EVIDENCE FOR COMPARTMENTALIZATION OF AQUIFER SYSTEMS: SOLUTE AND ISOTOPE GEOCHEMISTRY OF GROUNDWATERS IN THE MIDDLE SAN PEDRO BASIN, ARIZONA

By

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ABSTRACT

The Middle San Pedro Basin in southeastern Arizona is a typical alluvial basin in the semi-arid southwestern United States with a rapidly growing population that is dependent upon groundwater resources for water supply. This study investigated recharge areas, compartmentalization and potential mixing of water sources, and travel times of groundwater throughout the basin using variations in major ion chemistry (water type, Ca/Sr ratios, SO_4/Cl ratios) and isotope ratios (^{18}O, ^{2}H, ^{3}H, ^{34}S, ^{13}C, ^{14}C) of groundwaters, surface waters and precipitation in conjunction with hydrogeologic data (e.g. hydraulic head and hydrostratigraphy). Recent recharge (<50 years) has occurred within mountain systems along the basin margins, and in shallow floodplain aquifers adjacent to the San Pedro River. Groundwaters in confined aquifers in the central basin were recharged at high elevation in the fractured bedrock and have been extensively modified by water-rock reactions over long timescales (up to 34,600 years). These results can be used to constrain physical assumptions of future groundwater flow models designed to help make improved water management decisions.

1. INTRODUCTION

1.1 Motivation

Groundwater stored in the pore spaces of alluvial basin-fill sediments is an important source of water for domestic and agricultural uses in the southwestern United States (Anderson et al., 1992). In most arid to semi-arid regions in the southwest, groundwater is the sole source of water for growing populations due to limited surface water supplies. A better understanding of groundwater resources and water quality is needed to make more informed water policy decisions.

This study focuses on the Middle San Pedro Basin in southeastern Arizona (Figure 1), where populations solely dependent on groundwater supplies for irrigation and domestic uses are expected to rapidly increase over the next twenty years (Arizona Daily Star, 2005). Relatively little is known about the extent of finite water resources in this basin and how population increases will affect water resource supplies. In order to plan for sufficient water supplies for growing populations, ground water models could be improved with a better understanding of where groundwater is recharged throughout the basin, what the major groundwater flowpaths are, and how long groundwater resides in the subsurface. In addition, it is important to understand the quality of groundwater resources, as toxic elements, such as arsenic and fluoride, are common in concentrations above the EPA maximum contaminant levels in southwestern alluvial basins (Robertson, 1991). Groundwater helps to sustain base flow to some surface waters in the semi-arid southwestern US (e.g. Webb and Leake, 2006; Simpson, 2007; Zlatos, 2008); for example, shallow groundwater in the Upper San Pedro Basin has been shown to be a

major contributor to base flow of the San Pedro River (Simpson, 2007), one of the last

free flowing rivers in the southwestern US (The Nature Conservancy website,

www.nature.org, 2009). The extent of interaction between groundwater with surface

water along the middle reach of the San Pedro River is still unknown.

Extensive studies of groundwater hydrology and water quality have been

conducted in the adjacent Upper San Pedro and Tucson Basins (Freethey, 1982;

Cunningham et al., 1998; Pool and Coes, 1999; Eastoe et al. 2004; Baillie, 2005; Coes

and Pool, 2005; Wahi, 2005; Baillie, 2007; Simpson, 2007, Wahi, 2008). Although

similarities in hydrogeochemical processes likely can be drawn between the Upper San

Pedro, Tucson, and Middle San Pedro Basins, significant differences may exist due to the

presence of a thick regionally-extensive clay confining unit that is unique to the Middle

San Pedro Basin. The presence of the St. David Formation confining unit may limit

groundwater migration along the axis of the Middle San Pedro Basin, increase

groundwater residence times, and potentially alter groundwater quality. This study aims

to fill in this knowledge gap by coupling solute isotopes, age tracers, and solute chemistry

to determine how a confining clay unit affects groundwater flow paths, residence times,

and recharge to the basin.

The specific objectives of this study are to evaluate groundwater recharge areas,

flowpaths, compartmentalization and/or mixing of waters, and travel times in the Middle

San Pedro Basin using solute chemistry and isotope tracers of groundwaters, surface

waters and precipitation coupled to hydrogeologic data (e.g. hydraulic head, subsurface

structure, and hydrostratigraphy). In addition, geochemical data will be used to interpret

and analyze an existing groundwater model developed for this region based on physical hydraulic parameters. Geochemical modeling and geologic interpretation will demonstrate the importance of integrating knowledge of local geology and geochemical analysis when developing groundwater flow models.

Analytical and geochemical modeling results from this study are combined with particle tracking estimations of groundwater age in the Middle San Pedro Basin to address the following research questions:

(1) What is the location and seasonality of recharge to groundwater systems?

(2) What are the dominant flowpaths in the basin, how do waters evolve along these flowpaths, and what are the travel times of groundwaters?

(3) Are there any geochemical and/or isotopic differences between aquifer systems? Is there any evidence of compartmentalization or mixing of waters?

(4) How can these geochemical and isotopic results be used to better constrain groundwater modeling efforts?

2. BACKGROUND

2.1 Study Area

The San Pedro Basin is located within the Basin and Range Province in southeastern Arizona and is structurally and hydrologically typical of other basins in the region (Robertson, 1989). The San Pedro River flows for 220 km through the basin north from north-central Sonora, Mexico through southeast Arizona to its confluence with the Gila River. The Nature Conservancy declared the San Pedro River as one of America's top ten last great places due to its natural beauty and diversity of wildlife (The Nature Conservancy website, www.nature.org, 2009). The San Pedro River drains an area of 12,270 km^2 and includes the cities of Sierra Vista and Benson and other small towns. This study is focused on the Middle San Pedro Basin (Figure 1), between the Tombstone Gage and the Redington Gage (Figure 2), encompassing the towns of St. David, Cascabel, and Pomerene as well as the city of Benson.

Additional background information on the study area is included in Appendix A.

2.2 Climate

There are two distinct precipitation seasons in the San Pedro Basin: winter rains are generated from various regions in the Pacific Ocean and are of low intensity and long duration; summer rains are of high intensity and short duration (Anderson et al., 1992). Wright et al. (2001) utilized stable isotope ratios in precipitation and sea surface

temperatures to identify an area to the southwest of Baja California as a likely source of monsoonal moisture for the southwest.

Precipitation in the San Pedro Basin typically ranges from 20 to 65 cm per year and temperatures range from about 40°C in the summer to -5°C in the winter. However, recent climate change simulations project that mean temperature in the Colorado River Basin could increase between 1.2 to 4.4 °C by the year 2100, and precipitation could decrease by approximately 2% (Christensen and Lettenmaier, 2007), which could significantly alter recharge rates and evapotranspiration in southwestern US basins, such as the Middle San Pedro Basin.

3. PREVIOUS WORK

3.1 Geologic History

3.1.1 Basin and Range Faulting

The San Pedro Basin formed during Basin and Range faulting in the Tertiary (10-15 Ma) (Menges and Pearthree, 1989). The Basin and Range Province is categorized by steeply dipping normal faults that separate basins from surrounding mountain blocks. Beginning 15 million years ago, northeast-southwest extensional deformation occurred, forming local fault-block uplifts and clastic-filled basins in southeastern Arizona (Menges and Pearthree, 1989). Since this faulting occurred, the basin has been filled in with sediment of varying depths from surrounding mountain blocks.

