Chapter 2

BACKGROUND

2.1. Hydrology and Water Quality of the Colorado River

The Colorado River flows 2,317 km from its headwaters in the Southern Rocky Mountains to the Gulf of California (Figure 1). Together with its major tributary the Green River and their minor tributaries the Yampa, San Rafael, Gunnison, Dirty Devil, San Juan, Little Colorado, Virgin, and Gila Rivers, it drains ~632,000 km^2 of the American West and provides water for 24 million people and ~8,100 km^2 of farmland (Anderson 2002). The Colorado River Compact of 1922 divided the Colorado River Basin politically into Upper and Lower Basins at Lee's Ferry, a point in northern Arizona between Glen Canyon and Grand Canyon (Ingram et al. 1991). This division between the two basins has

Figure 1. The Colorado River Basin (Anderson 2002).

shaped scientific investigations into the water resources of the region.

Precipitation falls mostly as winter snow in the Upper Colorado Basin (Spahr et al. 2000), whereas the North American monsoon brings the majority of the precipitation in the Lower Basin (Webb et al. 2004). However, these contributions are quite unequal; most of the flow in the Colorado River comes from snowmelt in the Upper Basin, 60% of which lies above 2,000 m above sea level (asl) as compared to 16% of the Lower Basin (Bales et al. 2008). Precipitation is highly variable on multi-year time scales, leading to corresponding variability in Colorado River flows. Climate change is adding to this variability, leading to more precipitation as rain and earlier snowmelt (Barnett et al. 2008).

Flows past Lee's Ferry have historically been used to judge the amount of water in the river. Since the 1963 creation of Lake Powell, a reservoir just upstream from Lee's Ferry (see section 2.2), the estimated inflow to the reservoir has been used as the theoretical unregulated flow at Lee's Ferry. Thus, flow on the Colorado River as measured by the historical record at Lee's Ferry (dating to 1895) ranges from 4.7 km^3 yr^{-1} (3.8 million acre-feet (MAF) yr^{-1}) to 27.4 km^3 yr^{-1} (22.2 MAF yr^{-1}). The estimated mean is 15.3 km^3 yr^{-1} (12.4 MAF yr^{-1}), although if consumptive use in the Upper Basin were excluded, the flow would be about 18.5 km^3 yr^{-1} (15 MAF yr^{-1}; Webb et al. 2004).

While the effect of the Pacific Decadal Oscillation and the El Niño Southern Oscillation are incompletely understood, these climate patterns commonly influence precipitation and river flow across the entire Colorado River Basin (Webb et al. 2004, Kurtzman and Scanlon 2007). Extended droughts (i.e., > 10 years) are a realistic possibility (Meko and Woodhouse 2005). From 1999 to the present, the Colorado River

Basin has experienced a severe drought, with only 2 years of slightly above-average flow during this period and all other years markedly below average. Dendrochronologic reconstructions of streamflow at Lee's Ferry since 1490 indicate that this is the most severe, extended dry period since 1850, although three periods were identified during which there is a $\geq 25\%$ probability of lower flow than in the current drought (Woodhouse et al. 2006).

Estimated flow of the Colorado River at Lee's Ferry from 1895 to the present shows a decreasing trend (Webb et al. 2004) that can be attributed to several factors. First, the highest flows in the last 500 years occurred in the initial three decades of this time series (Woodhouse et al. 2006). Second, consumptive water use in the Upper Basin has steadily increased since the mid-1900s (Webb et al. 2004). Third, climate change appears to be shifting arid subtropical climatic patterns toward higher latitudes, leading to drier conditions on the Colorado Plateau (Seager et al. 2007). Together, these three phenomena may severely limit the water available for consumptive use, possibly leading to the draining of both major reservoirs on the Colorado River (Lake Powell and Lake Mead) in the coming decades (Barnett and Pierce 2008).

Water quality in the Colorado River can be impaired by high salinity, which results from evaporation, diversion of high-quality water, irrigation return flows, and dissolution of minerals from sedimentary rocks (Gloss et al. 1981). Salinity increases dramatically when the Colorado River leaves the Southern Rocky Mountains and enters the Colorado Plateau (Spahr et al. 2000), and it generally increases downstream, except when affected by flow through reservoirs (USBR 2008b). Mining in the Rocky Mountains contributes trace metals like copper, lead, zinc, and cadmium (Spahr et al. 2000), and these elements

are transported downstream in association with suspended sediment (Horowitz et al. 2001). Selenium, which can be leached out of the Mancos Shale formation of the Colorado Plateau and transported to the river by agricultural return flows, has warranted special attention (Engberg 1999, Naftz et al. 2005).

