# **Chapter 5**

# PHOSPHORUS RELEASE DURING SEDIMENT RESUSPENSION IN THE DELTA REGION OF A LARGE, OLIGOTROPHIC RESERVOIR (LAKE POWELL, UTAH, USA) DURING DECLINING WATER LEVEL

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# Abstract

At Lake Powell, a reservoir on the Colorado River, USA, low surface elevation may affect water quality. The exposed sediment delta is resuspended by the inflowing river, and this may release phosphorus into the water column. In the upper region of the reservoir, we measured dissolved phosphorus and trace elements during base and increased flow. We also performed phosphorus sorption experiments and sequential extractions on delta sediment. At base flow, resuspension of the exposed delta sediment increases the dissolved phosphorus concentration, whereas, at increased flow, sediment resuspension attenuates it. Seasonal advective currents appear to control solute transport in the lake. Phosphate is dominantly associated with calcite and apatite in sediment, and fine sediment sorbs much more phosphate than coarse sediment. Observed phytoplankton blooms during drawdown may result from a specific hydrologic condition in which sediment resuspension during base flow releases phosphate and an overflow or interflow current transports it to the photic zone.

### 1. Introduction

Dissolved phosphorus (P) availability limits primary productivity in many freshwater ecosystems, and addition of dissolved P to a lake can cause dramatic increases in phytoplankton abundance (Schindler et al. 2008). Such phytoplankton blooms can be a serious water quality concern, as they have been associated with the presence of algal toxins (Naselli-Flores et al. 2007) and hypolimnetic anoxia (Nürnberg 1995). Oligotrophic lakes are especially sensitive to small changes in dissolved P (Müller et al. 2007), which indirectly affect fish populations (Wüest et al. 2007).

In unpolluted rivers, the vast majority of P is transported in particulate form (Meybeck 1982), so P is deposited to bottom sediments in lakes by settling. Subsequent release to the water column, a process dependent on P speciation in the solid phase, can be an important source of bioavailable P in lakes (Gächter and Müller 2003). In various environments, P has been shown to associate primarily with calcium (Ca)-bearing and apatite minerals (Blecker et al. 2006, Zhang et al. 2004), iron (Fe)-oxide minerals, or organic carbon (Jordan et al. 2008). Although the partitioning of P between the dissolved and these various solid phases is expected to reach equilibrium during transport over hundreds of km in a river, sedimentation leads to a new set of chemical conditions (e.g., due to the absence of oxygen below the sediment-water interface) that induce new chemical reactions that can change the speciation of P. Specifically, reductive dissolution of Mn- or Fe-oxide minerals or decomposition of organic matter can release P into

porewater or a labile sediment-associated phase. Once these reactions have occurred, diffusion (Ahlgren et al. 2006) or sediment resuspension (Zhang and Huang 2007, Niemistö et al. 2008) can be important sources of P to overlying water in quiescent or turbulent settings, respectively.

Sediment resuspension is common in reservoirs subject to drawdown. When water surface elevation has been maintained for several years and sediment deltas have accumulated near river inflows, a significant decrease of water level induces resuspension of erodible delta sediment by reservoir tributaries (Riggsbee et al. 2007, Cheng and Granata 2007, Snyder et al. 2006). Sediment resuspension induced by drawdown is important at Lake Powell, a large reservoir on the Colorado River in Utah and Arizona. There, decreased water levels have resulted in a doubling of suspended load of the inflowing river (Vernieu 1997) and transport of  $> 1 \text{ km}^3$  of sediment more than 100 km down the length of the reservoir (Pratson et al. 2008).

In Lake Powell, P limits primary productivity (Gloss et al. 1980), which is directly linked to fish populations (Vatland and Budy 2007). During a current drawdown, increases in surface water chlorophyll may be linked to resuspension of delta sediment (Chapter 4), suggesting that this process represents an important new source of P to the water column. Therefore, this study assesses the potential for resuspension of delta sediment to supply bioavailable P for primary productivity in Lake Powell. Phosphorus release is expected to depend on physical and mineralogical characteristics of the sediment as well as the speciation of P in the solid phase.

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# 2. Sedimentation and Phosphorus in Lake Powell

Closed in 1963, Glen Canyon Dam (GCD) impounds the Colorado River in Lake Powell on the arid Colorado Plateau. This narrow, dendritic reservoir (Figure 1) can be up to 299 km long and up to 178 m deep. This reservoir is a major recreation destination as well as a crucial water storage component of the Colorado River, which supplies water to 25 million people and 6070 km<sup>2</sup> of farmland downstream. The Colorado River Basin has experienced a severe drought since 2000 (Woodhouse et al. 2006; Clayton 2008), yet GCD has maintained minimum releases as required by law, so the reservoir has been drawn down by as much as 42 m.

Sediment in the reservoir comes primarily from erodible sedimentary rocks of the Colorado Plateau and, to a lesser extent, from the Southern Rocky Mountains, which are formed by a variety of limestones, igneous, and metamorphic formations (Spahr et al. 2000; Anderson et al. 2003). In the lower portion of the reservoir, calcite precipitates (Reynolds 1978) and contributes ~0.08% of the sediment load to the entire reservoir (Condit et al. 1978). The sedimentation rate of the reservoir has been estimated at 21-52 Mt yr<sup>-1</sup> (Ferrari 1988, Horowitz et al. 2001), implying a lifetime of 601-1488 years. Two large sediment deltas have aggraded in the inflow regions of the two main tributaries, the Colorado and San Juan Rivers, which contribute 80% and 15% of the water to the lake, respectively, yet equal amounts of sediment (Potter and Drake 1989, Ferrari 1988). Aeolian deposition contributes ~0.03% of the entire sediment load to the reservoir (Condit et al. 1978) and no information is available about how this might vary during period of sustained dry or wet weather in the Colorado Plateau.

This sedimentation is important for P transport into the reservoir, since 96-98% of P enters the lake in particulate form and is deposited in the lakebed (Horowitz et al. 2001, Gloss et al. 1981). When Lake Powell is not drawn down, annual loads of P are correlated with inflows and thus highly variable, approximately ranging from 4000-14000 t yr<sup>-1</sup> total P and 240-390 t yr<sup>-1</sup> total dissolved P (Gloss et al. 1981, Horowitz et al. 2001). The particulate P load is generally associated with clay minerals, which are deposited primarily in the lower portions of the river deltas (Gloss et al. 1980, Chapter 4). The source of this phosphorus in the basin has not been precisely determined, but it is likely to come from the limited agricultural and urban land use in the Upper Colorado River Basin (Spahr et al. 2000).

