

INORGANIC PHOSPHORUS CHEMISTRY OF
UTAH LAKE'S EFFLUENT MIXING ZONES

By
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ABSTRACT

While restoration efforts for eutrophic lakes often target point sources containing high concentrations of total phosphorus, Utah Lake may present a challenging case wherein restoration efforts could be potentially overwhelmed by the natural loading and cycling of phosphorus in the lake. The effects of wastewater phosphorus on the effluent mixing zones of Utah Lake were investigated through water and sediment analyses, including mixing experiments, geochemical modeling, batch desorption, sequential extraction, and x-ray diffraction. Under the given experimental conditions, soluble reactive phosphorus appears to remain stable while in transit to the lake. Calcite is the only major mineral that precipitates within Utah Lake, and phosphate coprecipitation with calcite is the only inorganic sedimentation mechanism that renders phosphorus biologically unavailable in this setting. Quantifying this process is, therefore, an essential aspect of characterizing total phosphorus cycling in Utah Lake.

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LIST OF ABBREVIATIONS

Adsorbed.....	ADS
Amorphous Calcium Phosphate	ACP
Below Detectable Level	BDL
Calcite Equilibrated Solution	CES
Chlorapatite	CAP
Coprecipitated.....	CPT
Dicalcium Phosphate Anhydrous	DCPA
Dicalcium Phosphate Dihydrate	DCPD
Division of Water Quality	DWQ
Fluorapatite.....	FAP
Hydroxyapatite	HAP
Lake-water	LW
Octacalcium Phosphate	OCP
Soluble Reactive Phosphorus	SRP
Technology Based Phosphorus Effluent Limit	TBPEL
Total Dissolved Phosphorus	TDP
Total Dissolved Solids	TDS
Total Maximum Daily Load	TMDL
Total Phosphorus	TP
Wastewater	WW
X-ray Diffraction	XRD

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CHAPTER ONE

INTRODUCTION, PROBLEM DESCRIPTION, & LITERATURE REVIEW

1.1 Introduction

Utah Lake is a large, freshwater lake cradled between the Great Basin and the Rocky Mountains of north-central Utah (see Figure 1 for a reference map). Along with the Great Salt Lake, Utah Lake is a remnant of Lake Bonneville, a massive, late-Pleistocene paleolake that covered vast portions of western Utah between approximately 30,000-13,000 years ago (Murchison, 1989). Since Lake Bonneville's disappearance, Utah Lake has emerged as a basin-bottom lake. Utah Lake is also classified as a semi-terminal lake, being the recipient of multiple tributaries from the Rocky Mountains, but possessing only a single outflow, the Jordan River, which ultimately empties into the Great Salt Lake.

By surface area, Utah Lake is ranked the third largest lake in the contiguous United States west of the Mississippi River, falling behind Flathead Lake, Montana, and Lake Tahoe, California/Nevada (Fidel, S., 2012). Despite covering an area of about 380 square kilometers (145 square miles), the lake is relatively shallow, with an average depth of about 3 meters (9.8 feet). As is typical for large, shallow lakes, the lake-bottom sediments of Utah Lake are especially susceptible to wind-induced resuspension. This, along with the sediment that has been stirred up by the feeding activity of carp, causes the lake to have a turbid, grayish-green appearance. Additionally, Utah's semi-arid climate causes the lake to be somewhat saline due to high levels of evaporation, representing 40-50% of the lake's total outflow (PSOMAS, 2007).

Utah Lake functions as an important biological hub for north-central Utah. Positioned along one of the major routes for the Pacific Flyway, Utah Lake's wetlands are utilized as a

migratory waystation or breeding habitat for over 200 species of birds (URMCC, 2006). Utah Lake is also home to the June Sucker, a threatened fish species that reside exclusively in the lake. As of February 3, 2021, the June Sucker's conservation status was successfully elevated from endangered to threatened due to extensive projects involving the acquisition and management of water flows, habitat restoration, carp removal, and population augmentation. Conservation efforts in and around Utah Lake are expected to continue in order to help bolster the June Sucker's ongoing resurgence (FWS, 2021).

In addition to being an important natural resource, Utah Lake likewise serves as a valuable economic resource for the state of Utah, bringing in millions of dollars of revenue each year. Surrounding the lake is the Provo-Orem metropolitan area, home to over half a million residents, with the average Utah County resident living about 10 kilometers (6 miles) from the lake (DWQ, 2018). Recreational use of the lake includes motor boating, fishing, swimming, and shoreline activities such as walking and picnicking. Agricultural use of the lake includes using lake-water (LW) for irrigation and livestock watering.

Despite being a vital natural and economic resource, Utah Lake has long been considered an impaired water-body. For over a century, the lake has been plagued with problems ranging from raw sewage disposal to carp infestation. Multiple wastewater treatment plants and carp removal projects have since been introduced, and while they have certainly improved the lake's overall water quality, Utah Lake has continued to experience elevated levels of total phosphorus (TP) and total dissolved solids (TDS), even to the present day (PSOMAS, 2007).

With increasing frequency, Utah Lake has received widespread attention for its recurring algal blooms and associated closures (Penrod, 2016; Maffly, 2018; Donaldson, 2020). While the general public is often concerned with the blooms' impact on the recreational and aesthetic value

of Utah Lake and the outflowing Jordan River, such algal blooms likewise restrict agricultural usage of LW and hinder the conservation efforts being made for the June Sucker fish species (McKellar, 2016; Merritt, 2019; FWS, 2021). Algal blooms in Utah Lake are typically triggered by a combination of hot, dry, and calm weather conditions, consequently resulting in lower lake levels, decreased turbidity, increased light in the lake, and a warm aquatic environment ideal for growing algae in the lake's eutrophic waters (Penrod, 2016). Utah Lake's algal blooms are often assumed to be nutrient-limited and therefore induced by incoming wastewater (WW) effluent, the lake's most recognized source of phosphorus (Merritt, 2019).

Efforts to specifically limit total phosphorus (TP) loading to Utah Lake began in the mid-2000s when the Utah Division of Water Quality (DWQ) started the preliminary steps to establish a Total Maximum Daily Load (TMDL). This initiative included an in-depth study by PSOMAS of the lake's impairment. In their final report, it was concluded that before the TMDL process could move forward, Utah Lake's "individual lake system must be understood to comprehend the internal processes that may influence the cycling of TP and to identify the appropriate mechanisms for limiting TP in [its respective] watershed" (PSOMAS, 2007). After receiving PSOMAS's final assessment, DWQ chose to suspend Utah Lake's TMDL process in order to allow projects focused on the lake's invasive species to be more adequately addressed. (Penrod, 2016).

Instead of allowing the TMDL process to be resumed, the Utah Water Quality Board chose to bypass it in 2014 by enacting the Technology Based Phosphorus Effluent Limit (TBPEL). This new policy would require all discharges released into any of Utah's waterways to have an average TP content no greater than 1.0 mg/L by January 1, 2020 (DWQ, 2015). Any

affected facilities that strove to meet the January 1, 2020 deadline but were unable to do so could petition for a variance, extending their deadline to January 1, 2025 (Lancaster, et al., 2016).

While the TBPEL is expected to reduce TP concentrations in Utah Lake and other water-bodies throughout Utah, the policy has not been immune to criticism. Disapproval has arisen mainly because discharges from wastewater treatment plants (WWTPs) are not the only source for phosphorus to Utah Lake. The combined effects of agricultural runoff, sediment nutrients, and atmospheric deposition could potentially overwhelm the efforts being made to prevent future algal blooms through the removal of WW effluent phosphorus (PSOMAS, 2007; Randall, 2017; O'Donoghue, 2017; Merritt, 2019). There is also the question of whether Utah Lake's algal blooms are nutrient-limited in the first place. The lake is often turbid enough to argue that the lake's algal blooms are, in fact, light-limited rather than nutrient-limited (Merritt, 2019).

To add further gravity to the situation, there is also the matter of cost associated with enacting the TBPEL. Many WWTPs throughout Utah will require significant upgrades in order to become compliant, incurring costs for some plants upwards of hundreds of millions of dollars (Holmstrom, 2016; O'Donoghue, 2018). With such a hefty price tag associated with a policy fraught with unassured efficacy, it has become quite possible that Utahns are now collectively paying millions of dollars in a failed attempt to rehabilitate Utah Lake.

1.2 Problem Description

As it currently stands, the TBPEL remains an immovable policy in the face of ongoing criticism. Current and future studies on TP cycling in Utah Lake will now either serve to strengthen or weaken the TBPEL's stance that nutrient removal from WW effluent is integral to rehabilitating Utah Lake. As the WWTPs near Utah Lake are working towards becoming

compliant, now is an ideal time to study the behavior of WW phosphorus and its relationship to TP cycling before the TBPEL can take full effect on the lake.

In 2018, LimnoTech released a literature review evaluating 37 of the most relevant sources available on the water quality of Utah Lake. When discussing the topic *Internal Cycling and Biological Availability of Nutrients*, the review states that even though these studies "provide some insight into sediment phosphorus characteristics and fluxes... none of the studies quantify actual sediment nutrient flux rates, and no studies were available that quantified the biological availability of nutrients in lake sediments" (LimnoTech, 2018). While it is important to fill these knowledge gaps regarding TP cycling within Utah Lake, endeavoring to do so is invariably predicated upon answering a host of preliminary questions. More specifically, before sediment nutrient fluxes and bioavailability can be adequately quantified, the identity and behavior of Utah Lake's sediment nutrients must first be understood to ensure that all vital variables are both accounted for and addressed. As such, the two primary research questions for this study include:

- Which inorganic sedimentation mechanisms participate in the downward flux of phosphorus in Utah Lake's effluent mixing zones?
- How bioavailable is the phosphorus associated with these mechanisms?

1.3 Literature Review

The phosphorus cycle was discussed in considerable detail by Wetzel (2001) in which he explains that orthophosphate (PO_4^{3-}) is the primary manifestation of inorganic phosphorus in natural waters. It is also the most crucial form of phosphorus in plant nutrition (including algae) because it may be directly utilized. Dissolved orthophosphate can also be referred to as soluble reactive phosphorus (SRP) and usually constitutes < 5% of the TP content of temperate streams

and lakes. However, biologically productive water-bodies often possess a higher percentage of SRP and are identified as eutrophic when $TP \geq 30 \mu\text{g liter}^{-1}$. Together, TP and SRP are the most quantified phosphorus measurements among freshwater studies.

Of the various pathways for sedimentation to occur, Wetzel (2001) described two inorganic mechanisms by which sediment phosphorus arrives within lakes. These pathways include: 1) when phosphate minerals are physically transported from the drainage basin to the lake and are deposited nearshore upon entry, or 2) when phosphate forms minerals or sorbs onto suspended solids while in the water column and eventually settles onto the lake-bottom. This process includes the formation of calcium phosphate minerals (i.e., apatite), the adsorption and coprecipitation of phosphate with calcium carbonates (i.e., calcite), the coprecipitation of phosphate with iron and manganese compounds, and the adsorption of phosphate to clays, amorphous hydroxides, or other suspended solids.

Although these different forms of sedimentation are all part of the overall downward flux of phosphorus, they do not necessarily render the phosphorus biologically unavailable. Spears, et al. (2007) explained the process by which phosphorus is exchanged between the water column and lake sediments. Phosphorus that has been precipitated in calcium phosphates or coprecipitated with calcium carbonates can be released under acidic conditions and then coprecipitated again under basic pH conditions. Phosphorus that is coprecipitated with iron or manganese can be released under reducing conditions and then coprecipitated again under oxic conditions. Furthermore, phosphorus that is adsorbed onto clays, hydroxides, carbonates, and other sediments can readily be desorbed and resorbed depending on various physical, chemical, and biological conditions within the lake.

As part of his research regarding the sediments of Utah Lake, Randall (2017) conducted a sequential extraction procedure on ten lake-bottom samples to determine the phosphorus fractionation among the sediment's mineral phases. The experiment demonstrated that phosphorus is bound chiefly to iron oxyhydroxides (40-60%) followed by calcium minerals (25-50%). Lesser amounts are associated with clay minerals (2-6%) or are either loosely sorbed to various minerals, sediments, or their interstitial pore spaces (>5%). The iron oxyhydroxides in Utah Lake are only able to temporarily bind phosphorus, as the decomposition of organic matter in the sediments at warm temperatures can create reducing conditions and thus facilitate the release of phosphorus. Utah Lake's calcium minerals, on the other hand, can be considered a phosphorus sink because the combined effects of the lake's high pH and high alkalinity make it unsuitable for those minerals to release coprecipitated phosphorus (i.e., phosphorus that has become incorporated into the crystal lattice).

Calcite adds an interesting dynamic to TP cycling within lakes because of its ability to either adsorb or coprecipitate phosphorus from the water column. Li, et al. (2017) emphasized that phosphorus adsorption to calcite is significantly less stable than phosphorus coprecipitation with calcite. Wetzel (2001) reported that adsorption appears to be the predominant interaction between calcite and phosphorus in freshwater systems, with coprecipitation only occurring in small quantities. This observation was also reported by Sørensen, et al. (2011) who observed quick and complete sorption and desorption of phosphorus from calcite in their batch experiments.