3.1.2 Internal/External Drainage

Evaporite mineral assemblages suggest that the San Pedro Basin was an internal drainage basin, similar to the nearby Willcox Basin, for some depositional intervals (Towne and Stephenson, 2002). The San Pedro Basin transitioned from an internal drainage basin to an external drainage basin around 3.4 Ma with conditions that were correlated with less seasonal variability and potentially wetter conditions (Smith, 1994). This suggests that increased runoff changed the drainage pattern in the San Pedro Valley (Smith, 1994). Paleosol records indicate a warming trend between 2.5 Ma and 1.7 Ma and a decrease in winter rainfall and an increase in summer rainfall. Vertical textural

changes in clastic basin fill sediments can be explained as the result of climate change and a change in precipitation in semiarid areas or arid areas (Smith, 1994). Paleosols also indicate higher seasonal precipitation and a climate that was able to support shift from grasslands to a different plant regime dominated by woody plants (C3 plants) (Smith, 1994). These clay-rich paleosols are all slightly calcareous (Smith, 1994). Laminated gypsum beds intercalated with gypsiferous mudstones crop out in a few small areas throughout the basin (Smith, 1994). These beds originated in playa-like conditions during periods of internal drainage and are located along the axis of the basin.

3.2 Hydrostratigraphy

The Middle San Pedro Basin is bounded by the Dragoon Mountains (Jurassic and Tertiary granite), the Galiuro Mountains (Tertiary volcanics), and the Winchester Mountains (Cretaceous Jurassic sedimentary rocks and volcanics) to the east, and the Rincon Mountains (Tertiary and Proterozoic granite and gneiss) and the Whetstone Mountains (Paleozoic limestone and Precambrian granite) to the west (Huckleberry, 1996) (Figure 3). The majority of drainage from these mountains is focused into the San Pedro Basin (Huckleberry, 1996). Preliminary gravity studies (Gettings and Houser, 2000) indicate the depth to bedrock along the axis of the basin varies from 0 m below ground level near the Narrows to over 2500 m below ground level near Whetstone, Arizona (Meader, 1987).

Alluvial basin-fill in the Middle San Pedro Basin consists of up to 400 m of clastic sediments, evaporites, and stream alluvium (Robertson 1991, 1992). This alluvial

fill is comprises the Lower Basin Fill, Upper Basin Fill, confining unit and alluvial aquifer (Figure 4). The Lower Basin Fill was deposited under internal drainage conditions and contains more consolidated and fine grained sediments than the unit above it (Robertson, 1992). The younger (shallower) portions of the Lower Basin Fill consist of clay and silt with lenses of sand and gravel; these sediments are less consolidated and contain fewer volcanic rocks than the older (deeper) portion of the Lower Basin Fill (Robertson, 1991). The Upper Basin Fill is less deformed, tilted, and faulted than the Lower Basin Fill; it is also generally coarser grained and less cemented than the Lower Basin Fill due to accumulation during periods of through-flowing drainage conditions (Robertson, 1991).

The Middle San Pedro Basin confining unit (shown in dark grey in Figure 4), the St. David Formation, is composed of silts and clays with fine grained sediments, such as sand, fresh-water limestones, and paleosols (Gray, 1967). Based on analysis of geologists' and drillers' logs, the sediments that compose the St. David Formation are up to 300 meters thick and contain minor amounts of pyrite, hematite, magnetite, montmorillinite, and chert (Gray, 1967). Plio-Pleistocene sediments within the St. David Formation accumulated after cessation of significant basin-scale subsidence (Smith, 1994). Drainage patterns, paleosol records, and pond deposits suggest wetter conditions and seasonally variable precipitation during the Plio-Pleistocene that increased depositional rates (Smith, 1994). The areal extent of this clay confining unit is the source of on-going investigations.

3.3 Geochemistry

Multiple studies have been conducted on groundwater quality throughout the Upper and Middle San Pedro Basins due to increasing populations and interest in the San Pedro River riparian area. Robertson (1989) utilized solute and isotope chemistry of groundwaters throughout the basin to distinguish different water groups. In the aquifer beneath the confining unit (confined aquifer), he found low calcium and magnesium concentrations and high fluoride concentrations, likely due to dissolution of fluorite and calcite precipitation (Robertson, 1989; 1992). In contrast, groundwater in the mountain system had higher calcium, magnesium, and bicarbonate concentrations and lower fluoride values (Robertson, 1992). Floodplain aquifer waters were found to have variable water chemistries with elevated chloride, sulfate, and fluoride in select sites potentially from upward leakage of waters through gypsiferous deposits (Robertson, 1991). Pool and Coes (1999) reported that groundwaters in the alluvium (unconfined aquifer) originated from various sources, but in general had high specific conductance and higher δD and $\delta^{18}O$ values than groundwaters in the regional aquifer system.

Arsenic and fluoride are of water quality concern in many southwestern alluvial basins (Robertson, 1991). Robertson (1989) found that, in the San Pedro Basin, the highest concentrations of arsenic occurred in fine grained sediments, derived from weathering of igneous rocks, under confined conditions. High arsenic groundwaters were commonly enriched in fluoride and had high pH values (>8.5). Robertson (1989) determined that the arsenate ion (-3 charge) was the most likely contributor of arsenic to groundwater and adsorption of arsenate may have been affected by the iron content of the

basin fill, pH of the ground-water, and competition for adsorption sites by other negatively charged ions. Datta et al. (1996) suggested that common sources of fluoride to groundwater were natural mineral dissolution from igneous and sedimentary rocks, and phosphate fertilizers. One important aspect of this study will be to determine if fluoride is a useful indicator of groundwater residence times and/or compartmentalization of waters in the basin by comparing concentrations of fluoride of different aquifer systems.

Previous studies in the Upper San Pedro also used solute ratios to differentiate water sources. Sulfate to chloride ratios coupled with oxygen and hydrogen isotopes enabled Baillie (2005) and Wahi (2005) to calculate recharge rates in the Upper San Pedro Basin and to differentiate between alluvial aquifer waters that were derived from basin groundwater versus monsoon flood water. By using solute ratios and isotopic information, Wahi (2005) estimated that 70% of recharge through the mountain system occurred in the winter. Baillie (2005) determined that the San Pedro River had both losing and gaining reaches by following solute ratio trends along a stretch of the riparian corridor. This study will utilize SO_4 to Cl ratios to distinguish waters from various aquifers in the Middle San Pedro Basin and determine if there is significant mixing between the confined and unconfined aquifers.

Previous studies in the adjacent Tucson Basin and the Rio Grande Basin in New Mexico also provide valuable insight into hydrogeologic processes in the Middle San Pedro Basin. Eastoe et al. (2004) measured oxygen and hydrogen isotope values of Tucson Basin groundwaters and were able to infer the elevation of recharge (derived from precipitation) to the basin aquifer system. They determined that mountain front

recharge of winter precipitation was a large contributor to basin groundwater, similar to what was found in the Upper San Pedro Basin and other basins in the desert Southwest. Eastoe et al. (1994) published a map of tritium in groundwater that showed post-bomb recharge along certain washes in the Tucson Basin. Cunningham et al. (1998) found there was a modern component of recharge in the Santa Catalina Mountains along the ephemeral washes, as distinguished by tritium values above background levels (0.6 tritium units). Older groundwaters (up to ~10,000 ka) were found in the central basin along long flowpaths from high elevation mountain recharge. Stable isotopes were also useful in the Rio Grande Basin in New Mexico, which has similar climatic conditions, topography, and basin stratigraphy to those of the Tucson and San Pedro Basins. Plummer et al. (2004) showed that the δ^2H and δ^{18}O values of groundwater coupled with piezometric data in the Rio Grande Basin could be used to delineate flow directions and distinguish various hydrochemical zones. Many studies have been conducted on carbon isotopes of the San Pedro Basin that can provide insight into geologic processes in the basin; detailed regional carbon isotope information can be found in Appendix B.