Yearly hydrologic patterns affect phosphorus mobility in Lake Powell. Seasonal overflow (approximately May-October) and underflow (approximately January-March) density currents transport dissolved P through the epilimnion and hypolimnion of the reservoir, respectively (Johnson and Merritt 1979, Potter and Drake 1989, Gloss et al. 1980). However, these currents are not equal in volume: the majority of P enters the reservoir in an overflow during spring snowmelt, which brings 60% of the yearly inflow to the reservoir during May-July (Potter and Drake 1989). Once in the epilimnion, dissolved P is expected to be transported to the sediment by settling of biomass and scavenging by calcite precipitation (Gloss et al. 1980). Lake Powell retains 74% of dissolved P that enters via all sources, with the underflow currents probably moving the rest below the photic zone and eventually through the dam (Gloss et al. 1981). Although the yearly pattern of density currents in Lake Powell varies, underflow currents are thought to transport dissolved oxygen (DO) to the sediment surface to prevent

the frequent sediment anoxia that would promote diffusion of P from lakebed sediment into the hypolimnion (Gloss et al. 1980).

Monitoring measurements showing a dissolved N:P ratio of 29:1 (i.e., far in excess of the Redfield ratio), laboratory algal assays, and *in situ* experiments have shown that P limits primary productivity in Lake Powell (Gloss 1977). More recent measurements have shown that agriculture in the valleys of the Colorado Plateau contributes notable amounts of nitrogen (N), P, and sediment to the Colorado River (Spahr et al. 2000). While we know of no subsequent studies examining the effects of agricultural development that has occurred since the earliest studies on Lake Powell, it seems reasonable that incoming Colorado River water would still be deficient in dissolved P relative to dissolved N because of sorption of P to suspended sediment.

#### 3. Experimental

#### 3.1. Hydrology

Lake level data for this study are taken from U.S. Bureau of Reclamation records (UBSR 2008), and flow on the Colorado River into Lake Powell is estimated by adding U.S. Geological Survey (USGS) stream gaging data from the Colorado River near Cisco, Utah and the Green River near Green River, Utah (USGS 2008).

#### 3.2. Sample Collection and Processing

This study focuses on water and sediment chemistry of the Colorado River delta of Lake Powell, which is assumed to be generally representative of processes in the San Juan River delta. Water samples were collected on 21-23 March and 16-18 May 2006 from various depths along a longitudinal transect in the Colorado River inflow region of Lake Powell. Locations, identified by their distance from GCD (rounded to the nearest 0.5 km), were selected between the confluence of the Green and Colorado Rivers and the uppermost extent of Lake Powell (at 317.0 km above GCD), through the delta region (245.0 km, 241.0 km, 238.5 km, and 235.5 km), and below the delta (193.5 km and 178.0 km; Figure 1). Samples were collected from surface and bottom waters with a Van Dorn bottle. When the minimum DO (measured with a multiparameter instrument) did not occur in the surface or bottom water, a sample was collected at this depth as well. Not every location was sampled in both March and May. Water clarity was estimated with a secchi disk at 1-2 locations during each research cruise.

Shoreline effects were not considered in this study because shoreline runoff contributes < 1% of the total inflows to Lake Powell and because exchange of water between side canyons, where most of the shoreline perimeter is located, and the thalweg is minimal (Hart et al. 2004). Although the initial flooding of a reservoir is known to release nutrients from newly-submerged riparian biomass (Rydin et al. 2008), the region of Lake Powell studied is desert landscape with minimal vegetation and much of the thalweg is lined with vertical canyon walls. It is likely that nutrient release during initial reservoir flooding was minimal, and any such effects would have subsided well before the current study. More recently, riparian areas of the Colorado River, including those exposed by low water levels of Lake Powell, have been colonized by tamarisk (various species of the genus *Tamarix*). However, this plant is very tolerant of flooding (Potter and Drake 1989), so we do not expect the water level changes that occurred during the short time of this study to lead to nutrient enrichment due to decaying riparian biomass. Samples were filtered through 0.2 µm polypropylene filters and stored in new, acid washed (1 M HCl), high-density polyethylene bottles. To preserve samples intended for trace element analysis, concentrated ultrapure HCl was added to a final concentration of 2%. Samples intended for P analysis were preserved with the magnesium-induced coprecipitation (MAGIC) method (Thompson-Bulldis and Karl 1998) as modified by Colman et al. (*in preparation*). Briefly, 1 mL of 2.25 M MgCl<sub>2</sub> was added to a ~100 mL water sample, followed by 1.25 mL of 1 M NaOH. This leads to precipitation of a MgOH flocculent mass that quantitatively scavenges phosphate and remains stable indefinitely. All samples were transported on ice to the laboratory, where they were stored at 5°C.

"Lakebed" sediment samples were collected concurrently with water samples at locations in (245.0, 241.0, 238.5, and 235.5 km above GCD) and below (168.0 km above GCD) the main portion of Colorado River delta of Lake Powell (Figure 1). Since these locations probably only sample the lower portion of the delta (Pratson et al. 2008), a 1.5-m series of stacked sediment cores was collected from a shoreline location near Hite Marina, 249.5 km above GCD (Figure 1). At this location, Colorado River sediment deposited when lake levels were higher was exposed above the water level and accessible from land. Distinct sediment layers of coarse (mean size > 400  $\mu$ m) and fine (mean size < 20  $\mu$ m) particles (Chapter 4) imply that this location has received sediment deposited at very different lake levels such that it coincided with the uppermost part of the delta at low lake levels and the far downstream end of the delta at high lake levels. This provides a useful contrast to the lakebed samples, which were collected from different locations at very similar lake levels.

All sediment samples were collected in plastic,  $5 \text{ cm} \times 1 \text{ m}$  core liners, transported on ice to the laboratory, and frozen  $\leq 3$  d after collection. Cores were sampled anoxically based on visual inspection, leading to "surface" (0-30 cm) samples from all lakebed cores and "deep" (25-80 cm) samples from several cores. Eight samples were collected from the shoreline cores from layers of fine particle size at depth ranges -132 to -109 cm (negative values indicate depths above the sediment-water interface), -47 to 14 cm and 14 to 20 cm and from layers of coarse particle size at -109 to -77 cm and -77 to -47 cm. For more information on the sampling and characterization of sediment used in this study, see Chapter 4.

#### 3.3. Analysis of Dissolved Chemical Constituents

Water samples preserved for trace-element analysis were diluted as necessary and analyzed with an Agilent 4500 inductively-coupled plasma mass spectrometer (ICP-MS) for Li, Ti, Cr, Mn, Zn, As, Se, Br, Cd, Pb, and U. ICP-MS data were calibrated with multi-element calibration solutions prepared from ICP-grade single element standards for each element (EMD Chemicals). Analytical relative standard deviations were < 5%.