When phosphorus does manage to coprecipitate with calcite, x-ray diffraction will only detect calcite, as was observed by Kleiner (1988). X-ray diffraction work conducted by Randall (2017) determined that the lake-bottom sediments of Utah Lake are composed mostly of carbonates with an average of 46.1% (primarily as calcite at 39.7%), followed by quartz at

25.3%, feldspars at 15.4%, as well as clays at 9.8%. Despite constituting the largest fraction of sediment phosphorus in Utah Lake, iron oxyhydroxides, such as goethite, consisted of less than 1% of the lake's overall sediment by mass.

Regarding sediment TP in Utah Lake, a lake-wide study by Abu-Hmeidan (2017) measured an average TP content of 666 mg/kg among 85 samples of lake-bottom sediment. Areas with exceptionally high TP values were found near agricultural feedlots and WW discharge sites. In contrast, areas with lower TP values were located in areas thought to be under the influence of incoming groundwater. Abu-Hmeidan also compared the TP content of lake-bottom sediment with that of offshore geologic sediments surrounding the lake and found that there was no statistical difference in the phosphorus content between lake sediment and natural geologic materials.

Wetzel (2001) reported that most lakes have been found to have a weak to modest relationship between the phosphorus content of their sediments and the lake's trophic state. However, disturbances of the lake bottom can potentially double the rate by which phosphorus is released from the sediments. Abu-Hmeidan (2017) observed that this is especially the case with Utah Lake because its sediments are subject to frequent resuspension due to wind-induced waves and the feeding activity of carp, thus facilitating the transfer of loosely sorbed phosphorus from the sediments to the water column.

Batch sorption tests conducted by Randall (2017) revealed that Utah Lake's sediments are likewise quite capable of absorbing much of the water column's phosphorus when the aqueous concentrations are less than 1 mg/L. Randall's research also included an experiment monitoring phosphorus speciation between various mixtures of local WW effluent and LW from Utah Lake

over the course of 24 hours. The results showed no significant difference in TDP but a noticeable decrease in SRP.

In addition to lab experiments, phosphorus speciation can be calculated using geochemical models, such as PHREEQC. In *The User's Guide to PHREEQC*, Parkhurst (1995) explains that PHREEQC is a computer program that utilizes multiple models to conduct aqueous geochemical calculations. These models include the Lawrence Livermore National Laboratory model (to predict the behavior of electrolytes under non-ideal conditions), WATEQ4F model (to predict element speciation and mineral saturation in natural waters), a Pitzer specific-ion-interaction aqueous model (to predict the behavior of ions in natural waters), and the Specific Ion Interaction Theory aqueous model (to predict single-ion activity coefficients in highly concentrated electrolyte solutions). These models together enable PHREEQC to make speciation and saturation-index calculations, batch-reaction & one-dimensional transport calculations with reversible and irreversible reactions, and inverse modeling of mineral and gas transfers between waters.

To facilitate these calculations, PHREEQC utilizes a database containing kinetic data for various aqueous and mineral species. PHREEQC's database, however, does not contain information for most phosphate minerals and therefore requires manual entry of the desired kinetic data so that the software can account for those minerals in its calculations. Fortunately, kinetic mineral data for phosphorus can be readily found throughout scientific literature, as demonstrated in Wei, et al. (2013).

One of the main knowledge gaps that has emerged regarding Utah Lake is the lack of an understanding of how WW phosphorus behaves in the lake, especially in regards to phosphate mineral formation. As such, there has yet to be any published analyses of Utah Lake involving

PHREEQC. This study has sought to fill this knowledge gap by investigating which inorganic sedimentation mechanisms participate in the downward flux of phosphorus in Utah Lake's effluent mixing zones as well as determining the bioavailability of the phosphorus associated with those mechanisms.

CHAPTER TWO

METHODS AND MATERIALS

2.1 Water Analyses

With the primary focus of this study centered on the formation, sedimentation, and potential bioavailability of settled sediment phosphorus in Utah Lake's effluent mixing zones, the analytical methods of this study will be classified as either water or sediment analyses. The methods chosen for water analyses include: 1) mixing experiments to monitor phosphorus speciation and potential sedimentation throughout Utah Lake's effluent mixing zones, 2) geochemical modeling with PHREEQC to verify the results of the mixing experiments, and 3) batch desorption experiments to authenticate the modeled sorption of phosphate to calcite.

Water Sample Acquisition

LW samples were collected from the northern arm of Utah Lake State Park (40°14'28.1"N 111°44'43.2"W; see Figure 2) facing north towards Powell Slough. WW effluent samples were collected from the outflow of either the Orem Water Reclamation Facility (40°16'37.5"N 111°44'41.7"W; see Figure 3) or the Provo Wastewater Treatment Plant (40°12'41.4"N 111°39'06.3"W; also see Figure 3). Both LW and WW samples were collected on the same day that the mixing and batch desorption experiments were performed. The results from these analyses were plotted along a mixing line representing a spectrum of mixtures ranging from 0% LW to 100% LW. See Figure 4 for a conceptual representation of an effluent mixing zone and its mixing line.

Mixing Experiments

Patterned after the mixing experiments performed by Randall (2017) on different combinations of LW and WW, four mixing experiments were conducted monthly from July to October 2020. Samples of LW and WW were collected for each experiment alongside sonde data using an Aqua Troll 600 to measure the pH, temperature, density, and dissolved oxygen content for both types of water. WW effluent was collected from the Orem Water Reclamation Facility for the first three experiments and the Provo Wastewater Treatment Plant for the fourth experiment.

On the day each experiment was initiated, five sets of unfiltered solutions were prepared using the following ratios of LW to WW: 10:0, 9:1, 5:5, 1:9, and 0:10. The prepared solutions were taken to Brigham Young University's Environmental Analytical Laboratory at various time steps in order to monitor the change in phosphorus concentration with time among the different solutions. Each sample was tested for pH (excluding the samples from the first experiment) using a Thermo Orion 410A+ pH meter, for SRP using a FIALab Flow Injection Analyzer-2000 to perform the ascorbic acid method, and for TP using EPA 3015A microwave digestion and iCAP 7400 ICP-OES. Elemental detection was performed exclusively on the samples from the third experiment using iCAP 7400 ICP-OES. All mixed samples that reported concentrations at time-zero were mixed by laboratory personnel immediately prior to testing. Graphical representations of the mixing experiments' results are shown in Figures 5, 6, 9, and 11.

Geochemical Modeling

At the same collection times as the final three mixing experiments, two additional sets of LW and WW samples were acquired for measuring supplementary chemical data for this study's geochemical models. On the day of collection, one set of samples was taken to Brigham Young

University's Environmental Analytical Laboratory to be tested for bicarbonate using the alkalinity method prescribed by Gavlak, et al. (2005) as well as for elemental detection using iCAP 7400 ICP-OES. The remaining samples were likewise taken to Chemtech-Ford Laboratories the same day to be tested for chloride, fluoride, nitrate, and sulfate using the EPA 300.0 ion chromatography method. In addition to compiling water quality data, the original database for PHREEQC was manually augmented to include kinetic data for 23 different phosphate minerals. This adjustment made it possible for PHREEQC to predict and account for the possible formation of phosphate minerals while running geochemical models on the entered water quality data. See Table 1 for a list of these minerals, their $-\log k_{sp}$, and their sources.

Two geochemical models were created for this study. The first model was built to imitate the segmented mixing of LW and WW (to be denoted as the SM model), using the same mixing ratios as the mixing experiments (i.e., 10:0, 9:1, 5:5, 1:9, and 0:10). The second model was built to imitate the incremental mixing of LW to WW (to be denoted as the IM model) to simulate the gradual additions of WW as it flows from its parent tributary into the lake. See Figures 7 and 8 for conceptual depictions of these two geochemical models, and Figures 9, 10, and 11 for the results calculated by these models.

Batch Desorption Experiments

Based on the experiments conducted by Sørensen et al. (2011) on the desorption of phosphate from calcite, two batch desorption experiments were performed in January and February 2021 using LW, WW, and a 50:50 mixture of LW & WW as phosphate solutions. In addition to the sorbed and desorbed solutions produced in the experiments, duplicates of the original phosphate solutions (LW, WW, and a 50:50 mixture of LW & WW) were tested for TP using EPA 3015A

microwave digestion and iCAP 7400 ICP-OES at Brigham Young University's Environmental Analytical Laboratory.

For the sorption phase of the experiment, 50 mL of each phosphate solution had 2 grams of reagent grade calcite powder added to them and were allowed to equilibrate for 3.5 hours. The solutions were then centrifuged for 15 minutes at 2000 rpm, after which the liquid from each solution was collected and filtered through a 0.45 μm nylon filter before being tested for TP. For the desorption phase of the experiment, the remaining calcite residue from the sorption phase each had 50 mL of a calcite equilibrated solution (CES) added to them and was allowed to equilibrate for 30 minutes. The solutions were then centrifuged for 15 minutes at 2000 rpm, after which the liquid from each solution was collected and filtered through a 0.45 μm nylon filter before being tested for TP. Although 24 hours is the standard length of time for sorption and desorption experiments respectively, the time was shorted for these experiments in response to the quick reaction times observed by Sørensen et al. (2011).

Besides using water samples that were collected on differing days, the only difference between the two batch desorption experiments was the type of CES used in the experiments' desorption phase. The first experiment utilized a calcite equilibrated solution (CES) composed of deionized (DI) water equilibrated with reagent-grade calcite powder for 24 hours, centrifuged at 2000 rpm for 15 minutes, and was decanted before being used. The second experiment used unfiltered LW as its CES. See Figure 12 for graphical representations of these results.

2.2 Sediment Analyses

The sediment analyses chosen for this study included: 1) x-ray diffraction to identify the mineral phases present in effluent mixing zones, and 2) a sequential extraction experiment to determine the phosphorus fractionation among those sediments.

Sediment Sample Acquisition

Sediment samples were collected on October 30, 2020, during an excursion in an airboat (due to the shallowness of the tributaries) to the Powell Slough and Mill Race study areas (see Figure 3 for maps of those areas and Table 2 for the site coordinates). At each sampling site, the top several centimeters of sediment were collected by an Eckman Dredge and allowed to drain for approximately 30 seconds. The sediment was then stored in a centrifuge tube with the headspace filled with surface water. The opening of each tube was then covered with parafilm with the cap screwed on tight. The samples were then stored at 4°C until analysis could be performed on the samples.

Sequential Extractions

The sequential extraction method utilized in this study is the same method used by Randall (2017) due to its unique adaptation for Utah Lake and to ensure comparability between results. While a summary of his method and commentary on its replication will be included below, the specific instructions are outlined in his thesis.

Randall's sequential extraction method begins with an anoxic phase. While his instructions are vague in how these conditions were maintained, this study's iteration of the experiment was conducted within a small nitrogen-filled chamber to create an anoxic environment. From within the chamber, loosely sorbed phosphorus was extracted from 2.5 grams of wet sediment by rinsing it several times with 1 M ammonium chloride. The decanted rinses were then acidified with 1 M nitric acid and stored at 4°C. Redox-sensitive phosphorus was then extracted from the sediment residue by rinsing it with 0.11 M bicarbonate dithionite (a solution created from sodium bicarbonate and sodium dithionite) and an additional rinse with 1

M ammonium chloride. These rinses were likewise acidified with 1 M nitric acid and stored at 4°C. The remainder of the experiment was then performed under aerobic conditions.

Next, the phosphorus associated with either organic matter or exchangeable against OH⁻ ions was extracted by rinsing the residue twice with 1 M sodium hydroxide and once with 1 M ammonium chloride. Like the previous ones, these rinses were acidified with 1 M nitric acid and stored at 4°C. Phosphorus associated with calcium phosphate minerals and acid-soluble organic phosphorus was then extracted by rinsing the residue once with 0.5 M hydrochloric acid and once with 1 M ammonium chloride. These rinses were also acidified with 1 M nitric acid and stored at 4°C. Refractory organic phosphorus and non-extractable mineral phosphorus were extracted by drying the residue overnight at 105°C, heating it in a muffle furnace for 2 hours at 550°C, and then boiling it in 1 M hydrochloric acid for 10 minutes. The remaining liquid was combined with DI water and then stored at 4°C. The solutions from all extraction steps were taken to Brigham Young University's Environmental Analytical Laboratory to be tested for TP using EPA 3015A microwave digestion and iCAP 7400 ICP-OES. See Figure 13 for a graphical representation of these results.

X-ray Diffraction

To prepare samples for x-ray diffraction (XRD), the wet sediments were allowed to dry in a drying oven for three days at no warmer than 50°C to keep the clay minerals from becoming unstable. Once dry, each sediment sample was sealed within a container with aluminum oxide pestles and a couple of milliliters of methanol to suspend the sediment without causing the clay to swell. The containers were then sealed and shaken by a heavy-duty vibrator for 2 minutes to grind the sediment into powder. The sediments were then allowed to be dried again in a drying oven at 50°C for three days.

Once dry, the sediments were then placed inside small bottles along with a plastic pestle and about a milliliter of hexane. The bottles were shaken in a heavy-duty shaker for 20 minutes to randomly orient the clay particles. After drying overnight, the sediment was then placed into loading trays for examination using Rigaku MiniFlex 600 XRD. The produced diffraction patterns for each sample were then uploaded into PDXL2 and analyzed for potential mineral candidates until the calculated diffraction pattern matched the measured pattern and the associated *weighted-profile R* values (Rwp) were less than 10%. See Table 3 for a compilation of these results.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Results

Mixing Experiments

Phosphorus concentrations throughout all four mixing experiments were shown to be remarkably stable with respect to time regardless of their initial concentrations. This is made evident by the horizontal trendlines produced when phosphorus concentrations are plotted against time as shown in Figure 5, as well as the absence of concave upward trendlines when those same concentrations are plotted against dilution as shown in Figure 6. The high stability of the observed phosphorus concentrations (reported in ppm) is further emphasized by their average standard deviations among the four experiments, yielding 0.03, 0.03, 0.03, & 0.06 for SRP, and 0.05, 0.20, 0.03, & 0.07 for TP.