4. HYDROLOGY

4.1 Regional Recharge Studies

Recharge in the Upper San Pedro Basin occurs along the riparian corridor and along ephemeral washes. Floodwater from storm events has been shown to recharge the riparian aquifer through bank infiltration in the Upper San Pedro Basin (Baillie et al., 2007). Infiltration rates throughout the Upper San Pedro Basin were determined to range from 0.2 to 6 cm/year depending on location (Coes and Pool, 2005). Some washes were found to have higher infiltration rates than surrounding basin-floor sites (Coes and Pool, 2005). Infiltration through ephemeral stream channels in the Sierra Vista subwatershed indicated rapid infiltration to at least depths of 20 m; infiltration was found to occur up to 25.6 m downstream of the mountain front. During storm runoff events, infiltration rates ranged 0.4 to 2.8 m/hour. This infiltration to basin-fill aquifer systems is highly dependent upon the thickness and hydraulic properties of stream alluvium, permeability of sediments, streambed morphology and availability of stream flow (Coes and Pool, 2005).

Mountain system recharge consists of recharge occurring at both the mountain block and mountain front. Mountain system recharge is considered to be one of the primary sources of recharge to the heavily studied Upper San Pedro Basin (Wahi et al., 2008). Mountain system recharge estimates on the western side of the Upper San Pedro Basin were between $2x10^6$ m^3/year and $9x10^6$ m^3/year determined by groundwater fluxes by Wahi (2001). Although similar studies have not been conducted in the Middle San

Pedro Basin to date, results from the Upper San Pedro Basin may provide insight into hydrologic processes and properties that may be applied to the adjacent basin.

4.2 San Pedro Basin Hydrology

The aquifer system in the San Pedro Basin is comprised by confined and unconfined groundwater in unconsolidated and semi-consolidated basin fill, unconsolidated alluvium near the San Pedro River, and consolidated sedimentary and granitic rocks along the basin margins. Previous conceptual models of the basin groundwater system reported higher groundwater elevations along the basin margins near mountain fronts, and lower groundwater levels along the San Pedro River and towards the north. Groundwater generally flows from the basin margins to areas of lower elevation near the San Pedro River and down-gradient areas to the north, with assumed increasing residence time with flowpath distance (Usunoff, 1984; Fig 2). Groundwater flow in the confined aquifer occurs in two primary directions: from southeast to northwest, following the approximate pathway of the San Pedro River, and from the mountain ranges on the east and west of the basin towards the center of the valley, comprising a local component of recharge (Usunoff, 1984).

The Nature Conservancy walks portions of the San Pedro River annually on the summer solstice (June 21) in order to assess wet and dry portions of the river during the driest portion of the year. These wet and dry areas assessed on June 21, 2008 are overlain on Figure 2 and indicate gaining areas of the river (wet portions) and losing areas of the river (dry portions) (The Nature Conservancy, map, 2008). This information

is helpful in determining where groundwater contributes to surface water in the San Pedro River.

4.3 Groundwater Model

Multiple numerical models have been constructed to simulate groundwater flow in the San Pedro Basin. Goode and Maddock (2000) developed a physically-based groundwater model of the entire San Pedro Basin, using MODFLOW (McDonald and Harbaugh, 1988) software, including the Middle San Pedro Basin. The model assumed predevelopment hydrologic conditions for 1940, prior to major groundwater withdrawals in the basin; the model was then used to simulate pumping stresses on the groundwater system from 1940 to 1997. The authors based their model hydrostratigraphy (shown in Figure 5) on hydrogeologic units found in the southern portion of the study area (Upper San Pedro Basin). A cross section (Figure 5) was constructed for the purpose of this project based on the top elevation of model layers along the same transect as geologic cross sections.

Layer 1 consists of steep hydraulic gradients and hydraulic properties of the regional aquifer system; Layer 2 includes the Upper Basin Fill and the floodplain aquifer with variable hydraulic conductivities; Layer 3 corresponds to the Lower Basin Fill and has hydraulic properties similar to the regional aquifer; and Layer 4 represents consolidated sediments. No hydrogeologic units were included to represent the St. David Formation confining unit (Figure 5), which is prominent in the Middle San Pedro Basin and may have a significant effect on basin groundwater flow in this region.

Goode and Maddock (2000)'s model simulations show a reduction of stream flow in the San Pedro River due to increased groundwater pumping from 1940 to 1997, a reduction of evapotranspiration by riparian vegetation along the floodplain, and the formation of significant cones of depression near many communities and associated large losses of groundwater storage. This model is adequate for simulating regional flow and the regional hydrologic regime. However, the model may not be best representative of the Middle San Pedro Basin due to the presence (and exclusion in the model) of the St. David Formation, confining unit. This geochemical study will help to provide additional information to improve future modeling efforts in the Middle San Pedro Basin.

5. METHODS

5.1 Sample Collection

A total of 101 samples were collected from September 2007 to February 2009 in the Middle San Pedro Basin between the USGS Tombstone gage and the USGS Redington gage (Figure 6; Table 1). Seventy-eight groundwater samples were collected from municipal supply wells, private domestic wells, and springs (where possible). Groundwater wells for sampling were primarily targeted along two transects: 1) one west to east transect across the basin (Figures 3 and 4) and 2) one north to south transect along the San Pedro River (Figures 3 and 4). Well depths ranged from 18 to 408 meters below ground level.

Sixteen surface water samples were collected from stretches of the ephemeral San Pedro River from eight different sites when water was flowing at various times of the year. During periods that surface water was not present, groundwater was collected from shallow (<25 m depth) USGS piezometers adjacent to the river, following USGS methods (Claassen, 1982).

Seven precipitation samples were collected during summer and winter precipitation events. Screened five gallon buckets were set in areas with no human interference and open access to precipitation. A layer of mineral oil was placed in the buckets to ensure that any precipitation collected would not evaporate. Buckets were protected with a screen covering over top to prevent human or animal interference with sample collection. Precipitation buckets were left out for the duration of the storm season and water was sampled at the end of seasonal rainfall events. The elevation of bucket

locations ranged from the San Pedro Basin floor (1109 m) to varied steps along the surrounding mountain ranges (1665, 1688, and 2583 m) to account for influences of elevation on the isotopic composition of precipitation.

5.2 Field Methods

Water samples were collected by following the USGS NAQWA protocol, as listed in the USGS National Field Manual (Claassen, 1982) unless otherwise noted. This included collecting groundwater samples from the well head or nearest access point and running it through tygon tubing into the USGS NAQWA mobile laboratory for field parameter and sample collection. Sample site coordinates and altitudes were determined in the field using the Differential Global Positioning System and were measured at the well head (Table 1). Depth and geologic information was obtained from driller's well logs listed in the state well database maintained by the Arizona Department of Water Resources. Wells were purged of three casing volumes before sampling unless they were in continuous use. Orion meters were calibrated in the field using appropriate conductivity and pH standards, and dissolved oxygen was calibrated in relation to atmospheric pressure. Collected groundwater samples were measured for temperature, pH, specific conductivity, and the dissolved oxygen meter in the field in a flow-through chamber. Surface water samples were collected within reach of the riverbank and field parameters were measured directly in the stream flow. Precipitation samples were collected from buckets and filtered; no field parameters were measured and no solute chemistry analyses were performed on these samples.

