

PHOSPHORUS FRACTIONATION AND DISTRIBUTION ACROSS
DELTA OF DEER CREEK RESERVOIR

by

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ABSTRACT

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Master of Science

Eutrophication of reservoir systems, which causes deterioration of water quality through increased algal growth, is detrimental to our sustainable water supply and additionally impairs other beneficial reservoir uses. Limiting the amount of phosphorus (P) entering the system has been the key management tool for this problem, as P is the main limiting nutrient for plant and algal growth. These efforts have focused on controlling input of P from point sources, such as effluents from wastewater treatment plants, dairies, and industrial factories.

Even in systems (such as reservoirs) with significantly reduced external P loading, however, there has been continued eutrophication and slower than expected recovery of reservoirs in water quality restoration projects. Other nutrient sources have been studied to explain this phenomenon. The continual eutrophication has been potentially attributed to availability of nutrients from deposited sediments. This is referred to as nutrient recycling, as nutrients previously trapped within sediments may become available within the water column.

Deer Creek Reservoir (DCR), a significant water supply in Utah, has had greatly improved water quality after reduction of external P loading. However, there are still large algal blooms at times as well as other water quality issues without clearly attributable causes. Part of the explanation might lie within the deposited sediments, which are present both on the sediment delta and within the reservoir. This thesis provides data that can help researchers understand what role sediment has in the continuation of water quality problems at DCR. Sediment samples were taken across the delta to define both the spatial extent and distribution of P and chemical form, or 'pool', of the P. The pools can be used to estimate the ability of the sediment-bound P to move into the water column under various conditions. Results reported here indicate that significant amounts of P are found within these sediments, though not all of it can easily become available for algal growth.

We characterized P distribution by taking 91 samples on 6 transects across the exposed delta. Transects were separated by 200 m and samples were taken every 100 m along the transects. The samples were all analyzed for water soluble P content, and 19 samples were additionally characterized for KCl-, NaOH-, HCl-, and organic (by digestion) P fractions. Total P was determined for these as well by summation. The data showed that water soluble P ranged from 2.28E-03 and 9.81E-03 mg P g⁻¹ dry sediment and showed a decreasing trend along the reservoir. KCl-P ranged from 2.53E-03 and 1.10E-02, NaOH-P from 5.30E-02 to 4.60E-01, HCl-P from 1.28E-01 and 1.34E+00, and organic (residual) P from 8.23E-01 to 3.23E+00 mg·g⁻¹.

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Table of Contents

Acknowledgements	vii
List of Tables	xiii
List of Figures	xv
1 Introduction	1
2 Background and Literature Review	3
2.1 Nutrients in Soils	3
2.1.1 Soil-Solution Interactions	3
2.2 Nutrient Recycling Causes	6
2.2.1 Geochemical and Biochemical Interactions	6
2.2.2 Resuspension and Other Factors	9
2.3 Methodological Considerations	14
2.3.1 Sampling, Storage, and Preparation	14
2.3.2 Fractionation and Selective Dissolution Techniques	16
2.3.3 Measurement of Phosphorus in Solution	19
2.4 Deer Creek Reservoir	21
2.4.1 Basic Information	21
2.4.2 Water Quality	23
2.4.3 Local Sediment Studies	26

3	Plan and Methodology	29
3.1	Objectives and Preparation	29
3.2	Sampling	30
3.3	Fractionation of Samples	32
3.4	Measurements	35
3.5	Normalized Results	35
3.6	Geostatistical Analysis	36
4	Results	39
4.1	Results	39
4.1.1	Water Soluble Results	39
4.1.2	Complete Fractionation	40
4.2	Discussion of Results	44
4.2.1	Comparison with Surrounding Soil Samples	44
4.2.2	Repeat Fractionations	45
4.2.3	Assumptions and Limiting Factors	46
4.2.4	Verification of Results	52
5	Conclusions and Recommendations for Future Work	57
5.1	Conclusions	57
5.2	Future Work	58
5.2.1	Geostatistical Analysis of Phosphorus Distribution	59
5.2.2	Sampling Plan Extension	59
5.2.3	Protocols for Verification of Fractionation Results	60
5.2.4	Sediment-Water Interactions	61
	References	65

A	Sample Coordinate Locations	75
B	Protocols - SOPs	77
B.1	Water Content	77
B.2	Fractionation	77
B.2.1	Water Soluble P	77
B.2.2	Loosely Sorbed P	78
B.2.3	Aluminum and Iron-bound P	78
B.2.4	Calcium-bound (apatite) P	79
B.2.5	Residual (mostly organic) P	79
B.3	Equipment	80
B.3.1	Reciprocating Shaker	80
B.3.2	Ultracentrifuge	81
B.3.3	Vacuum Filtration	82
B.4	Measurement of P in Solution	82
B.4.1	Hach Amino Acid Method	83
B.4.2	Ion Chromatography	84
C	Results	87
D	Geostatistical Plots in GMS	91

List of Tables

3.1	Comparing Fractionation Schemes: Thesis v. Previous	34
4.1	Variation of Average Water Soluble P with Depth	41
4.2	Longitudinal Variation of Average Water Soluble P	41
4.3	Lateral Variation of Average Water Soluble P	41
4.4	Average Sediment P Concentrations for Various Fractions	41
4.5	Comparing Fractionation Results: Thesis v. Previous	43
4.6	P Content ($\text{mg P}\cdot\text{g}^{-1}$ sediment) of Background Soil Samples	44
4.7	Concentration Variability among Repeat Fractionations	45
4.8	Effects of Entrained Solution	48
4.9	Comparing P Measurement Techniques	51
4.10	Mineralogical Content (by wt. %) of Sediment	53
5.1	Parameters to be Measured in Sediment Samples	63
5.2	Water Quality Parameters to be Measured at Sample Locations	64
A.1	Coordinates for Sampled Locations	75
C.1	Background Soil P Concentrations ($\text{mg}\cdot\text{g}^{-1}$)	87
C.2	Summary of Adjusted P Concentrations	87
C.3	Summary of Sediment P Concentrations 1	88
C.4	Summary of Sediment P Concentrations 2	89
C.5	Sediment P Concentrations ($\text{mg}\cdot\text{g}^{-1}$) for Repeat Fractionations	90

List of Figures

2.1	Deer Creek Reservoir	22
2.2	Deer Creek Tributaries	22
2.3	Trophic State Variation of Deer Creek	25
3.1	Sample Distribution across Reservoir Delta	31
3.2	Sampling Delta Sediments Using a Hand Auger	32
3.3	Shaker Table and Tubes Used in Fractionation	33
3.4	Apparatus Used in Vacuum Filtration of Prepared Solutions	33
3.5	Solution Measurement Preparation	35
3.6	Placement of Solution into Spectrophotometer for Measurement	36
4.1	Water Soluble P Contours	42
D.1	HCl Extractable P Contours	91
D.2	NaOH Extractable P Contours	92
D.3	HCl Extractable P Contours	93
D.4	Organic P Contours	94

Chapter 1

Introduction

When present in excess, phosphorus (P) may negatively affect reservoir sustainability due to decreased water quality (through eutrophication) (Schindler, 1974). To reverse this process, many water quality restoration projects require the reduction of P quantities entering reservoirs, and these usually focus on P reduction from point sources such as industrial and wastewater treatment plants (Sas, 1989).

However, even after reduced external P loading, many water bodies have shown longer restoration times than expected. This has been attributed to internal P sources. Messer et al. (1984) notes that “phosphorus may also enter the euphotic zone from within the lake itself, as a result of releases from both oxic and anoxic sediments.” If sediments are not flushed from reservoirs, most P entering the reservoir is trapped, becoming a potential nutrient source for algal uptake. As Gibson (1997) notes,

a lake with little hydrological flushing is likely to accumulate nutrients and the regime promotes closed nutrient cycles in which sediment-water fluxes dominate the annual budget.

In reservoirs, most (and potentially all) hydrological flushing has been cut off; thus these water bodies are particularly susceptible to nutrient trapping (Gibson, 1997).

A number of studies confirm that P from within a reservoir itself (in deposited sediments) is responsible for delays in water quality restoration projects (Rossi & Premazzi, 1991; Granéli, 1998; Mayer et al., 1999), and this finding has been verified for local reservoirs in the intermountain west area, Utah and Wyoming (Messer et al., 1983; Messer & Ihnat, 1983; Messer et al., 1984) .

In order for these conclusions to be useful in reservoir management, it is necessary to understand the processes of internal P cycling. This can be difficult, as many factors contribute to the potential resuspension of sediments and release of P trapped in sediments to the water column. Sediments contain P in a number of different chemical forms, or ‘pools’, which are released to the water column under different physical and conditions (Sims & Pierzynski, 2005).

Though previous studies provide information regarding P in sediments of the local Deer Creek Reservoir (DCR) (Messer & Ihnat, 1983; Messer et al., 1984), no work has specifically looked at how sediments from the deposited delta affect nutrient dynamics. This is particularly critical for DCR at present, as the reservoir has recently been subjected to a drawdown process to be followed by refilling. Such processes affect phosphorus dynamics in reservoirs (Fabre, 1988). This thesis provides an initial step into understanding how delta sediments may affect nutrient dynamics within DCR by quantifying the types and amounts of different P pools across the delta, along with their spatial distribution. Previous studies did not look at spatial distributions.

Obviously, a number of other pieces of information are necessary for assessing the impact of these sediments on P dynamics within the reservoir. This work is part of a larger effort, and a number of other activities are ongoing to support the greater project. Other activities include collection and analysis of sediment samples from within the reservoir as well as measurement of water quality parameters important for understanding P dynamics. The results from this thesis are part of a comprehensive data set that will enable future researchers to examine potential impacts of nutrients currently contained in sediments.

Chapter 2 discusses background information including the relationship between sediment and nutrients, P dynamics in reservoirs (interactions between sediments and solutions), facts regarding the location of study, and potential methods. Chapter 3 overviews the plan and methods used in the research, including the chosen methods for P analysis and measurement as well as the locations and timing of sampling. Chapter 4 presents and discusses results while addressing assumptions. Finally, chapter 5 offers conclusions and recommendations for future work.

Chapter 2

Background and Literature Review

This chapter first details the problem of P (and other nutrients) in general, and discusses the role of sediment in relation to these nutrients. Additionally, it presents important issues and potential methodological procedures that we considered in developing the sample plan. Afterwards, information regarding the area of study, DCR, is provided. I included a record of reservoir water quality to help understand how past studies have addressed the problem of eutrophication, and also to use this information as the foundation for this work.

2.1 Nutrients in Soils

2.1.1 Soil-Solution Interactions

Excessive amounts of nutrients (particularly P and nitrogen (N), the primary limiting nutrients) may increase productivity in ecosystems, leading to problems with water quality (Schindler, 1974). Eutrophication control efforts in freshwater ecosystems have focused on P since it is the least abundant of these nutrients (Sas, 1989). Deposited sediments have been identified as a potential internal nutrient source since reducing external inputs of nutrients has had limited effect on eutrophication in some areas (Granéli, 1998; Mayer et al., 1999).

A basic understanding of sediment diagenesis processes can help explain how P (and N) can be deposited and stored in sediment deltas. Sediments contain both allochthonous (i.e., externally washed in) as well as autochthonous (i.e., produced within the reservoir) material. Allochthonous material consists of both inorganic and organic particulates that can contain P. The inorganic material can contain P in various mineral forms (obtained by passing through geologic formations), while the

organic material contains P from the remains of living organisms. Dissolved P can be precipitated to contribute to the inorganic reservoirs or be used by living organisms and contribute to the organic P reservoirs when these organisms die.

Autochthonous material is composed mainly of organism remains; P (a necessary nutrient for life) within decaying matter can be deposited in the sediments of lakes or reservoirs. Material entering the reservoir is detrital in origin, while the portion produced in the reservoir is authigenic. The P in the authigenic sediments originally came from dissolved P entering the reservoir with water or P cycling within the reservoir that becomes part of the sediment.

As external loading occurs, most nutrients within the water column are deposited with sediment. Morris & Fan (1998) notes that

phosphorus is removed from aquatic systems rather rapidly and becomes stored in sediments, where its concentration may be 2 orders of magnitude greater than the concentration in the overlying water.

Sediments are a determining factor for P levels within the water column of reservoirs. As described by Morris & Fan (1998),

Manipulation of water levels and sediments will potentially impact phosphorus levels and productivity in the reservoir and downstream ecosystems, making it important to have a conceptual understanding of the phosphorus cycle and its relationship to lake sediments.

Though much P is trapped within sediments (and thus is not available for algal growth), some portions of it may potentially be released by various mechanical and geochemical processes. Understanding how P is attached to sediments is critical in determining whether P pools (the specific form of P) may change into the soluble orthophosphate form (the ‘reactive’ and ‘bioavailable’ form of P), which is readily available for uptake. For a detailed discussion of P chemistry in soils (and sediments), see Golterman (2004), Sims & Pierzynski (2005) and chapter 6 of Pierzynski et al. (2005). These (or other chapters therein) additionally contain information regarding N chemistry in soils.

Most P pools are not biologically available, though under specific circumstances they may become available. Additionally, the particulate fraction (various P minerals) trapped in sediment generally is not bioavailable and does not contribute to eutrophication, though it is a potential source since this P may be released (e.g., by dissolution or desorption) under a number of conditions.

The particulate fraction also contains inorganic forms of P sorbed onto organic compounds. This binding of P to soil (sediment) or other materials can make it biologically unavailable as well. Morris & Fan (1998) note that this fraction additionally includes P that is “contained in or absorbed onto seston and/or inorganic complexes such as clays, carbonates, and ferric hydroxides.” They additionally note the importance of sediment as a source of P:

While most phosphorus in natural lakes is associated with seston, in reservoirs experiencing significant sediment loads much phosphorus may be associated with sediment, primarily the fine fraction that has a large surface area in relation to mass.

Fine sediments particularly display high capacity for trapping P, indicating that particle-size analysis may be important in understanding the role of P bearing sediment in a reservoir. My research did not analyze this parameter, though later work will.

P may be attached to and removed from sediments through a number of different processes. These include oxidation-reduction, adsorption-desorption, and precipitation-dissolution processes. P may be co-precipitated with various elements including iron (Fe), aluminum (Al), manganese (Mn), and calcium (Ca). Understanding the chemical and mineral composition of the sediments is critical for understanding how P may be distributed through sediments, what chemical forms it can take, and how it might be released to the water column making it bioavailable.

In addition to trapping P, sediments potentially may be a more direct nutrient source as they release P back into the water column from the autochthonous material, never leaving the biological cycle for long. This process is known as nutrient (re)cycling since nutrients move between the water and sediments on relatively

short time scales. The next section will describe potential mechanisms for nutrient movement through the sediment-water boundary.

2.2 Nutrient Recycling Causes

Nutrient (specifically, P) recycling is a complicated process with an extensive literature base, as it is affected by a variety of factors. For discussion, these will be divided into three types. First, P that can be released through geochemical processes. Second, sediment resuspension (potentially caused by a number of mostly mechanical factors) can affect internal nutrient cycling. Last, a number of other aspects (including temperature, organisms, etc.) may affect nutrient movement. Though these are not directly considered in this work, they are important to understand since this work is intended to provide data that will be used in evaluating these processes at a later time.

2.2.1 Geochemical and Biochemical Interactions

Chemically driven processes are responsible for a significant amount of P transfer between sediment and the water column. These include oxidation-reduction reactions involving Fe-P complexes as well as reactions involving P, Ca, and pH in calcareous sediments. Different P pools are released by different geochemical environments and processes.

Many studies have concluded that oxic sediment conditions retain P better than anoxic conditions (Einsele, 1936; Mortimer, 1941, 1971). There has also been significant work relating Fe to the P cycle, based on oxygen levels. Einsele (1936) first noticed an interesting relationship in which certain Fe compounds are precipitated when oxygen is prevalent. The Fe compound that precipitates in aerobic conditions is Fe(III) oxyhydroxide (Tessenow, 1974; Gunnars et al., 2002).

This compound is able to absorb or co-precipitate large amounts of P, however, when sediment conditions become anoxic, Fe(III) is reduced to Fe(II) which forms much more soluble compounds and P is released. A minimum molar stoichiometric Fe to P ratio ($\frac{Fe}{P}$) was found to be approximately 2 for precipitation of P (Gunnars et al.,

2002). If the ratio of ferrous Fe [Fe(II)] to phosphates is greater than 2, P can precipitate after enough O₂ has been added for oxidation and precipitation of all Fe present. If the ratio is less than 2, P remains in solution (Gunnars et al., 2002).

Ruban & Demare (2006) studied the effect of oxygen presence (or absence) on P release at the sediment-water interface. Release of P did not occur as long as the concentration of oxygen stayed above a level of 0.5 mg·L⁻¹. A drop of oxygen concentration accompanied by a change in redox potential (to greater reducing conditions) was found to result in the simultaneous release of both Fe and P. This is a common finding, and is in accordance with general chemistry principles when we consider that much P can be bound by Fe mineral complexes.

Gibson (1997) describes the process by which anoxic conditions may occur in the hypolimnion, creating the potential for P release. As allochthonous loading of P increases, autochthonous sources of P for sediment do likewise, reflecting greater amounts of organism growth. This increases both carbon and P within sediments. With more organic material (from carbon), oxygen demand increases and creates reducing conditions. When reducing conditions co-occur with greater P content, more P can be released from sediment.