2.2. Hydrology and Water Quality of Lake Powell

Lake Powell (Figure 2) is the second-largest reservoir in the United States and the second reservoir constructed on the mainstem of the Colorado River, after Lake Mead which is further downstream. Located 24 km upriver from Lee's Ferry and 17 km downstream from the confluence of the Green and Colorado Rivers, it fills Glen Canyon and lies between Canyonlands National Park and Grand Canyon National Park. It was formed by the completion of Glen Canyon Dam (GCD) in 1963 to generate hydroelectric power and to ensure that the Upper Basin could reliably deliver water to the Lower Basin as required by the Colorado River Compact (Farmer 1999). When full, its surface elevation is 1128 m asl, its length is 299 km, and its depth is 178 m. The tortuous shape of Glen Canyon gave rise to a long, narrow reservoir with > 95 "side canyons" that extend off the original channel of the Colorado River. The reservoir is a major recreation destination, welcoming ~2 million visitors per year for camping, fishing, and a variety of water sports (Granet and Anderson 2005; Potter and Drake 1989).

Releases from GCD do not match inflows to Lake Powell on either a yearly or multi-year time scale. In order to maximize hydropower revenue, releases from GCD are highest during the summer months, when demand for electricity is greatest. In the fall and

winter, inflows are low due to precipitation falling as snowmelt. As a result, the surface

elevation of the reservoir decreases from July until March. Dam releases are substantially
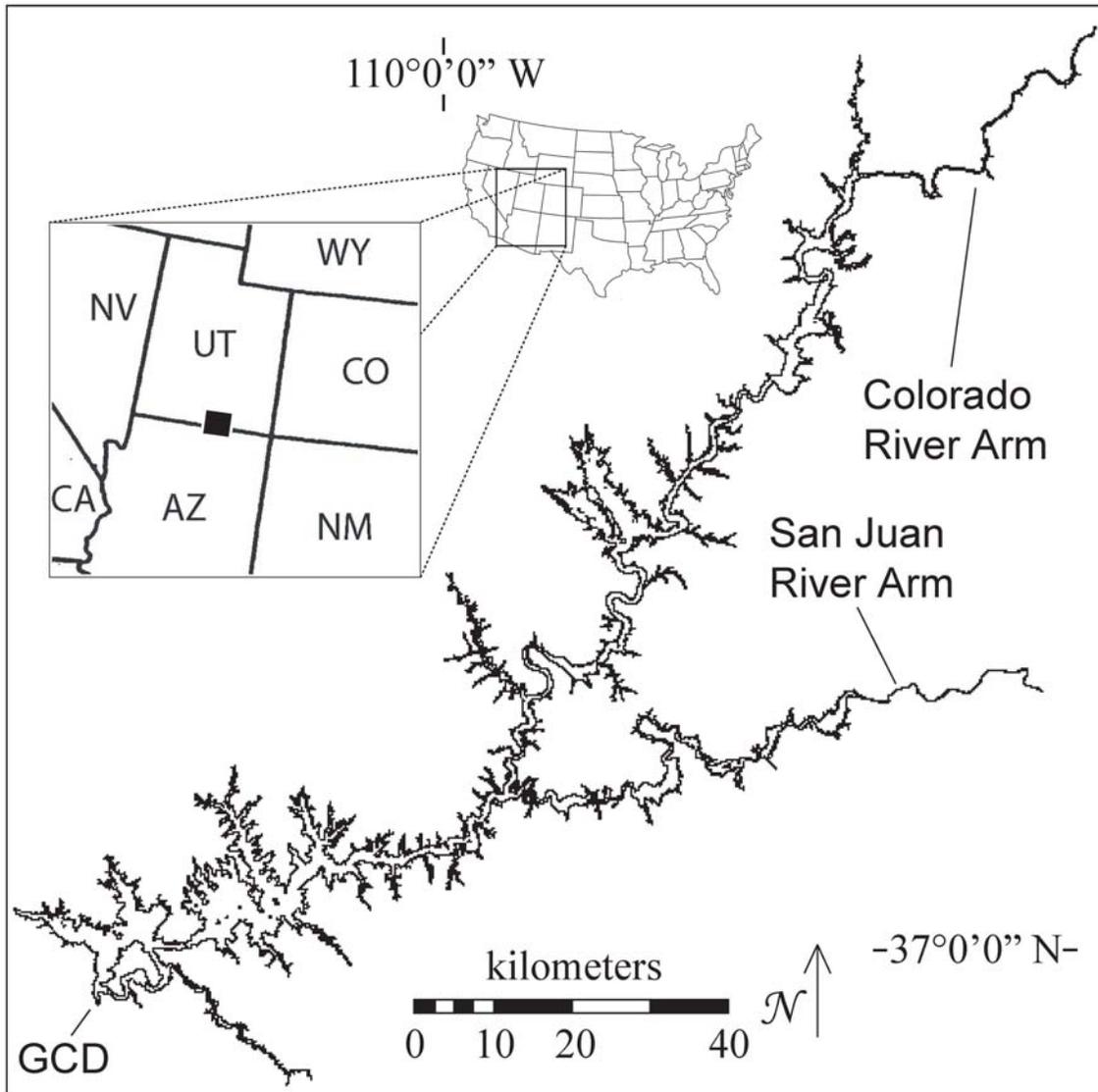

Figure 2. Lake Powell, impounded by Glen Canyon Dam (GCD) and located on the Utah-Arizona border, as denoted by the black rectangle on the inset map of the United States.

less than the spring inflows to the reservoir, which lead to a rapid increase of surface

elevation from April to June (Figure 3). Regardless of total inflows in a given year, GCD

must release 10.15 km^3 yr^{-1} (8.23 MAF yr^{-1}) to fulfill the legal obligations of the Upper

Basin states; frequently volumes in excess of this are released to balance storage between

Lake Powell and Lake Mead, which is downstream. As a result, Lake Powell experiences

multi-year periods when it is nearly full as well as extended periods of low water surface

elevation, or "drawdown" (Figure 3).