Filtered sample aliquots were collected at each site for anions, cations, trace metals, alkalinity, dissolved inorganic carbon (DIC) and stable carbon isotopes. Each sample was placed in a pre-rinsed filter housing and hand-pumped through a 45μm nylon filter. Dissolved inorganic carbon (DIC) and carbon stable isotope samples were collected in sample-rinsed 30 mL glass bottles and capped with no head space to prevent interaction with air. Anion and alkalinity samples were collected in sample-rinsed 60 mL HDPE bottles. Cation and trace metal samples were collected in acid rinsed 60 mL HDPE bottles and were acidified to a pH of 4 using nitric acid.

Unfiltered samples were collected for tritium, sulfur isotopes, water stable isotopes, and carbon-14. Both tritium and sulfur isotope samples were collected in sample-rinsed 1 L HDPE bottles. Oxygen and deuterium isotopes were collected in 60 mL glass bottles with rounded caps with no head space. Carbon-14 was collected one of two ways: either in two 500 mL amber glass bottles sealed with electrical tape or in one 50 L HDPE carboy. In both cases, special care was taken to minimize headspace. All samples were stored in coolers with ice in the field and at 4°C in the refrigerator in the laboratory with the exception of the carbon-14 carboys. Quality control samples (blanks and known standards) were collected in the field for solute chemistry to test for field contamination.

5.3 Laboratory Methods

Alkalinity was measured the same day as sample collection in the USGS Tucson Water Science Center laboratory using the Gran-Alk titration method as described in

Gieskes and Rogers (1973) (precision $\pm0.6\%$). Carbonate alkalinity is assumed to be equal to titration alkalinity, as all groundwaters, surface waters, and spring waters lacked appreciable organic acid anions and hydrogen sulfide. Solute concentration analyses and isotope analyses were performed at the University of Arizona in the department of Hydrology and Water Resources and Geosciences departments, respectively. Quality control samples collected in the field for anions and isotopes were also tested in the University of Arizona laboratories. Duplicate cation and anion samples were analyzed by the USGS National Water Quality Laboratory in Lakewood, CO. Blank samples resulted in negligible amounts of solutes. Samples tested for quality assurance and quality control met all protocols set by the USGS.

Anion (F, Cl, Br, NO_3, and SO_4) analyses were performed on a Dionex Ion Chromatograph (IC) model ICS-3000 using an AS23 analytical column (precision $<\pm2\%$). Internal standard checks were inserted into the sample sequence after every fifth sample for quality control. Major cation and trace metals (Ca, K, Na, Mg, Si, Sr, Zn) were analyzed using a Perkin-Elmer Optima 5300 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; precision $<\pm4\%$). The charge balance for all water samples was within 5%. Dissolved inorganic carbon (DIC = H_2CO_3 + HCO_3^- + CO_3^{2-}) concentrations were measured using an UIC 5014 carbon coulometer (precision $\pm2\%$).

Oxygen and hydrogen stable isotope analyses were performed using a Finnigan Delta S gas-source Isotope Ratio Mass Spectrometer (IRMS). Hydrogen isotope analysis was performed by reduction of Cr metal at 750°C (Gehre et al., 1996). Oxygen isotope analysis was performed by CO_2 equilibration at 15°C (Craig, 1957). Isotope values are

reported in per mil (‰) notation and were standardized relative to international standards VSMOW and SLAP (for δ^2H and $\delta^{18}O$). The analytical precisions (1-sigma) were 0.9‰ or better for δ^2H and 0.08‰ or better for $\delta^{18}O$ as determined by repeated internal standards. Carbon stable isotope analysis was performed on CO_2 samples generated by converting dissolved inorganic carbon to CO_2 through acid hydrolysis with phosphoric acid at room temperature for at least an hour. Samples were measured on a ThermoQuest Finnigan Delta Plus XL continuous-flow isotope ratio mass spectrometer coupled with a Finnigan Gasbench automated sampler. Carbon isotope ($\delta^{13}C$) VPDB values are reported in per mil (‰) notation and were standardized relative NIST-19 and NBS-19. The analytical precision was 0.30‰ or better.

To measure sulfur isotope ($\delta^{34}S$) values of dissolved sulfate, $BaSO_4$ was precipitated from water samples, and combusted with V_2O_5 and O_2 at 1030°C (a method similar to that of Coleman and Moore, 1978) on a Costech Element Analyzer. The isotope ratios of the resulting SO_2 were measured on a ThermoQuest Finnigan Delta PlusXL continuous-flow isotope ratio mass spectrometer. Values of $\delta^{34}S$ are reported in per mil (‰) notation relative to CDT with a precision of 0.15‰ or better. The International standards OGS-1 and NBS123 were used for calibration, and measurements were corrected using a linear calibration based on several laboratory standards between -10 to +30‰.

Tritium analyses were performed using a Quantulus 1220 spectrophotometer in an underground counting laboratory. Electrolytic enrichment and liquid scintillation decay counting methods were used (Theodorsson, 1996). Enriched samples were mixed 1:1 by

volume with an Ultimagold Low Level Tritium cocktail. Results are reported in Tritium

Units (TU) relative to the NIST SRM 4261 B and C standards. The detection limit is 0.5

TU.

Both Liquid Scintillation and AMS techniques were used for measurement of

carbon-14. Large (50 L) samples were measured at the Department of Geosciences

Radiocarbon Laboratory. DIC was precipitated as $BaCO_3$ at pH>11 and the resulting

slurry was reacted with HCl to yield CO_2. The carbon was converted to benzene (Polach

et al., 1982), and counted in one of two Quantulus 1220 spectrophotometers in an

underground counting laboratory (precision $\leq \pm 0.4$ pmc for full-size samples).   Results

are reported as percent modern carbon (pmc), and calibrated using the Oxalic Acid I

standard. One-liter samples were measured at the NSF-Arizona Accelerator Facility.

Carbon dioxide was extracted by acid hydrolysis, and was reduced to graphite that was

made into targets for Accelerator Mass Spectrometry. Standards used are the NIST

oxalic acid I and II. This method had a detection limit of 0.2 pmc.

5.4 Water Type and Solute Ratios

Water type was determined by converting mg/L concentrations to equivalents in

solution based upon molecular weight and charge. The dominant cations and anions in

terms of meq/L were then used to describe the water type. Solute ratios (Ca/Sr and

SO_4/Cl) were calculated on a mg/L per mg/L basis. A complete list of water types and

solute ratios can be found in Table 2.

5.5 NETPATH Modeling

The computer program NETPATH (Plummer et al., 1994) was used to model mass-balance changes in chemical composition of groundwaters along flowpaths from an initial well (upgradient) to a final well (downgradient), and to calculate corrected carbon-14 groundwater ages. Models were constrained using the mineralogy of the aquifer and mineral saturation states. The model was limited to the elements carbon, sulfur, calcium, sodium, fluorine, chloride, and silica and to the mineral constraints fluorite, carbon dioxide gas, pyrite, albite, anorthite, gypsum, halite, calcite, quartz, cation exchange, and proton-exchange. Calcite was forced to react in every model due to abundance of calcite in the mineral matrix of the basin.

The $\delta^{13}C$ value of soil CO_2 was assumed to be -23.1‰ as used by Robertson (1992), which is consistent with soil organic matter found in the basin that ranged from -14 to -24‰ (McPherson et al., 1993). The $\delta^{13}C$ value of calcite was assumed to be -4.5‰, as measured by Robertson (1992) for the Lower San Pedro Basin. Carbon isotope values of DIC in groundwater samples analyzed as part of this study were often much more positive than could be accounted for by simple incongruent dissolution of calcite. Therefore, proton exchange was added to the models, as suggested by Plummer et al. (1994), which would increase the $\delta^{13}C$ value of DIC without adding additional solutes from mineral weathering. In addition, due to the limited amount of carbon-14 data collected in recharge areas in the Middle San Pedro Basin as part of this study, only wells with carbon-14 data that were downgradient from a well with known carbon-14 values were modeled using NETPATH.