The data seem to suggest that lower P release rates and lower P concentrations within the water column naturally occur when oxic conditions in sediments are maintained. However, evidence has been found that P cycling at the sediment-water interface is not affected by maintaining oxic conditions in the hypolimnion (Gächter & Wehrli, 1998) (see also Schindler et al. (1973, 1977) and Levine et al. (1986)). Gächter & Müller (2003) aimed to identify a different model for the retention of P in lake sediments based on redox controls.

Others (Gächter et al., 1988; Gächter & Meyer, 1993; Hupfer et al., 1995) have looked at the role of benthic bacteria in this process. Gächter & Müller (2003) state that:

In the presence of O₂, some facultative aerobic bacteria deposit P as polyphosphate in their cells but release it as ortho-P under anoxic conditions. Advanced wastewater treatment technology profits from both processes to enhance P removal from wastewater.

Other elements have been examined as well. For example, Anderson (1982) discusses the effect of nitrate concentration within lake water on the release of P from sediments. Sulfur forms (e.g., sulfate) have also been found to affect P release from sediments (Caraco et al., 1993; Kleeberg, 1997; Suplee & Cotner, 2002). The Fe/P cycle can be disrupted by insoluble complexes of sulfide (FeS) after sulfates are reduced to sulfide. Ammonia (NH_4^+) was also found in a relationship to soluble reactive P at certain times of the year by Kleeberg (1997).

Water conditions were changed in columns by Eckert et al. (1997) to study pH and Eh (electron movement) along with carbon availability (which possibly affects P uptake). They found that the stability of Fe(III)-P complexes strongly depends on pH; additionally, when considering pH it is important to know whether the reservoir is calcareous.

Fisher & Wood (2004) studied the effect of the water column pH on P release rates. Their study was designed to differentiate pH increases due to increases in photosynthesis (resulting in greater concentrations of chlorophyll *a*) and pH increases that also resulted in alkalinity increases. Sediments were not able to uptake as much P at higher (than ambient or normal) pH levels. This was

probably because of the substitution of hydroxide ions for phosphate ions on iron hydroxides. This substitution is the geo-chemical process that, it was hypothesized, would cause rapid desorption of phosphorus from the sediments at high pH, i.e., internal loading.

Diffusion of nutrients from porewater is also possible. Fick's First Law was used by Lavery et al. (2001) for purposes of estimating nutrient fluxes. P gradients between pore water and bottom water samples are used. The utility of this method is described by Hille et al. (2005): "This method is quick and is preferred to more time consuming ones (e.g. incubation experiments) because a comparatively large number of stations could thus be investigated..." This experimental approach allows more dense spatial coverage of the area.

Obviously, this technique should only be used where other phenomena affecting transport (e.g., bioturbation, resuspension) are not present. The effects of these

assumptions were determined by Lavery et al. (2001) by comparing estimated fluxes (based on Fick's First Law) to measured fluxes from incubation experiments. They found that this method better estimated fluxes (predicted almost 100% of actual) from coarse sediments. It overestimated by about 40% for fine sediments. Additionally, the method is only recommended under favorable redox conditions. However, they note the possibility of modifying predicted values by taking into account redox conditions, biological activity, and hydrodynamics.

2.2.2 Resuspension and Other Factors

Resuspension is a mechanical process that allows deposited sediments to be suspended within the water column. This process, though not experimentally assessed in this work, is important in the present study with regards to effects on delta sediments as reservoirs levels decrease and increase (drawdown and refilling processes, see Fabre (1988)). These controlled reservoir processes can cause down-cutting and resuspension of sediments in the delta, which can in turn affect nutrient recycling. Koski-Vähälä & Hartikainen (2001) notes the following:

The P release from the solid phase to the water column is influenced by many biological and physico-chemical factors, and resuspension is a mechanism that may influence the internal P loading by mechanically mediating the P exchange between suspended material and the water column. In order to understand factors contributing to internal P loading, the effect of the resuspended sediment on the P fluxes in lakes must also be assessed.

A number of mechanisms causing resuspension have been studied for their effect on P-release. These include wind (Søndergaard et al., 1992; Kristensen et al., 1992), wave (seiche) action (Lijklema et al., 1994), ice cover (Niemistö & Horppila, 2007), climate change due to global warming (Niemistö & Horppila, 2007), and cold currents entering the reservoir. Disturbances by animals such as bottom-feeding fish (Lamarra, 1975) and chironomid larvae (Gallepp, 1979) may also trigger resuspension.

Some other aspects may affect resuspension as well as the transport of nutrients in aquatic systems. These will be discussed briefly as they are important to consider

in relation to results from this work, especially when assessing potential for P to be released from sediments in an aquatic environment.

First, animal interactions create movement of nutrients, though not all movement is through resuspension. Nitrogen and P can be excreted by animals at comparable rates to major nutrient sources. Nutrients can be recycled within a habitat, or be translocated across habitats or ecosystems by animals. Vanni (2002) reviews relevant work in this area, describing translocation:

When an animal feeds on benthic prey and excretes nutrients into the water, it translocates nutrients from benthic to pelagic habitats and converts nutrients from particulate to dissolved forms.

Fish are especially important in this process, as fish excretion of P can exceed watershed inputs, even when reservoirs are found below highly agricultural watersheds (Schaus et al., 1997; Vanni et al., 2001). Fish also can serve as nutrient sinks until death, as large amounts of nutrients are maintained within fish bodies.

Additionally, algae and bacteria affect nutrient cycling, both decaying into waste products of organic matter containing P and participating in P recycling (allowing P to be available again) from these wastes. Luxury uptake by bacteria could be important as well (Portielje & Lijklema, 1994; Khoshmanesh et al., 2002). Effects due to bacterial density were studied by Clavero et al. (1999).

Vegetation has also been considered in nutrient recycling. Macrophytes may act as potential nutrient pumps (Granéli & Solander, 1988). Littoral vegetation is probably important, as noted by Morris & Fan (1998), but this can be dependent on size of the reservoir.

Littoral vegetation also plays an important role in both the uptake and release of phosphorus in natural lakes. It may also be important in smaller reservoirs with stable water levels, significant vegetated shallows, and dendritic geometry that produces an elongated shoreline. However, littoral vegetation may be insignificant or absent in larger impoundments, in arid or alpine zones, and where steep slopes or variation in pool elevation precludes significant vegetative growth.

Growth of littoral vegetation is probably exposed by annual emptying and filling of reservoirs. The sediment delta of DCR is vegetated, but the majority of the shore line is not.

Drawdown of reservoirs creates exposed deltas. With continual filling and refilling of reservoirs, potential for nutrient movement exists, and this was studied by Fabre (1988).

Stratification is also important to consider. In the epilimnion (layer at the surface of a lake/reservoir), water is warm and vertically mixed. This results in a highly oxygenated area of water near the surface. In the metalimnion (below the epilimnion), temperature and density change rapidly. The lowest level is cold, dark, and oxygen-depleted. This is the hypolimnion (or profundal waters), and it is usually nutrient-enriched. For more productive lakes, Morris & Fan (1998) note that “the hypolimnic water which is trapped beneath the thermocline will become anaerobic because of the oxygen demand imposed by decomposers and organic sediments.”

Stratification in temperate zone lakes is caused by heating of surface waters in summer, while in winter complete mixing of the water column (turnover) occurs as the reservoir cools and the density gradient is eliminated (Morris & Fan, 1998). As turnover occurs, deeper waters return accumulated nutrients to the surface. This process is followed in the spring by temperature increases, longer days, and loss of ice cover. This cycle drives nutrient cycling and promotes growth of algae.

Water body characteristics also affect nutrient movement. The important characteristics for nutrient cycling are in large part dependent on whether the water body is a lake or a reservoir, and aspects that can affect nutrient loading are summarized by Morris & Fan (1998). Comparing productivity of lakes and reservoirs, Kimmel et al. (1990) concluded that reservoirs are more eutrophic than lakes. This could be due to the fact that reservoirs are built in locations that are exposed to a much greater drainage area as compared to lakes (Morris & Fan, 1998).

Age of the lake (or reservoir) may affect nutrient cycling in aquatic systems. Both lakes and reservoirs are susceptible to sediment accumulation, decreasing water levels, and nutrient enrichment. Even though reservoirs are much younger than lakes,

reservoirs are more greatly subjected to high sediment loading rates and thus age much more quickly than natural lakes (Morris & Fan, 1998).

The shape of the water body may also affect sedimentation. Natural lakes are usually oval-shaped, with shallow edges and deeper centers. Reservoirs are more elongated and have shallow upstream ends with depth increasing along the length of the reservoir. Morris & Fan (1998) state that reservoir geometry “produces strong longitudinal gradients in the physical, water quality, and biological characteristics in reservoirs which are largely absent in natural lakes.” Sampling within reservoirs must take these gradients into account (Thornton et al., 1982). Internal cycling of nutrients varies longitudinally along the reservoir due to such gradients.

The location within the reservoir may also influence nutrient dynamics. Reservoirs are divided longitudinally into three zones. The upstream zone (riverine) is narrow and shallow, and is “characterized by significant flow velocities and transport of silts and clays, while the coarse fraction of the inflowing sediment deposits to form a delta” (Morris & Fan, 1998). When deltas are formed, coarser particles settle out first due to their weight. In effect, particles are sorted longitudinally through the reservoir. This is important for nutrient distribution as finer particles tend to contain greater amounts of nutrients, while coarser particles do not contain many nutrients.

In this upper area of the reservoir, depth is limited, water is turbid, and stratification is absent. These factors allow the water column to remain aerobic, even with high amounts of organics. Production could possibly be light-limited in this zone, as high sediment loading increases turbidity. This can create shallow (possibly as low as 1 m) euphotic zones. This has an affect on production, as described by Morris & Fan (1998): “Vertical mixing in this environment can keep algae below the euphotic zone for prolonged periods, resulting in very low populations of primary producers and associated zooplankton.” Based on our observations, DCR does not exhibit high turbidity in this zone.

The most downstream zone (lacustrine) exhibits characteristics of natural lakes, including lower sediment loads, less turbid water, and stratified water columns. Algae may be sustained by significant nutrient loading in the source river. In the area

closest to the dam, autochthonous organic matter is important for the food chain. At this point, production is nutrient-limited instead of light-limited (Morris & Fan, 1998).

Hydraulic short-circuiting has also been discussed by Morris & Fan (1998), in which “storage areas off the main channel will receive much less sediment loading than the main reservoir.” Over time this process can be affected: “However, as sediment deposition from turbid density currents infill the original river channel, this horizontal focusing effect will be reduced or eliminated and the density current will tend to spread out laterally and dissipate.”

The trophic state of the lake can create differences in oxygen distribution, which in turn affects the chemical interactions described above. The hypolimnion of oligotrophic lakes is highly oxygenated and so P content varies minimally with depth. The oxygenated sediments function as a P sink. On the other hand, eutrophic lakes have profundal waters that are significantly depleted of oxygen and thus have anaerobic sediments. Because of this, P may be released continually into the water column from sediments. This causes P concentration to increase greatly with depth, as noted by Morris & Fan (1998): “Thus, water released from the hypolimnion of productive reservoirs tends to be nutrient-enriched, and circulation patterns within reservoirs that draw deeper anaerobic water into the epilimnion can increase nutrient availability, productivity, and the loading of organic sediments.”

As a final note, sediments within lakes of low productivity and low P loadings normally contain P in concentrations less than $1 \text{ mg}\cdot\text{g}^{-1}$ (dry sediment weight). The release of P from sediments could be dependent on the sediment concentration. Sas (1989) surveyed many lakes with reduced P inputs, concluding that P release from sediments tended not to occur where P concentrations less than $1 \text{ mg}\cdot\text{g}^{-1}$ sediment were present.

2.3 Methodological Considerations

2.3.1 Sampling, Storage, and Preparation

There is not much published information regarding design of sampling plans across reservoir sediment deltas, but this process should be somewhat similar to sediment sampling within reservoirs. A number of resources exist describing sediment sampling (Mudroch & MacKnight, 1994a), and these were used in the present work. An appropriately sized data set is important for any type of sampling plan, as sediment flux modeling depends on large data sets that allow for a complete understanding of all processes involved (DiToro, 2001).

Selection of sample locations should consider the purpose/objectives of the study, historical data reviewed, bottom dynamics, sampling area size, and available funds. The objective (what being measured) is important; MacKnight (1994) notes that:

generally, samples will be collected from the study area to investigate the distribution of parameters of interest at the project site. In studies of distribution of contaminants, sediment samples featuring the *most suitable grain size* for analyses and scheduled experiments...are preferred (p. 18, emphasis added).

Surveys and maps (topographic, bathymetric, sediment distribution) are also important, as they can show where fine-grained materials may exist and where more intense sampling needs to be undertaken. MacKnight (1994) notes that data from Håkanson (1981) and Håkanson (1984) “clearly show that there is considerable variability in the sediments at the mouth of the river compared to the homogeneous sediments in the lake.” Additionally, locations need to be chosen where there is the possibility for rapid and reliable repetition of sampling.

Though not critical for the present study, understanding bottom dynamics of reservoirs could be insightful for interpreting results from this study. Three areas of bottom dynamics were identified by Håkanson (1977). First, erosional areas contain exposed bedrock, gravel, sand, or hard glacial clays and tills. Secondly, areas of transportation temporarily accumulate fine-grained sediments while process such as

turbulence (from wind, waves, or ships) or currents allow for further transport. The accumulation areas typically contain the highest contaminant (and probably nutrient) concentrations, and are located in the deepest parts of lakes where fine-grained sediments eventually deposit.

These three areas are important to consider as a study is designed to try to maximize the probability of detecting areas with the greatest nutrient concentrations and minimize the cost of collecting improper (or worse, no) samples. Areas of accumulation typically provide the best locations for these goals. An interesting note regarding this is provided by MacKnight (1994):

A survey of sediment deposits and geochemistry in a lake can be a project. In such a case, sediment mapping will be carried out as a part of the project, and sampling stations will be selected to provide sufficient information for sediment mapping.

Sediment mapping can also display variability in gradients of sediment types, which is critical. As noted by MacKnight (1994), “the density of sampling stations required for the characterization of sediments is determined by the variability or gradients in the processes which control the distribution of the investigated sediment parameter or property.”

Traditionally, sediment sampling has been done at locations of easiest access. However, MacKnight (1994) notes that:

drawbacks of this approach include missing areas which should be sampled (i.e., an inadequate characterization) or requiring a good knowledge of a project area, information, or expertise which may not always be available. The result is considerable difficulty in applying a statistical treatment to the data and often an inability to resample at the same sites.

For this reason, statistical approaches are now frequently used for sampling distribution. These typically consist of a set of artificial grids (blocks, triangles) over an area. Sampling sites can be either in the middle of or at intersections of these blocks. The number of samples depends on the size of the area and the predicted constituent distribution. According to MacKnight (1994), this type of approach “permits subsequent manipulation of the data to determine trends or locations with high

concentrations of parameters of interest, or to assist in further sampling within a particular area.” A method for locating each site is critical.

2.3.2 Fractionation and Selective Dissolution Techniques

Knowing what P pools can be present in a soil is a start, but obtaining actual P content data is difficult as it is hard to separate these pools. This problem is held in common for all soil components. Many methods have been developed to extract different P pools from sediment into a solution for measurement, yet these methods have problems with overlapping of pools and other issues (Dean, 1938; Williams, 1950; Chang et al., 1983; Shang & Zelazny, 2008). Moore & Coale (2000) states that “it must be kept in mind that these are rather crude methods, with many extractants causing the dissolution of more than one type of P solid phase.” For this reason, it is difficult to determine the actual origins of any P measured in solution as extracted by these methods.

These fractionation (also known as sequential extraction or selective dissolution) procedures were first developed by soil scientists trying to examine soil P content for agricultural purposes (Dean, 1938; Chang & Jackson, 1957), but have later been extended for other purposes such as in fractionation of sediments (Williams et al., 1971; van Eck, 1982). We review extraction techniques here in consideration for use with delta sediments.

The main pools of P in soils/sediments that are extracted in these methods are: soluble (in interstitial water mostly), loosely bound or exchangeable, metal (Al-, Fe-, Mn-) bound (or adsorbed or occluded), Ca-bound (apatite), and organic. Various techniques have been used to extract each portion.

Soluble and loosely bound P can be extracted in one step using a salt (such as NH_4Cl (Chang & Jackson, 1957) or MgCl_2 (Ruttenberg, 1992)) or through the use of resin strips (Hedley et al., 1982). Water soluble P can be extracted prior to the use of salt or resins by simply mixing sediments in some fashion with DI water (Moore & Coale, 2000) in order to separate these fractions if desired.

A variety of methods have been used to extract P in metals (Al, Mn, Fe). Many of these (such as Williams et al. (1971) and Hieltjes & Lijklema (1980)) use NaOH (at different pH levels). However, a number (Chang & Jackson, 1957; Williams et al., 1980; Ruttenberg, 1992) combine (or use instead) another step involving Na-citrate, Na-bicarbonate, and Na-dithionite (CBD) (sometimes excluding the Na-dithionite) for Fe-bound P as well. This method essentially reduces all Fe^{3+} (highly insoluble) to Fe^{2+} (a more soluble form of Fe), so that all iron dissolves (and thus trapped P is released to solution). Shang & Zelazny (2008) note that:

there is a trend of replacing CBD with other extractants, because of the difficulty encountered in P analysis and multiple phase-extraction by CBD reagents. However, there are no other methods currently available that can perform better than CBD in removing Fe oxides.