The recent drawdown has resulted in a substantial amount of sediment transport

within the reservoir. In the Colorado River inflow region, sandy sediment eroded from

the uppermost region of the delta (the topset) was deposited on the region of maximum

slope (the forset), and, in the San Juan River arm, topset and forset sediment was

transported down the reservoir to Glen Canyon Dam (Pratson et al. 2008). The water

quality implications of fluctuating water levels are explored in later chapters of this thesis.
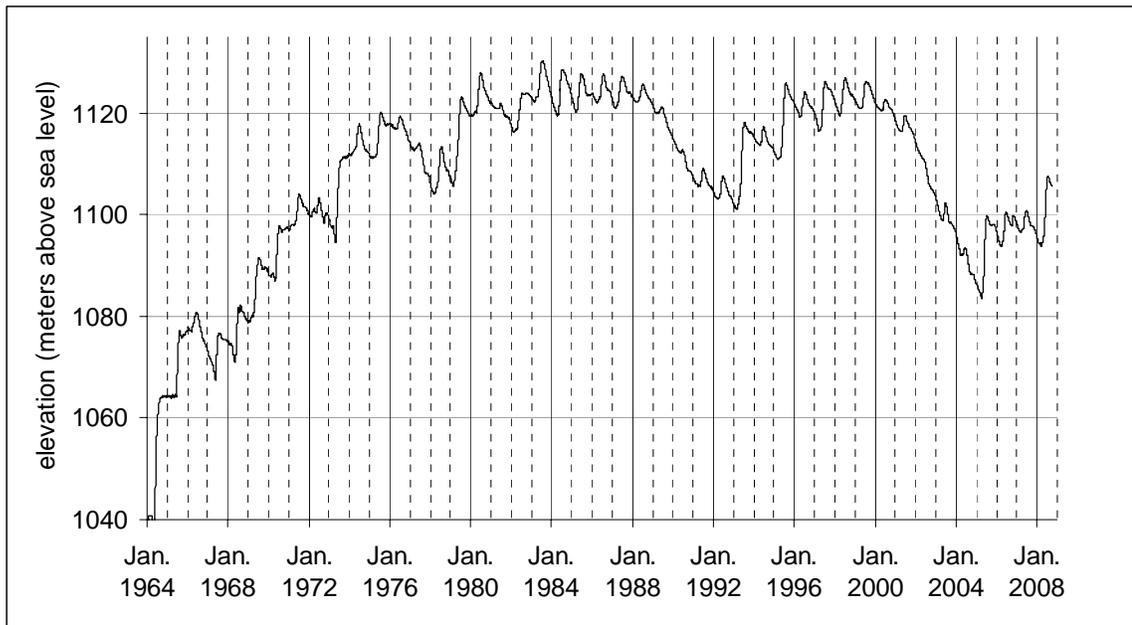
Figure 3. Surface elevation of Lake Powell (USBR 2008a).

Circulation in Lake Powell varies seasonally due to changing density of reservoir

and river water. During late winter (January-March), the inflow of the Colorado River is

cold and high in total dissolved solids (TDS), whereas the reservoir is still losing heat

from the previous summer. The denser river water enters the reservoir as an underflow

density current and either hugs the bottom for the entire length of the reservoir or

becomes an interflow current when it reaches a depth of similar density. Deep water in the path of the underflow current is pushed upward when it reaches the dam, and it then exits in the withdrawal current that passes through the dam. As a result, stagnant, deep water in Lake Powell is freshened and oxygenated not by convective mixing with surface water, but by advective transport of inflow water (Johnson and Merritt 1979, Potter and Drake 1989).

The spring snowmelt, which is warmer and more dilute than the wintertime river, and low summer inflows, which warm in response to summertime temperature increases more rapidly than the reservoir water, enter the reservoir as overflow density currents. These, coupled with intense summertime stratification characterized by a distinct thermocline ~20 m below the water surface, lead to several months of flow across the surface of the reservoir and stagnation at depth (Johnson and Merritt 1979). In the late autumn and early winter (November-December), convective circulation overturns the water column to a depth of ~60 m (Gloss et al. 1980) and the cooler river enters the reservoir as an interflow current (Johnson and Merritt 1979).

Nearly all water enters GCD through a combination of eight penstocks, located at 1058 m asl (70 m below the water surface when the reservoir is full), and exits through hydroelectric turbines (Hueftle and Stevens 2001). This depth is usually below the depth of summertime convective mixing, and, during fall overturn, the withdrawal current prevents overturn near the dam below a depth of 1020 m asl (Johnson and Merritt 1979). Epilimnetic and hypolimnetic water can be discharged through the spillway intakes (1114 m asl) and river outlet works (1029 m asl), respectively. While rarely used, releases from

the spillway and river outlet works can accelerate overflow and underflow circulation

patterns (Hueftle and Stevens 2001).