On the other hand, the pH of all samples, as shown in Figure 9, generally became more neutralized with respect to time. The initial pH for LW ranged from 8.1-8.6 and eventually dropped down to 7.5-8.2. The initial pH for WW ranged from 7.4-7.8 and eventually dropped down to 7.1-7.4 except for one case that maintained a pH of 7. Intermediate values for these constituents among the mixed samples were largely proportional to their ratio of LW to WW.

Among unmixed LW samples, the average values for SRP were 0.05, 0.10, 0.04, & 0.06, whereas the average values for TP were 0.17, 0.20, 0.18, & 0.22. In regards to unmixed WW samples, the average values for SRP were 1.14, 1.25, 0.87, & 1.25, and the average values for TP were 2.52, 3.03, 1.25, & 2.30. SRP constitutes a significant portion of the TP in both LW and WW, averaging 57% of TP throughout all experiments.

Geochemical Modeling

Of the 23 phosphate minerals added to the PHREEQC database for this study (listed in Table 1), only the apatite minerals ($\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$) were predicted to precipitate within the effluent mixing zones of Utah Lake. Even so, the SM and IM models in Figure 10 suggest that only one form of apatite mineral precipitates at a time, generally producing about 1 mg L^{-1} of total apatite (assuming the necessary chemical reactions are carried to completion). Besides apatite, the only other mineral predicted by PHREEQC to precipitate is calcite, also shown in Figure 10, with the SM model predicting steady formation until reaching 47 mg L^{-1} , whereas the IM model predicts delayed formation before suddenly reaching 94 mg L^{-1} .

In regards to dissolved speciation, both models were shown (as seen in Figure 11) to produce nearly identical results regarding the aqueous concentrations of calcium and phosphorus. When both models were set to predict these species without the formation of any minerals, the results closely matched the ones measured in the 3rd mixing experiment. Because of the similarity in the results between the four mixing experiments, it can be concluded that neither calcite nor apatite precipitation occurred in any of the mixing experiments. The models were also used to predict the dissolved speciation of calcium and phosphorus in the event that calcite and apatite do precipitate, understandably resulting in much lower aqueous concentrations.

Batch Desorption Experiments

As depicted in Figure 12, coprecipitation was unexpectedly shown to be the predominant fate of phosphorus in the batch desorption experiments, consistently accounting for anywhere between 46-58% of the TP among all water samples. On the other hand, adsorption accounted for anywhere between 6-28% of TP and was more inclined to occur in the presence of LW (both as a phosphorus solution and as a CES). The unaligned adsorption and coprecipitation isotherms

produced from these experiments confirm that only partial desorption is observed within these particular samples.

Sequential Extractions

Phosphorus fractionation was surprisingly similar between the Powell Slough and Mill Race Creek study areas. The largest fraction, at 57%, was associated with calcium phosphate minerals and acid-soluble organic phosphorus. This fraction was the only one to produce a trend based on location, having its greatest values in or near the main body of Utah Lake. The second-largest fraction, at 21%, was associated with redox-sensitive phosphorus bound to oxidized iron and manganese compounds. The third-largest fraction, at 13%, was associated with phosphorus that was exchangeable against the OH-ions in organic matter. The fourth-largest fraction, at 6%, was associated with refractory organic phosphorus and non-extractable mineral phosphorus. The fifth and final fraction, at 3%, was associated with loosely sorbed phosphorus. See Figure 13 for a graphical representation of these results.

X-ray Diffraction

Although the study areas for Powell Slough and Mill Race Creek were fairly similar in their mineralogy, the mass percentages of their minerals varied enough to require them to be reported separately. General trends between the two areas included quartz-dominated samples in the main body of Utah Lake and calcite prevalent samples in Provo Bay and the tributaries. Although apatite was detected throughout most of both study areas, there were no noticeable trends correlating concentration with location.

The average weight percent for the minerals in the Powell Slough Study Area are as follows: quartz at 39.4%, carbonates at 20.7% (predominantly consisting of calcite at 14.2%), feldspars at 19.9%, clays at 12.1%, apatite at 2.5%, ankerite at 2.0%, hornblende at 1.4%, pyrite

at 1.1%, and goethite at 0.6%. The average weight percent for the minerals in the Mill Race Creek Study Area are as follows: carbonates at 38.4% (predominantly consisting of calcite at 21.9%), quartz at 26.4%, feldspars at 13.9%, clays at 12.0%, hornblende at 3.6%, apatite at 3.3%, ankerite at 0.9%, goethite at 0.8%, and pyrite at 0.5%. See Table 3 for the weight percentages calculated for each sediment sample. See Table 3 for a complete compilation of these results.

3.2 Discussion

Unlike the mixing experiments performed by Randall (2017), all iterations of the experiment performed in this study showed no significant changes in SRP with time (see Figures 5 and 6). This observation even includes this study's fourth mixing experiment, which used WW effluent from the same wastewater treatment plant as Randall and recorded phosphorus measurements from time-zero up to 700 hours after sample collection. Randall's WW samples, however, contained more than double the amount of phosphorus that was measured in this study's WW samples, thus increasing the likelihood for SRP to undergo one or more chemical reactions under his experimental conditions.

With no changes seen in SRP concentrations over the course of several weeks, this study's mixing experiments suggest that – under these experimental conditions – SRP remains chemically inactive as it travels through Utah Lake's effluent mixing zones. This notion, however, is countered by this study's geochemical models, which claim that it is possible for apatite, a phosphate mineral ($\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$), to precipitate from the waters of these effluent mixing zones. It is important to note that apatite does not directly precipitate from surface waters. Sedimentary apatite is instead created when phosphate forms a surface complex with calcite via coprecipitation and is then repeatedly transformed into several intermediate

phases through dissolution and reprecipitation before apatite is finally produced (Avnimelech, 1983; Johnsson & Nancollas, 1992).

In addition to being a slow process, the "precipitation" of apatite is also dependent on the presence of calcite. Calcite precipitation, however, appears to be absent in this study's mixing experiments despite the predictions made by this study's geochemical models. When monitored, the only fluctuations observed concerning dissolved calcium were closely associated with the dilution ratio of LW to WW. Geochemical modeling of this system predicts the same concentrations of dissolved calcium as was measured in the mixing experiment when mineral precipitation is restricted in the model (see Figure 11). The lack of calcite forming in the water column of this study's mixing experiments consequently removes the possibility of apatite being able to form in these same experiments, thereby preventing SRP from being removed from the system through inorganic means.

Under geochemically saturated conditions, calcite precipitation can occur rapidly once initial crystals have been formed, thus creating nucleation sites upon which further calcite mineralization can be propagated (Murphy, et al., 1983). A corresponding increase in pH can likewise increase calcite insolubility. Calcite precipitation, however, can be hindered or even inhibited when its nucleation sites become overwhelmed by an overabundance of dissolved phosphorus or organic matter. Barriers such as these often require laboratory experiments to introduce calcite seed crystals in order to induce calcite precipitation (Danen-Louwerse, et al., 1994). This is likely why calcite and apatite were consequently unable to form in this study's mixing experiments despite the geochemical models predicting otherwise.

While calcite and apatite may not have formed under the conditions observed in this study's mixing experiments, x-ray diffraction detected both minerals within the sediments of the

Powell Slough and Mill Race Creek effluent mixing zones. These minerals could very well have been transported to the lake from throughout the watershed, but the geochemical models again suggest that calcite and apatite could also be formed in-situ. Calcite has been confirmed to actively precipitate in Utah Lake, with estimates of approximately 300 mg L^{-1} forming in the lake each year during the mid-1900s (Fuhrman, et al., 1981). Precipitation of calcite, therefore, provides an opportunity for phosphorus coprecipitation to occur, thus initiating the first stages of apatite formation within Utah Lake.

Several notable differences are seen when comparing the x-ray diffraction and sequential extraction results of this study with those reported by Randall (2017). Utah Lake's sediments, as observed by Randall, are generally dominated by calcium carbonate. While this was generally true for the sediments collected in Powell Slough, Mill Race Creek, and Provo Bay, the sediments collected in the main body of Utah Lake were quartz-dominated. This occurrence, however, is a local phenomenon caused by vigorous wave action and is commonly observed in the sands near the shorelines and the mouths of major rivers in Utah Lake (Brimhall & Merritt, 1981).

While the sequential extraction results obtained in this study (shown in Figure 13) and by Randall (2017) agree that redox-sensitive and calcium phosphate minerals are the most prominent forms of phosphorus within Utah Lake's sediments, this study's extraction results differ from Randall's in determining which of the two fractions is the largest. This discrepancy could be attributed to the differences in sampling location, with this study's samples being collected in the lake's effluent mixing zones and Randall's samples being collected throughout the lake. Another possible explanation could be the different approaches taken to keep the initial

sequential extraction steps anoxic. Replicated extractions of these sediments would likely be the most informative means of inquiring which fraction is indeed the largest.

Compared to the batch desorption experiments performed by Sørensen et al. (2011), the amount of coprecipitation observed in this study's desorption experiments as shown in Figure 12 is unexpectedly high. Most studies regarding the coprecipitation and adsorption of phosphorus on calcite indicate that adsorption is the primary mechanism observed. Differences between these results are likely due, at least in part, to the differences in experimental design. Some of the most notable differences include the amount of calcite powder used (2g/20mL used by Sørensen et al. and 2g/50mL used in this study), the range of phosphorus concentrations used (0.5-0.8 ppm used by Sørensen et al. and 0.1-1.9 ppm used in this study), the type of CES used (specialized solutions used by Sørensen et al. and calcite equilibrated DI water and LW for this study), and the measurement calcite surface area (accounted for by Sørensen et al. but not by this study). Coprecipitation, however, likely does not occur to the extent shown in the experiment as the calcite powder undoubtedly provided a superficially higher number of reaction sites than is naturally provided by the calcite within Utah Lake. Despite the observations made by Sørensen et al., greater amounts of phosphorus desorption from calcite could potentially occur in the waters of Utah Lake's effluent mixing zones if provided a desorption time that is longer than 30 minutes.

Regardless of the different outcomes that have been observed, this study's desorption experiment results imply that coprecipitation is an active mechanism influencing TP cycling within Utah Lake. The fact that calcite is less abundant in the lakeward sediments and yet contributes to a higher phosphorus fractionation than its counterparts upstream suggests that a fair amount of coprecipitation occurs in the main body of Utah Lake. Even at its lowest measurement, the phosphorus associated with calcium phosphates is still several times greater

than that of loosely sorbed (adsorbed) phosphorus. The coprecipitation of phosphorus with calcite could very well be more of a critical aspect in rendering phosphorus biologically unavailable in Utah Lake than was previously thought.

CHAPTER FOUR

CONCLUSION AND RECOMMENDED RESEARCH

4.1 Conclusion

Effluent mixing zones form a transitional boundary where tributaries containing wastewater intermix with their receiving water-body. SRP from WW discharges may limit or possibly prevent calcite precipitation from occurring within effluent mixing zones, causing SRP concentrations to remain stable while in transit to Utah Lake. Calcite is the only major mineral that forms and precipitates in the lake. Phosphorus is consequently more likely to coprecipitate with calcite after it has entered Utah Lake and likely influences the TP cycling in the lake more than was previously expected. In-situ formation of apatite in Utah Lake appears to be an extension of this process.

Precipitation of calcite and consequential coprecipitation of phosphorus with calcite appears to be the only inorganic sedimentation mechanism capable of rendering phosphorus biologically unavailable to algae in Utah Lake. Although it is unconfirmed how much of the calcium phosphate minerals found in the lake-bottom sediments are formed in response to coprecipitation in the lake, their prevalence suggests that their formation is an important mechanism for removing phosphorus from Utah Lake. Phosphorus can also be coprecipitated by redox-sensitive minerals or adsorbed to various other minerals or suspended solids, but these mechanisms only render phosphorus temporarily unavailable to algae. Further understanding in regards to phosphorus coprecipitation with calcite and redox-sensitive minerals is needed in order to better quantify the actual sediment nutrient flux rates and their associated bioavailability within Utah Lake.

This study's mixing experiments did not observe any mineral formation even when TP concentrations were below 1 mg L^{-1} . The restriction of WW phosphorus to 1 mg L^{-1} is likely not enough to induce early calcite formation and consequential phosphate coprecipitation in Utah Lake's effluent mixing zones due to phosphorus concentrations being too high and pH levels being too low. The results from this study are, therefore, unable to justify the enactment of the TBPEL by the Utah Water Quality Board.

4.1 Recommended Research

With calcium phosphate and redox-sensitive minerals shown to be the most significant fractions of phosphorus in the sediments of Utah Lake and its effluent mixing zones, further study is recommended regarding their ability to coprecipitate phosphorus. Such an endeavor would include monitoring coprecipitation under various conditions that affect Utah Lake, including the current rate of calcite precipitation, episodes of sediment resuspension, pH fluctuations throughout the year, and variations in oxidation state within the sediments. Doing so would answer key questions needed to quantify the actual sediment nutrient flux rates and bioavailability within Utah Lake.