Sims & Pierzynski (2005) notes that these Fe oxides are important P-trapping minerals in the environment.

Apatite P, a relatively insoluble form and thus probably all unavailable for algal growth, is extracted with a strong acid (usually HCl). This removes any carbonates-associated P as well. Some have tried to differentiate between different forms of P by prior extraction of weaker bound carbonate P with a weaker acid (such as acetic acid) (Ruttenberg, 1992) but this method seems problematic (Bickmore, 2009; Bickmore et al., 2009).

It is worth noting that another competing method for Fe- and Ca-bound P has been developed by Kouwe & Golterman (1976) (along with subsequent work such as Golterman (1982) and Golterman & Booman (1988)). These techniques use chelating agents such as nitrilo triacetic acid (NTA) and ethylene dinitrilo tetraacetic acid (EDTA). Golterman (1996) claims that the other extraction techniques (such as using NaOH) produce only operation results and that the pH changes due to the extractants cause P composition changes (which is probably an accurate description). The alternative is to use chelating compounds that will react with specific compounds in sediments (and do so at a pH approximately equal to the sediment pH), and Golterman (1996) compares these competing methods.

Finally, organic (or residual) P (orgP) is measured after destruction of organic matter to release P into solution as orthophosphates. This destruction is accomplished by wet oxidation or digestion procedures, using perchloric acid, nitric acid-sulfuric acid, or persulfate (Stieg et al., 2005). These all involve boiling of soil/sediment in acidic solutions and adjustment of pH afterwards. In digestion techniques a special hood must be used for safety. The measured P represents the amount of orgP.

Total P (totP) could be determined on a sample that hasn't been through any prior fractionation, through the same method. If inorganic P (inorgP) content is known, then orgP is calculated as follows:

$$orgP = totP - inorgP \quad (2.1)$$

Likewise, totP can be determined by the summation of concentrations for all P pools measured, up to and including orgP.

The soil (or sediment) tested is considered when choosing which procedure to use for destruction of organic matter. Use of perchloric acid is the most drastic and time-consuming, and is recommended only for particularly difficult samples such as sediments. Nitric acid-sulfuric acid is also difficult. Persulfate use is recommended due to its simplicity, but it is a good idea to verify results with those of one of the other methods before running a multitude of tests (Stieg et al., 2005).

Another possible way to determine orgP is through the use of loss-on-ignition (LOI) techniques, such as in (Dean, 1974). These involve destruction of organic matter by combustion at a certain temperature. After organic matter is destroyed, a simple washing step could extract P that was originally present in the organic matter and this could then be measured in solution.

Overall, it is important to remember that there are many different techniques for fractionation, all of which have varying advantages and disadvantages. It is quite difficult to actually determine what P fraction is being released into solution at each step, however this could be verified by mineralogical analysis between steps (Bickmore, 2009). There are many considerations in choosing a fractionation scheme, including

soil type, expected P pools, and the ultimate purpose of the data. van Eck (1982) tested a number of different proposed schemes, and reviews them. Shang & Zelazny (2008) provide a more up-to-date summary of fractionation schemes (including useful tables).

2.3.3 Measurement of Phosphorus in Solution

P can be found in many forms in the environment, only some of which are ‘readily’ available (accessible) for uptake by algae and plants. I emphasize readily due to the fact that P can be in constant flux between different types. An unavailable fraction may be converted (by a number of processes) into an available type, thus becoming available.

The available fraction of P, or orthophosphates, is the dissolved and suspended portion of P. This type is ‘reactive’ in that a small fraction of any condensed phosphate present is usually hydrolyzed. Therefore, not all the original phosphate is measured. Three common chemical methods for P (orthophosphates) measurement are reviewed here. In addition to these, other techniques will also be discussed.

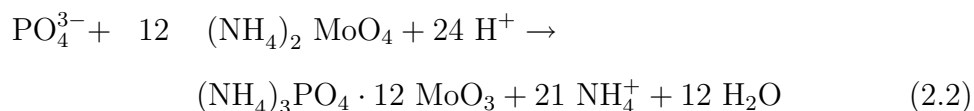
Prior to discussion of these methods, it is important to note that collected sediment samples must be handled correctly prior to measurement. If measurement cannot be completed immediately, samples should be preserved by freezing (at or below -10°C). For long periods of storage, it is important to add 40 mg HgCl_2 per L of sample. If there is a low concentration of P it is important not to store in plastic bottles unless soil is kept in a frozen state, so that phosphates do not absorb onto walls of the bottle.

A number of chemical measurement methods are available. First, gravimetric methods usually require that large amounts of P be present, which does not occur normally under natural conditions. Volumetric methods may be used if the concentration of phosphate is greater than $50\text{ mg}\cdot\text{L}^{-1}$. Formation of a precipitate, filtration, careful washing of the precipitate, and titration are required in this method. Once again, the concentrations tested by these methods are reached on very seldom occasions (e.g. in boiler waters, as anaerobic digester supernatant liquids), none of which

occur naturally (Stieg et al., 2005). For this reason, these methods (both gravimetric and volumetric) were not considered further for the present research.

Colorimetric techniques are the standard for testing water and wastewater, but result in a possible sacrifice of accuracy. In these techniques, concentrations are determined by Beer’s Law, which relates color of a sample (as indicated by light absorbed by the sample) to the concentration.

A variety of colorimetric methods exist for orthophosphate measurement, and are discussed by Stieg et al. (2005). One method is based on ammonium molybdate. Phosphate ion reacts with ammonium molybdate in acidic conditions to form a molybdophosphate complex. The reaction is:



With lower concentrations of P, a yellow colloidal sol is formed. This is the basis for colorimetric measurement of immediate concentrations. If the concentration of phosphate is less than 30 mg·L⁻¹ (common in water), the yellow color is not discernible and vanadium is added to form a vanadomolybdophosphoric acid complex. This provides a much more intense yellow color that allows phosphate detection as low as 1 mg·L⁻¹ or even lower.

Another colorimetric technique reduces molybdenum to produce a blue-colored sol. The color is proportional to the amount of phosphate present. Either stannous chloride or ascorbic acid is used for the reduction. For the first, the reaction is:



Other methods exist for measuring P. Ion chromatography may be used to measure orthophosphates. EPA Method 300 identifies a number of anions (SO_4^{2-} , PO_4^{3-} , NO_3^- , NO_2^- , *inter alia*) through this procedure. This method has some advantages. First, it allows for the measurement of several anions at the same time. These

other anions (nitrates, nitrites, sulfates) can be important to analyze P dynamics in aquatic systems and better characterize the geochemical environment. Additionally, this method allows for greater efficiency in measurement, as an auto-sampler may be used to analyze several samples with limited human interaction.

Another method involves x-ray fluorescence (XRF) spectroscopy, in which individual elements are analyzed. Thus, any answers from this method would be in total mass of P instead of phosphates. This method can be useful for solutions that might have interfering elements, as the solutions must be dried for analysis (Tingey, 2008). This could also cause problems as drying could cause the P to change chemical form.

2.4 Deer Creek Reservoir

This section provides information regarding the reservoir studied, including historical water quality data. Some relevant local studies are reviewed as well.

2.4.1 Basic Information

Deer Creek Reservoir (DCR) (pictured in Figure 2.1) is located on the Provo River, with other significant inflows from Snake Creek, Main Creek and Daniels Creek (shown in Figure 2.2). The watershed that drains into the reservoir is 171,663 acres. The area draining into Jordanelle Reservoir, a recently constructed major impoundment upstream of DCR, is not included in this number. Culinary water released from the reservoir for potable uses is diverted into the Salt Lake Aqueduct at the Olmstead Diversion, located a few miles downstream. The Murdock Diversion, approximately located at the canyon mouth, provides irrigation water.

It is necessary to understand beneficial uses of reservoirs, as these in effect set the water quality standards required. The Utah Division of Water Quality (UDWQ) has named the beneficial uses of this reservoir. It is used for culinary water, providing approximately 73,500 ac-ft of water annually for many water districts including areas in Salt Lake City, American Fork, Lehi, Lindon, Pleasant Grove, Orem, and Provo (serving approximate population of 480,000) (BOR, 2009). It is also used for recre-



Figure 2.1: Deer Creek Reservoir (BOR, 2009)

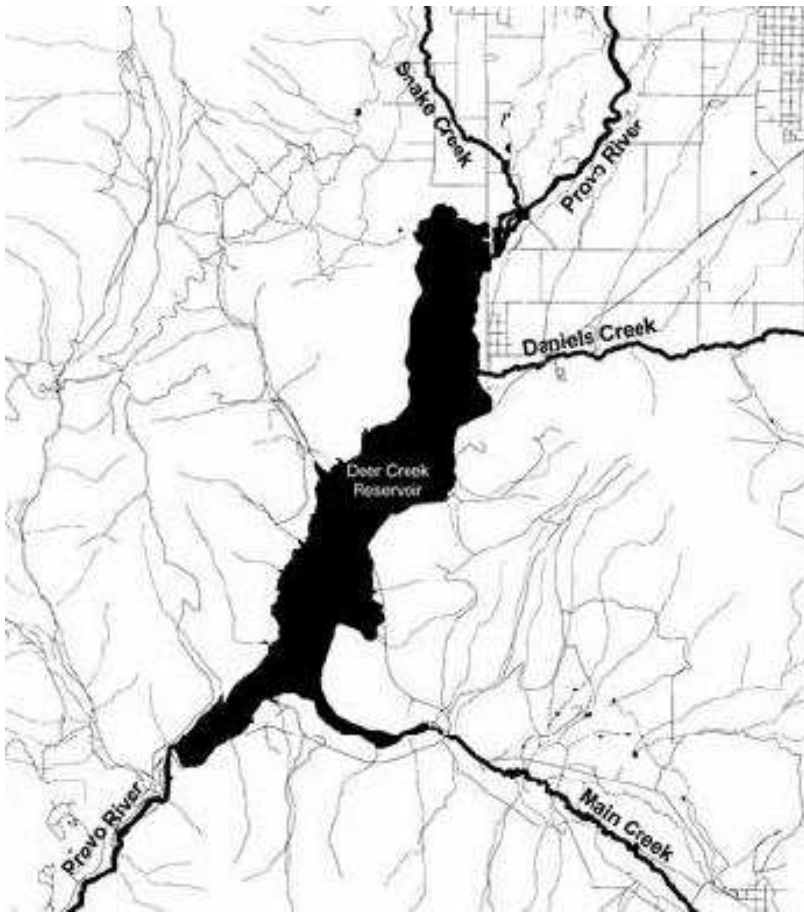


Figure 2.2: Deer Creek Tributaries (PSOMAS, 2002; Salah et al., 2005)

ational activities such as swimming and boating. Additionally, it is used for animal habitat (specifically cold water game fish and organisms within their food chain). Finally, it is used for agricultural purposes, providing irrigation water for more than 48,000 acres of farmland.

Annual precipitation in the area of the reservoir varies from 41 to 102 cm (16 to 40 in). The frost-free season of the area ranges from 80 to 100 days of the year (UDWQ, 2004).

Understanding the components (including nutrients such as P) of the delta sediments is a critical part of this study, and a number of sources contribute to their composition. First, geological formations surrounding the reservoir extensively control sediment constituents, as groundwater and surface water pass through them and dissolve minerals. Organic material, including trees and bushes, may also contribute to sediment composition as runoff makes its way to the reservoir. Additionally, any facilities (including farms) with effluents (point or nonpoint source) that reach the reservoir need to be noted. Even when these have been controlled, prior loading from these sources is probably mostly deposited in sediments in the hypolimnion (or within the delta).

The dam at DCR was constructed on alluvial deposits covering a foundation of limestone and sandstone. Vegetation of the surrounding watershed includes pine, spruce-fir, oak-maple, alpine tundra and sagebrush-grass. Additionally, some agricultural crops are located on the border of the reservoir and Heber Valley. Land use is varied, with much land owned by the United States Forest Service (USFS) and the Bureau of Land Management (BLM). Some grazing of domestic livestock occurs on private lands, but most private lands of the valley are either agricultural or urban (UDWQ, 2004).

2.4.2 Water Quality

Overall, Deer Creek's water quality is good, with relatively few parameters (P, dissolved oxygen, total coliforms) exceeding state quality standards based on the

assigned beneficial uses of the reservoir. The water in Deer Creek has relatively high hardness values ($\sim 180 \text{ mg}\cdot\text{L}^{-1}$ as CaCO_3).

P is a main concern here, and dissolved oxygen (DO) should also be considered since it has been shown to affect movement of P between sediments and the water column. Stratification at DCR causes anoxic conditions to develop, allowing trapped P in sediments to be released to the water column. For this reason, P concentrations throughout the water column at times greatly exceed the state pollution indicator for P, which is $25 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ (UDWQ, 2004).

Anaerobic environments seem to allow P to be released from sediments at Deer Creek, in agreement with other studies (including Mortimer (1941) and Mortimer (1971)). UDWQ (2004) also noted that in the latter portion of the summer the DO concentration lowers on a consistent annual basis. A dramatic example came on July 14, 1992, when DO levels in the hypolimnion reached to $0.5 \text{ mg}\cdot\text{L}^{-1}$. Any study of resuspension potential should thus take into account temporal variation in parameters measured. DO also shows a common diurnal variation.

When DCR was first built, impoundments were not created for purposes of potable water supply. However, the reservoir is now a major source of drinking water, as water demands in the Intermountain West have increased. Since reservoirs were not designed for potable water supply, Funk & Gaufin (1965) notes that “few studies have been made in this area to determine objectionable characteristics of algae or the feasibility of their control in water supplies.” Their study researched the application of copper sulfate at varying levels of alkalinity, for purposes of controlling algae that affect taste and odor of drinking water. Additionally, Gaufin & McDonald (1965) studied factors that control production of algae in Deer Creek Reservoir.

Deer Creek was found to be eutrophic in the 1970s (EPA, 1972), with anaerobic conditions found in the hypolimnion from July until September. Oxygen often was low under ice cover between January and April as well. P was the limiting factor for algal growth throughout the reservoir, though in some areas nitrogen limitations existed in August.

The reservoir was highly eutrophic from the late 1970s to the early 1980s. Since this time, management activities have reduced this problem by controlling point and nonpoint external sources. Figure 2.3 shows this reduction in the reservoir's trophic state index (TSI), as correlated with Secchi depth measurements by Carlson (1977).

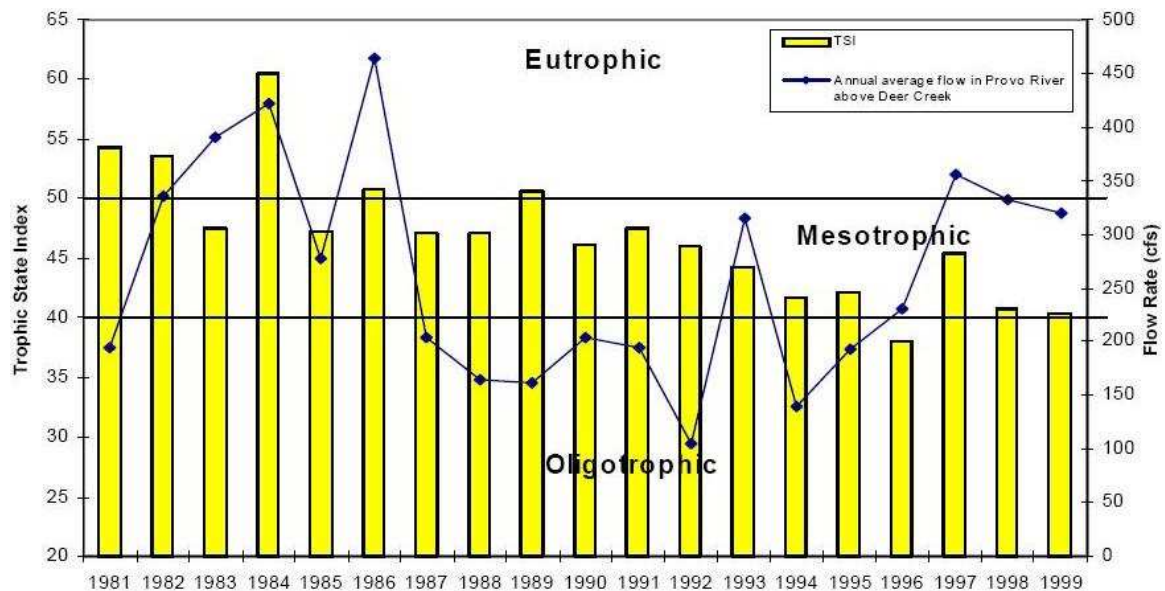


Figure 2.3: Variation of Trophic State Index of DCR from 1981-1999 (PSOMAS, 2002)

Even when water quality has improved within the reservoir, some problems remain. First, low DO concentrations during stratification are a concern. The reservoir was named an impaired water body by UDWQ (2000) due to low DO in the hypolimnion and high temperatures at the surface.

As TSI levels decreased, the dominant algae community has shifted from blue-green to green. However, UDWQ (2004), using information on plankton populations based on the Important Species Index (ISI) (method for assessing critical species in aquatic environments), notes that one strain of blue-green algae (*Aphanizomenon flos-aquae*) seems to have rebounded since (and this resurgence should be tracked):

Bluegreen algae together comprised approximately 17.2% of the flora when measured by summing ISI's. This total represents a significant increase

over the past few years. For example, bluegreen algae comprised only 1.5% of the flora for the 1990 year.