Water samples preserved by MAGIC were centrifuged and MgOH pellets were dissolved in 0.1 M trace-metal-grade HNO<sub>3</sub> following Colman et al. (*in preparation*). Samples were concentrated by re-precipitating MgOH through a second addition of 1 M NaOH. This new precipitate was again centrifuged and dissolved in acid. Samples were treated with a reducing agent to minimize arsenate interference (Johnson 1971) and analyzed for soluble reactive phosphorus (SRP) with the molybdate-blue method (Murphy and Riley 1962) on a UV-visible spectrophotometer at a wavelength of 883 nm. This method involves treatment of a sample with a "mixed reagent" containing 24 mM ammonium paramolybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O ), 2.42 M sulfuric acid, 0.31 M ascorbic acid, and 4.2 mM potassium antimonyl tartrate in a ratio of 1:2.5:1:0.5. The sample, reducing agent, and mixed reagent were combined at a ratio of 10:1:1. All analyses took place 30-120 minutes after the addition of the mixed reagent, as recommended by previous researchers (Sjosten and Blomqvist 1997). Results were calibrated with potassium hydrogen phosphate (K<sub>2</sub>HPO<sub>4</sub>) solutions in distilled water that were carried through the MAGIC procedure along with the samples, and the detection limit was 0.030  $\mu$ M.

Since this study focuses on the release of bioavailable P from sediment, only SRP was measured; this parameter can be taken to represent a minimum value for the bioavailable dissolved P in a system. Total dissolved P was not measured because it has been known to overpredict bioavailable P in the water column (Ellison and Brett 2006).

#### 3.4. Sequential Extraction

Speciation of P in the solid phase was assessed by a sequential extraction, a sequence of reactions of sediment dispersed in successive solutions designed to target phosphorus bound in operationally-defined geochemical phases. Although limitations to sequential extractions, such as lack of specificity or sorption or precipitation of solubilized phosphorus onto the remaining mineral surface, have been noted (e.g., Peltier et al. 2006), this measurement technique provides valuable information about the geochemical phases in which phosphorus is present. The method of Ruttenberg (1992) as modified by Zhang et al. (2004) was selected because it differentiates between reactive

Fe-oxide solids and calcite (Table 1), both of which are expected to be present in Lake Powell sediment. Major steps were: 1) magnesium chloride (MgCl<sub>2</sub>), targeting exchangeable P; 2) bicarbonate plus dithionite added in solid form (BD), targeting reactive Fe(III)-bound P; 3) sodium acetate buffered to pH 3.7 with acetic acid, targeting P bound to authigenic carbonate, fluoroapatite, calcite, or biogenic apatite; 4) hydrochloric acid (HCl), targeting P bound to detrital apatite; and 5) heating at 550°C followed by hydrochloric acid (ash+HCl), targeting organic P. To minimize error due to re-sorption or re-precipitation of extracted P, steps 1-3 were followed by at least one additional treatment of each of magnesium chloride and distilled water.

Samples were not dried before the extraction, which was performed in 50 mL polypropylene centrifuge tubes shaken end-over-end. After each treatment, tubes were centrifuged and the supernatant was filtered through a 0.45  $\mu$ m filter and analyzed for SRP with the molybdate-blue method using separate sets of calibration standards that matched the respective extractant solutions. Since color development of the molybdate-blue reaction is dependent on pH (Zhang et al. 2004), before the addition of the reducing agent and the mixed reagent, it was necessary to add 1.20 mL of 1 M NaOH to 1.35 mL of sample in an HCl matrix or 0.4 mL of 178 mM HCl to 0.1 mL sample in a BD matrix. Before analysis, all BD solutions were left open to air for  $\geq$  3 d to allow excess dithionite to oxidize and leave the solution as SO<sub>2</sub> (Zhang et al. 2004). The SRP concentrations of multiple parts of each step (i.e., the chemical unique to that step and any subsequent washes with water or MgCl<sub>2</sub>) were added together to give the SRP bound in a given geochemical phase.

### 3.5. Sorption Experiments

Sorption experiments were performed without drying sediment samples in order to avoid any geochemical changes (e.g., oxidation) to the sediment matrix and to retain the original porewater in the sediment samples. Frozen sediment was thawed and portioned into polypropylene centrifuge tubes such that wet masses ranged from 0.10-0.28 g (mean = 0.16 g, standard deviation ( $\sigma$ ) = 0.04). Separate portions of the sediment samples were freeze-dried to determine water content; the wet masses used for the sorption experiments correspond to dry masses of 0.06-0.17 g (mean = 0.09 g,  $\sigma$  = 0.02 g). Although it has been shown that anoxic resuspension of sediment releases much more P than oxic resuspension (Mitchell and Baldwin 1998), no effort was made to maintain anoxic conditions once sediment samples were thawed because it was assumed that the turbulent Colorado River would be oxygenated as it resuspends sediment.

Sediment samples were resuspended in 44 mL artificial Lake Powell water (ALPW) made following Reynolds (1978). Sodium bicarbonate ( $2.00 \cdot 10^{-3}$  M), calcium sulfate ( $1.30 \cdot 10^{-3}$  M), magnesium chloride ( $7.70 \cdot 10^{-4}$  M), magnesium sulfate ( $3.00 \cdot 10^{-4}$  M), potassium bicarbonate ( $7.00 \cdot 10^{-5}$  M), and sodium trisilicate ( $3.50 \cdot 10^{-5}$  M) were combined in distilled water with vigorous stirring overnight. After all solids had dissolved, pH was adjusted to 8.05 with 1 M HCl, following Mayer and Gloss (1980). Eight subsamples of each sediment sample were shaken on an end-over-end shaker for  $\geq$ 96 h in the dark (Zhang and Huang 2007, Müller et al. 2006). After this equilibration period, a total of 1 additional mL (final volume = 45 mL) of ALPW and K<sub>2</sub>HPO<sub>4</sub> was added to give final concentrations of 0.00  $\mu$ M, 0.05  $\mu$ M, 0.10  $\mu$ M, 0.25  $\mu$ M, 0.50  $\mu$ M, 0.75  $\mu$ M, 1.00  $\mu$ M, and 1.50  $\mu$ M and shaken for 24 h in the dark. These phosphate concentrations are generally representative of Lake Powell; monitoring data indicate that total P and SRP rarely exceeds  $3.23 \mu$ M and  $0.65 \mu$ M, respectively (Vernieu, *in preparation*). Samples were centrifuged, filtered through  $0.22 \mu$ m polypropylene filters, and analyzed with the molybdate-blue method using calibration standards made with potassium phosphate in ALPW.