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APPENDIX A – FIGURES AND TABLES

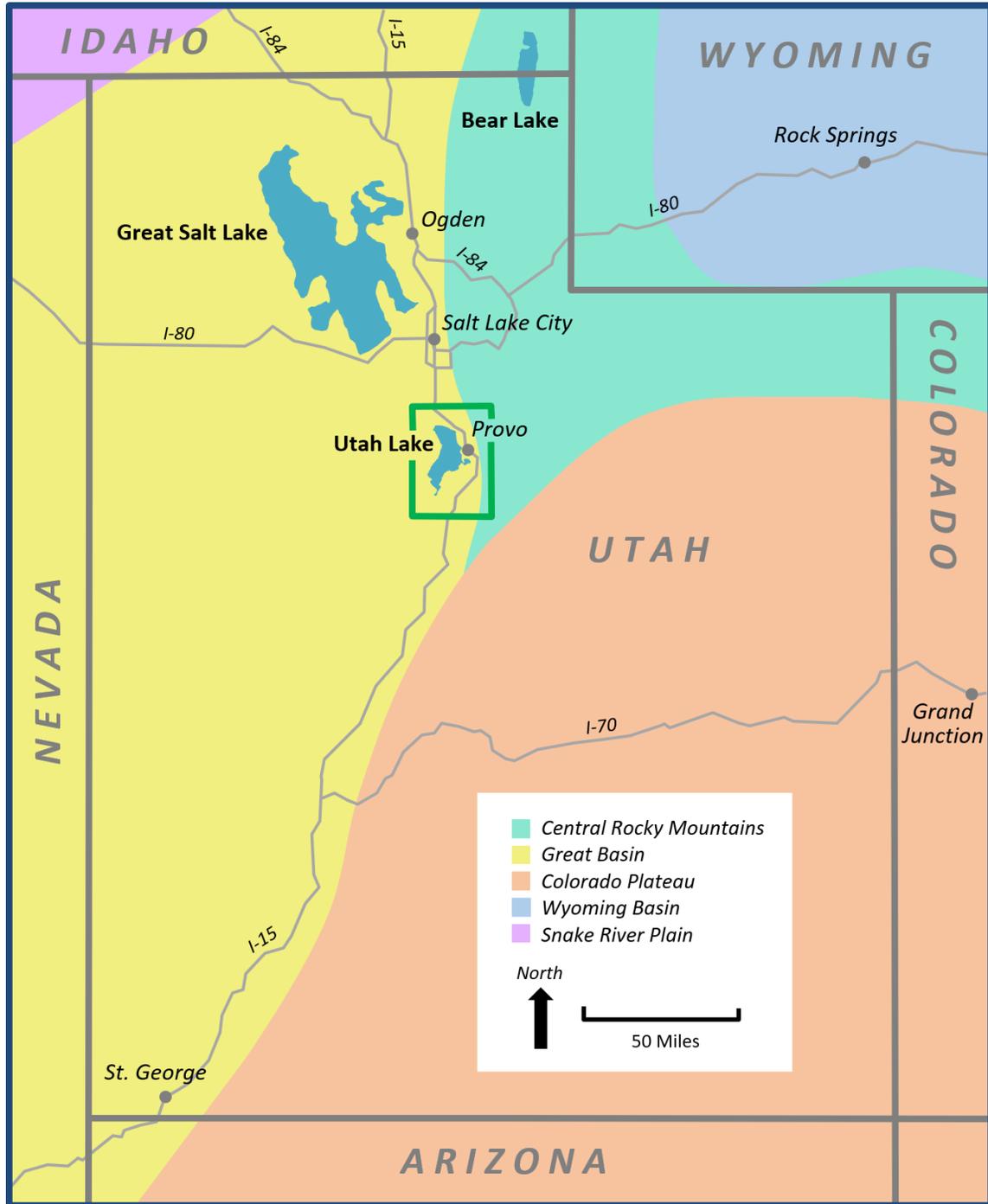


Figure 1. Reference map of the state of Utah, USA and the location of Utah Lake within the state (marked by the green box). Although Utah Lake is technically located in the Great Basin, its existence is heavily influenced by the physiographic characteristics of both the Central Rocky Mountains and the Great Basin.

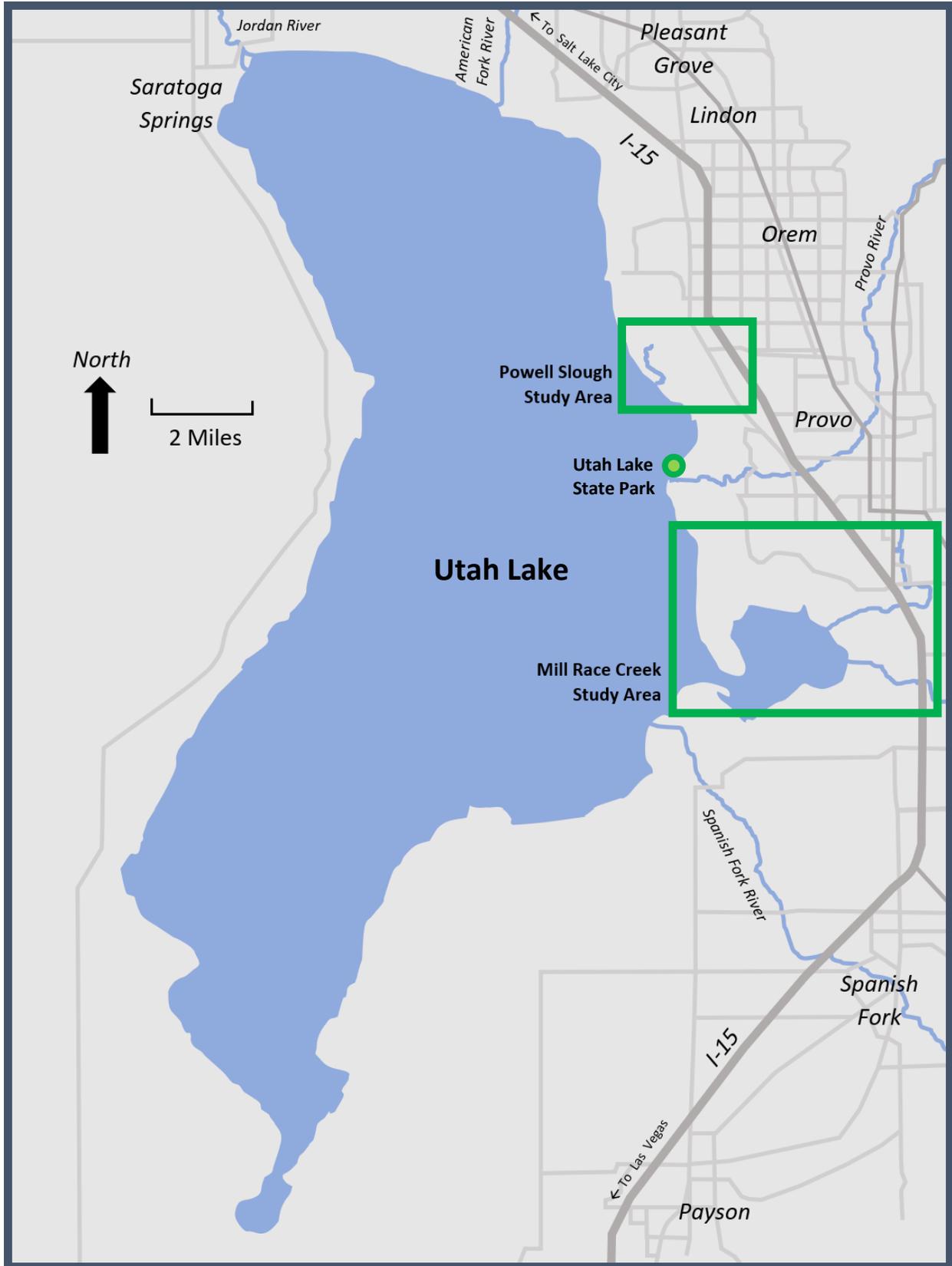


Figure 2. Reference map for Utah Lake and the location of the study areas mentioned herein.

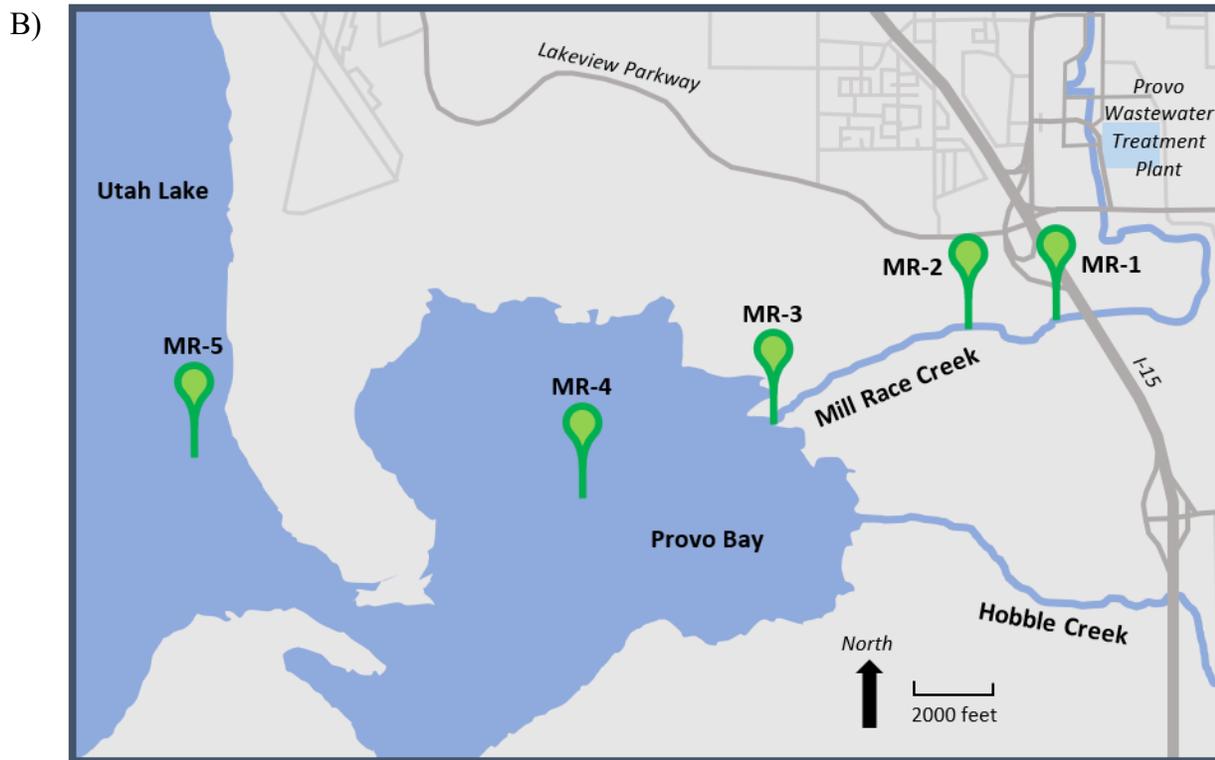


Figure 3. Reference map for A) the Powell Slough study area, and B) the Mill Race Creek study area. The green pins show the locations of where sediment samples were collected along with their corresponding sample name.

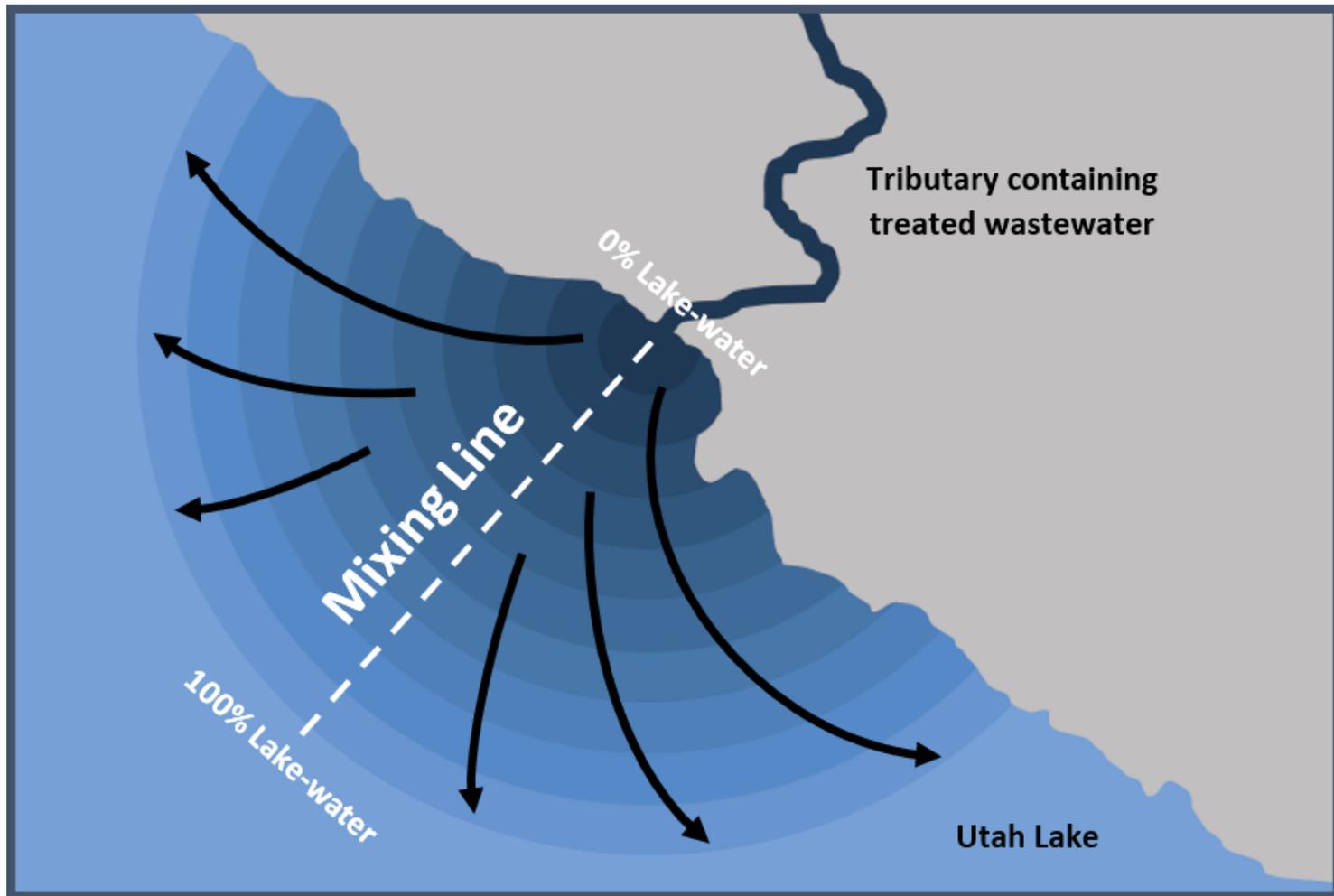


Figure 4. Conceptual representation of an effluent mixing zone and its mixing line, used to mark the dilution of tributary water in the lake. Many of the subsequent figures will be plotted along a mixing line to show how the concentrations of various constituents vary relative to their position within an effluent mixing zone.