Macrophytes, a set of plants that may affect nutrient dynamics by uptaking P, are not common and don't cause problems generally UDWQ (2004).

UDWQ (2004) also notes that "all the periods of record indicate that the reservoir is characterized as a nitrogen limited system." This needs to be considered, and indicates that nitrogen should be tested along with P. However, the study done by EPA (1972) indicated that P was the limiting nutrient (except for during blooms in August, when N became important).

2.4.3 Local Sediment Studies

Though many studies show that internal P loading is an important origin of P within reservoirs, Messer & Ihnat (1983) states that

virtually no information is available on the extent to which internal phosphorus loading is important in reservoirs in the Intermountain West, or on the factors controlling phosphorus uptake or release in these sediments.

For this reason, a series of preliminary sediment studies was conducted on reservoirs throughout the Intermountain West in the 1980s (Messer et al., 1983; Messer & Ihnat, 1983; Messer et al., 1984).

The studies aimed at increasing the understanding of sediment-water interactions in connection with the P cycle within these reservoirs. First, deposited sediments were tested for P chemistry. This included the types of P present (determined by fractionation methods) as well as their relative proportions. Secondly, simulations of P release from sediments to the above water column were carried out. Intact sediment cores gathered from the reservoir were used for this purpose. These tests assessed potential impacts of internal P loading in local reservoirs.

Messer et al. (1984) investigated DCR, and the study noted that the sediment surface becomes anaerobic at the upper portion of the reservoir during the late part of the summer. At this time and in this area of the reservoir, blue-green algal blooms seem to occur. The anaerobic conditions seem to provide an opportunity for P in the

sediments to become available for uptake within the reservoir water column. Large algal blooms can create an anaerobic environment at the sediment-water interface, as decaying algae produces high oxygen demand, reinforcing this cycle until colder weather causes turnover.

The sediment profiles within the reservoir indicated that apatite-P (mostly unreactive due to high unsolubility) comprised the majority of P entering the lake. Due to this finding, the researchers suggested that efforts to reduce external P loading into the reservoir should consider the availability of P entering the reservoir.

Messer et al. (1984) gathered sediment samples to analyze as a potential source of P for the water column. They found a possibility for moderate release of P under anaerobic conditions, while release was insignificant under aerobic conditions. Additionally, it seems that P release from sediments is partially dependent on the redox cycle of Fe. These findings seem to be in general accordance with work from other areas. Messer & Ihnat (1983) commented:

Although it is not possible to categorize the trophic state of a lake or reservoir based on the sediment P concentration alone, NaOH-P has been shown to be highly correlated with anaerobic P release rates from sediment cores taken from upper Flaming Gorge and incubated in the laboratory (Messer et al. 1983). Therefore, the NaOH-P concentration may provide a useful indicator of the potential for P release into an anoxic hypolimnion.

Their use of the term NaOH-P is P loosely bound to Fe, which can easily become available as orthophosphate ('reactive' P). Based on these results, Messer & Ihnat (1983) conclude that sediments of intermountain west reservoirs are expected to release P in significant amounts under anaerobic conditions in the hypolimnia.

Messer & Ihnat (1983) also discuss other parameters that could be important. These authors also studied Flaming Gorge Reservoir, located in Wyoming. The study was conducted in late summer in order to determine if internal P loading could be a contributor to algal blooms at this time of year. A number of potential follow-up studies are offered by Messer et al. (1983). These ideas aim to understand the process of internal P cycling to a greater extent for purposes of modeling.

Chapter 3

Plan and Methodology

This chapter outlines the objectives of the thesis, which involved sediment sampling on the delta of Deer Creek Reservoir for purposes of determining the spatial and chemical distribution of P and potential for P release from sediments. It provides the sediment sampling program, storage and measurement procedures, and analysis techniques.

3.1 Objectives and Preparation

There are many potential mistakes in sediment collection, including improper choice of sampling locations, inadequate numbers of samples collected, and incorrect techniques for sampling, handling, or analysis of sediments. In order to avoid these, Mudroch & MacKnight (1994b) suggest that “detailed information is necessary about the outline of the whole project prior to selecting sediment sampling techniques and proper methods for handling and analyses of the collected samples” For this reason, a sediment sampling program is provided here; details regarding developing these programs are found in MacKnight (1994) and Mudroch & MacKnight (1994b).

The ultimate purpose of the present work is to determine the potential for impact of sediment nutrient (specifically P) content on algal growth (and eutrophication) in DCR. Even with management of external nutrient loading, these problems may still exist due to trapped nutrients. The short term goal of this research is to characterize the spatial and geochemical distribution of P in the delta sediments. This will include determining the distribution of different geochemical P fractions across the delta both horizontally and vertically. Though not completed, I have begun to perform a geostatistical analysis of results to estimate P concentrations in areas not

sampled. This will also enable us to estimate total mass of P (including individual fractions) available in the reservoir delta. This follow-up work will be reported on in a different venue. The preliminary geostatistical analysis is presented.

In preparation for this study, a number of preliminary steps have been completed. We studied and evaluated many techniques. Participants in the thesis work have practiced the chosen methods, and written protocols (available in Appendix B) were developed for each method. We prepared an inventory of equipment available for the thesis as well. This preliminary work should increase the reliability of our results, ensuring better quality control.

The outline of work is as follows:

1. Develop a sampling plan
2. Obtain sediment samples with a hand auger
3. Prepare samples for measurement
 - Water soluble P only
 - Complete P fractionation (including water soluble and digestion)
4. Measure prepared samples for P
5. Determine water content of all sediment samples
6. Calculate P concentration in terms of dry sediment
7. Perform geostatistics calculations using data (to be done later)

3.2 Sampling

The sampling distribution plan across the DCR delta is shown in Figure 3.1; sample coordinates are given in Appendix A. Small black dots indicate where samples were taken in preliminary work. Points along transects are separated by 100 m, and transects are found at 200 m spacings.



Figure 3.1: Sample Distribution across Reservoir Delta

A surface sample was taken at each numbered point, with a few exceptions (points 1-6 and 60 were not sampled due to accessibility or other issues). Other points were moved slightly, as they were directly in the river. Red circles indicate that two additional samples were taken at depths of 6 inches and 1 ft to determine a vertical distribution. Additionally, samples from a 2 ft depth were taken at vertically sampled locations along one transect (points 12, 20, 30, and 42).

Sediment samples were taken using hand augers, and immediately placed into Ziploc bags for storage. The bags were labeled with information regarding location, sampling date, and depth. Figure 3.2 shows how samples were taken. Bags remained in coolers until arrival to the lab, when samples were stored in the freezer to await further preparation and measurements. A total of 91 samples were taken for analysis.

The sampling was done over a four week period, so that all samples collected could be prepared and analyzed within one week.



Figure 3.2: Sampling Delta Sediments Using a Hand Auger

3.3 Fractionation of Samples

Sediment samples were prepared for measurement of phosphates in solution, by a fractionation procedure generally following the scheme of Moore & Coale (2000) (from modification of van Eck (1982) by Moore & Reddy (1994)). Most steps involved mixing a certain extractant with sediment, shaking, centrifugation and filtration of the solution for measurement. Shaking was done with a Cole Parmer 51704 series shaker (see Figure 3.3).

For centrifugation, a Sorvall Superspeed RC2-B ultracentrifuge was used. Vacuum filtration was accomplished with $0.45\ \mu\text{m}$ Geotech geofilters using a Nalgene reusable filter holder (see Figure 3.4). The filter size ($0.45\ \mu\text{m}$) commonly defines the demarcation between dissolved and suspended particles. Notes and procedures on use of all equipment are available in Appendix B.3.

The fractionation scheme allowed for measurement P content in five different pools, with steps sequentially performed:

- Fr.W: water soluble P



Figure 3.3: Shaker Table and Tubes Used in Fractionation



Figure 3.4: Apparatus Used in Vacuum Filtration of Prepared Solutions

- Fr.KCl: loosely sorbed P
- Fr.NaOH: Al- and Fe-bound P
- Fr.HCl: Ca-bound (apatite) P
- Fr.PFD: residual P, probably mostly organic

Table 3.1 presents information regarding fractionation steps, briefly comparing the steps I used with steps used in the previous DCR studies (Messer & Ihnat, 1983; Messer et al., 1984). The main differences are that the first two steps I used were done in one step previously, and that the previous studies included an additional step to reduce iron (using Na-citrate, Na-dithionite, and Na-bicarbonate). The Fr.W step did not include shaking, and the Fr.PFD (post-fractionation digestion) step was accomplished by digestion of remaining sediment with persulfate and sulfuric acid (based on standard methods, Stieg et al. (2005)). I calculated total P content by the summation of the P content of each fraction. However, total P for the previous DCR studies was determined with a separate aliquot of sediment (which had not previously been subjected to fractionation).

Table 3.1: Comparing Fractionation Schemes: Thesis v. Previous

Current	t_{shake} (hr)	Previous	P Fraction
Water	-	-	interstitial water
1 M KCl	2/2	1 N NH_4Cl	anion-exchange sites, loosely sorbed
.1 M NaOH	17/18	.1 N NaOH	Al- or Fe-bound, adsorbed
-	-	CBD	Fe-bound, Fe-occluded by oxides
.5 M HCl	24/18	.5 M HCl	Ca-bound (apatite)
Persulfate	-	Persulfate	residual (organic), or total

We determined water soluble P for every sample taken, while the complete fractionation scheme was performed on a subset of the samples (19 total). We prepared a total of 167 solutions for measurement.

3.4 Measurements

For each prepared solution, phosphate content was measured using spectrophotometric means. Specifically, Hach method 8178 (amino acid method) was used with a Hach DR5000 spectrophotometer for measurement. This method is adapted from a standard colorimetric method (Stieg et al., 2005), and it is able to measure phosphate content from .23 to 30.00 $\text{mg}\cdot\text{L}^{-1}$. Figures 3.5 and 3.6 demonstrate this method. The method procedures are provided in Appendix B.4.



Figure 3.5: Preparing Solutions for Phosphate Measurement Using the Amino Acid Method

As part of this measurement step, we determined water content for each sediment sample. This was used to calculate P concentration of dry sediments.

3.5 Normalized Results

Prior to geostatistical analysis, all P content data must be available on the same basis. For the present research, we performed back calculations so that reported P content was based on the mass of dry sediment (i.e. $\text{mg}\cdot\text{g}^{-1}$ dry sediment). The



Figure 3.6: Placement of Solution into Spectrophotometer for Measurement

following base equation was used for these calculations, though it varied slightly depending on the fraction of P being calculated.

$$C_{P.in.sed} = \frac{C_{P.in.wat} \times \frac{L}{1000mL} \times V_{liq} \times D}{m_{dry.sed}} \quad (3.1)$$

where:

- $C_{P.in.sed}$ = concentration of P in dry sediment ($mg \cdot g^{-1}$)
- $C_{P.in.wat}$ = concentration of P in the solution ($mg \cdot L^{-1}$)
- V_{liq} = total volume of solution measured (mL)
- D = dilution factor
- $m_{dry.sed}$ = mass of dry sediment from which P extracted (g)

3.6 Geostatistical Analysis

I performed brief geostatistical analysis using GSLIB (Deutsch & Journel, 1992), which is freely available from Stanford University, and with the Groundwater

Modeling System (GMS, 2008). This analysis, though not completed, will allow us to estimate P concentrations in areas not sampled (and thus estimate total mass of P in delta) and additionally it will provide an idea of where more in-depth sampling should occur. This analysis will also help us determine spatial trends and correlations. With these data, we will estimate total amounts of P (from different fractions) available across the reservoir delta and provide an estimate of their spatial distribution. This work will be done as a follow-up to this thesis and will be reported on elsewhere.

Chapter 4

Results

Samples were collected in 4 sampling trips, over a period of 4 weeks in the summer (July-August) of 2008. We performed all analysis and measurement (except water content) of collected samples within one week of collection, so that analysis for each set of collected samples was completed prior to the next sampling trip. We carried out water soluble P tests for each (91 total) collected sample, while complete fractionations were completed for 19 selected samples. We later calculated P contents based on dry sediment weights; all values are reported on this basis. A complete set of the results is available in Appendix C.

4.1 Results

4.1.1 Water Soluble Results

Average water soluble P (WSP) content is displayed for a number of collected groups (by depth) in Table 4.1, while Table 4.2 and Table 4.3 examine average WSP values for surface samples along the length and width of the delta, respectively. The length is divided up into transects, with the first (transect 1) being most upstream. The width is divided up by columns, starting from the right side of the delta (as looking upstream). The number of samples (n) reflects how many actual samples were included in the averages for the specific groups. Some may be less than the actual number of samples taken due to error in analysis.

Overall, there is a trend toward lower WSP concentrations with depth. However, this should be investigated further since n decreases with depth. Change in concentration through depth might be attributable to decreasing water content with depth or greater quantities of organic matter with depth.

Longitudinal variation is generally apparent (Table 4.2), as WSP concentrations in the surface sediments decrease going from upstream to downstream. There is a notable exception at Transect 2 which needs to be considered though. This trend might be due to the fact that sediments further away from the reservoir (most upstream on the delta) have been uncovered for longer periods.

Considering lateral variation (see Table 4.3), two separate groups seem to be distinguishable. WSP concentrations in columns 1-4 generally are higher than those of columns 5-11. These data might be influenced by relatively sparse data (small number of samples n), but it appears that there is a general trend in lowering concentrations over the width of the delta. This could be due to the fact that as the column number increases, the distance from the river entrance to the delta decreases as well. The samples taken in the last columns were quite some distance from the river, and might have been uncovered for larger amounts of time.

Brief geostatistical analysis using tools in GMS support this idea of lateral variation, with higher water soluble P concentrations evident along the right side (looking upstream) of the delta (see Figure 4.1). Similar graphs for other P pools are provided in Appendix D, though these display different variation. We emphasize that these graphs are preliminary in nature, and further work with geostatistical analysis should confirm and expand on some of these initial findings (hypotheses).

4.1.2 Complete Fractionation

Table 4.4 provides data regarding average P concentrations for different fractions tested. Some results are based on only 18 (instead of 19) samples due to personnel error.

The sediments on average contained much less P in the water soluble and KCl-extractable pools than in the other pools, while there was significantly more (by 2+ orders of magnitude) of the NaOH-extractable, the HCl-extractable, and the residual P pools. Apatite P (extracted with HCl) was present in significant amounts, as expected from results of previous work (Messer & Ihnat, 1983; Messer et al., 1984) and due to the fact that these sediments are largely calcareous, as the location of the

Table 4.1: Variation of Average Water Soluble P with Depth

Depth	n	$C_{P.avg}$ (mg·g ⁻¹)
Surface	55	5.64E-03
6 in	15	4.43E-03
12 in	13	4.06E-03
2 ft	4	3.99E-03
All	87	5.12E-03

Table 4.2: Longitudinal Variation of Average Water Soluble P

Transect	n	$C_{P.avg}$ (mg·g ⁻¹)
1	10	7.29E-03
2	10	4.81E-03
3	11	6.31E-03
4	8	5.59E-03
5	5	3.82E-03
6	7	4.03E-03

Table 4.3: Lateral Variation of Average Water Soluble P

Column	n	$C_{P.avg}$ (mg·g ⁻¹)
1	3	1.53E-02
2	4	5.88E-03
3	4	9.68E-03
4	5	7.62E-03
5	5	4.10E-03
6	5	3.47E-03
7	6	4.54E-03
8	6	4.73E-03
9	6	4.04E-03
10	6	3.10E-03
11	2	3.23E-03

Table 4.4: Average Sediment P Concentrations for Various Fractions

Pool	n	$C_{P.avg}$ (mg·g ⁻¹)
Fr.W	19	4.66E-03
Fr.KCl	18	4.53E-03
Fr.NaOH	19	1.74E-01
Fr.HCl	18	9.26E-01
Fr.PFD	19	1.46E+00

