences, Brigham Young University, Provo, UT, USA.
[*]Lead PI, Corresponding author, lemonte@byu.edu, 801-422-7037.

Updated 26 May 2021

1.   Introduction and background information

Phosphorus loading is a major water quality issue in lakes, and P uptake by sediments may temporarily or permanently remove P from the water column. Sorption of P onto various cations may occur, including aluminum (Al) and iron (Fe) under acidic conditions and calcium (Ca) and magnesium (Mg) under alkaline conditions (Reddy et al. 1999). The major process(es) governing P binding vary by system and may be controlled by substrate availability, pH, redox, and sulfate (House and Donaldson 1986, House 1990, Caraco et al. 1999, Reddy et al. 1999). The reverse of these binding reactions may occur, with sediment release occurring when favorable environmental conditions reverse.

Calcite binding is an inorganic reaction whereby P is adsorbed to calcite and precipitates. This reaction is favorable under alkaline water column pH and high Ca^{2+} and P concentrations (House and Donaldson 1986, House 1990). The size of calcite granules may impact the degree of P binding as well (Berg et al. 2004). Although calcite precipitation is an inorganic reaction, biotic processes can affect rates of the process, most notably photosynthesis and respiration which alter pH (Hartley et al. 1997). Calcite precipitation is a major P sink in many lakes (Hamilton et al. 2009 and references therein) and may represent a semi-permanent P sink in waters with high Ca^{2+} and alkalinity (Reddy et al. 1999). Adding calcium hydroxide to induce calcite precipitation has been used as a management technique in some lakes (Dittrich and Koschel 2002).

Mass-balance data suggest that Utah Lake acts as a nutrient (P) sink. 90% of external P loading to Utah Lake is retained within the lake (Merritt and Miller 2016), though the response of in-lake P concentrations to external P inputs suggest this sink may be variable (Brett 2019). One probable mechanism for the P sink is calcite binding, as demonstrated in a recent sediment core experiment by Goel et al (2020). However, Randall et al. (2019) demonstrate sediment-bound P exists in different sediment fractions as well, including Fe oxides. Although likely sediment-bound P fractions have been identified through sequential chemical extractions, specific mineral forms have not been quantified. Further, the reactions driving P binding, including magnitude and environmental drivers (e.g., pH, P, cations), have not been fully described.

Utah Lake sediments may switch from acting as a sink to a source of P in response to a decrease in water column P concentrations below the equilibrium concentration. The timescale of eventual equilibration between the sediment and water column likely not only depends on the gradient of water column vs. sediment concentrations but also the degree of sediment resuspension and the amount and chemical forms of P in the sediment (Reddy et al. 1999). Further, nutrient criteria often focus on total P, including fractions of P that are unavailable to primary producers such as calcium phosphate. By developing a more thorough knowledge of P binding and speciation in Utah Lake, the

sediment P sink can be better quantified and the forms of P available to support primary production will be better defined.

Problem statements

- Currently the speciation of P in the water column and sediments of Utah Lake is not well characterized. Specifically, it is not clear what fraction of P is bound to calcite and to other sorbing substances (e.g. Fe, Mn).

- Currently, it is not clear how to predict P speciation and binding under varying water quality conditions (e.g. pH, redox), such as through sorption isotherms and/or partition coefficients.

- Currently the factors impacting P speciation in the water column and sediments of Utah Lake are not well characterized. Specifically, it is not clear to what degree and under what conditions P binding may be reversible.

- Currently it is not clear which forms of P are bioavailable in Utah Lake and how that bioavailability is impacted by P binding.

- Currently it is not clear how to predict the impact of spatial and temporal changes in Utah Lake under existing conditions (e.g., as a result of productivity, seasonal variations, etc.) and under future conditions (e.g., as a result of lake management) on the factors impacting the fate, transport and bioavailability of P.


2. Objectives and design of the investigation

The Brigham Young University research team will address the shortcomings identified in the problem statement and support the Science Panel in addressing questions about the current trophic state of the lake with respect to nutrients and phytoplankton ecology (Science Panel charge question #2). More specifically, this research will help inform charge question 2.3.5: What is the role of calcite "scavenging" [i.e., binding] in the phosphorus cycle? Objectives of this research are as follow:

- Characterize the chemical speciation of P in the water column and sediment, including free forms, soluble complexes, precipitates, and sorbed species under a series of specified water quality conditions representing existing and potential future conditions in Utah Lake.

- Create a reaction network of processes involving the chemical species of P in Utah Lake.

- Characterize P scavenging and release from the water column and sediments under a series of specified conditions (e.g., pH, redox, etc.) in order to identify contributing mechanisms such as precipitation and sorption and estimate of the expected fractional distribution of P in each form.