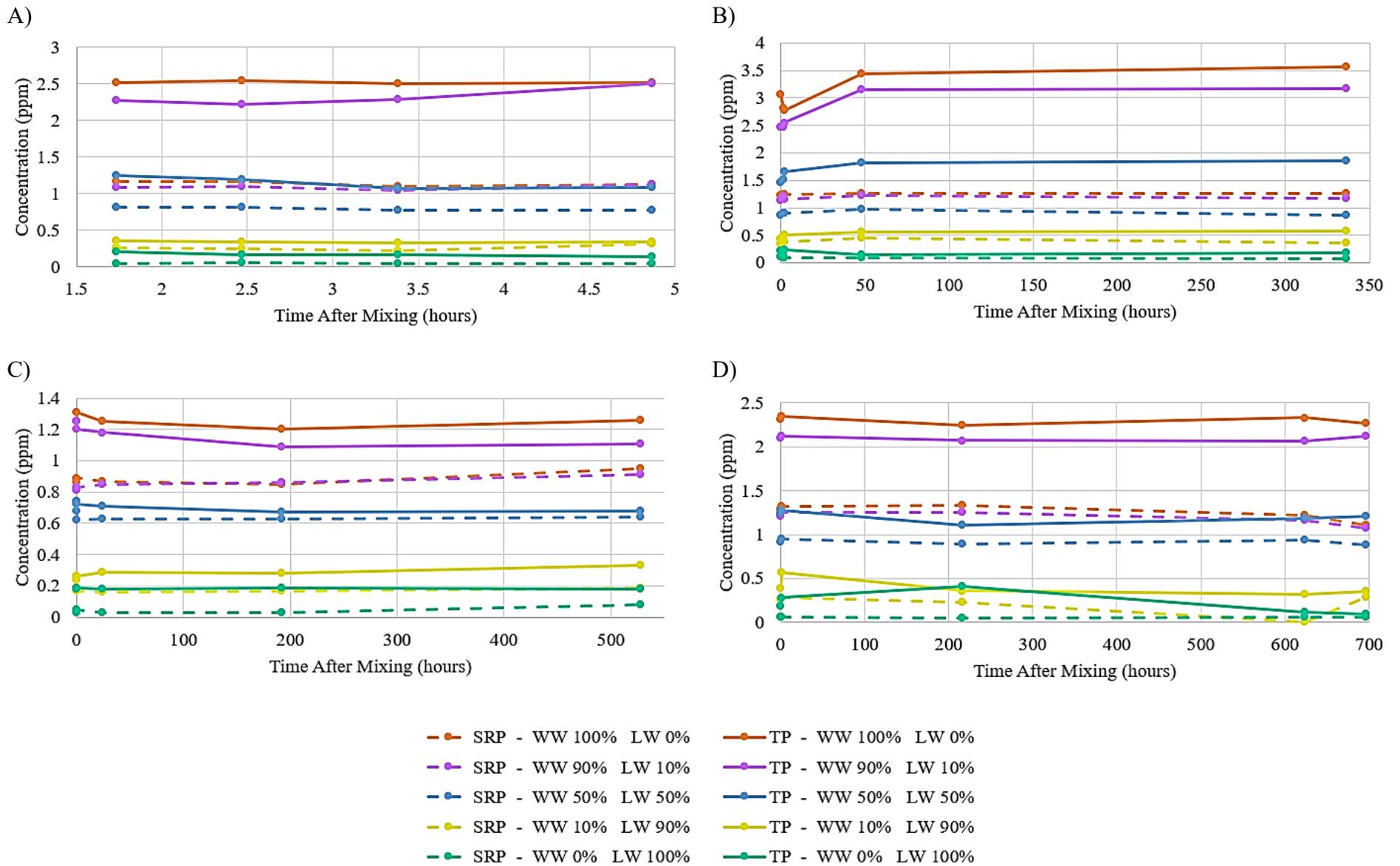


Figure 5. Mixing experiment results for concentration vs. time for A) the first experiment, B) the second experiment, C) the third experiment, and D) the fourth experiment.

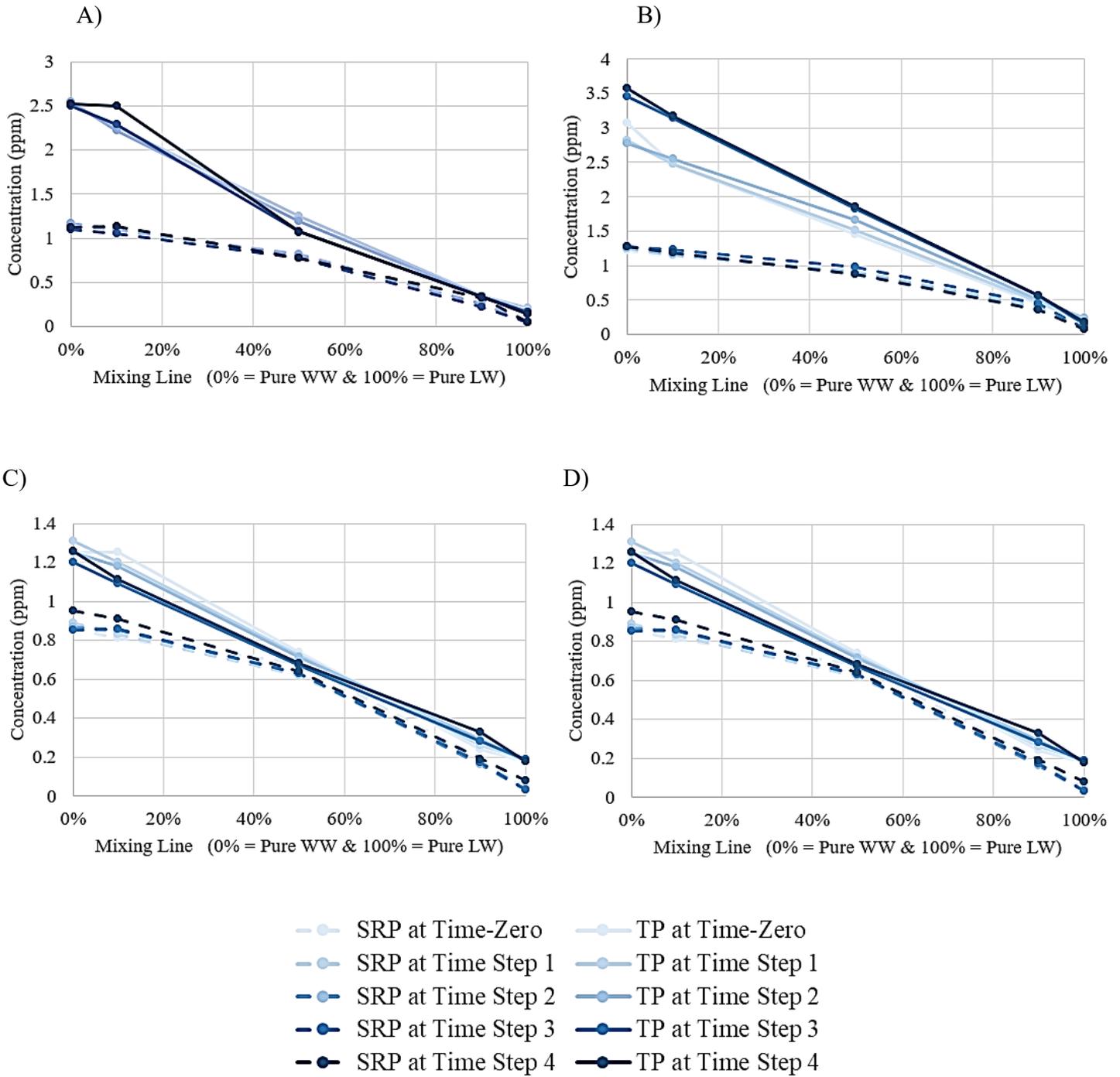


Figure 6. Mixing experiment results for concentration vs. dilution for A) the first experiment, B) the second experiment, C) the third experiment, and D) the fourth experiment. Although not shown here, the time steps do vary between experiments. See Figure 5 for the actual time steps.

SM Model (Segmented Mixing)

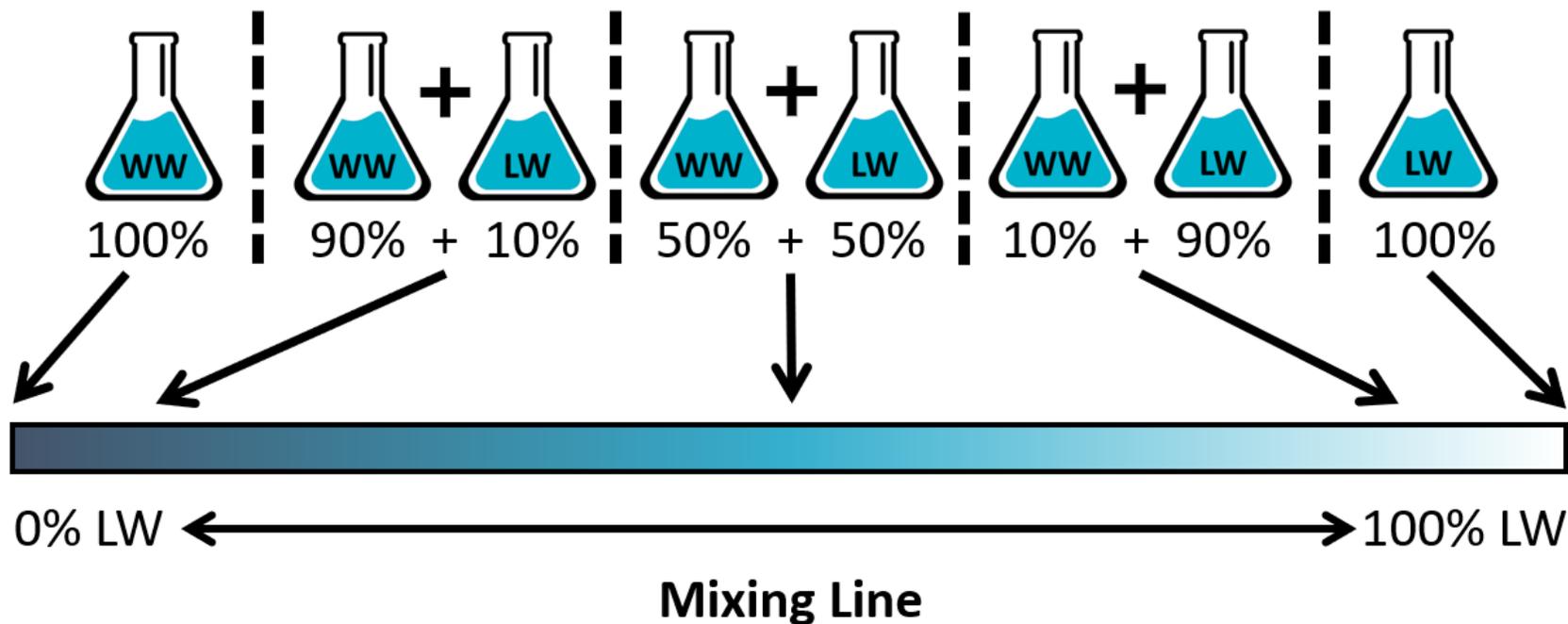


Figure 7. Conceptual representation of the segmented mixing (SM) model created in PHREEQC for this project. The model utilizes WW and LW samples as its endmembers along with three intermediate mixtures of WW to LW (ratios of 9:1, 5:5, & 1:9). Due to its simplicity, this model served as the basis for this study's mixing experiments.