Due to the limited amount of carbon-14 data collected along recharge areas within the basin, wells assumed to be in recharge areas based upon high tritium contents were assigned an initial carbon-14 value of 105.4 pmc which was the highest value measured in this study. This value is similar to the ^{14}C content of present-day vegetation (105 pmc) in the San Pedro Basin measured by Eastoe (personal communication, 2009).

5.6 Flowpath Modeling

Groundwater travel times obtained from NETPATH are compared to results from a particle tracking analysis using the numerical model of the Upper San Pedro Basin developed by Goode and Maddock (2000). The software MODPATH (Pollock, 1994) was used to calculate travel times using results from a steady state simulation of the numerical model. MODPATH uses a semi-analytical particle tracking scheme that computes particle positions using groundwater flow and direction output from the groundwater simulation software MODFLOW (McDonald and Harbaugh, 1988). To obtain travel times between wells, particles were tracked backward from the final well in the NETPATH analysis to an initial well based upon the groundwater flow system simulated by the Goode and Maddock model (2000). Particle travel time is determined using the relative length of a flowpath between two wells.

5.7 Aquifer Identification of Water Samples

Wells were classified into aquifer systems based upon their spatial location and the hydrologic unit in which they were located. Driller's logs and screened depth intervals

provided information about classifying the hydrologic source unit of each well. Wells were classified as follows: fracture system wells (located at least partially in fractured bedrock of mountain system), confined aquifer wells (located in the Lower Basin Fill, underneath confining unit), unconfined aquifer wells (located in the Upper Basin Fill above the confining unit), floodplain aquifer wells (located in the shallow alluvial aquifer along the river). Wells located in the fracture system are screened in bedrock within the mountain blocks and/or in unconsolidated sediments along the mountain front or ephemeral stream channels against the mountain base. In addition, surface water samples from the San Pedro River were categorized as river system samples and collected precipitation samples were classified as precipitation.

6. RESULTS

6.1 Geologic Cross-sections

Two geologic cross sections were constructed from information in driller's logs of domestic wells (shown in Figure 4): one transect from east to west across the basin (A-A') to capture the typical basin-and-range geomorphology, and one transect from north to south (B-B') to capture the extent of the clay confining layer in the central basin. Geologic units were then assigned based upon driller's descriptions of sediments. Solute and isotope chemistry of groundwater samples collected as part of this study were then overlain on the geologic cross-sections to help determine spatial and depth trends across the basin.

6.2 Field Parameters

Field parameters (conductivity, temperature, pH and dissolved oxygen) can help to determine major geochemical trends in the aquifer system. Electrical conductivity values ranged from 190 to 729 μs/cm in fracture system wells, 103 to 1409 μs/cm in confined aquifer wells, 180 to 1553 μs/cm in unconfined aquifer wells, and 330 to 1756 μs/cm in floodplain aquifer wells (Table 1). The river system had conductivity values of 190 to 546 μs/cm. The pH values also varied throughout the basin and within each water group. The fracture system wells had pH values of 6.72 to 8.58, values in the confined aquifer wells ranged from 6.94 to 8.88, values in the unconfined aquifer ranged from 7.15 to 8.34, and values in the floodplain aquifer wells varied from 6.96 to 7.79. The pH

values in the river system ranged from 6.88 to 8.45. Water temperature also varied

widely across the basin. However, due to our sampling methods (e.g. sampling from

domestic wells after pressure tanks, in some cases, and the seasonality of sampling),

temperature may not be an accurate proxy for in-situ hydrologic conditions.

6.3 Alkalinity

Alkalinity is the dominant parameter (in terms of meq/L) in the majority of

groundwater and surface water samples (83 out of 96), and is important for determining

charge balance. Alkalinity values ranged from 1.03 to 6.52 meq/kg in the fracture system

wells, 1.10 to 3.96 meq/kg in the confined aquifer, 1.74 to 8.02 meq/kg in the unconfined

aquifer, and 0.97 to 10.01 meq/kg in the floodplain aquifer (Table 2). River system

waters had alkalinity values between 2.32 and 4.99 meq/kg. Alkalinity is most likely

comprised of HCO_3^- at the near neutral pH values of the water samples, as confirmed by

the dissolved inorganic carbon (DIC) values, which closely match alkalinity.

6.4 Solute Chemistry

Water type is frequently used to determine major geochemical reactions occurring

in different parts of the aquifer and can be used to determine net reactions along a

flowpath (Table 2). Fracture system wells were dominated by calcium, sodium and

alkalinity, with concentration ranges of 13.88 to 145.03 mg/L and 9.21 to 103.93 mg/L

for Ca and Na, respectively (Table 2). The confined aquifer wells were dominated by

calcium, sodium, sulfate, and alkalinity, with concentration ranges of 1.82 to 290.61

mg/L, 7.92 to 259.60 mg/L, and 2 to 735 mg/L for Ca, Na, and SO_4, respectively.

Similarly, unconfined aquifer wells were dominated by calcium, sodium, sulfate, and

alkalinity, with concentration ranges of 17.00 to 95.84 mg/L, 8.30 to 237.31 mg/L, and

6.70 to 272.62 mg/L for Ca, Na, and SO_4, respectively. Floodplain aquifer wells were

also dominated by calcium, sodium, sulfate and alkalinity, with Ca, Na and SO_4 values

ranging from 48.19 to 135.11 mg/L, 15.08 to 387.88 mg/L, and 25.53 to 637.20 mg/L,

respectively. The river system was dominated by calcium and alkalinity, with calcium

concentrations ranging from 30.08 to 72.03 mg/L.

Strontium concentrations ranged from 0.14 to 1.26 mg/L in the fracture system,

0.14 to 1.45 mg/L in the unconfined aquifer, and 0.31 to 2.57 mg/L in the floodplain

aquifer. River system samples had strontium concentrations from 0.32 to 1.43 mg/L.

Samples from the confined aquifer had a large range of strontium concentrations from

0.03 to 5.08 mg/L.

The fracture system generally contained lower fluoride levels (most <2 mg/L)

than other water groups, but had a large range with values between 0.5 to 7.7 mg/L.

Lower fluoride levels were also found in the river system (0.4 to1.76 mg/L) and in the

unconfined aquifer (0.7 to 2.8 mg/L).   Higher fluoride concentrations were found in the

floodplain aquifer with values between 0.6 to 6.1 mg/L as well as in the confined aquifer

with values from 0.5 to7.4 mg/L.

Burtell (1989) and Towne and Stephenson (2002) examined the chemical

evolution of groundwater along flowpaths in the northern portion of the Middle San

Pedro Basin, north of the (Benson) Narrows. They found that groundwater in the

mountain systems is characterized by calcium bicarbonate or sodium bicarbonate type waters. Data from these studies suggest that groundwater in the unconfined aquifer is also calcium bicarbonate type water, indicating that both mountain systems and unconfined aquifers are areas of focused recharge in the basin. In addition, the lower concentrations of bicarbonate in the unconfined aquifer compared to the mountain system may indicate that less recharge is occurring in the unconfined aquifer. These results agree with the observation Towne and Stephenson (2002) made that calcium concentrations were highest in groundwaters from mountain system areas and decrease towards the basin center, likely due to mixing with deep alluvial aquifer waters that have been modified by water-rock reactions.