- Evaluate the kinetics of P sorption and desorption of P onto sorbing surfaces (e.g., calcite, Fe, Mn, organics) and evaluate desorption hysteresis (e.g., speed or irreversibility of desorption and under what conditions) for a series of relevant conditions for Utah Lake.

- Evaluate predictive relationships to characterize binding of P onto sorbing surfaces in the water column and sediments such as using sorption isotherms and/or partition coefficients over a range of specified conditions (e.g., pH, redox, etc.).

The investigation will follow a systematic design that includes field observations and sample collection; physical, geochemical, and mineralogical analyses; field-informed laboratory experiments; modeling for parameter determination; and data sharing (Fig. 1). Water column, porewater, and sediment samples will be collected from five locations Utah Lake in summer of 2021 for analysis and experimentation. Multi-level sediment redox sensors and porewater samplers will be installed at the same locales for continued monitoring for the duration of the study. These field observations and existing datasets will be used to inform laboratory experiments as to the environmental conditions of the lake. Laboratory experiments will replicate these environmental conditions and control for factors that may influence P sorption and desorption within Utah Lake. Experimentally derived data will be used to create models that will parameterize P behavior to inform Utah Lake water quality model development.
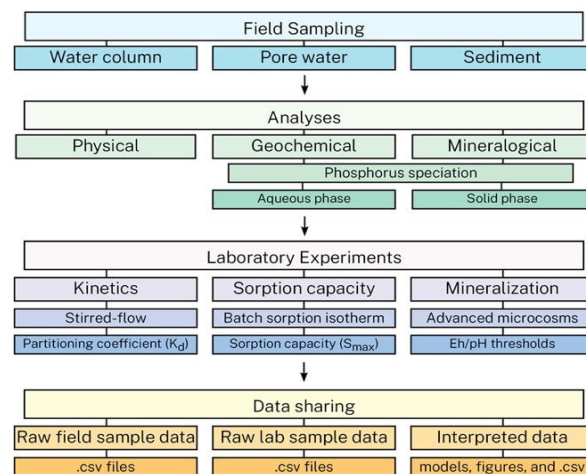
Figure 1. Project flow diagram including field sampling, analyses, laboratory experiments,

3. Special precautions and safety plan

Care will be taken to maintain the safety of all personnel while conducting both field and laboratory work. There will be a minimum of two personnel present at all times for both field and laboratory activities. All personnel will be trained on potential physical and/or chemical hazards including, but not limited to, water hazards, steep or unconsolidated banks and sediments, insects, chemical hazards or potential chemical hazards, and exposure to the elements. Appropriate personal protective equipment and safety gear for a given task will be worn/used at all times. This includes personal flotation devices while operating watercraft, waders, sunscreen, eye protection, gloves, etc. Immediately following field or laboratory research activities, all personnel will wash hands and arms thoroughly with antibacterial soap.

All personnel will be aware of the potentially hazardous conditions that can arise rapidly on Utah Lake. If weather is forecasted to create or does create hazardous and unfavorable conditions (i.e. high winds, waves, or lightning) for conducting research activities, personnel will reschedule research activities for another date/time.

Many of the experimental and analytical tasks associated with this work include working with potentially harmful substances, included concentrated acids (e.g. hydrochloric and nitric acids). All personnel will be familiar with the Safety Data Sheets (SDS) for all chemicals used, and the associated actions that must be taken if an individual experiences exposure, dermally or otherwise. The laboratories of BYU's Department of Geological Sciences in which these analytical and experimental procedures will be conducted is outfitted with 6 chemical fume hoods that are regularly serviced, and an eyewash and shower in each laboratory.