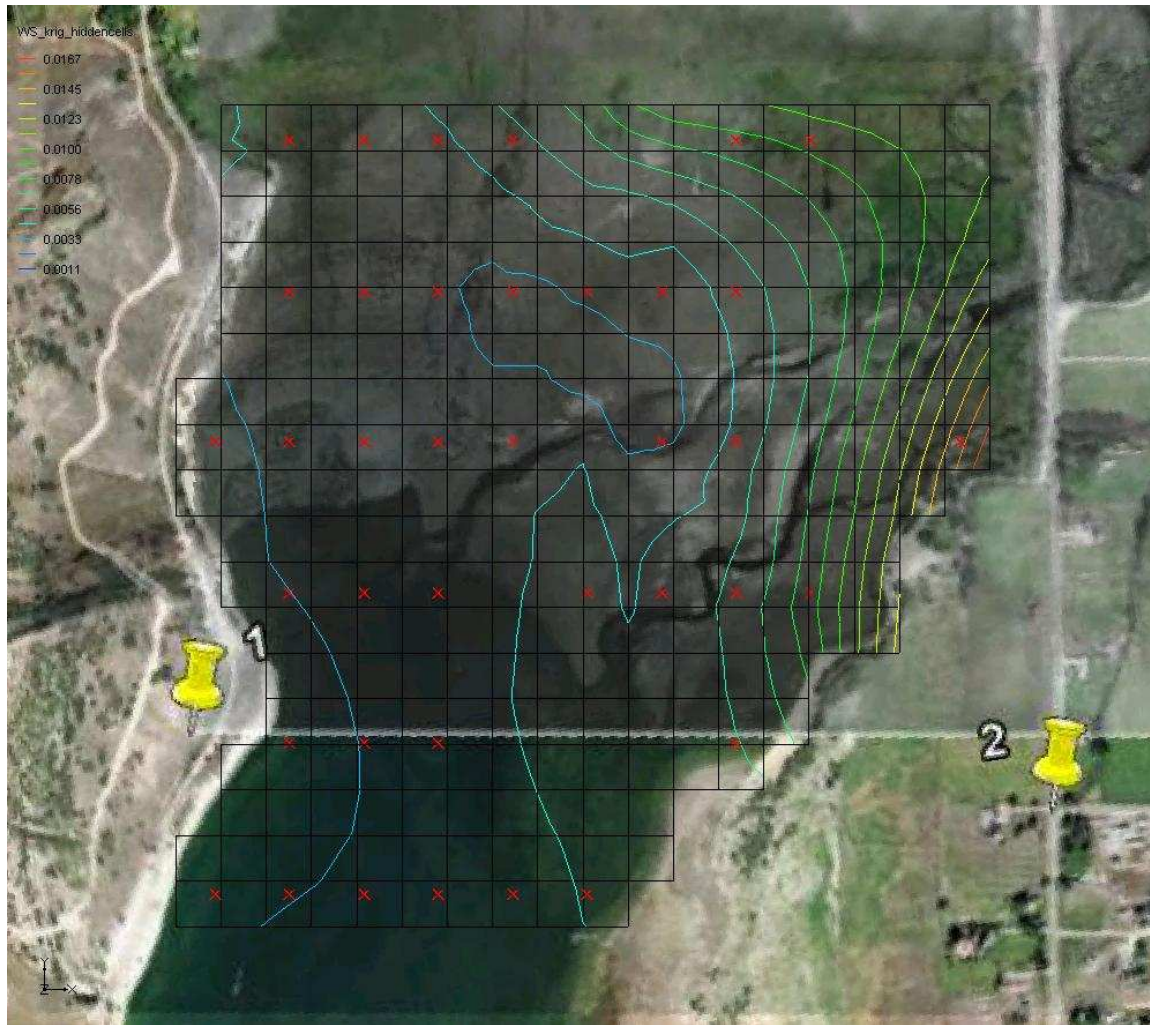


Figure 4.1: Preliminary Water Soluble P Concentration Contours across Delta

dam is on a limestone foundation (PSOMAS, 2002). The largest fraction of P present was residual, which is probably mostly organic P (plus whatever was not extracted in previous steps).

Table 4.5 compares average sediment P concentrations for similar fractions of the current work and the previous (Messer et al., 1984) DCR study. The fractionation schemes were slightly different, not only in extractants but also in other aspects such as shaking time and quantity of sediment extracted. Additionally, sediments collected in the previous study were taken from the bottom of the reservoir while those used in this study were taken from the delta. The number of collected samples was different as well.

The water soluble and loosely bound P (Fr.W and Fr.KCl) were determined through one step (Fr.NH₄Cl) in the previous work. Much less P was obtained in the current work, though this might be reasonable when considering location of sampled sediments (exposed v. in solution). Levels of Fr.NaOH P were very comparable, with slightly higher amounts in the current work. This is most likely due to the distinct environments (P may resorb to or co-precipitate with Fe minerals upon drying of sediments). Apatite P content was much higher in the sediments from the current work; this could be due to other P pools (perhaps from CBD, which wasn't performed in this work) dissolving into solution with the strong acid. Authigenically formed apatite might be part of the explanation as well; these Ca-P complexes are more likely to dissolve in solution than detrital forms of apatite.

There were significant amounts of residual P present. This is another point of departure between the two studies. For the current work, total P was calculated from the summation of individual pools while in the previous work total P was determined by digestion of a separate aliquot of sediment (with no previous fractionation performed on it). To calculate residual (or organic) P for the previous study, we could subtract inorganic P from the total P obtained but this was not done. Non-apatite inorganic P (NAIP) refers to the summation of P contained in Fr.NaOH and Fr.CBD (i.e., all the inorganic P that is not apatite).

Table 4.5: Comparing Fractionation Results: Thesis v. Previous

Current	$C_{P,avg}$ (mg·kg ⁻¹)		Previous
	Current	Messer	
Fr.W	4.66	-	-
Fr.KCl	4.53	-	-
Fr.W+Fr.KCl	9.19	54.3	Fr.NH ₄ Cl
Fr.NaOH	174.07	155.2	Fr.NaOH
-	-	355.8	Fr.NaOH + Fr.CBD (NAIP)
Fr.HCl	926.31	542.0	Fr.HCl
Fr.PFD	1460	-	Total - (NAIP+Fr.HCl)
Total (by sum)	2569.6	1107.3	Total (by sum)
Total (by digestion)	-	825.6	Total (by digestion)

4.2 Discussion of Results

Results presented above will be further addressed. Specifically, discussion involves trying to determine whether results are reasonable. First, P content of sediments will be compared to the P content of background (BG) (in area surrounding the delta) soils. Assumptions are also addressed to see the effect they could have had on results. Finally, methods for verification of results are given. This includes a brief discussion of some preliminary results from some of the methods.

4.2.1 Comparison with Surrounding Soil Samples

Fractionations were completed on 5 other soil samples (taken from nearby locations surrounding the delta (but outside the deposition zone of the reservoir), though this was difficult to verify) in order to provide an idea of how P content varied from BG soils to deposited sediments. Table 4.6 compares fractionation results from these BG samples with the average concentrations from fractionation of sediments.

Table 4.6: P Content ($\text{mg P}\cdot\text{g}^{-1}$ sediment) of Background Soil Samples

	BG1	BG2	BG3	BG4	BG5	Mean Sediment
Fr.W	4.49E-3	6.12E-3	3.42E-3	7.28E-3	-	4.66E-3
Fr.KCl	2.90E-3	2.72E-3	2.26E-3	9.66E-3	1.20E-2	4.53E-3
Fr.NaOH	1.52E-1	1.62E-1	1.20E-1	1.14E-1	6.52E-2	1.74E-1
Fr.HCl	1.68E-1	2.17E-1	1.91E-1	1.12E+0	1.56E+0	9.26E-1
Fr.PFD	1.54E+0	1.94E+0	1.38E+0	6.05E+0	4.21E+0	1.46E+0

There is not much difference in P content between the sediments and BG samples, with some BG samples even having greater P content than sediments. However, the land where soil samples were taken from cannot be considered too ‘normal’ for determining BG P concentrations, as it was obvious that it had been used for agricultural/farming pursuits. Much of the P content of sediments was originally created due to runoff from agriculture (prior to regulations leading to reductions in external P loading), so this might not be too surprising. It is still important to verify whether BG soil is different in terms of P content. This might only be possible by further searching for an area where no other activities have taken place (i.e., an area that can

be considered in a natural state). Such locations only seem to be available on surrounding hillsides, with steep slopes. However, these areas are probably particularly susceptible to erosional processes.

4.2.2 Repeat Fractionations

After completion of work, it was recommended that we perform the CBD fractionation step as well. For this purpose, we ran fractionations again for six of our sediment samples. This additionally allowed us to fill in some missing information and to compare how results varied with a repeated fractionation. Table 4.7 shows how P concentrations compared (by ratio $\frac{C_{second}}{C_{first}} \cdot 100\%$) between the two fractionation procedures for Fr.W, Fr.KCl, and Fr.HCl.

Concentrations shown in square brackets indicate measurements that were problematic and might not be as reliable as others. Information for the other pools is not yet available for the second set of fractionations. Additionally, we note that there were two additional steps added in these fractionations (and both were performed prior to Fr.HCl).

We note that in almost all cases (and in fact all of Fr.W and Fr.KCl), measured P on the second fractionation was lower. This could be due to the length of time between the fractionations (~ 4 months) as chemical changes might have occurred.

The situation is much more complicated for Fr.HCl, with two samples (24.S, 32.1 ft) being measured at almost the same concentration (though one was lower and one was higher than 100% of the original) and two other samples (22.S, 35.S) being significantly higher in concentrations on the second fractionation.

Table 4.7: Concentration Variability among Repeat Fractionations

Sample	W	KCl	HCl
12.2ft	48.6	54.8	-
22.S	72.6	33.7	225.8
24.S	36.5	[19.9]	92.2
32.S	[53.1]	62.4	42.8
32.1ft	[72.5]	52.7	108.8
35.S	[42.2]	61.9	165.5

The fact that Fr.HCL samples came out higher in concentrations is somewhat surprising considering the fact that two additional steps (Fr.CBD, Fr.Na-Ac) were carried out prior to the Fr.HCl stage. It might be possible that those two additional steps released P but that entrained solutions (discussed in more detail later) increased the P concentrations by this later step. A more likely scenario could involve the fact that the earlier P pools (Fr.W and Fr.KCl) had lower concentrations on these repeat fractionations, perhaps indicating that some of this P had been lost to other pools.

We did not perform many repeat fractionations to verify results, but these few provide evidence of interesting differences. In any case, we believe that this information demonstrates a need to be careful with fractionation timing as well as in evaluation of results obtained from these procedures. The complete fractionation scheme should be performed soon after collection of samples, and methods should be established to verify results. Even if there is some variety between repeat fractionations, some methods (to be described later) should allow for greater credibility in the results.

4.2.3 Assumptions and Limiting Factors

A number of assumptions and limiting factors probably affected results. These are addressed in order to provide ideas for improvement of future studies, in addition to relating shortcomings of the current study. These basically fall into the following categories: personnel error, fractionation methodology, and measurement methodology.

Personnel error is a problem with any study. In the present study, we endeavored to minimize this through practicing all techniques prior to using them in the actual work performed for the study. However, differences between operators probably were not completely eliminated. For example, in the spectrophotometric work samples had to be inverted a few times but the word ‘few’ probably was not interpreted the same by all operators (and maybe even wasn’t the same for each time a certain operator performed the measurement). Such things should be checked in greater detail and minimized. A number of other errors could occur. These include

mixing up samples, incorrect (or forgetting to do so) recording of results (both in the laboratory as well as in the office), problems in measurements of solutions or solids used in analysis, inadvertent disposal of prepared samples, and errors in calculations. We attempted to minimize some of these by specific labeling of containers and by frequently checking to ensure correct recording.

A number of issues could complicate the fractionations performed in this study. First, the ratio of sediment to extracting solution used in fractionation could potentially affect the release of P from sediment to solution, resulting in discrepancies for different ratios. Though we kept our ratios equivalent (for the most part, with minor discrepancies), comparisons with other studies using different ratios might be problematic.

One of the main problems with fractionation involves the entrainment of solutions in the sediments between fractionation steps. The supernatant is decanted from centrifuge tubes for measurement of P in solution after each step. However, some of the solution almost always remained in the tube (this portion is the entrained solution). Obviously, this remaining solution probably contained the same P concentration as the decanted solution. For the next step of fractionation, this solution could have either diluted or increased the concentration of P obtained from a particular step.

One possible indication of this problem involves a few Fe content tests performed on samples from Fr.NaOH and Fr.HCl. Results indicated that significant amounts of Fe (2.25 ppm in one case) was present in solutions obtained from the Fr.HCl step, even when that step wasn't designed to obtain Fe-bound P. This could be due to entrained solutions from the previous step, which was designed to release Fe-bound P (and as expected, Fr.NaOH samples also contained Fe). There are possibly other reasons for this (such as reduction of iron through the Fr.HCl step), but these have not been verified.

To determine exactly how entrained solutions were affecting final results, all sample concentrations (for Fr.KCl, Fr.NaOH, Fr.HCl) were additionally calculated taking the amount of P from entrained solution into account. This was done with a

slight modification of the equation above. The difference took into account the fact that the prior solution contained P already. The equation was modified to be:

$$C_{P.in.sed} = \frac{C_{actual.P.wat} \times \frac{L}{1000mL} \times V_{liq} \times D}{m_{dry.sed}} \quad (4.1)$$

We adjusted the concentration of P in the solution ($C_{actual.P.wat}$) by subtracting the concentrations present in the entrained solution:

$$C_{actual.P.wat} = C_{measured} - C_{prior,entrained} \quad (4.2)$$

Adjusting the concentrations for the Fr.PFD step is somewhat different. There are some issues with this that need to be addressed. First, we used leftover sediment (from the fractionation process through Fr.HCl) in the digestion. If we want to calculate the actual amount of P per mass of dry sediment, the water content of this leftover sediment must be known (unless we had dried the leftover prior to digestion, which wasn't done). Since we did not measure the water content, we are left with two possible options: 1) assume that sediment has same water content as initial sediment or 2) determine water content with the assumption that entrained solution mixed uniformly throughout leftover sediment. Due to how we sampled sediment for the digestion, the second option is not very applicable. We used the first option for comparison with our original results.

Table 4.8 compares average concentrations ($mg \cdot g^{-1}$) obtained for the four P pools (all but Fr.W), using both the original and the entrained solution adjusting equations.

Table 4.8: Effect of Entrained Solution on Results ($mg \cdot g^{-1}$)

Fraction	n	$C_{avg.P}$ -Original	$C_{avg.P}$ -Adjusted	% of Original
Fr.KCl	18	4.93E-03	4.54E-03	92.1
Fr.NaOH	19	1.82E-01	1.71E-01	94.3
Fr.HCl	18	9.39E-01	9.39E-01	99.9
Fr.PFD	19	1.46E+00	2.30E+00	157.2

Obviously, there is some slight discrepancy but it is not extreme (except maybe in the case of Fr.PFD, as expected). Perhaps in the future it will be alright to only minimize problems with the entrained solution. However, we will address some ways that this problem might be further mitigated.

To address this problem of entrained solutions, there are a few possibilities. First, changing the centrifuge tube might prove helpful. A smaller centrifuge tube with a complete opening (not lipped openings as were used in this study) would allow for solution to be removed to a greater extent. Doing so would create a need to change the shaking process, the centrifuge and speed of centrifugation as well. However, even with slower speeds, a fractionation performed with smaller tubes (15 and 50 mL conical base) should result in better separation of the supernatant and the leftover sediment pellet. One other advantage of this is that better contact between solutions and sediments would be possible.

Another possible fix for this would be to add some washing steps in between each fractionation step, as was done by Ruttenberg (1992). This would be able to clear up any leftover phosphates in solution to some degree, but would result in greater time spent in the fractionation process as many additional steps would be added. However, there still might be problems with entrained solutions and this might not completely remove all phosphates that have been released from sediments. This could additionally cause other problems.

It is also possible that the high sediment to solution ratio (~ 10 g sediment to 20 mL solution) used in this study intensified the entrained solution problem. Having a smaller ratio would ensure that solutions did not become oversaturated with P, which could potentially inhibit P from leaving sediments. Additionally, a smaller ratio would provide for better contact with solution and would result in less sediment lost while decanting the supernatant. This should be considered in future work.

The Fr.PFD step also could have been problematic. Boiling for this digestion step was supposed to be gentle, but there was a variety in how gentle our solutions boiled. Additionally, the pH of these samples was supposed to be adjusted at the end

but the process was difficult. The solutions were probably measured at a variety of pH levels after preparation, which would have affected final measurements.

The final limiting factor deals with measurement of P in solution, which was problematic for some of the fractionation steps, as solutions were highly colored or had different pH values. Fractionation steps Fr.NaOH, Fr.HCl, Fr.PFD (as well as Fr.CBD and Fr.Na-Ac, performed in repeat fractionations) created problematic solutions. These problems were taken care of in this work by dilution of the sample to remove color (in Fr.NaOH and Fr.HCl steps) but this probably had an affect on actual measured P concentrations, even after adjustment for dilution. We determined discrepancies in P content of sediments (in mg P g^{-1} of dry sediment) when testing different dilutions. For example, one sample contained $8.11\text{E-}2 \text{ mg}\cdot\text{g}^{-1}$ with a smaller dilution (31) while with a larger dilution (126) it contained $1.07\text{E-}1 \text{ mg}\cdot\text{g}^{-1}$. Another contained $1.6\text{E-}1 \text{ mg}\cdot\text{g}^{-1}$ with a dilution of 126, while with a dilution of 251 it contained $2.7\text{E-}1 \text{ mg}\cdot\text{g}^{-1}$. Though these are relatively close, they do demonstrate possible effects by dilution. Future studies might be able to address this by using other techniques, such as ion chromatography (IC) or total element analysis (discussed to a greater extent later).

The spectrophotometric technique we used (Hach amino acid method with Hach DR5000 spectrophotometer) should measure quantities of orthophosphates in solution, but might be problematic. We assumed that this measured all forms of orthophosphates (PO_4^{3-} , HPO_4^{2-} , and H_2PO_4^-) though upon checking in further detail the technique supposedly only measures orthophosphates in PO_4^{3-} form (but perhaps this is generic for all orthophosphate forms), which is only present in significant quantities after reaching highly basic levels ($\text{pH} > 10$, for disassociation of phosphoric acid $[\text{H}_3\text{PO}_4]$, $\text{pK}_3 = 12.4$). The pH of the solution ($\text{pK}_1 = 2.1$ and $\text{pK}_2 = 7.2$) would affect how much of each of these orthophosphate species was present, and we did not adjust pH levels for solutions unless it was specified (which was only the case in the digested Fr.PFD samples). The amino acid methodology needs to be verified with the manufacturer to determine what orthophosphate species it actually measures.