Water in Lake Powell is generally very low in trace metals and anthropogenic

organic chemicals (Hart et al. 2004). Concentration gradients may exist between the head

and the mouth of a side canyon, although the basis for these has not been rigorously

investigated. Gradients persist because side canyons are generally quiescent (Hart et al.

2004). Precipitation of calcite is an important summertime process that is more likely to

occur in the lower region of the reservoir due to inhibition by organic compounds that are

present in the inflow region (Reynolds 1978). In the inflow region of Lake Powell,

sorption reactions between water and sediment limit the range of dissolved phosphorus (P)

concentrations, yet silica varies in a range outside that predicted by laboratory sorption

experiments (Mayer and Gloss 1980). The circulation patterns described above are very

important for the dynamics of P, the limiting nutrient in the reservoir. When P enters in

an underflow current, it bypasses the photic zone and does not contribute to primary

productivity, but when it enters as an overflow current, it contributes to summer

phytoplankton blooms (Gloss et al. 1980). Sediment resuspension during drawdown can

double suspended sediment concentrations and may release additional nutrients into the

water column (Vernieu 1997).

Storing water in Lake Powell affects water quality downstream. Precipitation of

calcite offsets the increase of TDS that occurs due to evaporation such that there is no net

change in TDS concentration (Gloss et al. 1981). An important additional consequence of

storage in Lake Powell is the moderation of annual variability in TDS (USBR 2008b),

which facilitates management of salinity downstream. Furthermore, Lake Powell retains

> 90% of total P, > 70% of dissolved P, > 20% of total nitrogen, and > 10% of total silica that enters from all sources (Gloss et al. 1981). Releases from Glen Canyon Dam, which draws water from the middle of the water column, are clear and cold, and this significant difference from historical conditions has damaged sensitive ecological habitat immediately downstream in Grand Canyon. Additionally, reservoir processes that are not completely understood can lead to seasonal plumes of anoxic water within Lake Powell (Vernieu et al. 2005), and, under certain hydrologic conditions, these can pass through the dam and impair water quality in the Colorado River (Williams 2007).

2.3.   Early Diagenesis and its Implications for Inorganic Contaminants

Early diagenesis, the quantitative description of chemical changes during sediment deposition before lithification occurs, is characterized by chemical reactions that are generally a result of microbial metabolism of organic matter. During aerobic respiration, organic matter acts as an electron donor and is oxidized to carbon dioxide. Oxygen is the most thermodynamically favorable electron acceptor for this process. In most sediment, deposition of organic matter is such that diffusion of oxygen from surface water into porewater is insufficient to support microbial respiration. In this case, the concentration of dissolved oxygen in sediment porewater decreases with depth below the sediment-water interface, and, where it approaches zero, microbial respiration uses other electron acceptors in a sequence determined by their reduction potential. Reduction of nitrate (NO_3^-) to N_2 is the most favorable anaerobic process and an important means of reducing NO_3^- contamination in groundwater (e.g., Domagalski et al. 2008). When NO_3^- is depleted, manganese (Mn), iron (Fe), and sulfate (SO_4^{2-}) are reduced (Berner 1980,

Stumm and Morgan 1996, Froelich et al. 1979). Importantly, a single microbial species does not carry out each reaction. Rather, different species dominate the microbial population as the geochemical conditions change with depth. Furthermore, environmental conditions may change the relative availability or energetic yield of different electron acceptors, and thus the sequence of reduction described here may not always be clearly observed due to overlap of electron acceptor utilization (McGuire et al. 2002).

Redox reactions can control partitioning between the solid and the dissolved phase. The environmentally-important reduced species Mn(II) and Fe(II) can occur in solution as Mn^{2+} and Fe^{2+} ions, whereas their oxidized forms, Mn(III/IV) and Fe(III), generally occur in solids with very low solubilities (Morel and Hering 1993). Thus, the absence of oxygen and NO_3^- in sediment porewater leads to the reductive dissolution of Mn and Fe (Froelich et al. 1979, Kneebone et al. 2002). These elements can be removed from porewater by oxygenation, which leads to the precipitation of Mn(III/IV)-oxide and Fe(III)-oxide minerals, or by precipitation of reduced carbonate (e.g., siderite ($FeCO_3$) or rhodocrocite ($MnCo_3$)), sulfide (e.g., pyrite (FeS) or albandite (MnS)), or phosphate (e.g., vivianite ($Fe_3(PO_4)_2$)) solids. Sulfide (S^{2-}) produced during sulfate reduction can lead to precipitation of pyrite, which is more likely than that of albandite, since S^{2-} and Fe^{2+} react preferentially (Canfield 1989, Báez-Cazull et al. 2007) and undersaturation of albandite is generally observed in sulfidic porewater (Naylor et al. 2006). Isomorphic substitution of Mn^{2+} during vivianite ($Fe_3(PO_4)_2$) precipitation can reduce dissolved Mn^{2+} concomitantly with PO_4^{3-} (Taylor and Boult 2007).