4. Field sampling methods and documentation

To capture spatial and geochemical heterogeneity of Utah Lake, sites will be selected near UDWQ buoys and other established monitoring locations for field sampling, monitoring, and characterization. These sites include Provo Bay, Utah Lake State Park, the western shore, the northeastern shore, and the southern shore (Goshen Bay). Sampling, observations, and subsequent analyses will pay particular attention to those factors that commonly control P cycling in sediments: nutrient loading, bottom water oxygen concentration, quality and quantity of organic matter, pH, Eh, mineral content and reactivity, ionic strength and competition, and temperature.
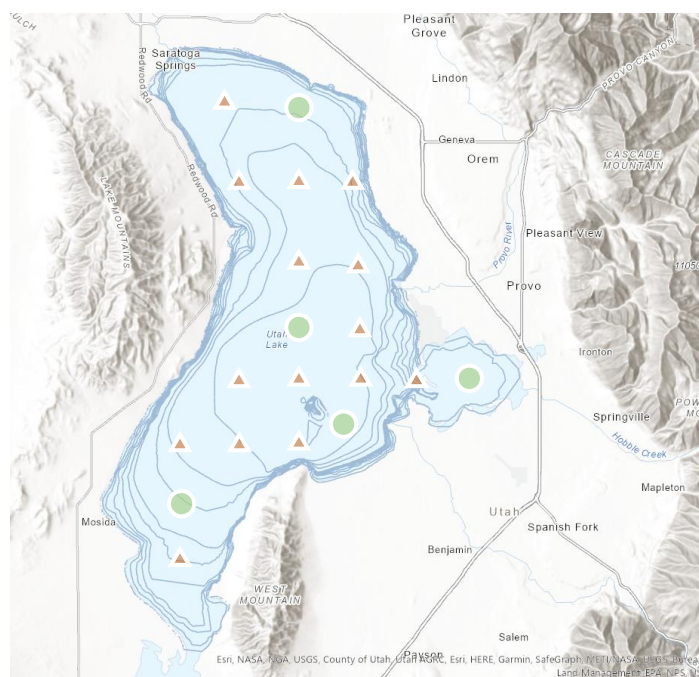
Figure 2. Sample locations. Green circles indicate primary sites where instrumentation will be deployed. Sediment and water column samples will be collected at each primary site and at each secondary site (orange triangles).

4.1. Sediment cores

Sediment cores will be collected from each of the sites at Utah Lake (n=5) from the sediment surface to 1 m below the surface. Once recovered, cores will be immediately capped and wrapped in polyethylene film to inhibit oxidation of the core, then stored in a cooler on ice for immediate transportation to the lab (within 6h). Sediment cores will then be stored in the dark at 4°C for 24h or less prior to being logged, including *in-situ* analysis via proximal x-ray fluorescence every 2-5 cm. Additional freeze cores (n=5) will be collected to a depth not to exceed 1 m and stored at -20°C for core logging and subsample collection. Freeze cores allow for the preservation of the material without compaction or distortion of sedimentary structures, mitigation of redox changes, pore water recovery, and *in-situ* porosity. Cores will then be subsampled every 10 cm at minimum for physico-chemical characterization of the sediment. Physico-chemical characterization will include pH, total C, total organic C, total inorganic C, NH_4-N, NO_2-N, NO_3-N, anions (Cl, PO_4, and SO_4), particle size distribution, extractable metals and cations, and microwave-aided digestion for total metals (EPA method 3051a). Mineralogy will be determined using XRD and calcite crystallinity and grain size will be estimated. Additionally, specific surface area of sediments will be determined via BET. *In-situ* sediment redox potential will be measured and logged every 10 cm below the sediment surface to a terminal depth not to exceed 2 m using Pt redox sensors embedded in fiberglass/epoxy probe (Paleo Terra,

Amsterdam, Netherlands). Prior to installation, exact placement (depth and intervals) will be informed by redox measurements made from the sediments collected via freeze core.

To provide insight into P geochemistry and reactivity, Utah Lake sediment P will be fractionated into loosely-sorbed P (via $MgCl_2$); Fe and Mn-bound P (via CBD); biogenic, OH^- exchangeable, and Al-bound P (via NaOH); Ca-bound P (via HCl); refractory P (via ashing and HCl); and organic phosphates (P_o) using sequential chemical extraction of field samples (Hupfer, 2009).

Additional subsamples will be collected for synchrotron-based analysis at U.S. Dept. of Energy user facilities, where Dr. LeMonte has extensive experience. Synchrotron-based x-ray diffraction (sXRD) utilizes a high-flux x-ray source with a micrometer (or smaller) beam size to identify mineralogical heterogeneity that may otherwise be imperceptible by traditional bulk mineralogical techniques. This technique is commonly paired with micro-x-ray fluorescence (u-XRF) for elemental mapping at the micron scale, and X-ray absorption spectroscopy (XAS). XAS is an in-situ synchrotron-based technique that requires minimal sample preparation, no chemical alteration of the sample, and utilizes unique spectra from known standards to serve as geochemically distinct fingerprints or signatures. This element-specific method can be used to speciate and determine the molecular ("local") structural and compositional environment of the atom in question. For example, recently this technique has been used to identify the formation of $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite) in calcareous soils, and speciate forms of P in various soil types (Colocho Hurtarte et al., 2020; Gamble et al., 2020; Hesterberg et al., 2017; Ingall et al., 2011). This method is complementary to X-ray diffraction and can enhance confidence in identifying particular species of a given element in the environment. See section 6.4 of this document for more detailed protocol regarding synchrotron-based sample preparation and analysis.

Table 1. Sediment physicochemical parameters.