#### 3.6. Sorption Isotherms

In these sorption experiments, SRP was added to sediment containing some amount of labile P, and thus the concentration of SRP in the system can be written as

$$SRP_{sorbed} + SRP_{final} = SRP_{added} + SRP_{labile}$$
(1)

where  $SRP_{sorbed}$  is the concentration of SRP sorbed to the sediment,  $SRP_{final}$  is the measured concentration in solution at the end of the experiment,  $SRP_{added}$  is the concentration added to solution at the beginning of the experiment, and  $SRP_{labile}$  is the concentration of sediment-associated SRP that is labile under the experimental conditions. The difference between the added and final concentrations of SRP was used to calculate the amount sorbed (positive values) or desorbed (negative values) such that

$$\Delta SRP_{sed} = (SRP_{added} - SRP_{final}) \cdot 0.045 / m_{sed}, \qquad (2)$$

where  $\Delta$ SRP<sub>sed</sub> is the amount sorbed or desorbed (in µmol g<sup>-1</sup> of dry sediment), SRP<sub>added</sub> and SRP<sub>final</sub> are expressed in µM, 45 is the volume of solution in each experiment (in mL), and m<sub>sed</sub> is the mass of dry sediment (in g) calculated from the mass of wet sediment added. This value can be modeled from SRP<sub>final</sub> with a modified Freundlich equation (see Limousin et al. 2007 for a review of sorption modeling),

$$\Delta SRP_{sed} = F \cdot SRP_{final}^{n} - A.$$
(3)

The empirical parameters F (in L g<sup>-1</sup> dry sediment), n (dimensionless), and A (in  $\mu$ mol g<sup>-1</sup> dry sediment) were determined by using a computer program (written in the software package R 2.8.0; RDCT 2008) to find the values of each that minimized the residual sum of squares between the calculated and measured values of  $\Delta$ SRP<sub>sed</sub>. Ranges tested were 0.1-2.0, 0.1-1.0, and 0.1-1.5 for F, n, and A, respectively, and each parameter was incremented in steps of 0.1. The parameter A was introduced into the Freundlich equation to account for SRP desorbed from sediment at low SRP<sub>added</sub>. When determining parameters, one obvious outlier was removed from each of: the lakebed sample collected at 238.5 km, 40-50 cm depth; a lakebed sample collected at 235.5 km, 0-15 cm depth; a shoreline sample representing -77 to -47 cm depth; and a shoreline sample representing - 47 to 14 cm depth. The equilibrium phosphorus concentration (EPC, in  $\mu$ M), the value of SRP<sub>final</sub> when  $\Delta$ SRP<sub>sed</sub> = 0 and thus that at which no adsorption or desorption occurs, was calculated.

#### 4. Results

# 4.1. Lake Level and River Flow

During the March 2006 sampling, the surface elevation of Lake Level decreased from 1094.0 to 1093.9 m above sea level (asl) and the mean Colorado River flow was 192.6 m<sup>3</sup> s<sup>-1</sup>. In May, rapidly increasing springtime snowmelt increased the river flow from 619.4 to 716.5 m<sup>3</sup> s<sup>-1</sup> during the sampling trip, and the lake surface increased from 1096.5 to 1096.7 m asl. At the 245.0 km sampling location, there was substantial current from the inflowing river and an anchor was necessary to maintain a steady position of the sampling boat. By the 238.5 km location, the current was substantially less and no anchor was necessary, though periodic motoring was needed to offset drift.

In March, an obvious plungeline between the 241.0 km and 238.5 km sampling locations was observed, consistent with an underflow density current that occurs in winter and early spring (Johnson and Merritt 1979). Visual observations in May indicated that sediment-laden water remained on the surface of the lake many km below the inflow region, consistent with a summer overflow current (Johnson and Merritt 1979). In the delta region, the suspended sediment concentration was qualitatively substantially higher in May than in March. At the 168.0 km location, the secchi depth was estimated at 10 m in March; at the 178.0 km location, it was estimated at 1.5 m in May. In May, at the 178.0 km location, surface water appeared more green than brown, suggesting turbidity due more to phytoplankton (i.e., chlorophyll) than suspended sediment.

#### 4.2. Dissolved Trace Elements

Consistent with previous research (Hart et al. 2004), Lake Powell water is very low in trace elements (Table 2), with no elements exceeding primary or secondary drinking water standards of the U.S. Environmental Protection Agency (US EPA 2008). Concentrations of Br measured by ICP-MS are assumed to correspond to bromide, a conservative environmental tracer (Harvey et al. 2005). In March, Br concentrations in deep samples are closer to that of the inflowing river (317.0 km) than those in shallow samples, supporting the visual observation of an underflow density current entering the reservoir in March. The river inflow has much lower Br concentrations in May than in March, consistent with the spring snowmelt being more dilute in most solutes (Johnson and Merritt 1979). In May, the inflow concentration of Br resembles that in surface water at the 193.5 km location, but not at the 178.0 km location, implying that the overflow density current had reached the former location, but not the latter.

Concentrations of P, Mn, and Se increase substantially in March from the 317.0 km location to the 245.0 km location. Below this location, deeper samples are consistently higher in P, Mn, Li, U, and, with the exception of the deep sample at the 241.0 km location, Se than shallower ones. In May, P is the only element with higher concentrations at the 317.0 km location than in March. The concentration of P is lower at the 245.0 km and 238.5 km locations than at the 317.0 km, which is also different from the other elements. Concentrations of Mn, Br, Se, Li, and U all increase from the 317.0 km location to the 245.0 km location in May. Concentrations of all elements, including P, are highest in the deep water at the 193.5 km location.

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4.3. Phosphorus Speciation in Sediment Samples

Total concentrations of SRP estimated from sequential extraction of Lake Powell sediment are 55.4-99.9% (mean = 79.0%,  $\sigma$  = 12.0%) of total concentrations measured by X-ray fluorescence (Chapter 4). SRP is dominantly associated with fractions extracted by acetate (1.7-11.6 µmol P g<sup>-1</sup>; mean = 7.7 µmol P g<sup>-1</sup>,  $\sigma$  = 2.8 µmol P g<sup>-1</sup>) and by HCl (2.4-5.1 µmol P g<sup>-1</sup>; mean = 4.0 µmol P g<sup>-1</sup>,  $\sigma$  = 0.8 µmol P g<sup>-1</sup>; Figure 2, Table 3). A much smaller fraction of phosphorus was extracted by BD (0.5-2.1 µmol P g<sup>-1</sup>; mean = 1.5 µmol P g<sup>-1</sup>,  $\sigma$  = 0.6 µmol P g<sup>-1</sup>), with approximately equal, still smaller amounts extracted by MgCl<sub>2</sub> (0.1-1.0 µmol g<sup>-1</sup>; mean = 0.7 µmol P g<sup>-1</sup>,  $\sigma$  = 0.3 µmol P g<sup>-1</sup>) and ash+HCl (0.3-1.7 µmol P g<sup>-1</sup>; mean = 1.0 µmol P g<sup>-1</sup>,  $\sigma$  = 0.4 µmol P g<sup>-1</sup>). While no sequential extraction is perfectly accurate, these results can be interpreted with confidence because general trends are clear and because Ruttenberg rigorously verified the specificity and efficiency of the extraction method (Ruttenberg 1992).