Trace elements and P commonly sorb to the surfaces of Fe- and Mn-oxide minerals (Belzile et al. 2000, Dixit and Hering 2003, Lee et al. 2002, Tonkin et al. 2004, Gächter

and Müller 2003). Thus, reductive dissolution of these minerals can also release trace

elements into sediment porewater (Kneebone et al. 2002, Campbell et al. 2008).

Furthermore, some trace elements, such as arsenic and uranium, are redox active and will

thus respond to the redox state of sediment porewater determined by the major redox

species of a system (Campbell et al. 2006, Finneran et al. 2002).

2.4. Reservoir Sedimentation and Transport of Sediment-Bound Elements

Globally, sedimentation in reservoirs traps 20% of sediment transported by rivers;

Lake Powell, which traps > 99% of the sediment that enters it, far exceeds global

averages for its continent, ocean basin, climate, and elevation (Syvitski et al. 2005, Potter

and Drake 1989). The ability of flowing water to entrain and transport particles depends

principally on fluid density, fluid viscosity, and flow velocity. The first two of these

remain approximately constant when a river is impounded; a decrease in flow velocity

decreases particle transport (Prothero and Schwab 2004). As sediment particles in a river

enter a reservoir, they will settle according to Stokes's law, which implies that, as the

river flow slows, coarse particles will settle before fine ones. Specifically,

$$v_p = \frac{\Delta\rho}{\rho} \cdot \frac{g}{18v} \cdot D_p^{\,2}$$

where v_p is the sinking velocity (in m s^{-1}), $\Delta\rho$ is the density difference between particles

and water (in kg m^{-3}), ρ is the density of water ($\approx$ 1000 kg m^3), g is the gravitational

acceleration (= 9.81 m s^{-2}), v is the viscosity of water ($\approx$ 1-1.5 · 10^{-6} m^2 s^{-1}), and D_p is the

particle diameter (in m) (Friedl and Wüest 2002). As the energy of a river decreases upon

reaching the flat surface of a lake, its turbulent upwelling will decrease in velocity and

will fail to counteract the higher sinking velocity of large particles. The slowing river will

carry fine particles further into the reservoir and deposit them as it continues to slow.

Thus, sediment deltas are usually deposited in gradients of particle size, with coarse

particles closest to the river and fine particles deepest into a lake (Prothero and Schwab

2004). In a narrow lake, such as a reservoir that has filled a narrow valley, the shape of

the sediment delta can lead to a clear gradient in sediment particle size. Sedimentation in

the inflow region of a reservoir is derived from allochthonous sources, whereas, in the

part of a reservoir that resembles a lake, sedimentation is autochthonous as in natural

lakes (Friedl and Wüest 2002). Only deposition of river sediment will be reviewed briefly

here.

Gradients of particle size in sediment deltas have been observed in several

reservoirs most clearly when sediment deltas do not reach the dam (e.g., Riggsbee et al.

2007, Cheng and Granata 2007). Large deltas will be strongly influenced over time by

changes in reservoir level, with decreases in water level allowing the river to mobilize

coarse sediment from the upper region of the delta further into the reservoir, and

subsequent increases in water level depositing fine sediment on top of coarse sediment

(Snyder et al. 2006). Thus, vertical variations in sediment particle size will be closely tied

to the management history of a reservoir.

Trace elements are generally enriched in particles < 0.125 mm in size. Small

particles are high in both organic carbon and clay minerals, so it is not clear which of

these phases contributes most to trace element sorption (Horowitz and Elrick 1987).

Reservoirs have been observed to retain both inorganic contaminants, especially when

downstream from mines (Castelle et al. 2007, Lee et al. 2008), and nutrients (Teodoru

and Wehrli 2005) in their sediment. While the concentration of chemicals in reservoir

sediment is a means of purifying downstream river water, this sedimentation is an important sink for organic carbon (Downing et al. 2008). Both the rapid sedimentation of organic matter and the submergence of riparian biomass lead to greenhouse gas emissions (i.e., nitrous oxide and methane) from reservoirs that are much higher than those from lakes or undammed rivers (Guérin et al. 2008, 2006, Kemenes et al. 2007).

2.5. Phosphorus in Lakes

The bioavailability of P has long been understood to limit primary productivity in freshwater ecosystems, an assertion most recently stated by Schindler et al. (2008). The amount of P in the water column of a lake is dependent on input from land, rivers, and sediment diagenesis, loss to sedimentation and outflow, and consumption by primary productivity (Müller et al. 2007). The quantity of dissolved P in a lake has generally been thought to depend on lake depth and flushing rate, but recent research suggests that P input and water residence time may be more important (Brett and Benjamin 2008).