Sediment Parameter Classification	Analyte(s)
Physical	Particle size distribution, bulk density, porosity, total solids, volatile solids
Nutrients	Total N, ammonium, nitrate (via 2M KCl, FIA), total P, orthophosphate, TOC
Bulk metals (ICP-OES, EPA method 3051a)	Aluminum, Arsenic, Barium, Boron, Cadmium, Calcium, Chromium, Copper, Iron, Lead, Magnesium, Manganese, Mercury, Nickel, Phosphorus, Potassium, Selenium, Silver, Sodium, Zinc
Bulk metals (pXRF, EPA method 6200)	Aluminum, Arsenic, Barium, Boron, Cadmium, Calcium, Chromium, Copper, Iron, Lead, Magnesium, Manganese, Mercury, Nickel, Phosphorus, Potassium, Selenium, Silver, Sodium, Zinc
Mineralogy	Bulk mineralogical composition (via powder XRD); micro mineralogical composition (via synchrotron XRD)
Molecular structure (synchrotron)	Oxidation state (via X-ray absorption near edge spectroscopy, XANES), bond structure (via extended X-ray absorption fine structure spectroscopy, EXAFS), elemental colocation (via micro X-ray fluorescence)
Phosphorus fractionation within lake sediments (sequential chemical extraction)	Loosely-sorbed P (via $MgCl_2$); Fe and Mn-bound P (via CBD); Biogenic, OH^- exchangeable, and Al-bound P (via NaOH); Ca-bound P (via HCl); refractory P (via ashing and HCl)
In-situ chemistry (multilevel redox probes)	Oxidative-reductive potential (Eh)

4.2. Porewater

Porewater will be collected using peepers and modified Hesslein peepers near the sediment surface and at distinct depths below the surface at each of the sites at Utah Lake. Where possible, pore water will be immediately analyzed in the field for pH, dissolved oxygen, Eh, salinity, TDS, and temperature via a YSI Professional Plus handheld multiparameter meter (Yellow Springs, Ohio, USA). Following these analyses, samples will be immediately filtered using a 0.2 um nylon filter. Once filtered, samples will be analyzed for unstable species in solution as follows: ferrous iron (Fe^{2+}) via the phenanthroline method using field colorimetric analysis (CHEMetrics V-2000,

Washington, D.C., USA), sulfide via the USEPA methylene blue method (Hach), ammonium via the high range salicylate method (Hach), and alkalinity via the bromcresol green-methyl red indicator using the Hach digital titrator. A subsample aliquot will be acidified to 2% trace metal grade HNO_3 and stored at 4°C for total metal analysis via inductively coupled plasma spectroscopy. A second filtered aliquot for dissolved organic carbon (DOC) analyses will be stored under cool, dark conditions for transport back to the lab where it will be stored frozen (-20°C) until analysis via high temperature catalytic oxidation (Vario TOC Cube, Elementar Americas, Mt. Laurel, NJ, USA).

4.3. Overlying water

Overlying water will be collected from 2 discrete depths within the water column: 0.5 m below the surface and 0.5 m above the sediment. Tygon® high purity tubing will be lowered to the designated depth and then water column samples will be pumped to the surface using a peristaltic pump. Water pH, dissolved oxygen, Eh, salinity, TDS, and temperature will be measured using a YSI Professional Plus handheld multiparameter meter (Yellow Springs, Ohio, USA). Water column subsamples samples will be collected, treated, and analyzed following the additional methods outlined above for the pore water. See Table 2 for a comprehensive set of water chemistry parameters to be analyzed for. Understanding P speciation and behavior is an integral portion of this work. Therefore, water samples will be analyzed for total P, SRP, and orthophosphate.

Table 2. Water Chemistry Parameters

Water Parameter Classification	Analyte(s)
Dissolved nutrients (0.45 um filter)	Total N, ammonia, nitrate, nitrite, total P, orthophosphate, SRP, DOC
Bulk nutrients (no filter)	Total N, ammonia, nitrate, nitrite, total P, phosphate, TOC
Dissolved metals and trace elements (EPA method 200.7)	Aluminum, Arsenic, Barium, Boron, Cadmium, Calcium, Chromium, Copper, Iron, Lead, Magnesium, Manganese, Mercury, Nickel, Potassium, Selenium, Silver, Sodium, Strontium, Titanium, Vanadium, Zinc
Bulk metals and trace elements (EPA method 3015A)	Aluminum, Arsenic, Barium, Boron, Cadmium, Calcium, Chromium, Copper, Iron, Lead, Magnesium, Manganese, Nickel, Potassium, Selenium, Silver, Sodium, Strontium, Titanium, Vanadium, Zinc
General chemistry	Alkalinity, chloride, dissolved oxygen[1], specific conductance [1], ORP[1], pH[1], sulfate, sulfide, temperature[1], total dissolved solids[1], total suspended solids, volatile suspended solids