To check the accuracy of our phosphate measurements, a few sample solutions (with known phosphate content, not from this study) were measured for phosphate using spectrophotometry and ion chromatography (IC). IC was performed using Dionex equipment, specifically an AS40 Automated Sampler connected to a ICS-90 Ion Chromatography System with a IonPac AS14 column.

The solutions tested were prepared from water taken from Utah Lake, and were spiked with sodium phosphate to contain known PO_4^{3-} concentrations for isotherm studies. Utah Lake water was assumed to contain $0.1 \text{ mg}\cdot\text{L}^{-1}$ but contained slightly more when measured. Table 4.9 compares expected concentrations with measured concentrations for these solutions.

Results from IC matched well with expected P (in form of phosphate) concentrations, while those from spectrophotometry were significantly higher. Part of this discrepancy could be due to evaporation of the solution prior to spectrophotometric measurement, but this doesn't seem reasonable as solutions were covered and under refrigeration. Additionally, evaporation could not have occurred at such great levels as to explain the great change in concentration.

This discrepancy might also be due to the form of orthophosphate that is being measured, but this seems doubtful. The eluent (carrier liquid for solution) used in the IC method buffers the pH to about 8.3, creating a situation where most (if not all) of the phosphate is in the same species (HPO_4^{2-} , recall that $\text{pK}_2 = 7.2$) (Tingey, 2009; Bickmore, 2009). Although it is useful to have a standard pH for all solutions (provided by IC, but uncertain in spectrophotometry unless adjust all solutions to desired pH), this probably isn't the cause for the difference in concentrations between

Table 4.9: Comparing P Measurement Techniques

Expected Concentration	IC	Spectrophotometry
Utah Lake (assumed 0.1)	0.26	0.49 (after strong dilution)
1.5	1.59	-
3.0	2.86	12.93
4.5	4.80	20.89
6.0	6.24	-

these two methods either. However, varying pH levels probably effected measured P concentrations from spectrophotometry, a fact which needs to be checked since we are unsure about the actual form measured by the Hach amino acid method.

Overall, we are not sure why there is such a discrepancy. This should be determined if we are to have correct P (phosphate) concentrations. For comparing internal results (i.e. only results from this study), it should not be a problem though, since we can compare relative concentrations since all were based on the same method.

IC should be a better method for measurement for a number of reasons, including the possibility for automation which allows for more efficient use of time. However, the problematic solutions prepared from fractionation of sediment samples also cause problems for IC methods, and probably are damaging to the IC column (Tingey, 2008). One way around this is to perform a total element analysis for P (instead of phosphate) only. This was done using x-ray fluorescence spectroscopy for another study performed (in which similar problematic solutions had to be measured for P) (Bickmore et al., 2009). Solution matrices do not cause problems in this technique since they are dried on a clear film on which dissolved solids remain after evaporation (Tingey, 2008).

4.2.4 Verification of Results

In order to verify whether present results seem reasonable, we can compare other results obtained (from other work) using a nearby sediment sample. We briefly report these results here to demonstrate how they might be of use in verifying fractionation results, though all findings are preliminary and these methods need to be further developed for the specific purpose of verification.

During the period of this study, some other work was being completed to determine procedures for obtaining sediment samples from within the reservoir. One of these samples, taken in July of 2008 using an Ekman grab sampler, was used for a number of different tests that could potentially help to provide credibility to the results from this as well as future studies. This sample was taken from a location near the upper portion of DCR, not too far from the delta. However, obviously, this

sample probably differed somewhat in content from delta sediments due to contact with water.

First, a mineralogical analysis was completed using x-ray diffraction (XRD) by the method of Środoń et al. (2001) (using a Scintag XDS 2000 X-Ray Diffractometer), and with pattern analysis performed with RockJock software (Eberl, 2003). The analysis was performed twice, once with sediment containing soil organic matter (SOM) and once with sediment in which SOM had been destroyed by treatment with NaOCl (bleach) (method described by Soukup et al. (2008)). Table 4.10 reports mineralogical content of the sediment sample by weight percent of select components (some lumped together in groups). Of the most interest here are the carbonates, iron minerals, and apatite. Clays should also be of interest for some purposes.

Table 4.10: Mineralogical Content (by wt. %) of Sediment

Non-Clays	w/ SOM (% by wt.)	w/o SOM (% by wt.)
Carbonates	5.88	10.88
Gypsum	0.57	0.52
Quartz	29.22	24.70
Iron Minerals	1.86	4.19
Alkali Feldspars	24.32	16.88
Plagioclase Feldspars	14.56	13.78
Apatite	1.59	2.50
Total Non-Clays	~77.9	~73.7
Clays		
Kaolinites	1.81	5.44
Smectites and Illites	10.15	8.49
Other Clays	10.12	12.33
Total Clays	22.1	26.3

Total Fe (TI) analysis was also performed separately using a modification of Holmgren (1967) developed by Loeppert & Inskeep (1996). Sodium-citrate and sodium-dithionite were used to ensure all Fe is reduced to ferrous (Fe^{2+}) and then released to solution. This method is very similar to the CBD fractionation performed by Messer et al. (1984), so theoretically we could have determined P content of this

solution as well. This would have provided an idea of how much P was co-precipitated with or sorbed to Fe in the sediment.

Atomic Adsorption Spectroscopy (AAS) (using a Perkin Elmer Atomic Adsorption Spectrophotometer) was used for measurement of Fe in solution. TI analysis showed that iron was found at a concentration of $5.02 \text{ g Fe kg}^{-1}$ sediment, or approximately 0.5% by weight. Note that this cannot be directly compared with the weight percentage reported for Fe minerals above, as these minerals (including goethite and hematite) contain more than just Fe. However, this number does seem reasonable as it is a fraction of the weight percentage of iron minerals reported.

To verify Fe results further, we might test solutions obtained from the Fr.NaOH step for iron. This would indicate how much iron was released into solution during the step, and thus could provide (by combining with P results) an idea of how much P attaches to Fe in the sediment. Fe content was determined for five samples (one Fr.W, two Fr.NaOH, two Fr.HCl) using LaMotte wet chemistry kits. As expected, no Fe was found in the water soluble step. Iron was found in the Fr.NaOH samples, and also within the Fr.HCl samples. This could indicate either or both of the following: 1) that entrained liquid from the Fr.NaOH step was present in the Fr.HCl samples; 2) that the Fr.HCl step also somehow reduces Fe^{3+} and thus sediments release both Fe and P by this step into solution. The brief results seem to indicate that HCl is pulling out more Fe (one diluted Fr.HCl sample contained too much Fe to be measured), so mechanism 2 should be important. Further calculations and work with this should allow us to determine which of these (if not both) is primarily responsible.

Organic content and carbonate content were also determined using loss on ignition (LOI) techniques, according to Dean (1974). Organic content was found to be 43.2 g C kg^{-1} sediment, while inorganic carbon was present at a concentration equal to 69.1 g C kg^{-1} sediment. Soil pH (equal to 8.16) was determined for the sediment, using the method of Thomas (1996). This parameter could have a great effect on P constituents present. Cation exchange capacity (CEC) was also determined (equal to $49.9 \text{ mmol cation charge kg}^{-1}$ sediment) using the method of Amrhein & Suarez

(1990), summarized by Sumner & Miller (1996). Surface area was determined to be $1.41\text{E-}02 \text{ km}^2\cdot\text{kg}^{-1}$ sediment, using the method of Blum & Eberl (2004).

Through knowledge of the forms of minerals, as well as other characteristics such as organic content and soil pH, we should be able to calculate a rough estimate for potential P content of different pools. This could be compared to values obtained through fractionation methodology, and provide some credence to results. Development of these ideas is recommended for future studies. We have briefly discussed it here, but it needs to be extended specifically for verification purposes. One possible idea would be to test the mineralogy of the sediment after each fractionation step (Bickmore, 2009); this would allow us to determine what minerals/elements went into solution during each step.

Chapter 5

Conclusions and Recommendations for Future Work

As noted, this work is part of a larger project trying to understand and model water quality issues at DCR. One specific purpose of this was to identify how deposited delta sediments might provide a recycled nutrient (specifically P) source to the water column, in case of reservoir flooding (refilling after drawdown) over the exposed delta. This study provides information that can be used in further work. Here we offer some insights that will be of use in future work and additionally provide ideas for such work.

5.1 Conclusions

A number of important inferences may be concluded from the work contained herein. These deal with both the most effective methodologies to use as well as the actual results from this study.

First, though we thought that entrained solutions would have a large effect on measured P concentrations, this does not seem to be the case based on our three sets of calculations. Future fractionation studies should still seek to minimize the problem though, since this should be relatively easy to do and would result in more representative P concentrations.

Second, it is critical to determine how to best measure P in solution. Extremely complex matrix solutions are prone to measurement problems that are difficult to overcome. For this reason, we believe that P can be more accurately measured by methodologies that incorporate total element analysis.

Third, P (at least WSP) concentrations display at least slight anisotropy across the delta and through depth. Though there were only sparse data for other fractions of P, it is assumed that concentrations of these also vary across the delta. The

preliminary findings provided in the previous chapter are a start at understanding this phenomenon, but should be verified and extended with further geostatistical analysis. If such findings can be confirmed, they would have important implications as to how refilling of the reservoir would affect nutrient concentrations in the water column. For example, we could avoid refilling the reservoir over an area especially prone to loss of nutrients in sediment solutions.

Finally, this work confirms past studies that found apatite-P in large quantities of DCR sediments while extending this finding to exposed delta sediments. However, these initial results suggest that there is more apatite-P in the exposed delta sediments than in sediments that had been deposited in the reservoir (comparing our results with those of Messer et al. (1984)). This could have repercussions on refilling the reservoir, as some of the apatite-P found in delta sediments might be of authigenic (precipitated in area previously covered by water) instead of detrital origin. This could especially be true due to the extended droughts of recent years. This P might more easily become available as the reservoir is refilled.

This increased apatite fraction also indicates that the external P loading reductions starting in 1981 (as described by PSOMAS (2002)) have been successful. Apatite-P is the least bioavailable pool due to high insolubility (highly immobile) and would thus not be targeted for reduction. An increased overall percentage of this pool thus provides evidence of reduction in the other pools (which were targeted). When considering this in combination with the fact that P concentrations in discharged water from the dam have been significantly reduced, we believe that the loading reduction plan has been successful in targeting the actual bioavailable P pools within the reservoir. This has been accompanied by an improvement in water quality, as a near elimination of blue-green algal blooms (from cyanophyta) has been achieved.

5.2 Future Work

A number of recommendations for future work are listed below, followed by brief discussions of each.

1. complete geostatistical analysis of P distribution
2. extend sampling plan along length of reservoir
3. perform fractionation studies for varying particle sizes
4. establish protocols to verify fractionation results
5. explore interactions between delta sediments and inflowing water
 - incorporate results in a model for prediction
 - use geochemical software to determine release potential
 - complete experiments using sediments and river water

5.2.1 Geostatistical Analysis of Phosphorus Distribution

Geostatistical analysis using GSLIB has not been completed extensively enough to be reported on here. However, it has been started and it should be completed soon; a preliminary step has been taken using GMS which contains geostatistical tools. This analysis consists of creating variograms to understand any anisotropy (or learn about the lack thereof) in P concentration distribution across the delta. Though results indicate slight anisotropy in P concentrations (longitudinally and laterally across delta), complete geostatistical analysis should provide a more extensive analysis. Additionally, kriging techniques will provide the ability to predict P content (for all fractions) at unsampled locations across the delta. This complete analysis should allow for determination of potential P release to the reservoir when it is refilled (when exposed delta is covered again by reservoir).

5.2.2 Sampling Plan Extension

To understand the fate of P throughout the reservoir, it will be important to establish a sampling plan along the complete length of the reservoir. Any new plan need not necessarily be so extensively sampled across the width of the reservoir as was done in this study of delta sediments. Fractionation studies for longitudinally

sampled sediments should provide an idea of how P is distributed through the entire reservoir.

Particle size distribution (PSD) also can dramatically affect the P content of sediments, as smaller particles tend to sorb contaminants (including nutrients) to a much greater extent than larger particles. Future work should provide an analysis of PSD, and additionally studies could include fractionations on individual particle sizes (ranges of sizes) of sediment samples to determine how P is distributed through sediment size.

Future studies should also consider extending the fractionation scheme employed here. The CBD step used by Messer et al. (1984) should be important in determining how different fractions of Fe-bound P become available in solution. We used this method briefly when we processed (through complete fractionation scheme) a few of the same samples a second time. This was suggested due to the potential importance of information obtained from the CBD step.

Another possible extension to the fractionation scheme involves a search for methods to differentiate between different fractions of apatite-P. Ruttenberg (1992) was the first to try to distinguish authigenic from detrital apatite-P, and others have continued this work. This was also implemented for samples that we processed a second time. The best method for the differentiation would probably involve the use of microprobes, which allow us to visualize the grain structure and determine individual elements present (Bickmore, 2009). Differentiation of these pools should allow researchers to determine what fraction (if any at all) of apatite-P could become available.

5.2.3 Protocols for Verification of Fractionation Results

Fractionation (or extraction or selective dissolution) techniques can be highly variable and might not be very accurate. In order to verify whether results are reasonable, a number of other tests could be performed. These should be designed to determine content of sediments (or soils) by various methods. A number of initial suggestions were offered in the previous chapter, and the microprobes mentioned

above should be another important component of confirming findings of fractionation. These have been used in other work, but they show promise in verification of fractionation results. Additionally, it might be possible to use results from these tests to reasonably predict results of fractionation.

5.2.4 Sediment-Water Interactions

The overall purpose of the larger study is to determine how deposited sediments might be a source of nutrients to the water column. However, this has not been specifically treated in this work. The results from this study, along with results from future work suggested above, provide the data to be used to explore potential interactions between sediments and water.

With an idea of the P distribution in the sediments (both from this and future studies), we can begin to look at how trapped nutrients may become available to the water column under varying conditions. Potential work could include an exploration of these interactions in two ways. First, data can be incorporated into computational models designed to predict what may happen to trapped P with changes in the system behavior (e.g. drawdown and refilling of the reservoir). We could use both geochemical software (such as MINTEQ or PHREEQ-C) as well as modeling software such as CE-QUAL-W2 in this effort. Second, experiments may be designed to use natural sediments and river water to directly determine what effect these changes have on trapped P release. This will be important as reservoirs are emptied and then refilled, as exposed delta sediments are again allowed to interact with the water column. Any future work in this could consider studies by Fabre (1988) and Moore & Reddy (1994).

Another important consideration involves nitrogen. Though not considered here, this critical nutrient has been identified as a limiting nutrient (at least at times; seem to coincide with large algal blooms) at DCR (PSOMAS, 2002; UDWQ, 2004). Understanding the nitrogen content of the sediments would probably involve another fractionation scheme, and this could be an important step in the overall study (determining how algal growth is affected by release of trapped nutrients from sediments).

Tables 5.1 and 5.2 respectively summarize sediment and water quality parameters that have been found to affect P binding in sediments. These should be important to consider in studies of sediment-water interactions. Many of these have been measured as part of the larger project.

As a final consideration, PSOMAS (2002) discusses the production of Geosmin by algae. This substance was identified as the likely cause for taste and odor problems that occurred in January 2001, after a large algal bloom in November 2000. Prior turnover probably provided the nutrients contributing to rapid algal growth.