Complete chemical analyses were conducted to determine charge balances of waters and can be found on Table 2. This dataset can be used in future studies of basin groundwater.

6.5 Solute Ratios

In addition to information gained through solute chemistry, solute ratios (Ca/Sr and SO_4/Cl) were utilized to better constrain groundwater geochemical reactions along flowpaths and between aquifer systems. The divalent cation ratio Ca/Sr offers information regarding residence time of groundwaters and the amount of interaction between geologic sources and groundwaters while the mixed valence ratio SO_4/Cl provides information pertaining to the presence and type of evaporites, while excluding the effects of evaporation.

Calcium to strontium ratios (reported on a mg/L to mg/L basis) were lowest in the confined aquifer with values between 21 to 222 and in samples collected from the river system with Ca/Sr ratios from 46 to 158. Ca/Sr ratios were highest in fracture system wells, ranging from 34 to 463 (Table 2) while the unconfined aquifer wells similarly demonstrated high Ca/Sr ratios of 42 to 526. The floodplain aquifer wells had Ca/Sr ratios ranging from 27 to 182.

Similarly, sulfate to chloride ratios (on a mg/L to mg/L basis) varied throughout the basin. The lowest SO_4/Cl ratios were found in the river system wells, fracture system wells, and unconfined aquifer wells with values between 3 to 9, 1 to 2, and 1 to 7, respectively (Table 2). The floodplain aquifer wells had SO_4/Cl ratios from 3 to 26. The highest sulfate to chloride ratios were found in the confined aquifer wells with values ranging from 0.5 to 59.

6.6 Stable Isotopes

Stable isotopes of water are helpful in determining the sources of recharge, while solute isotopes (C and S) are useful in distinguishing geochemical reactions that occur along a flowpath. Oxygen and hydrogen isotope values of groundwater samples in the Middle San Pedro Basin ranged from -11.8 to -6.8‰ and -82 to -50‰, respectively (Table 3), and plot along the Local Meteoric Water Line (LMWL), developed from Baillie (2005) with a linear equation of $\delta^2H = (7.38 \pm 0.21) \times \delta^{18}O + (5.10 \pm 1.82)$ (Fig. 8). Because all samples collected as part of this study plot along or near the LMWL, discussion is limited to oxygen isotope values below. Isotope values of precipitation

samples varied seasonally and plot within the range of groundwater samples. In general, river system samples have more positive $\delta^{18}O$ values, ranging from -4.9 to -8.1‰. The confined aquifer had the largest range of $\delta^{18}O$ values ranging from -11.8 to -7.4‰. Fracture system groundwaters have $\delta^{18}O$ values between -10.8 and -8.2‰. The unconfined aquifer and floodplain aquifer had $\delta^{18}O$ values plotting between the fracture system and river system samples with values of -9.2 to -7.4‰ and -9.2 to -6.8‰, respectively.

Carbon isotope values of dissolved inorganic carbon (DIC) in groundwaters varied throughout the basin: fracture system groundwaters had $\delta^{13}C$ values from -11.2 to -3.8‰; confined aquifer groundwaters ranged from -9.5 to -2.9‰, unconfined aquifer groundwaters ranged from -12.0 to -7.9‰, and floodplain aquifer groundwaters ranged from -11.8 to -5.2‰ (Table 3). River system waters had $\delta^{13}C$ values from -8.9 to -6.3‰.

Sulfur isotope values of dissolved sulfate varied greatly (-8.4 to 11.7‰) in groundwaters throughout the basin with no clear trend between water groups (Table 3). Likely sulfate sources in the Middle San Pedro Basin are localized pyrite and gypsum deposits, precipitation, and the San Pedro River (upstream sources of sulfate). Burtell (1989) measured the $\delta^{34}S$ value of gypsum deposits in several mountain blocks in the San Pedro Basin. Permian gypsum from the Epitaph Formation in the Whetstone Mountains had a $\delta^{34}S$ value of 11.7‰. Pyrite in igneous rocks in the Winchester and Dragoon Mountains had $\delta^{34}S$ values of 2.0‰ and 4.3‰, respectively.

Sulfur isotope values of precipitation were not measured as part of this study. Gu (2005) reported a $\delta^{34}S$ value for SO_4 of 4.9‰ in Tucson Basin precipitation collected in

2003. Gu's study (2005) also provides an end member for local reworked Permian marine gypsum within the basin, yielding a δ^{34}S value of 14‰. Eastoe et al. (2004) observed a seasonal variation in δ^{34}S values in precipitation between 2.1 and 8.5‰; sulfur isotopes of past precipitation are not known.

6.7 Radioactive Isotopes

Radiogenic isotopes, such as radioactive carbon-14 (half-life: 5730 years) and tritium (half-life: 12.32 years) are useful for determining relative groundwater residence times over short (<50 years) to long (up to ~30 to 50 ka) timescales (Clark and Fritz, 1997). Carbon-14 has also been utilized to estimate average recharge rates to regional aquifer systems to verify numerical flow models (Zhu, 2000). In this study, carbon-14 and tritium were analyzed to help identify recharge areas and calculate residence times of groundwater in the Middle San Pedro Basin. Tritium was primarily measured on groundwater samples that were suspected of having short residence times (e.g. mountain system and unconfined aquifer wells) (Table 3). Carbon-14 was then measured on samples that were suspected to have little to no tritium or that were expected to be part of the confined aquifer system (Table 4).

Carbon-14 values of groundwater vary throughout the basin from 1.2 pmc to 105.4 pmc. Groundwaters in the confined aquifer have the lowest carbon-14 values between 1.2 and 33.7 pmc. The one sample analyzed from the floodplain aquifer had a carbon-14 value of 95.9 pmc. Fracture system groundwaters and unconfined aquifer groundwaters tended to have the highest carbon-14 concentrations, ranging from 23.6 to

78.8 pmc and 37.8 and 105.4 pmc respectively. Urban air in the adjacent Tucson Basin

contained 107 pmc ^{14}C in 2002, as measured by Eastoe et al. (2004). Rural air around

Tucson is 0 to 2 pmc more enriched in ^{14}C than urban air; and surface waters in the

Tucson Basin were found to contain 85 to 107 pmc (Eastoe et al., 2004). Organic plant

matter sampled in the San Pedro Basin by Eastoe in 2008 measured 105 pmc (Eastoe,

personal communication, 2009).

Uncorrected radiocarbon ages for groundwater samples measured in the Middle

San Pedro Basin range from modern to 37,000 years before present. Because of the

evidence for calcite dissolution in the basin, which can significantly dilute carbon-14

concentrations and increase apparent groundwater ages, NETPATH was used to help

account for water-rock reactions and correct travel times between wells along assumed

flowpaths. Corrected travel times for the system ranged from 1,700 to 34,600 years

before present throughout the basin. Corrected carbon-14 ages were insensitive to

changes in δ^{13}C and carbon-14 values of endmembers (e.g. calcite and soil CO_2).

Groundwaters in the Middle San Pedro Basin had tritium concentrations from

below the detection limit (<0.5 TU) to 6.9 TU. Confined aquifer groundwaters had the

lowest tritium concentrations, with all but two samples having less than 1 TU; these two

anomalous wells contained 2.6 and 1.8 TU. The highest tritium values were measured in

fracture system and floodplain aquifer groundwaters (<0.3 to 6.9 TU, and <0.6 to 4.9 TU,

respectively). Groundwaters in the unconfined aquifer had tritium values from <0.6 to

3.7 TU. Although tritium was not measured for precipitation samples in the Middle San

Pedro Basin, it is likely that pre-bomb rainwater would now contain less than 0.6 TU due

to radioactive decay. In addition, modern precipitation in the Tucson Basin has contained

6 ± 1 TU since 1992 (Eastoe et al., 2004).