The specificity of Ruttenberg's extraction is most suspect with regard to organic P; however, potential artifacts were examined by conducting the full extraction procedure on freshly collected phytoplankton and zooplankton that were freeze-dried before extraction. In these samples, she observed that 80% of P was extracted in the first step (MgCl<sub>2</sub>, targeting exchangeable P) and the remaining 20% was extracted in the fifth step (targeting organic P). It is likely that freeze-drying may have liberated P during cell lysis; this has little bearing on our study since the MgCl<sub>2</sub>-extractable P was the smallest fraction. Ruttenberg observed no extraction of P in steps 2-4, indicating that the variation in pH during these steps does not hydrolyze non-exchangeable organic P from fresh organic matter (which might also be present in surface sediment of the Lake Powell inflow region).

The rather large variability in the concentrations of SRP extracted from each geochemical phase results from the influence of particle size; coarse sediment contained significantly less (t-test, p < 0.05) SRP than fine sediment in every fraction. When coarse samples were removed from the data set, the ash+HCl-extractable fraction was the only geochemical phase with a significant difference (t-test, p < 0.05) between shoreline and lakebed samples, with higher concentrations in samples from the lakebed. Among lakebed samples, there was no significant difference (t-test, p < 0.05) between those collected in March or May 2006. Lakebed surface samples contained more acetic-acid-extractable SRP (t-test, p < 0.1) and less HCl-extractable SRP (t-test, p < 0.05) than deep samples. Fine and coarse sediment contained much more and slightly less acetate-extractable SRP than HCl-extractable SRP, respectively.

BD- and ash+HCl-extractable SRP increased slightly towards GCD in the 245.0-235.5 km lakebed samples (Figure 3). The other fractions showed no trends with distance, but, notably, the 168.0 km location contained slightly higher acetic-acid-extractable SRP than the other locations.

#### 4.4. Phosphorus Sorption

In experiments with SRP<sub>added</sub> = 0, values of  $\Delta$ SRP<sub>sed</sub> are < 0, which represents desorption of some SRP<sub>labile</sub> during resuspension in oxic conditions at 25°C. Desorbed SRP ranged from 0.03-0.14 µmol g<sup>-1</sup> dry sediment (mean = 0.07 µmol g<sup>-1</sup>;  $\sigma$  = 0.03 µmol g<sup>-1</sup>). Interestingly, shoreline samples of fine particle size were significantly (t-test, p <

0.05) higher in desorbed SRP than lakebed samples; no other pairings of sample groups are significant.

The modified Freundlich equation provided an adequate model to describe P sorption in Lake Powell sediment. Both F and n were significantly higher (t-test, p < 0.01) in fine samples than in coarse ones, indicating a much higher affinity for P in fine sediment (Figure 4, Table 4). This agrees with previous research at Lake Powell, which shows that bulk P is associated with sediments of small particle size and high clay content (Chapter 4). The isotherms from the lakebed cores overlap those of the fine shoreline sediment and show no significant trend with location (i.e., distance from the dam). Values of EPC ranged from 0.05-0.37  $\mu$ M (mean = 0.19  $\mu$ M,  $\sigma$  = 0.07  $\mu$ M) and no significant differences existed between groups of samples. These EPC values are much lower than 1.3 ± 0.6  $\mu$ M reported for Lake Powell delta sediment by Mayer and Gloss (1980), who used air-dried sediment. This is generally consistent with previous research showing that submerged lakebed sediment has a higher affinity for phosphate than air-dried sediment from the shoreline of the same lake (Baldwin 1996).

#### 5. Discussion

#### 5.1. Colorado River Inflow to Lake Powell during Drawdown

The two sampling events captured notably different hydrologic conditions. March sampling was conducted with the Colorado River at base flow, and both visual observations and Br data indicate that an underflow density current existed at this time and began between the 241.0 km and 238.5 km sampling locations. In May, sampling occurred during both an overflow current and increased flow caused by snowmelt runoff

in the Rocky Mountains. During this study, the surface elevation of the reservoir was > 31 m below its maximum; hence, the river entered the lake near the 245.0 km sampling location after passing through as much as 55 km of exposed sediment delta.

Although suspended sediment concentrations were not measured in this study, visual observations indicate that the inflow in May was substantially more turbid than that in March. This increase in suspended sediment is most probably due to a combination of increased river flow, which leads to increased suspended sediment load (Potter and Drake 1989), and flow through the exposed Colorado River delta of Lake Powell, a process observed to double the suspended sediment load during low surface elevations of this reservoir (Vernieu 1997).

Flow through the sediment delta appears to affect concentrations of solutes in the inflow region. In March, an increase in SRP from 0.065  $\mu$ M at the 317.0 km location to 0.090  $\mu$ M at the 245.0 km location suggests that resuspension of exposed delta sediment may represent a source of P to Lake Powell that did not exist when the lake was full. Other sources of P in this reach are unlikely, as the river flows through arid, sparsely vegetated land that is quite remote and subject to little direct human influence. This finding agrees with the study of a previous, less extreme drawdown at Lake Powell (Vernieu 1997).

Based on the measured SRP concentrations, a river flow of 192.6 m<sup>3</sup> s<sup>-1</sup> in March corresponds to loads of 1082 and 1498 mol SRP d<sup>-1</sup> at the 317.0 km and 245.0 km locations, respectively. Based on an average desorption of 0.07  $\mu$ mol SRP g<sup>-1</sup> of dry sediment, this 38% increase in SRP load suggests resuspension of 5.9 kt d<sup>-1</sup> of sediment. Horowitz et al. (2001) report an average yearly suspended sediment load of 16.8 ± 9.3 Mt

entering Lake Powell via the Colorado River. If we assume that 20% of the yearly sediment load enters Lake Powell with the 40% of the water that enters at base flow (August-April), then this implies a suspended sediment load of  $12.5 \pm 7$  kt d<sup>-1</sup> at base flow. The estimated amount of sediment required to be resuspended to produce the observed increase in SRP load is about half of the estimate of the suspended load at base flow.