In unpolluted rivers, the vast majority of P is transported in particulate form (Meybeck 1982, Horowitz et al. 2001), and, once in a lake, several processes can move the remaining dissolved P into the solid phase as well. Phosphorus sorbs abiotically to Fe-oxide minerals, aluminum-oxide minerals, and carbon (Arias et al. 2006, Novak et al. 2006). Sorption characteristics change with salinity; increasing the salinity of freshwater to a range of 5-12 salinity units induces P desorption (Spiteri et al. 2008). Apatite precipitation or scavenging during calcite precipitation may be important in some lakes (Kleiner and Stabel 1989). Most importantly, uptake by biomass decreases dissolved P concentrations. If this biomass dies and degrades in surface water, then P re-enters the

dissolved pool. However, settling of dead biomass to sediment retains it in the solid phase for a much longer time (Kalff 2002).

To contribute to primary productivity, P must be in the photic zone of a lake. Bioavailable P that reaches the photic zone is generally taken up by biomass growth rapidly, and thus concentrations of P are often higher in bottom water than in surface waters. P can reach bottom waters by transport by underflow density currents (Gloss et al. 1980), diffusion from sediment porewater (Gächter and Müller 2003), or decay of sinking particulate organic matter (Kalff 2002). In this case, convective overturn of the water column is an important step that leads to primary productivity in surface waters, and the depth of overturn determines the extent to which hypolimnetic P reaches surface water (e.g., Baldwin et al. 2008, Kalff 2002). The importance of overturn events is magnified in reservoirs that release water from the middle or bottom of the water column, since advective circulation allows hypolimnetic P to exit the reservoir without entering the photic zone when overturn does not bring it to surface waters (Matzinger et al. 2007).

Once in sediment, chemical processes enrich P concentrations in porewater so that it diffuses back into bottom waters. Dissolution of Fe-oxides is generally cited as the main mechanism for this process. When water near the sediment-water interface is anoxic, Fe reduction can occur in surface sediment, liberating both Fe^{2+} and P to the dissolved phase. If these reach an oxic region of the water column, Fe will precipitate and scavenge P. However, if S^{2-} is present, it can sequester Fe^{2+} as FeS and allow P to accumulate in the water column (Baldwin and Mitchell 2000, Berner and Rao 1994, Jordan et al. 2008). Internal loading of a water body in this manner can maintain high dissolved P concentrations even if external loading is decreased (Ahlgren et al. 2006). Microbial

decomposition of organic matter in sediment can also contribute P to sediment porewater, where it will either sorb to particles or diffuse into overlying water. Sediment-associated calcite may be less likely to release P to the water column, but the implications of this have not been adequately determined.

2.6. Water Resources and Water Use in the Lower Merced River Basin, California

The Central Valley of California is a large, northwest-trending structural trough filled with alluvial and marine sediment, the southern half of which is the San Joaquin Valley (Figure 4). The valley floor is a productive agricultural region that receives water primarily from rivers that flow southwest from the Sierra Nevada range (Gronberg and Kratzer 2007). About 80% of the annual precipitation to the Valley falls between November and March, yet only 40-50% of the streamflow occurs at this time, as the remainder of precipitation is stored in the snowpack and reservoirs (Dubrovsky et al. 1998). This water is delivered to row crops and orchards throughout the
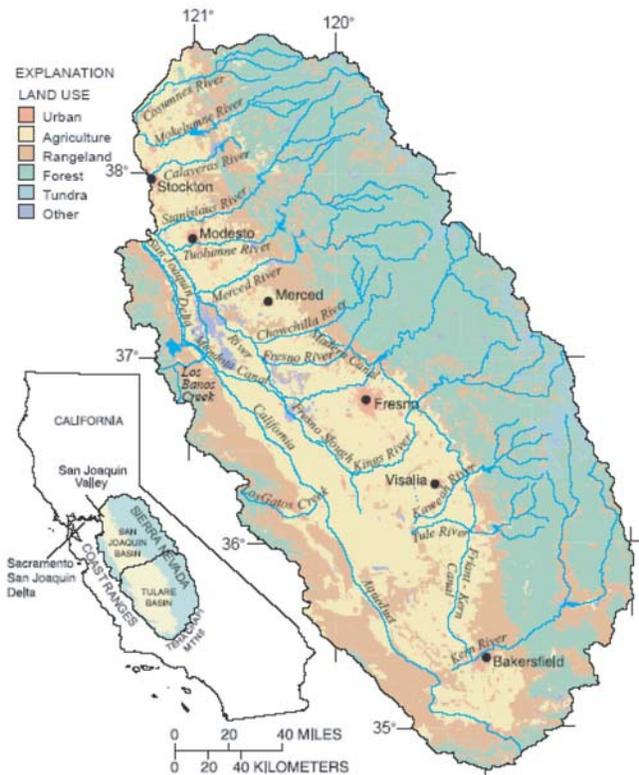
Figure 4. The San Joaquin Valley, from Dubrovsky et al. (1998).

summer growing season by an extensive network of irrigation canals (Gronberg and

Kratzer 2007).