Table 5.1: Parameters to be Measured in Sediment Samples

Parameter	Purpose	Reference(s)
orthophosphates	'readily' available P	Sas (1989), all studies
total P	sediments tend to retain P when under certain concentrations	Sas (1989)
nitrates	affects P-binding	Anderson (1982)
sulfates/sulfides	may bind iron, inhibiting P binding	Caraco et al. (1993); Kleeberg (1997); Suplee & Cotner (2002)
iron	can bind P	Einsele (1936); Mortimer (1971); Tessenow (1974); Gunnars et al. (2002)
manganese	potential binding site for P	Messer & Ihnat (1983); Christensen (1997)

Table 5.2: Water Quality Parameters to be Measured at Sample Locations

Parameter	Purpose	Reference(s)
pH	higher levels affect sediment P-retention	Eckert et al. (1997); Fisher & Wood (2004)
temperature	useful for modeling, affects density and stratification	
suspended solids	affect water density, and thus movement	Morris & Fan (1998)
turbidity	mapped with suspended solids, limits light and thus productivity	Morris & Fan (1998)
dissolved oxygen	oxic conditions possibly retain P better	Mortimer (1941, 1971); Ruban & Demare (2006)
total N	ratio of tot-N to tot-P possibly indicative of P release	
total P	same as for total N	
redox potential	similar to purpose for oxygen	Eckert et al. (1997); Gibson (1997); Gächter & Müller (2003)

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Appendix A

Sample Coordinate Locations

Table A.1: Coordinates for Sampled Locations

Sample	Longitude	Latitude	Sample	Longitude	Latitude
1	-111.469757	40.4786989	31	-111.478968	40.4733033
2	-111.470901	40.4769083	32	-111.478956	40.4715174
3	-111.470913	40.4786942	33	-111.478943	40.4697315
4	-111.472070	40.4786895	34	-111.480099	40.4697267
5	-111.472057	40.4769036	35	-111.480112	40.4715126
6	-111.472044	40.4751177	36	-111.480124	40.4732985
7	-111.473201	40.4751130	37	-111.480137	40.4750844
8	-111.473213	40.4768989	38	-111.480150	40.4768702
9	-111.473226	40.4786848	39	-111.480163	40.4786561
10	-111.474382	40.4786800	40	-111.481319	40.4786513
11	-111.474370	40.4768941	41	-111.481306	40.4768654
12	-111.474357	40.4751082	42	-111.481293	40.4750796
13	-111.474344	40.4733223	43	-111.481280	40.4732937
14	-111.475500	40.4733176	44	-111.481268	40.4715078
15	-111.475513	40.4751035	45	-111.481255	40.4697219
16	-111.475525	40.4768894	46	-111.482411	40.4697170
17	-111.475538	40.4786753	47	-111.482424	40.4715029
18	-111.476694	40.4786705	48	-111.482437	40.4732888
19	-111.476682	40.4768846	49	-111.482449	40.4750747
20	-111.476669	40.4750987	50	-111.482462	40.4768606
21	-111.476656	40.4733128	51	-111.482475	40.4786465
22	-111.476644	40.4715269	52	-111.483631	40.4786417
23	-111.477800	40.4715222	53	-111.483618	40.4768558
24	-111.477812	40.4733080	54	-111.483606	40.4750699
25	-111.477825	40.4750939	55	-111.483593	40.4732840
26	-111.477838	40.4768798	56	-111.483580	40.4714981
27	-111.477850	40.4786657	57	-111.483567	40.4697122
28	-111.479006	40.4786609	58	-111.484723	40.4697074
29	-111.478994	40.4768750	59	-111.484762	40.4750651
30	-111.478981	40.4750892	60	-111.484787	40.4786368

Appendix B

Protocols - SOPs

B.1 Water Content

1. weigh ceramic bowl, record weight (m_{bowl})
2. add sediment sample
3. reweigh bowl with wet sediment, record weight ($m_{wet.bowl}$)
4. heat in oven at 105 °C for 24 h
5. reweigh bowl, record weight ($m_{dry.bowl}$)
6. determine water content

B.2 Fractionation

This fractionation scheme is based on Moore & Coale (2000), roughly equivalent to van Eck (1982) as modified by Moore & Reddy (1994).

Weigh centrifuge tube (w_t) prior to placement of sediment sample in tube. The weight of each successive fraction is needed to calculate the entrained liquid (containing soluble P) from the prior extraction.

B.2.1 Water Soluble P

1. place ~10 g sediment sample into tube
2. reweigh tube with sediment (w_{t+s}), determine wet weight of sediment
3. add 20 mL of DI water to tube

4. centrifuge for 20 minutes at 7500 rpm
5. filter through 0.45 micron membrane filter (use vacuum filter)
6. save sample for analysis/measurement, refrigerate ASAP to avoid evaporation

B.2.2 Loosely Sorbed P

1. reweigh tube to determine how much water removed ($w_{wat.sol}$)
2. homogenize pellet left in tube with a spatula
3. add 20 mL of deaerated 1 M KCl to tube
4. shake for 2 h on reciprocating shaker
5. centrifuge for 20 minutes at 7500 rpm
6. filter immediately through 0.45 micron membrane filter
7. save sample for analysis/measurement, refrigerate ASAP to avoid evaporation
8. reweigh tube to determine weight after loosely sorbed P released (w_{loose})

B.2.3 Aluminum and Iron-bound P

1. add 20 mL 0.1 M NaOH to tube
2. shake for 17 h on reciprocating shaker
3. centrifuge at 7500 rpm for 20 minutes
4. filter with 0.45 micron filter
5. save sample for analysis/measurement, refrigerate ASAP to avoid evaporation
6. reweigh tube to determine new weight (w_{Fe+Al})

B.2.4 Calcium-bound (apatite) P

1. reweigh tube prior to Ca-bound P extraction
2. add 20 mL of 0.5 M HCl
3. shake for 24 h on reciprocating shaker
4. centrifuge at 7500 rpm for 20 minutes
5. filter through 0.45 micron filter
6. save sample for analysis/measurement, refrigerate ASAP to avoid evaporation

B.2.5 Residual (mostly organic) P

We used the persulfate digestion method with remaining sediment after step #4 (apatite-P). This can also be used with a new sediment aliquot for determination of total P.

Materials:

- hot plate
- glass scoop (to hold persulfate crystals)
- sulfuric acid solution
- potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) solid
- 1 N (1 M) NaOH

Procedure:

1. obtain 50 mL (or suitable portion) of thoroughly mixed sample
 - for sediments, mix ~ 60 mg sediment sample (record weight) to 50 mL H_2O
2. add 1 mL sulfuric acid solution

3. add 0.5 g solid potassium persulfate
4. boil gently on preheated hot plate for 30-40 min (or until 10 mL left)
5. cool and dilute to 30 mL (with DI water)
6. neutralize solution with NaOH
7. dilute to 100 mL with distilled water

B.3 Equipment

B.3.1 Reciprocating Shaker

This shaker can be found in 395 CB.

1. place bottles together on board of shaker
2. wrap them together using tape
3. ensure that it is on ‘reciprocating’ mode (if necessary move knob to that side)
4. set speed to highest setting (10)
5. turn on shaker
6. leave on until shaking time ends

NB: There is a top for the shaker (which holds individual tubes/bottles), but we didn’t find it until after the fractionation work had commenced. In order to ensure that all samples were shaken in the same manner, we followed the above protocol (wrapping tubes together) for all the work. The purpose of shaking is to ensure enough contact between sediment and solution so that sediment components can be released to the solution, and for this reason we decided to ensure that contact would be similar for all samples.

B.3.2 Ultracentrifuge

This can be found in the hydrogeology lab (in the ESC). Additional directions for use are found above the ultracentrifuge in the lab.

1. turn on centrifuge by pressing button, wait until inside cold (10-15 min)
2. add tubes (250 mL PP bottles) to centrifuge
 - ensure caps tightended on tubes
 - ensure that bottles are balanced (2, 4, or 6 tubes placed across from one another)
3. screw caps onto top of centrifuge, ensure that it is tightened (note directional arrows)
4. ensure that inside is cold (arrow should be below blue indicator)
5. completely close the door on top of centrifuge (should snap in place)
6. set speed to 1000 rpm for starting up
7. ensure that auto brake is off, hit start button
8. once to speed (wait a couple minutes), increase speed sequentially (waiting between increases) to desired speed
9. set timer to desired time (or just hit stop button if counting time by yourself)
10. once time is up (if you didn't set time, hit stop button), turn on the auto brake if desired
11. wait until spinning ceases, obtain samples from centrifuge

NB: There is also a small centrifuge available that could be used for 50 mL conical base centrifuge tubes. It has a maximum speed of 3500 rpm. The concept of use is similar, but there is no need to ensure that the centrifuge is cool (no refrigeration necessary).

B.3.3 Vacuum Filtration

We used the filter holder available in the hydrogeology lab, though we could do something similar in 395 CB.

1. put together vacuum ensemble
 - put circular piece on top of bottom piece and put filter on top
 - screw in top piece
 - add black stopper to one side of bottom piece
 - connect tubing to other side of bottom piece
2. turn on vacuum by flipping the switch
3. pour liquid to be filtered through the filter
4. turn off vacuum when all liquid is filtered
5. pull off the stopper and pull out the tubing
6. pour solution in bottom piece through one of the side tubes on bottom piece into labeled container

NB: The entire ensemble should be thoroughly cleaned (rinsed with DI water) and dried prior to the next use, in order to avoid contamination from previously filtered solutions.

B.4 Measurement of P in Solution

All results reported here were determined using the Hach amino acid method for phosphate measurement. We give the procedure for this method here, and additionally provide the procedure we used for measurement of phosphate using ion chromatography.

B.4.1 Hach Amino Acid Method

We needed to dilute our solutions prior to measurement with this method. In all cases, it was because we didn't have enough solution to use this method. In some of the cases, we had to do greater dilution due to darker solutions that we thought would interfere with measurement. It is important to keep track of the dilution that you use. After dilution, the method proceeds as follows:

1. ensure that 1 inch square cell holder is facing user
2. choose the amino acid program (#485) from stored programs on DR5000
3. obtain 12.5 mL of sample
4. add 0.5 mL of first reagent (molybdate)
5. add 0.5 mL of second reagent (amino acid)
6. invert solution a few times to mix (turns blue if phosphates present)
7. tap the timer button on DR5000 screen (in amino acid program) and hit 'OK'
8. place inverted solution in a 10 (or 25) mL 1 in cuvette
9. place blank sample (solution without any reagents) into another cuvette (same size)
10. use wipes to ensure cuvettes are clear of smudges
11. once time is up, place blank sample cuvette into centrifuge and press 'Zero'
12. remove this cuvette and place other (prepared) sample into holder
13. record reading from the screen (in $\text{mg}\cdot\text{L}^{-1} \text{PO}_4^{3-}$)

NB: The method reports some possible interferences, including colored samples. Instead of dilution (as we did), the method says to add 1 mL of a sulfuric acid standard solution (10 N) to the blank sample. This was not used in this work.

B.4.2 Ion Chromatography

The ion chromatography system we practiced with is in the hydrogeology lab (ESC). There is a system being prepared in 395 CB as well.

Materials:

- tubes and stoppers 5 (now 6) for standards plus one for each water sample to be run
- stopper plunger
- auto-sampler trays (enough to hold all tubes, 6 tubes per tray)
- five standard solutions and DI water
- previously prepared solutions for measurement

For each of the standards and water samples (first do DI water, then standards #1-5, and then the water samples in desired order), perform the following:

1. pour liquid into IC tube to ~ 1 cm below top of tube
2. put on stopper, push down with plunger until top-most part of the stopper is aligned with top of the tube
3. dry out as well as possible any liquid remaining on top of the stopper
4. place stopper in the auto-sampler tray
 - first tube in each tray will be placed on side with the black dot
 - place DI water and then five standards in first tray
 - make sure to record order that samples are placed in trays

After all water samples are loaded, place trays into the auto-sampler. First tray will be the most forward tray in the left rack, and the second will be next (and so on).

The black dots align with the right side of that rack. After this is completed, the run can be prepared and started.

Running the samples:

1. choose File Save as (name what you want)
2. rename, delete, create samples according to how many water samples that will be running and desired distinction by name
3. set dilutions factor if desired and necessary
4. select batch - start
5. tap hold/run button on the auto-sampler
6. check back later for results

NB: You should check with lab assistant (or Dave Tingey) to ensure that there is enough eluent available for the run.

Appendix C

Results

Table C.1: Background Soil P Concentrations ($\text{mg}\cdot\text{g}^{-1}$)

BG	WS	KCl	NaOH	HCl	PFD	Total P
1	4.49E-03	2.95E-03	1.60E-01	1.84E-01	1.54E+00	1.89E+00
2	6.12E-03	2.84E-03	1.71E-01	2.32E-01	1.94E+00	2.35E+00
3	3.42E-03	2.34E-03	1.30E-01	2.07E-01	1.38E+00	1.72E+00
4	7.28E-03	1.06E-02	1.37E-01	1.38E+00	6.05E+00	7.59E+00
5	-	1.32E-02	7.80E-02	1.91E+00	4.21E+00	-

Table C.2: Summary of Adjusted Sediment P Concentrations ($\text{mg}\cdot\text{g}^{-1}$)

Location	Depth (ft)	KCl	NaOH	HCl
near9	0	4.85E-03	5.30E-02	1.28E-01
12	0	4.97E-03	1.21E-01	1.20E+00
12	2	3.44E-03	8.98E-02	-
20	0	4.73E-03	9.89E-02	7.25E-01
20	2	3.40E-03	1.61E-01	1.10E+00
22	0	1.07E-02	4.33E-01	6.77E-01
22	1	6.52E-03	2.62E-01	5.01E-01
23	0	2.82E-03	1.74E-01	9.57E-01
24	0	-	9.28E-02	1.34E+00
29	0	2.33E-03	1.86E-01	9.46E-01
29	1	2.96E-03	1.69E-01	1.14E+00
30	0	3.33E-03	1.35E-01	1.25E+00
30	2	4.65E-03	2.25E-01	8.54E-01
31	0	3.23E-03	1.69E-01	1.08E+00
31	1	6.00E-03	2.11E-01	1.03E+00
32	0	3.53E-03	1.31E-01	1.01E+00
32	1	3.99E-03	1.72E-01	9.61E-01
33	0	5.80E-03	2.00E-01	1.09E+00
35	0	4.48E-03	1.69E-01	8.98E-01

Table C.3: Summary of Sediment P Concentrations ($\text{mg}\cdot\text{g}^{-1}$) for Points 7-29

Location	Depth (ft)	WS	KCl	NaOH	HCl	PFD	Total P
7	0	2.80E-02	-	-	-	-	-
8	0	9.46E-03	-	-	-	-	-
9	0	8.45E-03	-	-	-	-	-
near9	0	9.71E-03	4.92E-03	5.30E-02	1.28E-01	1.39E+00	1.59E+00
10	0	5.93E-03	-	-	-	-	-
10	0.5	3.97E-03	-	-	-	-	-
10	1	4.00E-03	-	-	-	-	-
11	0	4.96E-03	-	-	-	-	-
11	0.5	6.95E-03	-	-	-	-	-
11muck	0	5.97E-03	-	-	-	-	-
12	0	6.14E-03	6.19E-03	1.27E-01	1.20E+00	1.38E+00	2.72E+00
12	0.5	3.39E-03	-	-	-	-	-
12	1	3.70E-03	-	-	-	-	-
12	2	3.89E-03	3.58E-03	8.98E-02	-	8.23E-01	-
13	0	6.48E-03	-	-	-	-	-
near13	0	5.38E-03	-	-	-	-	-
14	0	7.14E-03	-	-	-	-	-
15	0	4.75E-03	-	-	-	-	-
16	0	4.70E-03	-	-	-	-	-
17	0	2.21E-02	-	-	-	-	-
18	0	9.81E-03	-	-	-	-	-
18	0.5	3.19E-03	-	-	-	-	-
18	1	4.06E-03	-	-	-	-	-
19	0	5.52E-03	-	-	-	-	-
19	0.5	4.52E-03	-	-	-	-	-
19	1	5.48E-03	-	-	-	-	-
20	0	4.06E-03	5.74E-03	1.34E-01	7.27E-01	1.16E+00	2.04E+00
20	0.5	4.93E-03	-	-	-	-	-
20	1	4.94E-03	-	-	-	-	-
20	2	4.49E-03	3.67E-03	1.73E-01	1.10E+00	1.48E+00	2.76E+00
21	0	1.27E-02	-	-	-	-	-
21	0.5	9.52E-03	-	-	-	-	-
21	1	4.49E-03	-	-	-	-	-
22	0	6.02E-03	1.10E-02	4.60E-01	6.78E-01	1.81E+00	2.97E+00
22	0.5	7.93E-03	-	-	-	-	-
22	1	4.66E-03	6.58E-03	2.70E-01	5.01E-01	8.31E-01	1.61E+00
23	0	2.80E-03	3.22E-03	1.86E-01	9.58E-01	9.32E-01	2.08E+00
24	0	5.81E-03	-	1.07E-01	1.34E+00	9.11E-01	-
25	0	3.53E-03	-	-	-	-	-
26	0	4.50E-03	-	-	-	-	-
27	0	3.88E-03	-	-	-	-	-
28	0	2.52E-03	-	-	-	-	-
29	0	2.70E-03	2.53E-03	1.86E-01	9.46E-01	1.44E+00	2.58E+00
29	0.5	2.80E-03	-	-	-	-	-
29	1	2.87E-03	3.02E-03	1.71E-01	1.14E+00	2.68E+00	4.00E+00

Table C.4: Summary of Sediment P Concentrations ($\text{mg}\cdot\text{g}^{-1}$) for Points 30-59

Location	Depth (ft)	WS	KCl	NaOH	HCl	PFD	Total P
30	0	2.28E-03	3.72E-03	1.35E-01	1.25E+00	2.64E+00	4.04E+00
30	0.5	2.55E-03	-	-	-	-	-
30	1	2.37E-03	-	-	-	-	-
30	2	4.42E-03	5.00E-03	2.38E-01	8.54E-01	3.23E+00	4.33E+00
31	0	4.48E-03	3.94E-03	1.88E-01	1.08E+00	1.00E+00	2.28E+00
31	0.5	3.69E-03	-	-	-	-	-
31	1	5.60E-03	6.56E-03	2.24E-01	1.03E+00	1.03E+00	2.30E+00
32	0	-	4.00E-03	1.51E-01	1.01E+00	1.06E+00	-
32	0.5	3.01E-03	-	-	-	-	-
32	1	-	3.99E-03	1.72E-01	9.61E-01	1.12E+00	-
33	0	5.34E-03	5.93E-03	2.01E-01	1.09E+00	1.53E+00	2.83E+00
34a	0	3.47E-03	-	-	-	-	-
34b	0	5.40E-03	-	-	-	-	-
35	0	-	5.18E-03	1.83E-01	8.98E-01	1.34E+00	-
36	0	2.91E-03	-	-	-	-	-
37	0	2.80E-03	-	-	-	-	-
38	0	4.80E-03	-	-	-	-	-
39	0	7.86E-03	-	-	-	-	-
40	0	3.23E-03	-	-	-	-	-
41	0	5.01E-03	-	-	-	-	-
42	0	5.76E-03	-	-	-	-	-
42	0.5	3.37E-03	-	-	-	-	-
42	1	3.99E-03	-	-	-	-	-
42	2	3.15E-03	-	-	-	-	-
43	0	6.01E-03	-	-	-	-	-
43	0.5	3.28E-03	-	-	-	-	-
43	1	3.49E-03	-	-	-	-	-
44	0	4.53E-03	-	-	-	-	-
44	0.5	3.33E-03	-	-	-	-	-
44	1	3.08E-03	-	-	-	-	-
45	0	3.83E-03	-	-	-	-	-
46	0	4.42E-03	-	-	-	-	-
47	0	3.10E-03	-	-	-	-	-
48	0	2.71E-03	-	-	-	-	-
49	0	5.54E-03	-	-	-	-	-
50	0	3.22E-03	-	-	-	-	-
51	0	5.24E-03	-	-	-	-	-
52	0	3.89E-03	-	-	-	-	-
53	0	3.16E-03	-	-	-	-	-
54	0	3.23E-03	-	-	-	-	-
55	0	3.01E-03	-	-	-	-	-
56	0	2.67E-03	-	-	-	-	-
57	0	2.65E-03	-	-	-	-	-
58	0	3.10E-03	-	-	-	-	-
59	0	3.37E-03	-	-	-	-	-