6.8 Geochemical Modeling

Geochemical modeling through NETPATH yielded general trends of net

geochemical reactions that likely occur along flowpaths throughout the basin. Fluorite,

halite, and gypsum dissolved between all initial and final well pairs, indicating these

reactions are important throughout the basin. Calcite also dissolved and/or precipitated

along all flowpaths; proton exchange was included in some models to help account for

the incongruent dissolution of calcite. Pyrite and quartz precipitated or dissolved in small

quantities to account for changes in sulfur and silica species between wells. Cation

exchange is also an important process responsible for increases in sodium concentrations

along flowpaths. These results are consistent with previous geochemical modeling

studies (Burtell, 1989) that found the formation of clays and oxides, calcite dissolution,

fluorite dissolution and silica precipitation to be common in Lower San Pedro Basin

groundwaters.

6.9 Flowpath Modeling

In order to compare modeled NETPATH residence times with ages estimated by

the numerical modeling of the San Pedro Basin, particle tracking was employed using the

Goode and Maddock (2000) MODFLOW model. Simulated particles were tracked from

their final destinations back to the origination sites to estimate travel times between an

initial area and final wells. Due to variations in flowpaths and the location of wells

sampled as part of this study, only four of the flowpaths that were simulated by particle

tracking closely matched flowpaths modeled through NETPATH. Travel times from the

particle tracking model were calculated to be between 20 to 275 years and are listed in

Table 7 next to the resulting NETPATH ages. These modeled travel times are lower than

the NETPATH travel times calculated using carbon-14, carbon-13 and solute chemical

data collected as part of this study. This difference may suggest that the numerical model

needs to be refined to more accurately represent the Middle San Pedro Basin flow system

and/or there are important geochemical reactions that still need to be accounted for in the

NETPATH modeling.

7. DISCUSSION

7.1 Location and seasonality of focused recharge to groundwater systems

Tritium and carbon-14 are useful age tracers of groundwater residence times and identifying locations of focused recharge in the Middle San Pedro Basin. Concentrations of tritium and carbon-14 are plotted spatially in Figure 7. Groundwaters with detectable tritium (above 0.5 TU) and/or elevated carbon-14 concentrations (above ~100 pmc) are indicative of waters recharged within the last 50 years. Detectable tritium (0.6 to 6.9 TU) is found in groundwaters in the fracture system, floodplain aquifer, and unconfined aquifer; these sample locations identify areas of recharge to the basin within the last 50 years.

Uncorrected carbon-14 values can also be used to qualitatively identify locations of recharge to the Middle San Pedro Basin; samples with higher carbon-14 indicate relatively recent recharge while lower carbon-14 values indicate longer residence time within the basin. One groundwater sample in the unconfined aquifer has a carbon-14 value above 105 pmc, similar to the 105 pmc value of modern organic matter in the San Pedro Basin measured by Eastoe (personal communication, 2009). This groundwater sample is also consistent with a precipitation sample collected in the Tucson Basin measuring 107 pmc in 2002 (Eastoe et al., 2004); this sample contained detectable tritium (3.7 TU) (Figure 7). There are a few groundwater samples from the fracture system that have lower carbon-14 values (23.6 to 29.9 pmc) suggesting longer residence times. Two samples from the confined aquifer contain low carbon-14 values (13.1 and 20.2 pmc), but

detectable tritium (1.8 and 2.6 TU). These two samples (C20 and C29) are located near a gaining portion of the river by St. David (Figure 2). These anomalous samples may have resulted from mixing of older waters from the confined aquifer and younger waters from the overlying unconfined aquifer and/or potential dilution of carbon-14 by addition of dead carbon via calcite dissolution or organic matter oxidation or potentially from a long screened interval; additional samples would need to be collected to test these hypotheses.

Oxygen and hydrogen isotopes were analyzed to further elucidate the location, elevation and seasonality of recharge to the Middle San Pedro Basin. Groundwater, surface water, and precipitation samples plot along the local meteoric water line (as determined by Baillie, 2005) in Figure 8, indicating that these waters are derived from meteoric sources and have not experienced extensive evaporation and/or water-rock alteration. Groundwater samples in the floodplain aquifer have relatively positive $\delta^{18}O$ values (-9.2 to -6.8‰), plotting close to surface water samples from the San Pedro River (-8.1 to -4.9‰). This is consistent with previous results from the Upper San Pedro Basin, which showed close communication between the river system and adjacent alluvial aquifer (Baillie, 2005). Low elevation summer precipitation samples also fall close to the range of floodplain aquifer samples, indicating that summer precipitation (monsoon storms) is most likely the largest contributor to recharge in the floodplain aquifer. $\delta^{18}O$ values of winter precipitation were much more negative (-10.6 to –9.4‰) than summer precipitation (-8.2 to –7.6‰) and did not show a strong influence on floodplain aquifer samples. Unconfined aquifer samples, however, fall between summer and winter precipitation values, thus indicating recharge of year-round precipitation.

The lower $\delta^{18}O$ values found in the confined aquifer, fracture system, and unconfined aquifer are affected by seasonality and elevation. Figure 9A shows the differences in oxygen isotope values between summer and winter seasons from precipitation collected during this study. This plot indicates that $\delta^{18}O$ values of precipitation decrease with elevation; however, the only way to attain $\delta^{18}O$ values more negative than -9.5‰ is from seasonal effects (i.e. winter precipitation). This plot helps to illustrate that any groundwaters with $\delta^{18}O$ values less than -9.5‰ are probably due to a dominance of winter precipitation recharge. Most unconfined aquifer, confined aquifer and fracture system waters fall closer to winter precipitation values, suggesting that winter precipitation is the dominant source of recharge to these groundwater systems. Cross sections overlain with oxygen isotope data (Figure 15) raise the possibility that recharge is occurring at high elevations through the fracture system and migrating downgradient into the confined aquifer.

In order to more fully understand precipitation values in the San Pedro Basin, oxygen and hydrogen isotopes from this study were plotted with average summer and winter precipitation values from the Upper San Pedro Basin from Baillie (2005) and with altitude corrected values from Wright (2001) from the Tucson Basin (Figure 9B). Wright (2001)'s data from the Tucson basin was extrapolated for three elevation stations (1000m, 1400m, 2600m) that represent elevation in the San Pedro Basin. Wright (2001)'s study is the only available source of long term averaged precipitation data for the region and gives a more accurate signature of seasonal isotope values than the precpitation samples collected during this short study. The local meteoric water line as determined by

Baillie (2005) was included on this plot. Precipitation values spanned a large range and indicate that groundwater from the floodplain aquifer appears to originate mostly from summer precipitation or low elevation recharge.

Since oxygen isotope ratios are useful in distinguishing the different water groups (e.g. water samples from the fracture system and confined aquifer have distinct $\delta^{18}O$ values from those in the floodplain aquifer), tritium results are plotted versus $\delta^{18}O$ values (Figure 10) to distinguish which groups are currently experiencing recharge and what the isotopic signature of recharge is. Tritium is particularly important in helping to target the isotopic signature of recent recharge throughout the basin; Figure 10 indicates that the majority of modern recharge has a $\delta^{18}O$ value from -9.5 to -6.5‰.