[1]Data generated using a YSI Professional Plus handheld multiparameter meter

5. Laboratory sample handling procedures

Care will be taken to minimize alterations to the natural conditions at which sediments and water samples are sampled. Solid phase sediments that will be used for synchrotron analyses will be dried and stored in an anaerobic chamber. Sediments used for bulk analysis will be stored at 4°C in the dark until the point of analysis. Aqeuous samples that will be analyzed via ICP-OES will be acidified to 2% trace metal grade HNO_3^- and stored at 4°C in the dark until the point of analysis, samples that will be analyzed for anions will be frozen at the point of collection and until immediately prior to analysis. All laboratory samples will be labeled with the following information: date of collection, researcher name, project name, analysis method, sample details (i.e. depth, lat/long, collection/preservation method), and a unique lab number. All samples will be cataloged in triplicate: on a PC hard drive, back up cloud drive, and physical notebooks.

6. Analytical methods and laboratory documentation

A series of laboratory experiments will be conducted using sediment and water collected from Utah Lake, informed by the observed conditions of the sediment and waters at collected at the field sites. The experimental objectives for this work are to empirically derive 1) partitioning coefficients (K_d), and 2) sorption capacity (S_{max}) of P species in Utah Lake sediments and important sediment constituents under conditions that may affect P binding and release, and 3) elucidate which factors control P binding and release across redox gradients. We hypothesize that binding and release of P in the presence of sediment minerals is controlled by P loading (lake sediment P concentration ranges from 200 – 2000 mg kg^{-1}), pH, organic matter quantity/quality, redox conditions, and ionic competition.

The rates of chemical reactions at soil/sediment mineral surfaces are dictated by several transport and chemical reaction processes, and these processes can vary over a wide time scale (microseconds to years). For instance, the chemical reactions occurring on a mineral/soil surface (e.g. adsorption and desorption) are usually very rapid and not rate-limited. However, transport processes are dominated by diffusion, and can be much slower than the chemical reactions happening at mineral surfaces. These processes can be seen in sorption data and are referred to as biphasic process, because they are composed of a quick chemical reaction followed by a second, slower diffusion process. Proper experimental design can help elucidate the rates of these different reactions, therefore choosing proper protocols are integral for fully characterizing a system.

Experimental Method	Target Parameter	Proposed Models
Batch sorption	K_d, S_{max}	Langmuir
Stirred-flow kinetics	Partitioning coefficient (K_d), S_{max}	Chem_Transport chemical kinetic sorption and transport
Microcosm biogeochemical thresholds	Thresholds for P sorption and precipitation (pH, Eh, loading levels)	Geochemists WorkBench

6.1. Batch Sorption

Batch experiments are quick and relatively simple experiments good for rapid determination of equilibrium parameters (e.g. sorption constant, K_d, equilibrium time). To this end, batch sorption isotherm experiments will be conducted to derive sorption capacity of P in sediments and sediment constituents. To improve understanding of these sorption phenomena, sediment and sediment constituents (i.e. Fe-, Mn-, Ca- and Al-hydroxides identified via XRD) known to drive sorption in sediments will be used for experimentation. As specific surface area, crystallinity, and particle size have been shown to influence calcite-phosphorus interactions, efforts will be made to utilize calcite materials that are like those found in Utah Lake sediments (Berg et al., 2004). Previous work has identified major oxides and minerals in Utah Lake sediments via WDXRF and XRD, respectively (Randall 2019). The extent to which these sediment constituents influence the geochemical behavior of P is complex and poorly understood.

A systematic series of batch sorption/desorption experiments will be conducted to determine the sorption capacity and partitioning coefficients of P in Utah Lake. These experiments will create a sorption baseline by using sediments from Utah Lake. As the sediment within the lake is heterogeneous and its geochemical composition can vary widely across Using previously reported data as a guide, major sediment constituents will be identified and used in batch sorption

While P/phosphate sorption has been studied for decades, the present research will replicate the novel environmental conditions (pH, EC, P loading, etc.) specific to Utah Lake. In particular, pH ranges up to 10 will be investigated.

Table 3. Potential surfaces for P sorption/desorption experiments.

Surface	Formula	Abundance range, %[*]
Utah Lake Sediment, Site A	Heterogeneous sediment	
Utah Lake Sediment, Site B	Heterogeneous sediment	
Utah Lake Sediment, Site C	Heterogeneous sediment	
Calcite	$CaCO_3$	12-75
Dolomite	$MgCO_3 \cdot CaCO_3$	2-30
Ferrihydrite	$Fe^{3+}_{10}O_{14}(OH)_2$	
Goethite	$\alpha\text{-}Fe^{3+}O(OH)$	
Hematite	Fe_2O_3	1-3
Gibbsite	$Al(OH)_3$	
Aluminum oxide	Al_2O_3	3-6

[*]Abundance range is based off previously reported mineralogy data obtained via XRF in Randall et al., 2019.