Table C.5: Sediment P Concentrations ($\text{mg}\cdot\text{g}^{-1}$) for Repeat Fractionations

Location	Depth (ft)	WS	KCl	NaOH	HCl	PFD
12	2	1.89E-03	1.96E-03	-	1.45E+00	-
22	0	4.37E-03	3.71E-03	-	1.53E+00	-
24	0	2.12E-03	2.67E-03	-	1.24E+00	-
32	0	1.81E-03	2.49E-03	-	4.32E-01	-
32	1	3.22E-03	2.10E-03	-	1.04E+00	-
35	0	2.30E-03	3.20E-03	-	1.49E+00	-

Appendix D

Geostatistical Plots in GMS

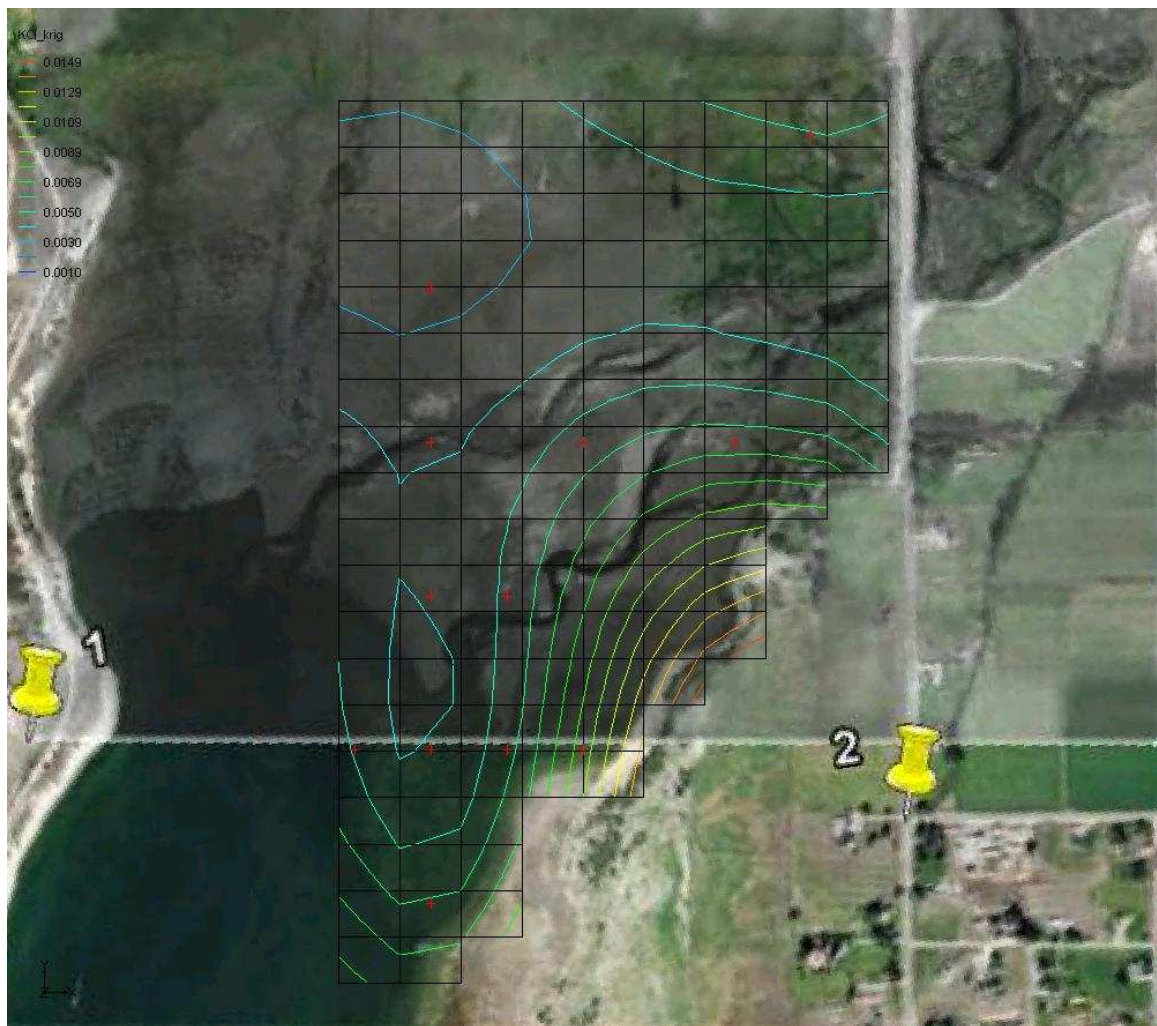


Figure D.1: Preliminary KCl Extractable P Concentration Contours across Delta

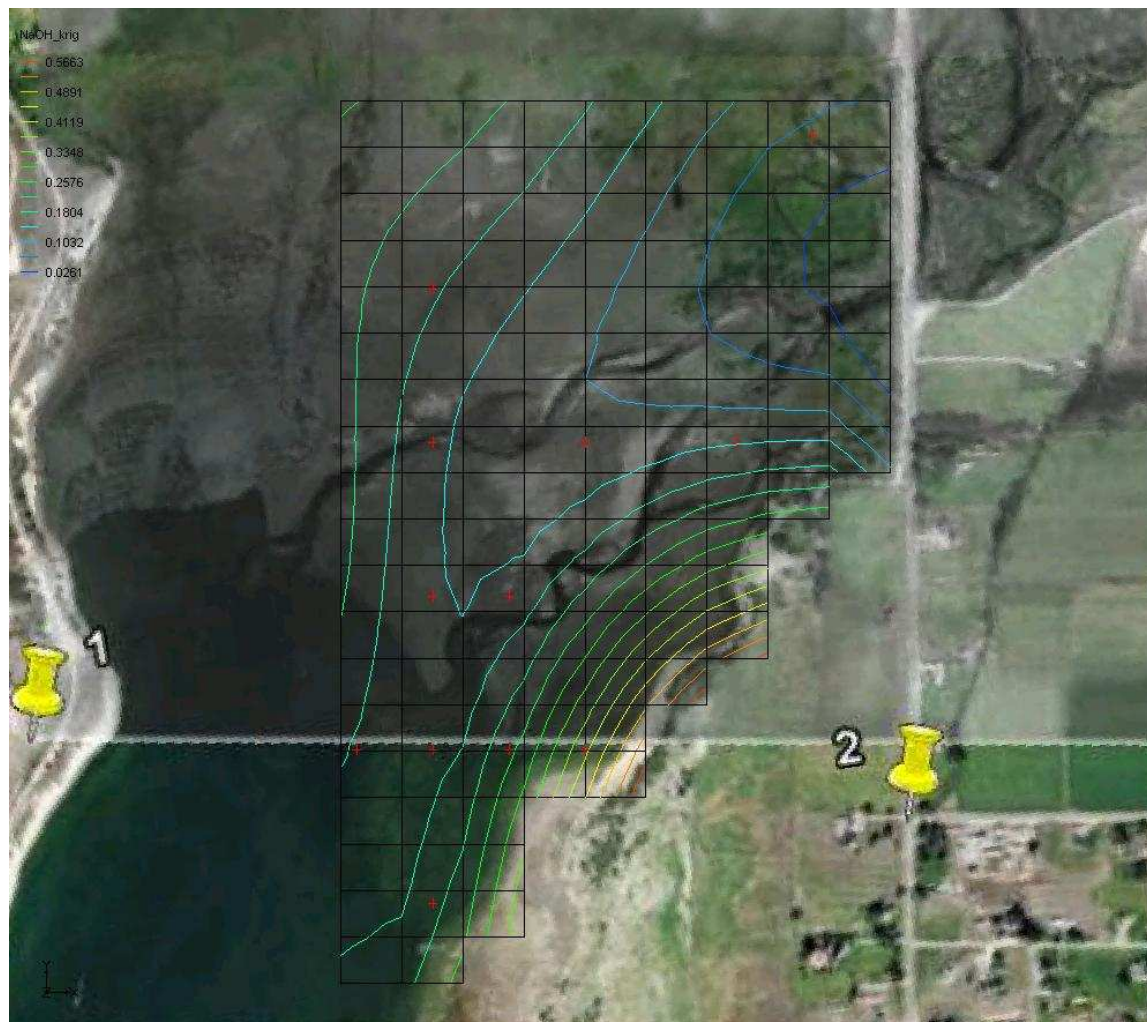


Figure D.2: Preliminary NaOH Extractable P Concentration Contours across Delta

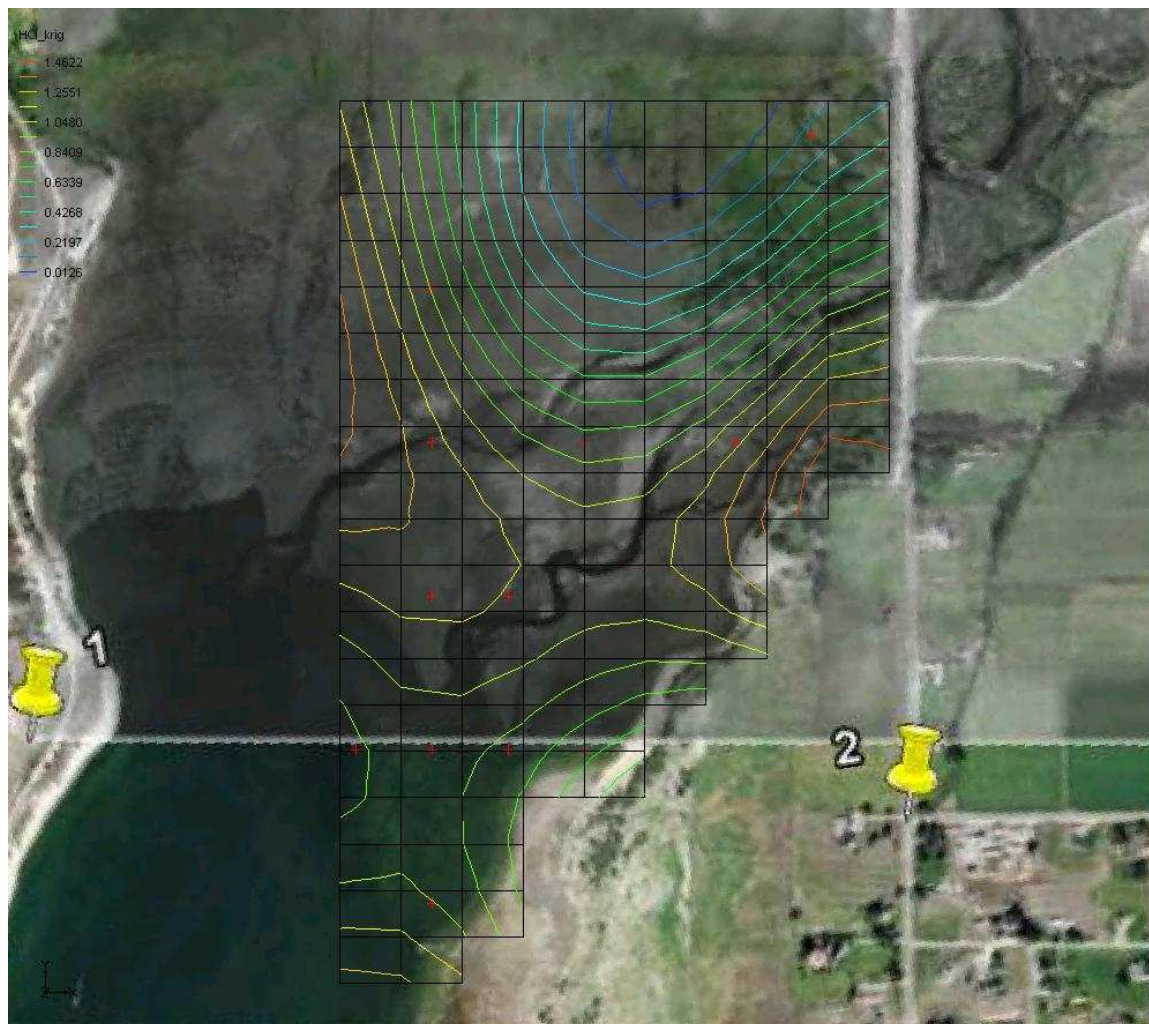


Figure D.3: Preliminary HCl Extractable P Concentration Contours across Delta

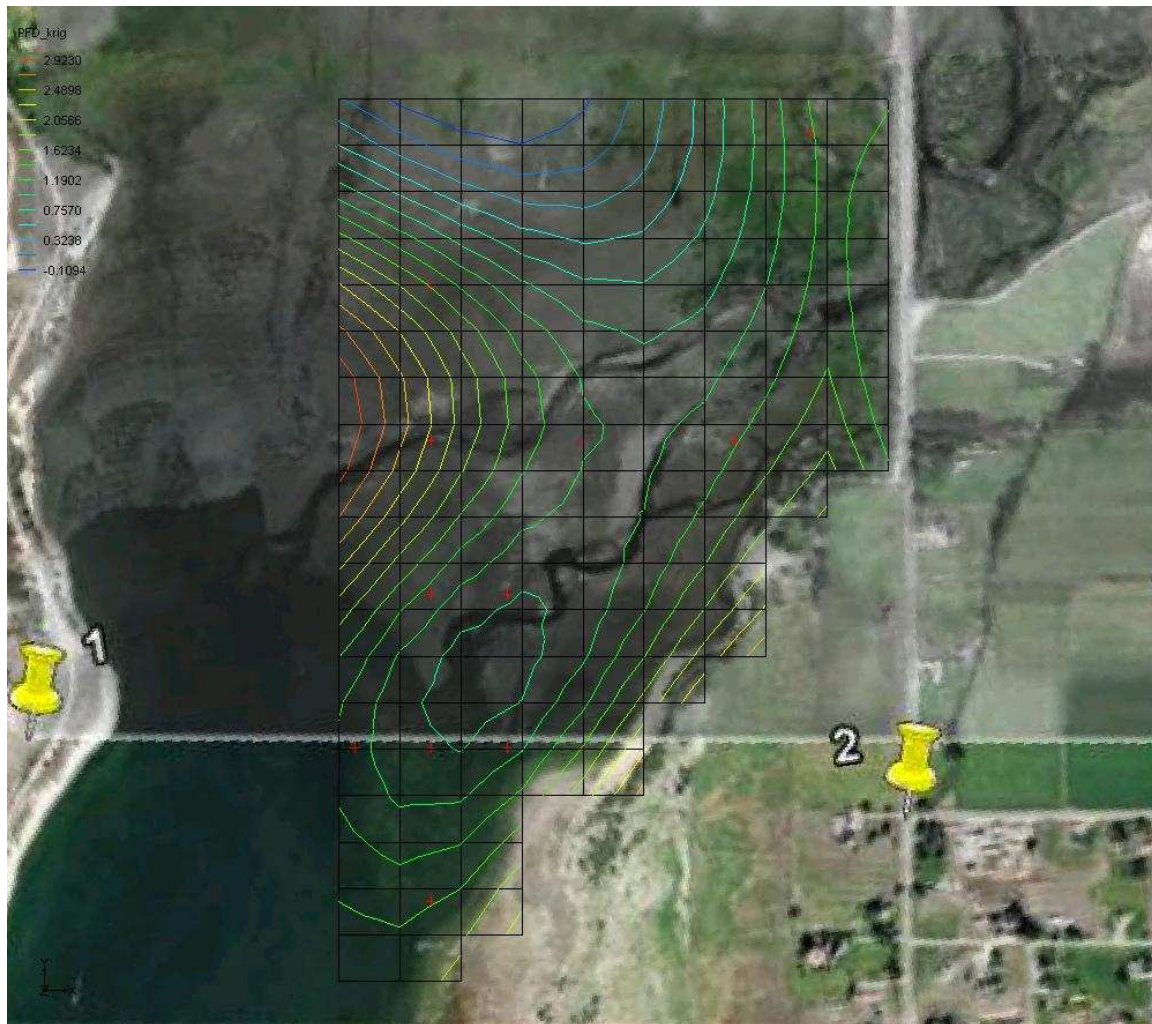


Figure D.4: Preliminary Organic (by digestion) P Concentration Contours across Delta