The Lower Merced River (Figure 5), a major tributary of the San Joaquin River, has

been a focus of the United States Geological Survey Agricultural Chemicals Transport

Study, which is part of the ongoing National Water Quality Assessment program. The

semi-arid climate of the San Joaquin Valley leads to a mean annual precipitation of 31

cm with mean temperatures of 25°C and 8°C in July and January, respectively. The

annual average flow of the Merced River at its confluence with the San Joaquin River is

19.4 m^3 s^{-1} (Capel et al. 2008). This is modified both by releases from the McSwain Dam,
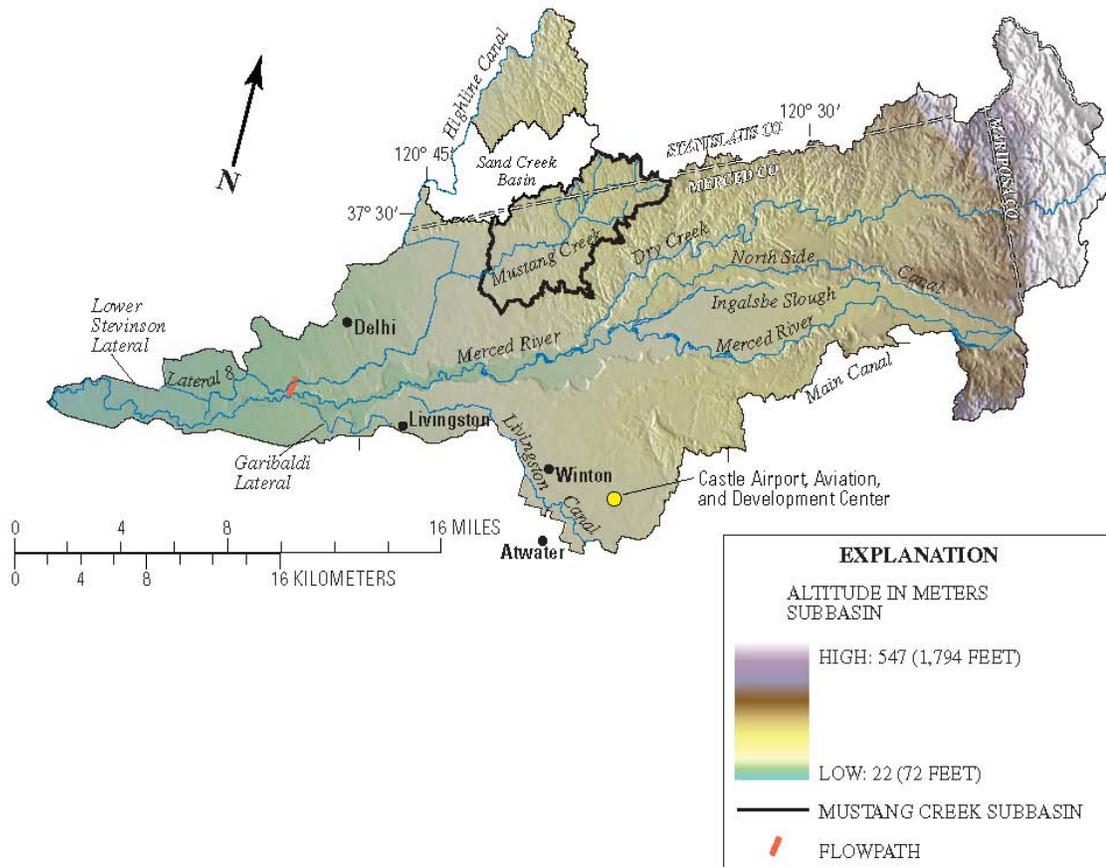

Figure 5. The Lower Merced River Basin, from Gronberg and Kratzer (2007). Water flow is from east to west. The location of the field site described in Chapter 6 is approximately where the Merced River intersects the flowpath labeled on the map.

which is just upstream of the boundary that defines the Lower Merced River basin, and

five major irrigation and drainage canals that discharge to the river (Gronberg and

Kratzer 2007). In this reach, the river is underlain by an unconfined aquifer that is

bounded beneath by the Corcoran Clay formation, which is 28-85 m below ground

surface (Capel et al. 2008).

More than half (55%) of the Lower Merced River Basin is used for agriculture,

mostly almond orchards, with some corn and grain fields and vineyards (Capel et al.

2008). Irrigation seasonally raises the water table, inducing a gradual flow to the Merced

River (Phillips et al. 2007). As a result, in the reach studied in Chapter 6, the Merced

River usually gains water from the local aquifers, except when high river stage pushes

water into the subsurface (Essaid et al. 2008). Groundwater-surface water exchange is

minor, however, due to small differences in hydraulic head across the sediment-water

interface, which may be due to the location of the study reach just downstream from a

transition from a losing stream to a gaining stream, to negligible surface water slope, and

to a wide channel for groundwater discharge (Essaid et al. 2008, Puckett et al. 2008).

Furthermore, the residence time of groundwater in the streambed between the sediment-

water interface and a depth of 3 m is on the order of 2 months (Puckett et al. 2008).