6.2. Stirred-flow kinetics

Stirred flow (SF, Figure 2) methods are another approach to measuring chemical rate parameters for adsorption and desorption processes. SF techniques combine aspects of both batch and more traditional continuous flow methods (e.g. column experiments and miscible displacement experiments). An advantage of the SF method is that studies can be conducted at solid to solution ratios that better simulate field conditions compared to traditional batch studies. In SF experiments, the adsorbent is exposed to a greater mass of ions than in a static batch system, and the flowing solution removes the desorbed and detached species (i.e. reaction products), which can help prevent secondary precipitation reactions that may not accurately represent real world conditions. Therefore, SF experiments will be conducted to collect kinetic data with enhanced temporal resolution that are more representative of natural systems under similar experimental conditions to the batch reactions.
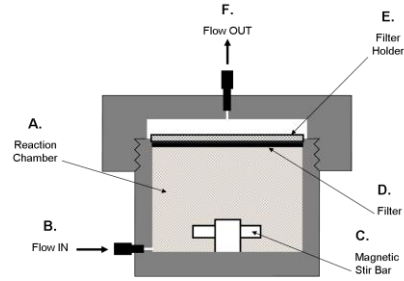
Figure 3. Schematic of stirred-flow reactor

6.3. Biogeochemical microcosm threshold experiments

Whereas batch sorption isotherms and SF experiments are good for parameterizing sorption and desorption of P, a more controlled system is preferred to investigate the impact of redox on this system. It has been shown that reduced species of P, such as phosphite and hypophosphite are both accessible as nutrients and can comprise a significant proportion of total P in a water body under reducing conditions (Pasek et al., 2014). This will play a role in the scavenging of P. In order to ascertain potential prevalence of calcite and binding and optimal conditions for this phenomenon, it will be necessary to conduct large-scale sorption equilibrium experiments that allow for the collection and analysis of solid phase samples for mineralogy and molecular level binding conditions. Therefore, an advanced automated biogeochemical microcosm (MC) system will be used to control and simulate conditions that may drive calcite P scavenging, including pH, Eh, and Ca and P loading and speciation (UIT, Dusseldorf, Germany). Dr. LeMonte and others have used this method successfully to demonstrate how a dynamic environment can impact elemental cycling (Frohne et al., 2011; LeMonte et al., 2017; Shaheen et al., 2015).
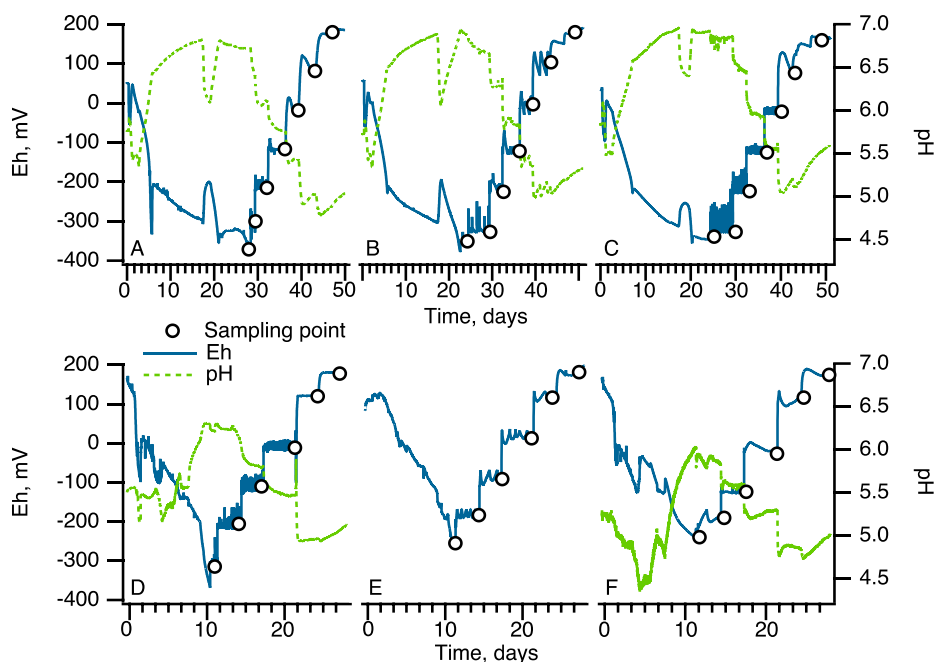
Figure 4. Example rendering of redox potential (Eh) and pH monitoring over the course of a controlled microcosm experiment.