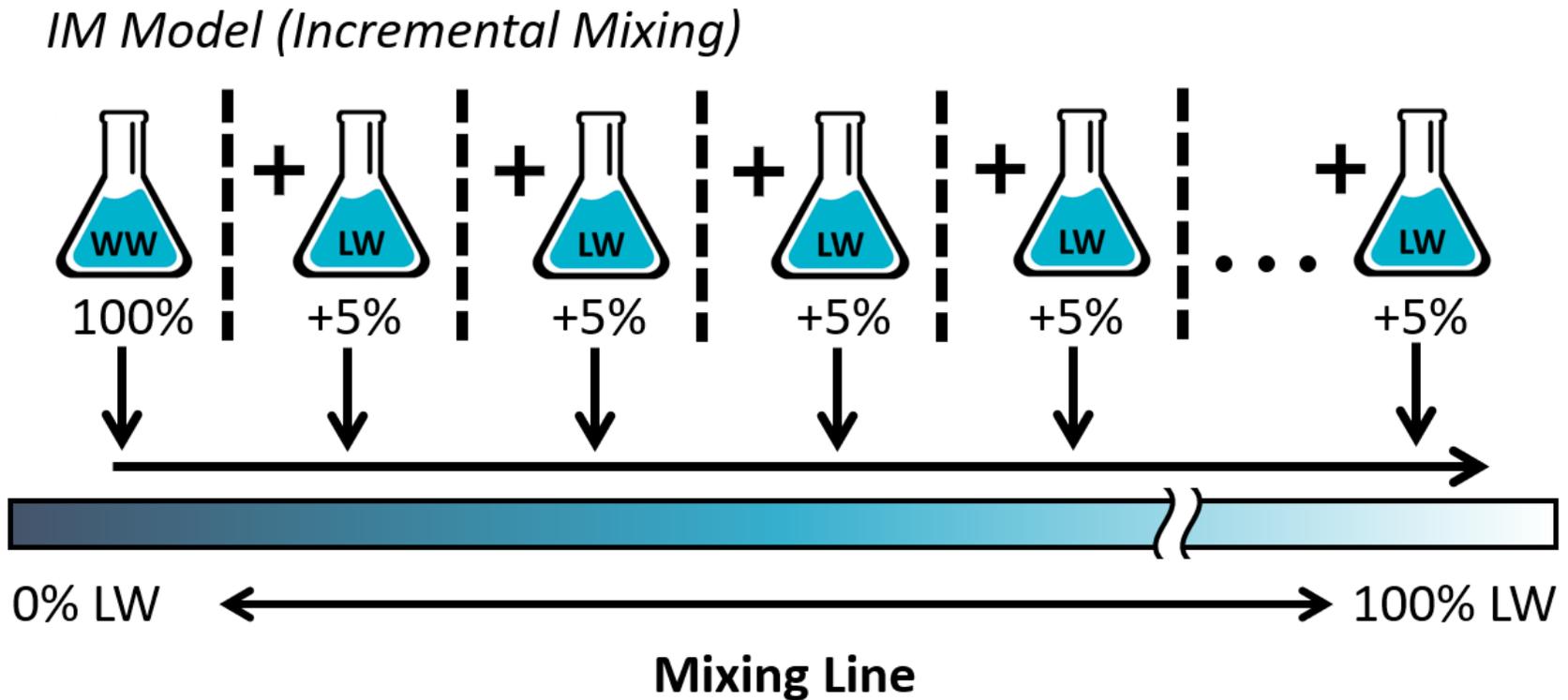


Figure 8. Conceptual representation of the incremental mixing (IM) model created in PHREEQC for this project. The model begins with a sample of 100% WW and had LW added to it in 5% increments (by mass) until the WW solution became infinitely diluted with LW. This model is considered to be more accurate than the SM model in representing Utah Lake's effluent mixing zones.

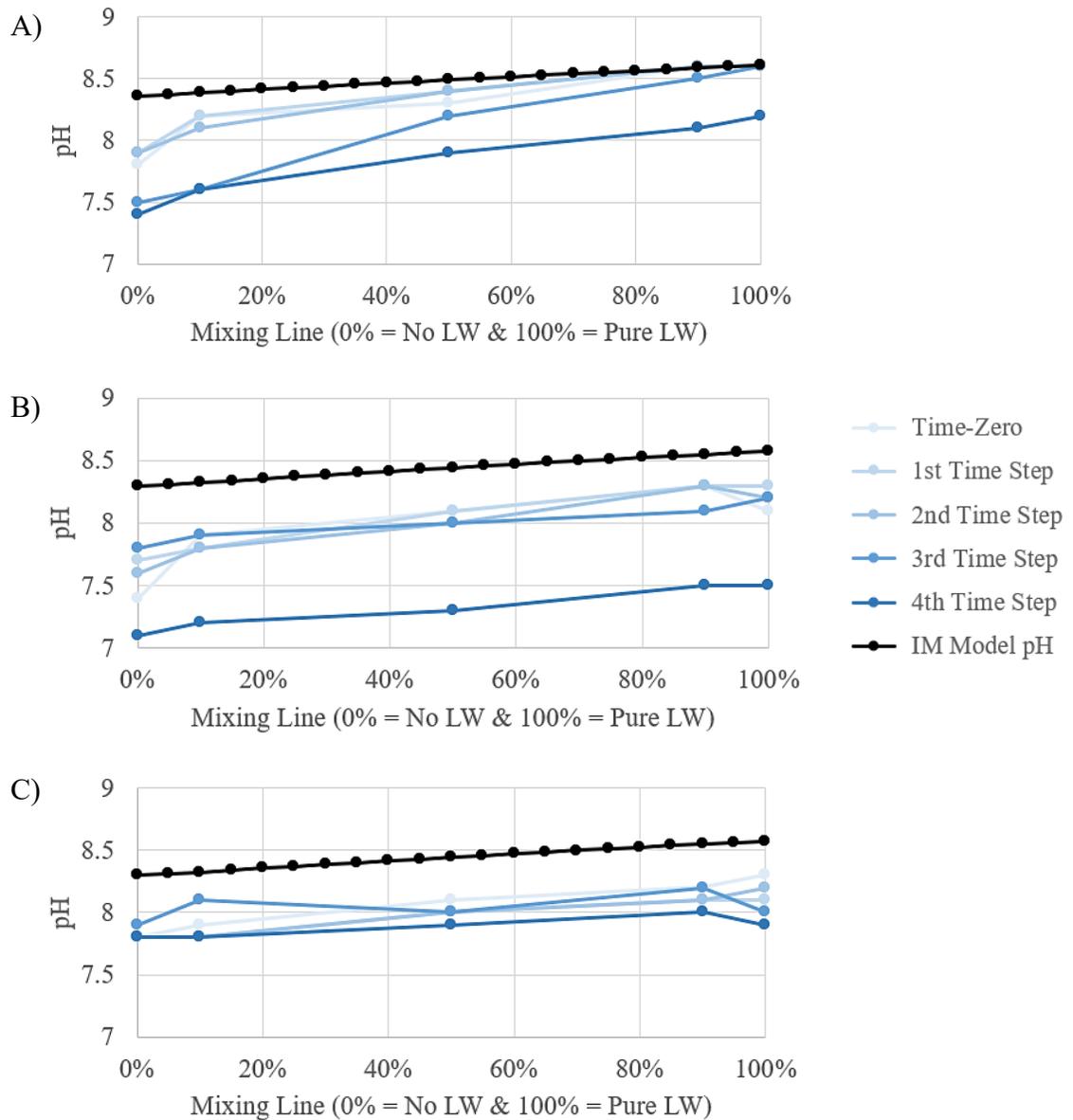


Figure 9. Mixing experiment and IM model results for pH vs. dilution for A) the second mixing experiment, B) the third mixing experiment, and C) the fourth mixing experiment. SM model results for pH were essentially identical to the IM model results. While modeled pH tended to be higher than measured pH, this was most likely caused by utilizing an estimated value for $p\text{CO}_2$ in the models. Incorporating $p\text{CO}_2$, however, had no noticeable effect on the predicted values for mineral precipitation or concentration for dissolved phosphorus or calcium.

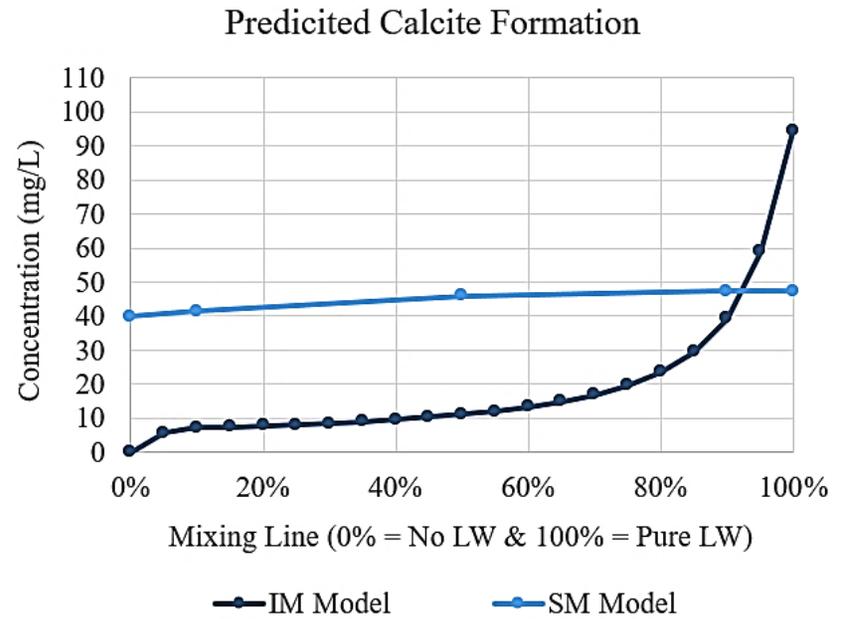
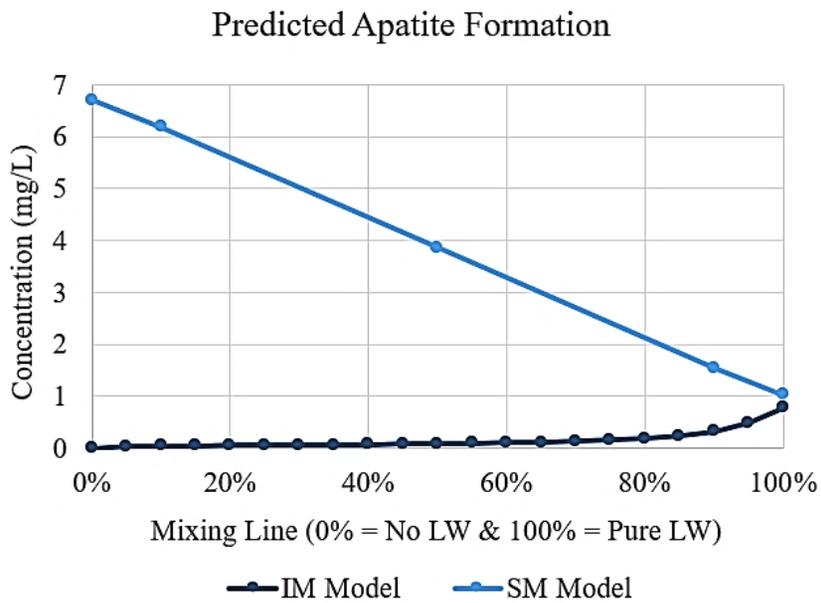


Figure 10. Geochemical models for the potential formation of apatite and calcite within Utah Lake's effluent mixing zones. While other potential minerals phases could potentially form, their concentrations are so low that their presence becomes essentially negligible.