The SRP values measured in the Lake Powell inflow region in March are near the minimum EPC values calculated from the sorption experiments, yet they are closer to values measured in the inflow region during a previous drawdown ( $< 0.1 - 0.2 \mu$ M, mean = 0.1  $\mu$ M,  $\sigma$  = 0.05  $\mu$ M; Vernieu 1997). This suggests that our laboratory experiments may not have accurately replicated sorption processes in the Colorado River. Variation of the solid:solution ratio has been observed to significantly affect sorption of P to river sediment (Müller et al. 2006) and sorption results show an significant influence of particle size, so the experiments in this study may not have matched the concentration or composition (i.e., coarse vs. fine sediment) of the suspended load entering Lake Powell. Furthermore, sorption of P to sediment has been observed to decrease as salinity increases from 0 to a range of 5-12 salinity units (Spiteri et al. 2008). The ALPW used for the sorption experiments was based on average reservoir composition and may not have matched the specific conditions in the inflow region during the sampling times. Lastly, the temperature conditions in the laboratory experiments are likely to have been higher than the ambient temperature of the river in the spring (not measured). Previous research using Mn-oxides as sorbents shows that higher temperatures lead to a relatively minor decrease in sorption of P (Mustafa et al. 2008), which suggests that our

experimental conditions may have led to lower sorption in the laboratory relative to the field. However, other studies of similar sorbates (i.e., arsenic) and sorbents (i.e., Fe-oxides) show the opposite effect (Banerjee et al. 2008), and thus we note that the response of sorption to temperature may vary between different study systems, yet is not a major influence at environmentally-relevant temperature ranges.

In May, higher river flows dilute the incoming load of most trace solutes, yet SRP increases, an observation consistent with previous results (Gloss et al. 1980). In contrast to March, SRP decreases between the 317.0 km location and the 245.0 km location, despite an apparent increase in suspended sediment between these locations. The similarity of the March (0.090  $\mu$ M) and May (0.077  $\mu$ M) SRP concentrations at the 245.0 km location suggest that these values may represent a true EPC value at this site. Since sorption results indicate that fine sediment has a significantly greater affinity for phosphate than coarse sediment, the low EPC measured at the 245.0 km site may be driven by abundant fine particles in suspension.

# 5.2. Mechanisms of Phosphorus Release and Sorption

Resuspension of sediment in Colorado River water is most similar to step 1 of the sequential extraction; loosely-sorbed, exchangeable SRP is the most likely geochemical phase to partition into the water column. The SRP desorbed from sediment without P added (mean =  $0.07 \ \mu mol \ g^{-1}$ ) is much lower than the total exchangeable SRP of fine sediment (mean =  $0.80 \ \mu mol \ g^{-1}$ ) and about half that of coarse sediment (mean =  $0.16 \ \mu mol \ g^{-1}$ ). Total exchangeable SRP accounts for only ~10% of the total extractable SRP; thus, only a small fraction of the total P appears to desorb from sediment in ALPW with

no P added. The higher affinity of fine sediment for SRP suggests that its low desorption of exchangeable SRP might be explained by resorption to other geochemical phases.

The large increase of dissolved Mn between the 317.0 km and 245.0 km locations in March may help explain the low desorption of SRP. At circumneutral pH, only  $Mn^{2+}$ , the environmentally-relevant, reduced form of Mn, is soluble, so the presence of dissolved Mn indicates low reduction potential. However, microbially-mediated reactions oxidize dissolved  $Mn^{2+}$  to solid Mn(III/IV)-oxide minerals in the presence of dissolved oxygen on a time scale of hours (Bargar et al. 2000). The observed increase in dissolved Mn probably comes from resuspension of exposed delta sediment with reducing porewater, and, upon resuspension, oxidative precipitation of Mn-oxides is likely. A similar process is likely for Fe, based on its geochemical similarity to Mn (Stumm and Morgan 1996). Newly precipitated Fe- and Mn-oxide minerals in suspension are likely to sorb SRP; thus, sediment resuspension may decrease SRP through sorption processes while also increasing it through the release of exchangeable SRP. That the apparent EPC of the Colorado River is lower than the EPC calculated in sorption experiments may suggest that sorption of exchangeable SRP to freshly precipitated Fe- and Mn-oxides is more prevalent in the Colorado River than in the laboratory experiments of this study.

Although sorption to Fe- and Mn-oxides may be an important sink for desorbed SRP upon resuspension, calcite and apatite minerals appear to be the dominant sink for P in Lake Powell. Organic compounds were found to inhibit calcite precipitation in the inflow region of Lake Powell (Reynolds 1978), so association of P with calcite is expected to be even greater in areas of the lake below those at which we collected samples, a hypothesis consistent with the highest calcite-associated SRP concentration

occurring at the 168.0 km location. Minor trends of increasing association of SRP with easily reducible or organic geochemical phases in the delta sediment may be related to weak trends in particle size in the region studied (Chapter 4).

#### 5.3. Phosphorus in Lake Powell

Downstream of the 245.0 km location, higher concentrations of SRP and Br suggest that P transport is controlled by the seasonal underflow density current in March. This implies that P is transported below the photic zone, which is shallow due to turbidity in the upper 30-60 km of the reservoir (Gloss et al. 1980) and the depth of wind-driven circulation (~20 m, Johnson and Merritt 1979). This phenomenon has been cited as a mechanism for oligotrophication at Arrow Lakes Reservoir, British Columbia, Canada (Matzinger et al. 2007). Thus, when base flow and an underflow current occur together, most SRP released from sediment resuspension may not be available to support primary productivity. If this occurs, then the additional P load may be removed by summertime calcite precipitation in the lower portion of Lake Powell, or it may be eventually exported through GCD.

In May, the incoming SRP load appears to be decreased by sorption to resuspended sediment. The upstream location with two depths measured for SRP (238.5 km) shows a higher concentration in surface water, consistent with the overflow current indicated by Br. Decreased surface water SRP at the 193.5 km location could be the results of uptake by biomass, which is consistent with qualitative observations of green-colored surface water at this location.

These observations suggest that resuspension of the exposed sediment delta should not contribute additional SRP to the surface water of Lake Powell, where it would lead to an increase in primary productivity. However, monitoring data indicate that, during drawdown, summertime chlorophyll has increased by about an order of magnitude in the surface water of the upper part of the reservoir (Chapter 4). The most likely explanation for this discrepancy is the synoptic nature of our sampling. We did not observe base flow entering the reservoir as an overflow or interflow current, which would contribute SRP added from delta sediment resuspension to the photic zone. These conditions would be expected in April, when the river has warmed enough to end the underflow current, yet the high-elevation snowpack in the headwaters of the Colorado River Basin has not increased flow substantially.