Sediment collected from the Utah Lake locales listed above will be air-dried, and passed through a 2-mm sieve for homogenization and used in the reaction vessel. Overlying water from Utah Lake will be collected and passed through a 0.45 µm filter. The microcosms will be filled with a sediment:solution mixture with a 1:8 solid-to-solution ratio using these natural materials collected from Utah Lake. For the Eh to reach a minimum, microbial respiration is necessary. Glucose (5 g) and powdered plant biomass (10 g) collected from the shores of Utah Lake will be added as C sources for the microbial community within each microcosm. Periodic C inputs may be required until the Eh level stabilizes at a soil-dependent minimum. However, DOC and TOC levels will be monitored so as to avoid creating an artificial C-spiked system that is not representative of what is found in Utah Lake. A targeted Eh level will be set with ±20 mV precision and automatically controlled with the addition of N_2 or O_2 gases. Redox windows will be set in 50 mV to 150 mV increments from reducing to oxidizing, totaling 5 to 10 unique Eh levels. The vessel will be given 48 h to equilibrate following the input of a targeted Eh level. Redox potential, pH, and temperature will be monitored every 10 minutes. An example of data collected using these microcosm systems is presented in Figure 4. Aliquots will be taken after this equilibration period and immediately centrifuged to separate solid from liquid phases. The supernatant will be filtered under N_2 atmosphere through a 0.2 µm nylon filter and analyzed for total P via ICP-OES, other metals of interest, DOM, and anions via ion chromatography. Solid phase samples will be dried, resin-embedded, and thin sectioned (all under N_2 atmosphere to prevent oxidation changes) for XAS analysis. This resin-embedding process will preserve the

oxidation state of the solid samples. Thin sections of the resin-embedded samples will be mounted on slides with Kapton tape for analysis at the beamline.

6.4. Synchrotron (XAS) analyses

Beam time proposals will be submitted to the National Synchrotron Light Source II at Brookhaven National Laboratory to perform advanced synchrotron analyses of solid phase samples to determine the in-situ molecular speciation of P-mineral complexes. This will be accomplished via a bimodal approach. One aspect of the approach will be conducted at the Tender Energy Source beamline (TES). TES optimized for the tender-energy range, offering routine operations from 2.0 to 5.5 keV, with capabilities to reach down to 1.2 or up to 8 keV with configuration change, making it an optimal choice for P ($K\alpha_1$ edge = 2 keV) and Ca ($K\alpha_1$ edge = 3.7 keV) analyses. Another aspect of the approach will be conducted at the X-ray Fluorescence Microprobe beamline (XFM). XFM is optimized for the 2.05 - 23 keV energy range (Phosphorus to Technicium K edges). XFM is ideal to investigate P chemical interactions with Fe ($K\alpha_1$ edge = 6.4 keV) and potentially Mn ($K\alpha_1$ edge = 5.9 keV).

Solid samples will be analyzed μ-XAS, μ-XRF, and μ-XRD to determine elemental speciation, the co-localization of P with other metals, and mineralogy. Informed by bulk XRD analysis, 5-10 reference standards will be selected and prepared for XANES analysis. Incident energy to excite fluorescence from Ca, Fe, Mn, and P for XRF mapping will be used to determine metal associations and distribution at the micron scale. X-ray fluorescence maps ($1-3$ mm^2) will be created to observe distinct elemental correlations and to identify regions of interest ("hotspots") for micro-XAS and micro-XRD speciation analysis. These micro-techniques can detect minor, yet potentially more reactive species/complexes that are not detectable via bulk methods. With the monochromator calibrated for the element of interest (i.e., P or Ca), μ-XANES will be collected from approximately 200 eV below the absorption edge energy to k values of 10 Å^{-1} with longer counting times in the XANES region. Attention will be paid to any changes in the white line, which represent alterations of the original oxidation state. Because sediment is a heterogeneous matrix, it is essential to collect μ-XANES from many identified "hotspots". To produce data that can be adequately fit by principal component analysis and linear combination fitting in Athena, 2-3 scans will be collected at each hotspot. This will improve signal:noise ratio while minimizing radiation damage of the sample. These scans will each be normalized and then merged into one spectrum. The merge file will then be fit using principal component analysis and linear combination fitting with the reference standards spectra.

7. Project quality control requirements

All measurements, analyses, and experiments will be conducted in triplicate (at minimum) with blanks for quality control. All reagents used will be analytical grade. Standards used in analyses will all be certified reference standards.