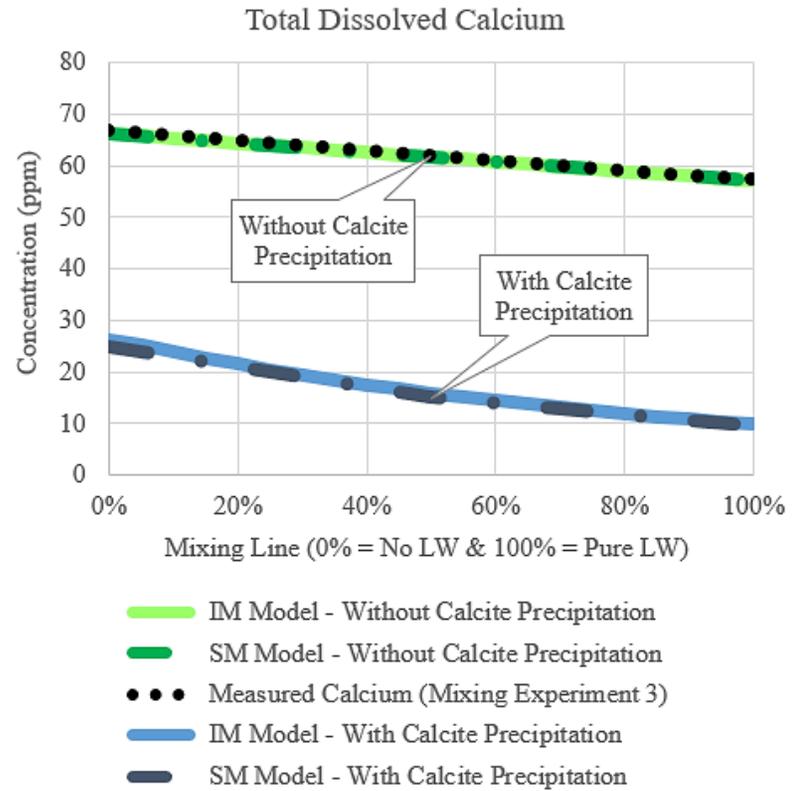
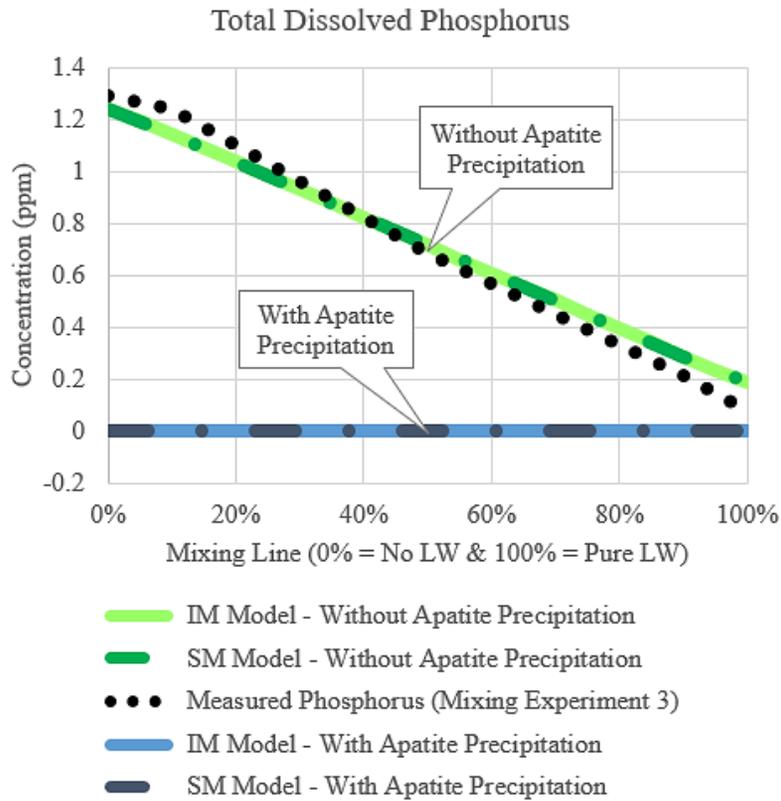


Figure 11. Geochemical model for the potential concentrations of dissolved phosphorus and dissolved calcium in Utah Lake's effluent mixing zones. The models portray two scenarios, one with mineral precipitation and the other without mineral precipitation.

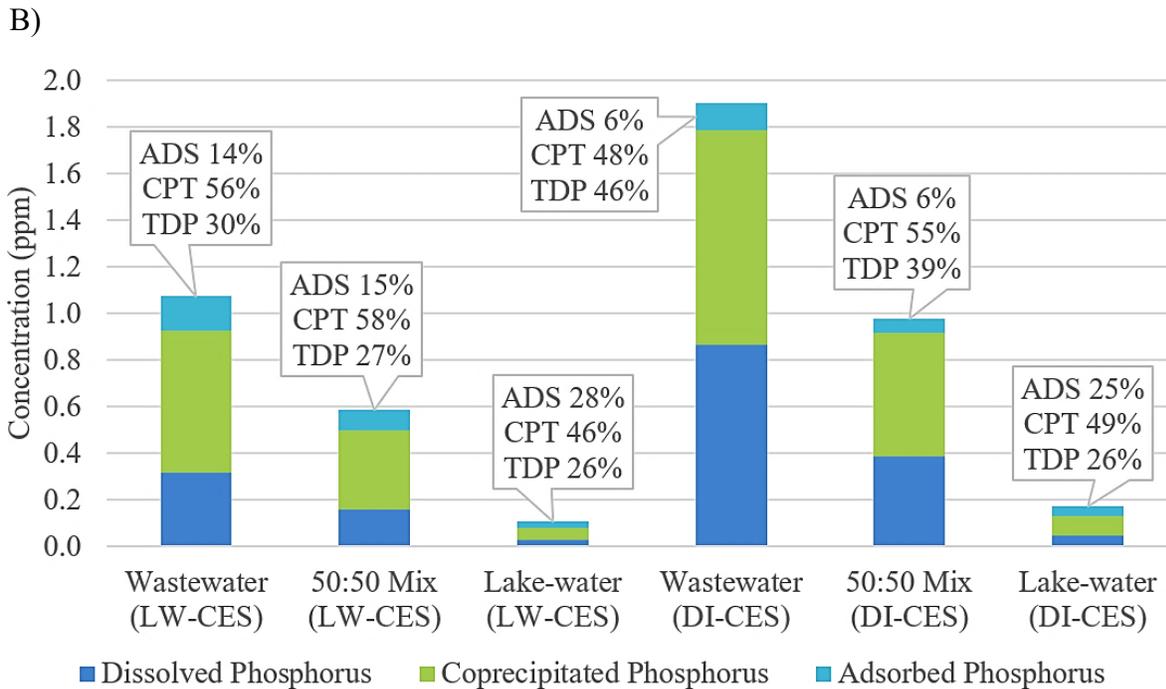
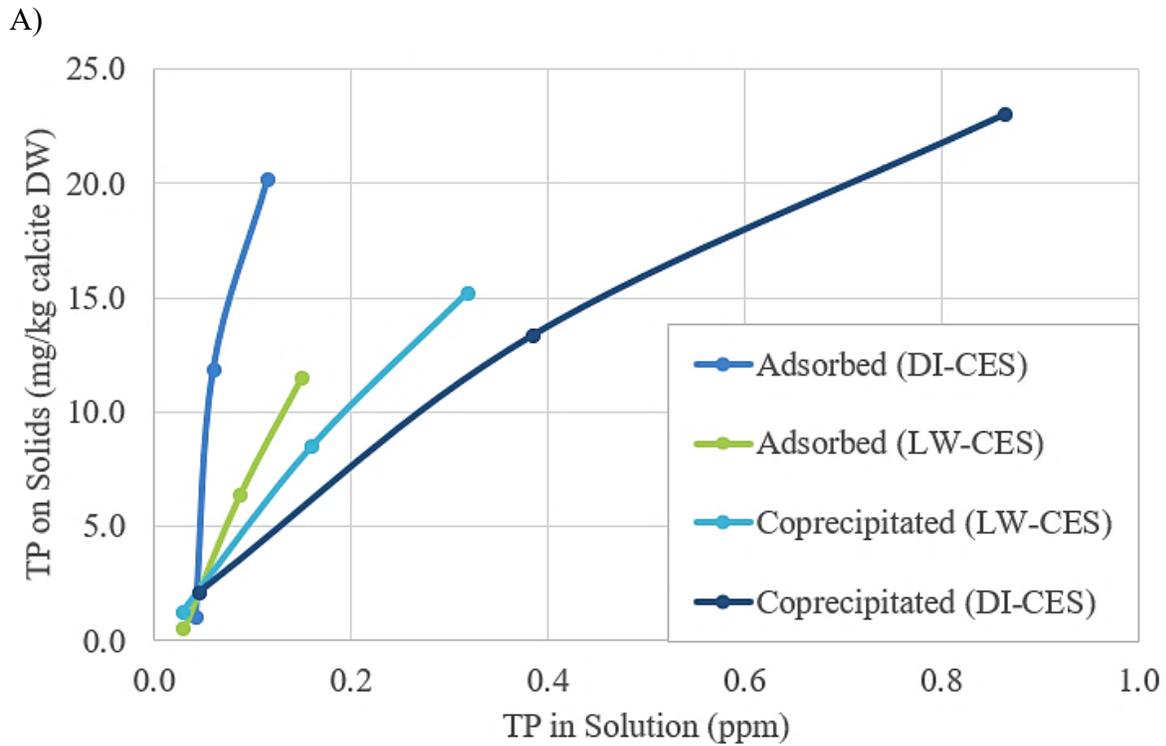


Figure 12. Batch desorption results showing A) the isotherms for adsorption and coprecipitation, and B) the comparative amounts of coprecipitated (CPT), adsorbed (ADS), and dissolved phosphorus (TDP) associated with each batch.

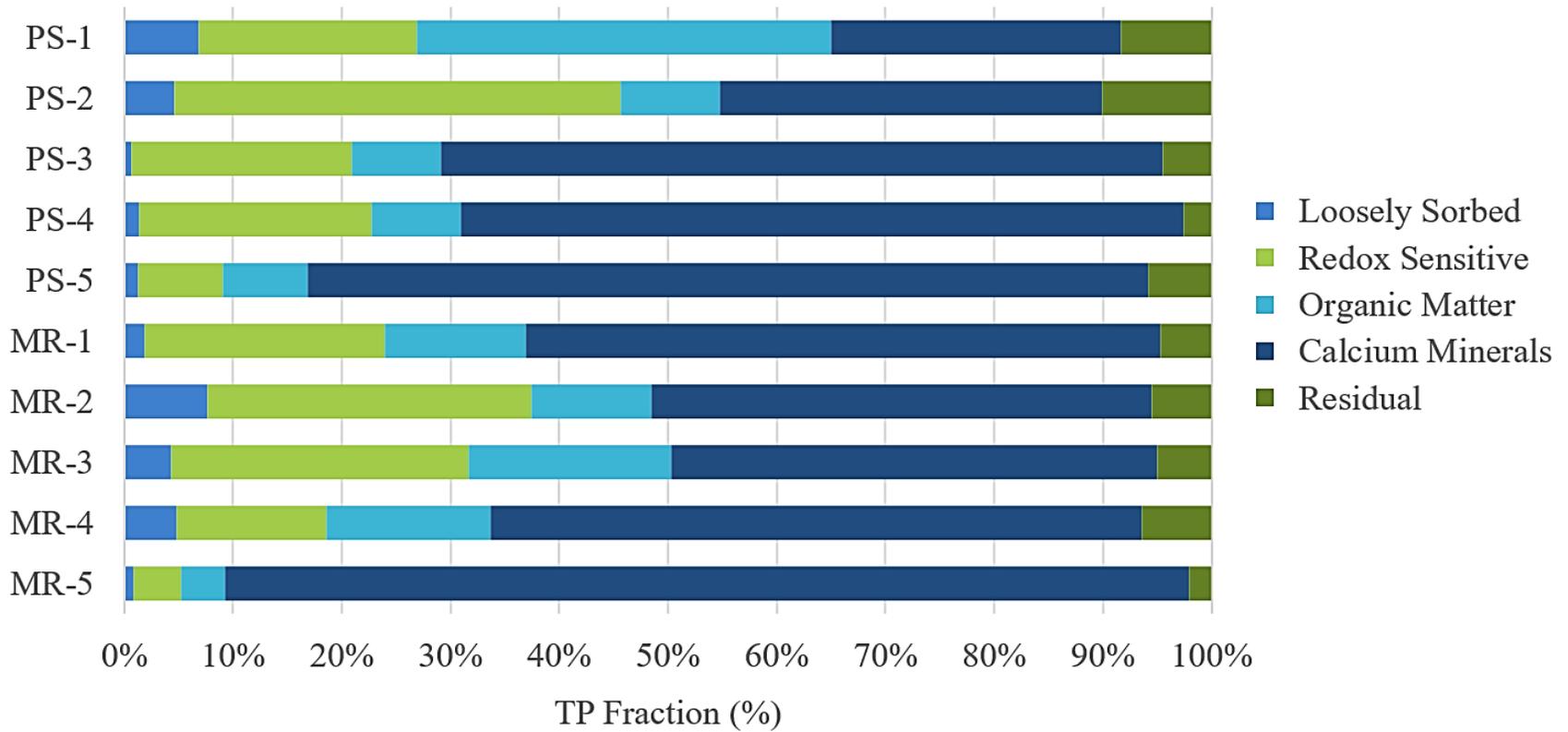


Figure 13. Sequential extraction results for the sediments in the Powell Slough and Mill Race Creek study areas. See Figure 3 for maps showing the location where each sample was collected.