Thus, increased concentrations of chlorophyll during drawdown may result from a pulsed addition of P to surface water that results from specific hydrologic conditions in this reservoir. This mechanism differs substantially from the mechanism of increased chlorophyll concentration during reservoir drawdown in Lake Hume, New South Wales, Australia. There, the very shallow depth of the nearly-empty reservoir allowed wind-driven circulation to bring anoxic, nutrient-rich bottom water to the photic zone (Baldwin et al. 2008). In this setting, nutrients are supplied to bottom water by diffusion from sediment, a situation of apparently minor importance in Lake Powell. The mechanism for increased primary productivity during reservoir drawdown therefore depends on both the chemical speciation of nutrients in sediment and the hydrology of river inflows, which may lead to significant variability in water quality during times of low water levels in different reservoirs.

#### 6. Conclusions

- During drawdown of Lake Powell and subsequent exposure of several km of delta sediment, sediment resuspension appears to increase SRP concentration at baseflow through desorption of P yet decrease SRP concentration at increased flow through sorption of P.
- Sediment resuspension appears to involve opposing effects of desorption and resorption of P. The desorbed fraction is probably loosely-sorbed, exchangeable SRP and subsequent sorption could be to newly precipitated Mn- and Fe-oxide minerals.
- 3. The amount of SRP desorbed from sediment samples in laboratory experiments is small compared to the measured exchangeable SRP, which is about 10% of the total extractable SRP. The majority of SRP is released by extractions targeting calcite, biogenic apatite, and hydroxyapatite phases.
- 4. The EPC estimated through sorption experiments conducted at 25°C in ALPW is higher than the apparent EPC measured in the Lake Powell inflow region.
- 5. Fine sediment sorbs significantly more SRP than coarse sediment, although there is no significant difference between the two in the amount of SRP desorbed by sediment resuspension in ALPW.
- 6. Seasonal density currents transport inflowing solutes, including SRP, to bottom waters in March and surface waters in May. Increased primary productivity during drawdown may result from a specific hydrologic scenario in which baseflow enters Lake Powell as an overflow or interflow current in the late spring.

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# 5 - 32 **Tables**

#### step extractant(s) time target exchangeable or 1A $1 \text{ M MgCl}_2$ 2 h 1B $1 \text{ M MgCl}_2$ 2 h loosely-sorbed P dH<sub>2</sub>O 1C 2 h dH<sub>2</sub>O 1D 2 h 1 M NaHCO<sub>3</sub> + 8 h easily reducible or reactive 2A 1.125 g Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> Fe(III)-bound P 2B 1 M MgCl<sub>2</sub> 2 h 2C dH<sub>2</sub>O 2 h 3A 1 M NaH<sub>2</sub>C<sub>3</sub>O<sub>2</sub> buffered 6 h P bound to authigenic carbonate, fluoroapatite, calcite, to pH 3.7 with H<sub>3</sub>C<sub>3</sub>O<sub>2</sub> or biogenic apatite 3B 1 M MgCl<sub>2</sub> 2 h 3C 1 M MgCl<sub>2</sub> 2 h dH<sub>2</sub>O 3D 2 h 3E dH<sub>2</sub>O 2 h 4 1 M HCl 16 h P bound to detrial apatite 5 heating at 550°C for 2 h, 16 h organic P followed by 1 M HCl

Table 1. Sequential extraction conditions<sup>a</sup> used to determine operational speciation of sedimentary SRP

<sup>a</sup> Extractions were performed with an initial dry mass of  $\sim 0.5$  g, at a temperature of 25°C, and in solution volumes of 50 mL, except for step 2A, which was 45 mL, following Ruttenberg (1992) as modified by Zhang et al. (2004).

inflow reg	gion of L	ake Po	well					
loc	ation			e	element			
distance <sup>b</sup>	depth <sup>c</sup>	Li	Р	Mn	Zn	Br	Se	U
	March, 2006							
317.0	0.5	3.5	0.065	0.053	0.092	0.63	0.031	0.019
245.0	0.5	3.7	0.090	0.677	0.039	0.64	0.050	0.020
241.0	1.3	3.9	0.045	0.230	BDL	0.57	0.033	0.019
241.0	6.3	4.6	0.058	0.282	BDL	0.62	0.030	0.020
238.5	0.5	3.5	BDL	0.115	0.332	0.48	0.027	0.018
238.5	19	4.1	0.052	0.377	BDL	0.57	0.042	0.019
235.5	0.5	3.4	0.032	0.109	0.056	0.47	0.030	0.018
235.5	27	3.8	0.055	0.230	BDL	0.56	0.035	0.019
		May, 2006						
317.0	0.5	1.5	0.130	BDL	BDL	0.27	0.029	BDL
245.0	0.2	1.6	0.077	0.152	BDL	0.32	0.036	0.010
238.5	0.6	2.7	0.087	0.038	BDL	0.40	0.035	0.014
238.5	19.1		0.058					
193.5	1.5	1.9	BDL	BDL	BDL	0.29	BDL	0.010
193.5	19.5	2.3	0.045	0.042	0.044	0.36	0.042	0.012
193.5	54.5	3.7	0.058	0.624	0.173	0.52	0.030	0.018
178.0	6	2.3		BDL	0.032	0.77	BDL	0.010
178.0	12	1.9	0.032	0.117	0.188	0.57	BDL	0.010
178.0	66.5	3.6	0.081	0.554	0.051	0.53	0.045	0.018
statistics and elemental information								
	mean	3.1	0.064	0.257	0.112	0.50	0.035	0.016
	σ	1.0	0.026	0.219	0.101	0.14	0.007	0.004
EPA limit <sup>d</sup>				0.910	76.4		0.633	0.126
detection limit		0.29	0.030	0.036	0.031	0.025	0.025	0.008

Table 2. Dissolved inorganic elemental concentrations  $^{a}\left( \mu M\right)$  in the

<sup>a</sup> Concentrations of Ti, Cr, As, Cd, and Pb were below detection <sup>b</sup> Distance is measured in kilometers from Glen Canyon Dam.
<sup>c</sup> Depth is measured in meters below the lake surface.
<sup>a</sup> EPA limit is a primary maximum contaminant level for Se and U

and a secondary standard for Mn and Zn (US EPA 2008).