8. Data analysis, record keeping, and reporting requirements

8.1. Data analysis

Data analysis will be conducted referencing accepted protocol in the literature. The reaction network will be informed by the data collected in the field and in the lab and entered into geochemical modeling software such as PHREEQC, Geochemist's Workbench, or Visual Minteq. Fitting and mineral identification of the XRD data from solid phase samples will be performed using the Jade, RockJock, or PDXL2 software packages. Principle component analysis, linear combination fitting, elemental mapping, and spectra corrections of the synchrotron-based solid phase analyses will be conducted using the Athena, Larch, and GSE Map Viewer software packages (https://xraypy.github.io/xraylarch/).

The batch sorption isotherms (representing the triplicated sorption data) will be modeled using the Langmuir model, as:

$$Q_{eq} = \frac{S_{max} K_L C_{eq}}{K_L + C_{eq}} \quad [1]$$

where, K_L = the Langmuir partition coefficient and S_{max} = the asymptotic concentration representing the maximum P sorptive capacity (equilibrium concentration) of the sediment. For simplicity, the Langmuir affinity constant will be modeled as $1/K_L$. Sorption isotherms will be fitted using the *nlsList* function in the "nlme" R package (Ritz and Streibig, 2009), which contains a "self-starter" function that calculates the initial values for the Langmuir constants from the linearization of the Langmuir equation. Modeling of the data in this way will allow for the determination of maximum loading capacity of P in sediments at equilibrium for each P type, sediment, and pH tested.

There are different models available in the literature for parameterizing stirred-flow kinetic data including zero-order kinetic models, first-order kinetic model, second-order kinetic model, continuous stirred tank reactor with step loading model, Shi model 1 with single k, Shi model with two and three ks, Bar-Tal kinetic models, and the Chem_transport model (Selim 2016). Dr. LeMonte has previously determined that the Chem_transport model is typically the most suitable for stirred flow experiments. However, if this model fails in this experimental system (poor accuracy, poor replicability, etc.), another model will be considered to determine kinetic parameters. Kinetic parameters can be modeled based on the combination of mass-balance and kinetic relationships.

The general equation for SF experiments is:

$$C_iJ = JC_{out} + V\frac{dC}{dt} + M\frac{dS}{dt}$$ [2]

where,
C_i = solute influent concentration (mol m^{-3})
C_{out} = solute effluent concentration (mol m^{-3})
C = solute chamber concentration (mol m^{-3})
V = solution volume in chamber (L), J = flow rate (m^3 min)
t = time (min), S = amount adsorbed (mol kg^{-1})
M = mass of adsorbent

The first term represents advective flow through the chamber with the assumption of a well-mixed system (based on chamber design) verified through previous experimentation. This means that the SF experimental procedures can be designed to avoid common issues with physical dis-equilibrium in natural soils and sediments. The second term represents input solute gradient in solution while the third term represents the solute removal from solution strictly by sorption processes.

8.2. Record Keeping
All reports will be provided in .docx and .pdf format. All raw and interpreted data will be provided as .csv files. All documents will be stored via a shared Box folder in the cloud with download and upload permissions shared with UDWQ.

9. Schedule

Monthly visits will occur throughout the duration of the project. Sampling during winter months will continue, so far as weather and ice conditions permit.

TASK DESCRIPTION	2021 (J F M A M J J A S O N D)
1.1. Literature review and preliminary reaction network	▉ (J–F, red)
1.1.1. Draft technical lit review memo	▉ (J–F, red)
1.1.2. Final technical lit review memo	▉ (F, red)
1.2. Sampling and analysis plan (SAP)	▉ (F–M, orange)
1.2.1. Draft SAP	▉ (F, orange)
1.2.2. Final SAP	▉ (M, orange)
1.3. Mineralogy experiments and data reporting*	▉ (M–O, yellow)
1.3.1. Collect and archive sediment, pore water, and water column sample	▉ (M–N, yellow)
1.3.2. Data and metadata on samples*	▉ (M–N, yellow)
1.3.3. Sediment and water mineral characterization*	▉ (M–N, yellow)
1.3.4. Data and metadata on laboratory experiments*	▉ (M–N, yellow)
1.3.5. Deliver raw and interpreted data to the Science Panel in electronic format	▉ (M, yellow)
1.4. Review and analysis	▉ (M–J, green)
1.4.1. Preliminary report detailing the results of the analyses of field and laboratory data	▉ (M–J, green)
1.5. Prepare technical report	▉ (J–O, blue)
1.5.1. Draft technical report	▉ (J–A, blue)
1.5.2. Final technical report	▉ (O–D, blue)
1.5.3. Final electronic deliverable of raw and interpreted data	▉ (O–D, blue)

* Field data collection, experimentation, and laboratory experimentation will experience a vastly improved dataset with longer exposure/monitoring/experimental times. Therefore, it is proposed that these subtasks continue as long as possible prior to final reporting.