In addition to irrigation water, 1 million kg of pesticides, 7.3 million kg of nitrogen,

and 1.3 million kg of phosphorus were applied to crops in 2003 in the Lower Merced

River Basin (Capel et al. 2008). Pesticides generally degrade in soil and aquifer material,

with atrazine and metolachlor occurring in lower concentrations in groundwater than

their degradates (Steele et al. 2008). Denitrification removes most fertilizer-derived

nitrate as groundwater flows through the riparian zones into the river subsurface, most

likely due to substantially more reducing conditions in the riverbed subsurface than in the

nearby aquifer (Domagalski et al. 2008, Puckett et al. 2008).

2.7. Subsurface Hydrologic and Biogeochemical Processes in Rivers and Streams

Exchange between stream water and groundwater can affect surface water

chemistry due to reactions in the river subsurface. The region of the riverbed groundwater

that is hydrologically linked to surface water such that exchange occurs on short length

and time scales is known as the hyporheic zone (Figure 6, Findlay 1995). Particle size is a

particularly important parameter determining the amount of infiltration to the hyporheic

zone; contact time with riverbed sediment can limit chemical reactions in sandy

streambeds, whereas cobble streambeds provide a lesser physical barrier (Jackman and
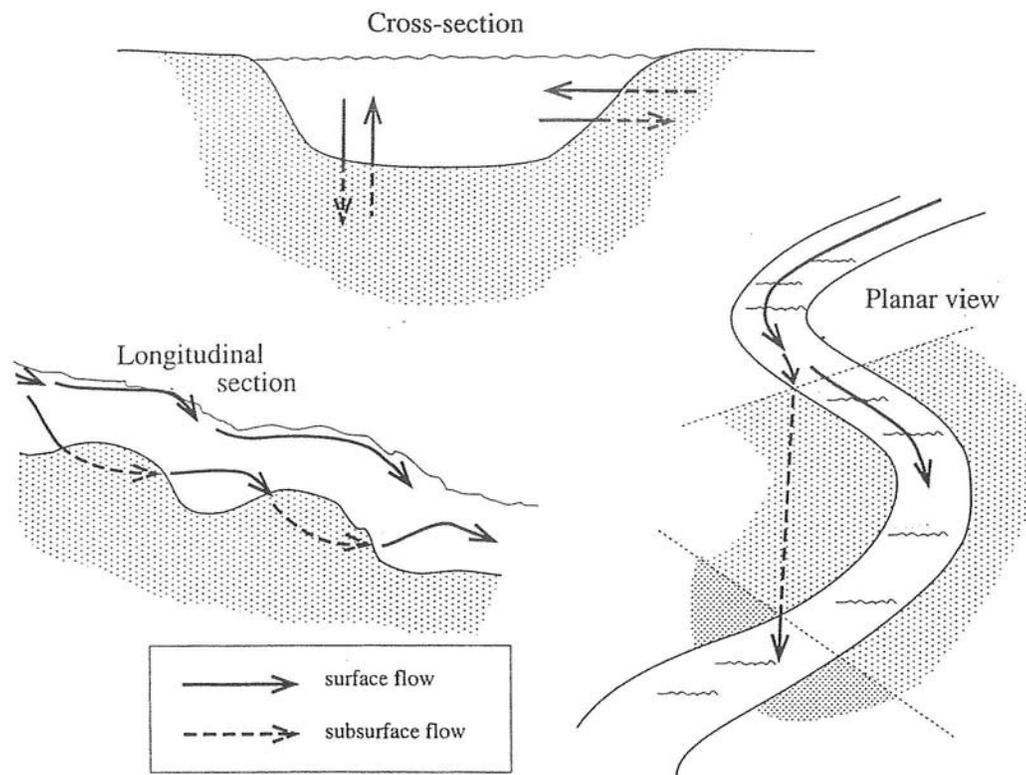

Figure 6. Schematic representations of hyporheic zone flowpaths (Findlay 1995).

Ng 1986). A coarse "armor" layer on top of finer sediment has been observed to have no effect on the advection of water into the river subsurface (Marion et al. 2008), yet streamflow does, with more surface-subsurface exchange occurring at lower streamflow than at higher streamflow (Harvey et al. 1996). The extent of infiltration is a master variable that controls the residence time of water in a river reach, which, in turn, is often the best explanation for observed differences in biogeochemical activity (Findlay 1995, Valett et al. 1996).

Interaction of solutes within the hyporheic zone depends on both the contact time of river water with the riverbed matrix and the type of solute. The mechanism of retention is generally believed to be chemical, often ion exchange or sorption, as injection experiments demonstrate that the downstream advection of inorganic solutes (Kennedy et al. 1984) or nutrients (Valett et al. 1996, Haggard et al. 2005) is retarded relative to a conservative tracer. Due to infiltration by stream water, the hyporheic zone is generally oxic, although pockets of reducing zones can exist where sediment is less permeable (Salehin et al. 2004). Thus, organic matter degradation is common, and this acts as a source of nutrients to surface water (Findlay 1995). Contact with sediment surfaces can also promote redox reactions: loads of dissolved Mn in a contaminated stream have been observed to decrease due to subsurface oxidation (Harvey and Fuller 1998).

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