Table 3. Amount of phosphorus" extracted in sequential fractions						
location (km) <sup>b</sup>	depth (cm) <sup>c</sup>	MgCl <sub>2</sub>	BD	acetate	HC1	ash+HCl
lakebed samples						
245.0	15-30	0.83	1.53	8.20	4.58	1.29
245.0	60-75	0.77	1.39	8.08	4.86	0.95
241.0	0-5	0.95	1.87	11.25	3.35	1.26
241.0	0-12.5	0.86	1.64	9.63	3.34	1.48
241.0 <sup>d</sup>	5-15	0.51	1.09	6.66	3.92	0.82
238.5	0-15	0.83	1.87	10.15	3.20	1.12
238.5	25-40	0.73	1.91	7.90	5.14	1.17
238.5	0-12.5	0.77	1.89	9.68	3.45	0.95
238.5	40-50	0.78	1.78	9.30	4.47	1.26
238.5 <sup>d</sup>	0-5	1.03	2.13	9.88	3.89	1.35
235.5	0-15	0.88	2.01	8.57	4.19	1.35
235.5	0-15	0.87	2.01	8.21	4.45	1.63
235.5	25-40	0.81	2.04	7.63	4.19	1.68
168.0	5-15	0.83	2.11	11.56	4.43	1.12
lakebed mean		0.82	1.81	9.05	4.10	1.24
lakebed $\sigma$		0.12	0.30	1.40	0.60	0.25
shoreline samples						
249.5	-132 to -109	0.52	0.85	7.26	4.79	0.67
249.5	-132 to -109	0.53	0.88	8.77	4.69	0.58
249.5	-109 to -77	0.13	0.46	1.74	2.43	0.33
249.5	-109 to -77	0.15	0.61	2.44	3.05	0.32
249.5	-77 to -47	0.17	0.70	2.12	2.80	0.36
249.5	-77 to -47	0.19	0.47	2.66	2.86	0.26
249.5	-47 to 14	0.97	1.84	8.20	4.88	0.80
249.5	-47 to 14	0.74	1.89	7.39	4.54	1.33
249.5	14 to 20	0.93	1.71	9.91	3.60	0.69
shoreline mean		0.48	1.05	5.61	3.74	0.59
shoreline $\sigma$		0.34	0.59	3.30	0.99	0.34
<sup>a</sup> Phosphorus was measured as SRP and is expressed in µmol g <sup>-1</sup> of dry						

Table 3. Amount of phosphorus<sup>a</sup> extracted in sequential fractions

<sup>a</sup> Phosphorus was measured as SRP and is expressed in μmol g<sup>-1</sup> of dry sediment.

<sup>b</sup> Distances are upstream from Glen Canyon Dam.

<sup>c</sup> Depth is positive below the sediment-water interface; negative depths denote sediment exposed to air.

<sup>d</sup> These samples are from May 2006; all other samples are from March 2006.

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location (km) <sup>a</sup>	depth (cm) <sup>b</sup>	$\Delta SRP_{sed} \ (\mu mol \ g^{-1})$ when $SRP_{init} = 0$	F <sup>c</sup>	n <sup>c</sup>	A <sup>c</sup>	EPC (µM) <sup>d</sup>		
lakebed sampl								
245.0	15-30	0.05	0.9	0.9	0.2	0.188		
245.0	60-75	0.06	1.4	0.5	0.6	0.184		
241.0	0-5	0.05	1.0	1.0	0.2	0.200		
241.0	0-12.5	0.04	1.3	0.8	0.3	0.160		
$241.0^{e}$	5-15	0.05	0.8	07	01	0.051		
238.5	0-15	0.09	1.8	0.5	0.9	0.250		
238.5	25-40	0.03	1.8	1.0	0.2	0.111		
238.5	0-12.5	0.09	1.6	0.8	0.5	0.234		
238.5	40-50	0.07	1.9	0.4	0.8	0.115		
238.5 <sup>e</sup>	0-5	0.09	1.4	0.6	0.6	0.244		
235.5	0-15	0.07	1.7	0.4	0.9	0.204		
235.5	0-15	0.07	1.4	0.8	0.4	0.209		
235.5	25-40	0.05	1.8	0.5	0.7	0.151		
168.0	5-15	0.03	1.8	1.0	0.2	0.111		
shoreline samples								
249.5	-132 to -109	0.06	1.3	0.3	0.7	0.127		
249.5	-132 to -109	0.07	0.9	0.6	0.3	0.160		
249.5	-109 to -77	0.03	0.5	0.1	0.4	0.107		
249.5	-109 to -77	0.09	1.5	0.1	1.3	0.239		
249.5	-77 to -47	0.04	0.3	0.2	0.2	0.132		
249.5	-77 to -47	0.07	1.0	0.1	0.9	0.349		
249.5	-47 to 14	0.09	2.0	0.7	0.6	0.179		
249.5	-47 to 14	0.13	1.9	1.0	0.7	0.368		
249.5	14 to 20	0.14	2.0	0.5	0.9	0.203		

Table 4. Sorption isotherm parameters and results

<sup>a</sup> Distances are upstream from Glen Canyon Dam.

<sup>b</sup> Depth is positive below the sediment-water interface; negative depths denote sediment exposed to air.

<sup>c</sup> Freundlich isotherm parameters determined according to equation (3) (see text).

<sup>d</sup> The equilibrium phosphorus concentration.

<sup>e</sup> These samples are from May 2006; all other samples are from March 2006.





Figure 1. Sampling locations at Lake Powell. White and black circles represent shoreline and lakebed sampling sites, respectively. Dissolved and lakebed sampling sites denoted by river km from Glen Canyon Dam (GCD). The black box on the border of Arizona (AZ) and Utah (UT) denotes the approximate location of the upper panel, and the box in the upper panel denotes the location of the lower panel.





Figure 2. Results from phosphorus sequential extractions. Fractions displayed are magnesium chloride (MgCl<sub>2</sub>), bicarbonate + dithionite (BD), sodium acetate buffered to pH 3.7 with acetic acid (acetate), hydrochloric acid (HCl), and heating at 550°C followed by hydrochloric acid (ash+HCl). *Upper panel*: Lakebed sediment samples denoted by distance from Glen Canyon Dam, with depth (in cm) below the sediment water interface in parentheses. Asterisks denote samples from May 2006; all others were collected in March 2006. *Lower panel*: Shoreline sediment samples denoted by depth above (negative values) and below (positive values) the sediment water interface (in cm).





Figure 3. Phosphorus extracted by bicarbonate + dithionite ( $\diamond$ ) and heating at 550°C followed by hydrochloric acid ( $\Delta$ ) plotted against distance from Glen Canyon Dam.





Figure 4. Results from phosphorus sorption experiments on lakebed samples (*upper panel*) and shoreline samples (*lower panel*). Only lakebed samples from surface sediment collected in March are shown. For clarity, only replicates from the 241.0 km location are shown; other replicates are identical. These results generally bracket the variability of the other lakebed samples.