Table 1. List of Phosphate Minerals

<i>Common Name</i>	<i>Chemical Formula</i>	<i>-log K_{sp}</i>	<i>Source</i>
Berlinite	AlPO ₄	20.01	Ofoegbu (2019)
Variscite	AlPO ₄ :2H ₂ O	30.5	Ofoegbu (2019)
Monetite (DCPA)	CaHPO ₄	6.90	Ofoegbu (2019)
Brushite (DCPD)	CaHPO ₄ :2H ₂ O	6.60	Ofoegbu (2019)
Amorphous Calcium Phosphate (ACP)	Ca ₃ (PO ₄) ₂ :xH ₂ O	25.46	Daneshgar, et al. (2018)
Chlorapatite (CAP)	Ca ₅ (PO ₄) ₃ Cl	53.08	Ofoegbu (2019)
Fluorapatite (FAP)	Ca ₅ (PO ₄) ₃ F	59.08	Wei, et al (2013)
Hydroxyapatite (HAP)	Ca ₅ (PO ₄) ₃ OH	57.72	Wei, et al. (2013)
Octacalcium Phosphate (OCP)	Ca ₈ H ₂ (PO ₄) ₆ :5H ₂ O	46.97	Ofoegbu (2019)
FePO ₄	FePO ₄	22	Ofoegbu (2019)
Strengite	FePO ₄ :2H ₂ O	34.3	Ofoegbu (2019)
Fe ₃ (PO ₄) ₂	Fe ₃ (PO ₄) ₂	29.89	Ofoegbu (2019)
Vivianite	Fe ₃ (PO ₄) ₂ :8H ₂ O	35.755	Ofoegbu (2019)
K-Struvite	KMgPO ₄ :6H ₂ O	10.632	Enchemica LLC (2017)
K-Taranakite	K ₃ Al ₅ (PO ₄) ₈ H ₆ :18H ₂ O	178.8	Enchemica LLC (2017)
MgHPO ₄	MgHPO ₄	14.80	Lothenbach, et al. (2019)
Newberyite	MgHPO ₄ :3H ₂ O	17.93	Lothenbach, et al. (2019)
MgNH ₄ PO ₄	MgNH ₄ PO ₄	12.6	Brezonik & Arnold (2011)
Struvite	MgNH ₄ PO ₄ :6H ₂ O	13.26	Daneshgar, et al. (2018)
Farringtonite	Mg ₃ (PO ₄) ₂	22.41	Lothenbach, et al. (2019)
Bobierite	Mg ₃ (PO ₄) ₂ :8H ₂ O	25.30	Lothenbach, et al. (2019)
Cattiite	Mg ₃ (PO ₄) ₂ :22H ₂ O	23.03	Lothenbach, et al. (2019)
NH ₄ -Taranakite	(NH ₄) ₃ Al ₅ (PO ₄) ₈ H ₆ :18:H ₂ O	175.5	Stewart (1991)

Table 2. Sediment Sample Information

Sample Name	Location Description	Coordinates
PS-1	Powell Slough Upstream	40°16'34.6"N 111°44'46.6"W
PS-2	Powell Slough Downstream	40°16'01.8"N 111°44'25.6"W
PS-3	Powell Slough Confluence with Utah Lake	40°15'54.6"N 111°44'34.7"W
PS-4	Utah Lake Near Shore	40°15'53.0"N 111°44'36.1"W
PS-5	Utah Lake Offshore	40°15'50.6"N 111°44'40.5"W
MR-1	Mill Race Upstream	40°12'06.5"N 111°39'23.7"W
MR-2	Mill Race Downstream	40°12'03.9"N 111°39'51.6"W
MR-3	Mill Race Confluence with Provo Bay	40°11'42.9"N 111°40'53.4"W
MR-4	Provo Bay Near Shore (by DWQ's sonde)	40°11'20.7"N 111°41'55.4"W
MR-5	Provo Bay Offshore (Utah Lake)	40°11'32.6"N 111°43'58.9"W

Table 3. X-ray Diffraction Results

<i>Major Mineral Assemblage</i>  <i>Trace Mineral Assemblage</i>	PS-1 Powell Slough Upstream	PS-2 Powell Slough Downstream	PS-3 Powell Slough Confluence	PS-4 Utah Lake Near Shore	PS-5 Utah Lake Offshore	MR-1 Mill Race Upstream	MR-2 Mill Race Downstream	MR-3 Mill Race Confluence	MR-4 Provo Bay	MR-5 Utah Lake (near Provo Bay)
	<i>Mass Percentage</i>									
Quartz	32.0	16.0	47.0	53.0	49.0	31.0	20.0	9.0	19.0	53.0
Calcite	23.0	25.0	12.0	4.7	6.3	33.0	45.0	43.0	34.0	4.7
Aragonite	4.4	2.2	BDL	6.8	0.7	1.9	3.5	4.0	2.0	4.1
Dolomite	4.0	9.0	4.0	0.8	0.8	0.7	2.9	3.0	7.3	3.0
Kaolinite	3.0	2.2	1.1	0.6	2.6	1.4	3.6	1.0	2.9	0.6
Montmorillonite	0.3	1.7	5.0	1.1	0.3	1.7	1.1	2.0	1.1	0.3
Illite	BDL	4.9	3.4	1.5	1.1	5.2	2.0	4.0	0.2	2.5
Muscovite	9.0	7.0	9.0	1.7	4.8	7.0	0.8	4.0	18.0	0.7
Albite	11.0	18.0	13.0	17.0	10.4	9.5	12.0	2.0	10.0	20.0
Anorthite	5.0	4.8	BDL	1.0	16.8	1.4	0.6	8.0	BDL	BDL
Microcline	1.3	0.8	BDL	0.3	0.2	0.9	0.1	2.0	0.8	2.2
Goethite	0.5	1.2	0.8	0.4	0.2	1.4	1.1	0.2	0.4	0.8
Ankerite	0.9	BDL	3.1	4.1	1.9	1.1	0.2	0.0	1.1	2.1
Hornblende	1.4	0.9	0.4	1.9	2.2	2.2	4.0	10.0	BDL	1.9
Pyrite	1.0	3.4	0.6	0.2	0.1	0.4	0.5	0.8	0.9	BDL
Apatite	2.7	2.8	BDL	5.2	2.0	1.1	2.7	7.0	2.4	3.2

APPENDIX B– PHREEQC INPUT FILES

Segmented Mixing (SM) Model

TITLE Simulation 1 – Solution 1
SOLUTION 1 Wastewater [Date]

temp _____
pH _____
units ppm
density _____
Al _____
Alkalinity _____ as HCO3
B _____
Ba _____
Ca _____
Cl _____ charge
Cu _____
F _____
Fe _____
K _____
Mg _____
Mn _____
N(5) _____
Na _____
O(0) _____ O2(g) 0.21
P _____
S(6) _____
Si _____
Zn _____
-water 1 # kg
SAVE solution 1

TITLE Simulation 2 – Solution 2
SOLUTION 2 Lake-water [Date]

temp _____
pH _____
units ppm
density _____
Al _____
Alkalinity _____ as HCO3
B _____
Ba _____
Ca _____
Cl _____ charge
Cu _____
F _____
Fe _____

K _____
 Mg _____
 Mn _____
 N(5) _____
 Na _____
 O(0) _____ O2(g) 0.21
 P _____
 S(6) _____
 Si _____
 Zn _____
 -water 1 # kg
 SAVE solution 2
 END

TITLE Simulation 3 - Mixture 1 (WW-99:LW-01)
 USE solution 1
 USE solution 2
 MIX 1

1 0.99
 2 0.01

EQUILIBRIUM PHASES 1
 CO2(g) -3.5
 Calcite 0 0
 Hydroxyapatite 0 0
 SAVE Solution 3
 END

TITLE Simulation 4 - Mixture 2 (WW-90:LW-10)
 USE solution 1
 USE solution 2
 MIX 2

1 0.90
 2 0.10

USE EQUILIBRIUM PHASES 1
 SAVE Solution 4
 END

TITLE Simulation 5 - Mixture 3 (WW-50:LW-50)
 USE solution 1
 USE solution 2
 MIX 3

1 0.50
 2 0.50

USE EQUILIBRIUM PHASES 1
 SAVE Solution 5
 END

TITLE Simulation 6 - Mixture 4 (WW-10:LW-90)
 USE solution 1
 USE solution 2
 MIX 4
 1 0.10
 2 0.90
 USE EQUILIBRIUM PHASES 1
 SAVE Solution 6
 END

TITLE Simulation 7 - Mixture 5 (WW-01:LW-99)
 USE solution 1
 USE solution 2
 MIX 5
 1 0.01
 2 0.99
 USE EQUILIBRIUM PHASES 1
 SAVE Solution 7
 END

Incremental Mixing (IM) Model

TITLE Simulation 1 – Solution 1
 SOLUTION 1 Wastewater [Date]

temp	_____	
pH	_____	
units	ppm	
density	_____	
Al	_____	
Alkalinity	_____	as HCO3
B	_____	
Ba	_____	
Ca	_____	
Cl	_____	charge
Cu	_____	
F	_____	
Fe	_____	
K	_____	
Mg	_____	
Mn	_____	
N(5)	_____	
Na	_____	
O(0)	_____	O2(g) 0.21
P	_____	
S(6)	_____	
Si	_____	

Zn _____
-water 1 # kg
SAVE solution 1

TITLE Simulation 2 – Solution 2
SOLUTION 2 Lake-water [Date]

temp _____
pH _____
units ppm
density _____
Al _____
Alkalinity _____ as HCO3
B _____
Ba _____
Ca _____
Cl _____ charge
Cu _____
F _____
Fe _____
K _____
Mg _____
Mn _____
N(5) _____
Na _____
O(0) _____ O2(g) 0.21
P _____
S(6) _____
Si _____
Zn _____
-water 1 # kg

SAVE solution 2
END

TITLE Simulation 3 - Mixture 1 (WW-99:LW-01)

USE solution 1
USE solution 2

MIX 1
1 1.000
2 0.010

EQUILIBRIUM PHASES 1

CO2(g) -3.5
Calcite 0 0
Hydroxyapatite 0 0

USE EQUILIBRIUM PHASES 1

SAVE Solution 3
END

TITLE Simulation 4 - Mixture 2 (WW-95:LW-05)
USE solution 3
USE solution 2
MIX 2
 3 1.000
 2 0.043
USE EQUILIBRIUM PHASES 1
SAVE Solution 4
END

TITLE Simulation 5 - Mixture 3 (WW-90:LW-10)
USE solution 4
USE solution 2
MIX 3
 4 1.000
 2 0.058
USE EQUILIBRIUM PHASES 1
SAVE Solution 5
END

TITLE Simulation 6 - Mixture 4 (WW-85:LW-15)
USE solution 5
USE solution 2
MIX 4
 5 1.000
 2 0.065
USE EQUILIBRIUM PHASES 1
SAVE Solution 6
END

TITLE Simulation 7 - Mixture 5 (WW-80:LW-20)
USE solution 6
USE solution 2
MIX 5
 6 1.000
 2 0.074
USE EQUILIBRIUM PHASES 1
SAVE Solution 7
END

TITLE Simulation 8 - Mixture 6 (WW-75:LW-25)
USE solution 7
USE solution 2
MIX 6
 7 1.000
 2 0.083

USE EQUILIBRIUM PHASES 1
SAVE Solution 8
END

TITLE Simulation 9 - Mixture 7 (WW-70:LW-30)
USE solution 8
USE solution 2
MIX 7
8 1.000
2 0.095
USE EQUILIBRIUM PHASES 1
SAVE Solution 9
END

TITLE Simulation 10 - Mixture 8 (WW-65:LW-35)
USE solution 9
USE solution 2
MIX 8
9 1.000
2 0.110
USE EQUILIBRIUM PHASES 1
SAVE Solution 10
END

TITLE Simulation 11 - Mixture 9 (WW-60:LW-40)
USE solution 10
USE solution 2
MIX 9
10 1.000
2 0.128
USE EQUILIBRIUM PHASES 1
SAVE Solution 11
END

TITLE Simulation 12 - Mixture 10 (WW-55:LW-45)
USE solution 11
USE solution 2
MIX 10
11 1.000
2 0.152
USE EQUILIBRIUM PHASES 1
SAVE Solution 12
END

TITLE Simulation 13 - Mixture 11 (WW-50:LW-50)
USE solution 12

USE solution 2
MIX 11
12 1.000
2 0.182
USE EQUILIBRIUM PHASES 1
SAVE Solution 13
END

TITLE Simulation 14 - Mixture 12 (WW-45:LW-55)
USE solution 13
USE solution 2
MIX 12
13 1.000
2 0.222
USE EQUILIBRIUM PHASES 1
SAVE Solution 14
END

TITLE Simulation 15 - Mixture 13 (WW-40:LW-60)
USE solution 14
USE solution 2
MIX 13
14 1.000
2 0.278
USE EQUILIBRIUM PHASES 1
SAVE Solution 15
END

TITLE Simulation 16 - Mixture 14 (WW-35:LW-65)
USE solution 15
USE solution 2
MIX 14
15 1.000
2 0.357
USE EQUILIBRIUM PHASES 1
SAVE Solution 16
END

TITLE Simulation 17 - Mixture 15 (WW-30:LW-70)
USE solution 16
USE solution 2
MIX 15
16 1.000
2 0.476
USE EQUILIBRIUM PHASES 1
SAVE Solution 17

END

TITLE Simulation 18 - Mixture 16 (WW-25:LW-75)

USE solution 17

USE solution 2

MIX 16

17 1.000

2 0.667

USE EQUILIBRIUM PHASES 1

SAVE Solution 18

END

TITLE Simulation 19 - Mixture 17 (WW-20:LW-80)

USE solution 18

USE solution 2

MIX 17

18 1.000

2 1.000

USE EQUILIBRIUM PHASES 1

SAVE Solution 19

END

TITLE Simulation 20 - Mixture 18 (WW-15:LW-85)

USE solution 19

USE solution 2

MIX 18

19 1.000

2 1.667

USE EQUILIBRIUM PHASES 1

SAVE Solution 20

END

TITLE Simulation 21 - Mixture 19 (WW-10:LW-90)

USE solution 20

USE solution 2

MIX 19

20 1.000

2 3.333

USE EQUILIBRIUM PHASES 1

SAVE Solution 21

END

TITLE Simulation 22 - Mixture 20 (WW-05:LW-95)

USE solution 21

USE solution 2

MIX 20

```
    21  1.000
    2  10.000
USE EQUILIBRIUM PHASES 1
SAVE Solution 22
END
```

```
TITLE Simulation 23 - Mixture 21 (WW-01:LW-99)
USE solution 22
USE solution 2
MIX 21
    22  1.000
    2  80.000
USE EQUILIBRIUM PHASES 1
SAVE Solution 23
END
```