Samples with detectable tritium (>0.5 TU) occur in the confined aquifer, unconfined aquifer, fracture system, and floodplain aquifer. Two samples from the confined aquifer have detectable tritium (1.8 and 2.6 TU) and indicate high elevation recharge through low oxygen isotope values (-8.9 and -8.0 ‰ respectively). Three samples from the unconfined aquifer have detectable amounts of tritium (3.0, 3.6, and 3.7 TU) and have a wide range of oxygen isotope values (-8.0, -8.4 and -8.8 ‰ respectively), indicating recharge is occurring at different elevations or during different seasons. Numerous samples from the floodplain aquifer have detectable tritium but higher oxygen isotope values (~-7.2 ‰), indicating modern recharge occurring in this aquifer has a summer seasonal signature. Many fracture system wells with low oxygen isotope values (~-9.0 ‰) have detectable tritium, indicating that recharge is occurring somewhere along the mountain system. These conclusions agree with Coes and Pool (2005) who found

that a large percentage of recharge to the Upper San Pedro Basin occurred through ephemeral streams near the base of the mountain systems.

Major ion chemistry of groundwaters can also be used to identify locations of focused recharge. The majority of waters in the fracture system and floodplain aquifer, and several wells in the unconfined aquifer were dominated by Ca-HCO$_3$ or Na-HCO$_3$ (Table 2), which are typical of waters with relatively short residence times in recharge areas (Burtell, 1989; Towne and Stephenson, 2002). Many groundwater samples in the confined aquifer were enriched in SO$_4$, likely due to increased residence time and water-rock reactions in downgradient wells.

7.2 Groundwater flowpaths, transit times and geochemical evolution of waters

Water levels measured by the Arizona Department of Water Resources in 2005 for groundwater wells throughout the Middle San Pedro Basin are shown on Figure 2 (Arizona Department of Water Resources, 2005). Groundwater flow lines constructed from the potentiometric surfaces suggest that in general flow is directed from the mountain blocks (fracture system) towards the center of the basin (confined aquifers) and from south to northwest along the axis of the basin (confined aquifers). Solute and isotope chemistry were used to confirm these flow paths.

As mentioned in the previous section, groundwaters in recharge areas in the fracture system and unconfined aquifer have detectable tritium and modern carbon-14 values. A spatial map of tritium and carbon-14 (Figure 7) shows a systematic decrease in values from the high elevation fracture system towards the basin center in the confined

aquifer, which likely indicates an increase in groundwater residence times along these general flowpaths. The same trend can be seen in cross-section (Figure 15).

Oxygen and hydrogen isotope composition of groundwaters help to confirm the source elevation of basin groundwaters. Interestingly, groundwaters in the confined aquifer system have $\delta^{18}O$ values within the same range as the fracture system waters (Figure 8), suggesting that these deep central basin waters originated from high elevation recharge along the margins of the basin. There are several groundwater samples in the confined aquifer that have more positive and more negative $\delta^{18}O$ values than the fracture system. These waters may have originated from higher or lower elevations than samples collected as part of this study. Alternatively, waters could have been recharged from winter precipitation with different isotopic compositions than what was measured as part of this study.

Variations in oxygen and hydrogen isotope composition of confined aquifer waters may also be a function of climate change; for example, the relatively negative values (-11.8 to −11.5‰) observed in wells C16 and C33 may be due to recharge under cooler climatic conditions at the end of the last glacial period (~18 ka). Samples with low carbon-14 values and low $\delta^{18}O$ values (-11.2 and -11.7‰) have been found in the Middle San Pedro Basin at Hooker Hot Springs by Eastoe (personal communication, 2009). To test this hypothesis, $\delta^{18}O$ values were plotted versus carbon-14 (Figure 11A); most samples with carbon-14 measurements have $\delta^{18}O$ values between -9 and -7‰, regardless of carbon-14 age. However, three samples with less than 30 pmc ^{14}C have $\delta^{18}O$ values below -10‰ and may indicate climate change. This phenomenon may be

due to the altitude affect; sample C16 is also near an area of discharge from Ash Creek, which drains the Rincon Mountains, potentially indicating the source of high elevation recharge.

Groundwaters in the floodplain aquifer have $\delta^{18}O$ values similar to the San Pedro River and range between winter and summer precipitation (Figure 8). These waters likely have short flowpaths and are closely connected to the river system. Waters in the unconfined aquifer have a varied oxygen isotope signature that spans the range between summer and winter precipitation and indicates year round recharge.

Groundwater travel times within the Middle San Pedro Basin were determined using both quantitative and qualitative methods. Carbon-14 can be used to estimate groundwater apparent ages, while solute ratios (e.g. Ca/Sr) can be used to provide insight into groundwaters ages due to increased water-rock reactions with increased residence times. The geochemical modeling program NETPATH was used to calculate net geochemical reactions and corrected carbon-14 ages of waters between selected wells in the basin. Results from the NETPATH modeling are reported in Table 4. The corrected ages represent the travel time between two input wells (an initial upgradient well and final downgradient well), and the minimum amount of time that water parcels have resided in the aquifer system. The actual residence time of samples may be greater than the corrected ages shown in Table 4, due to using initial wells in the model that are already slightly downgradient of likely recharge areas (function of availability of well sample locations).

The NETPATH modeling results confirm that calcite dissolution is an important process occurring in Middle San Pedro Basin groundwaters, which can significantly dilute the carbon-14 concentrations and make groundwaters appear to be much older than their actual age. Corrected carbon-14 travel times, accounting for calcite dissolution, cation exchange and proton exchange, are listed in Table 4. Groundwaters in the fracture system had carbon-14 travel times from 2,400 to 9,951 years before present (ybp). One sample from the unconfined aquifer yielded a travel time of 3,250 ybp; there were no corrected travel times in the floodplain aquifer due to a lack of adequate upgradient wells sampled as part of this study. The oldest groundwaters (10,000 to 34,600 ybp) in the Middle San Pedro Basin are located along the axis of the basin, beneath the confining unit, in the confined aquifer system.

Calcium to strontium ratios can be used as a qualitative indicator of groundwater residence times, as calcium and strontium are both released to solution during carbonate mineral dissolution. If waters become supersaturated in calcite with increased water-rock reaction, a pure form of calcite may precipitate leaving strontium in solution. Therefore, Ca/Sr ratios of groundwaters in carbonate and silicate aquifers typically decrease with increasing residence times (Edmunds and Smedley, 2000). The highest Ca/Sr ratios in the Middle San Pedro Basin were observed in fracture system wells (Figure 12 A, B), consistent with their relatively short residence times. Groundwaters in the confined aquifer system have significantly lower Ca/Sr ratios and lower carbon-14 concentrations (longer residence times). The positive correlation between Ca/Sr ratios and carbon-14 concentrations (Figure 12 A) suggests that Ca/Sr may be a useful and relatively

inexpensive tracer of groundwater ages in the Middle San Pedro Basin and other alluvial basins in the southwestern United States. Ca/Sr ratios were plotted with $\delta^{18}O$ values in Figure 11 B and indicate similar trends as carbon-14 data mentioned above. Samples with $\delta^{18}O$ values below -9‰ mostly have Ca/Sr ratios below 100 mg/L/ mg/L, indicating these more depleted waters have longer residence times.

Increased residence times may correspond to increased salt contents of groundwaters due to dissolution of gypsum, oxidation of pyrite, and/or dissolution of halite in the Middle San Pedro Basin; dissolution of gypsum-dust in surface environments may also provide additional sources of SO_4 to groundwater. Sulfate to chloride ratios provide an indicator for inputs of SO_4 or Cl, while neglecting the effects of evaporation (which would not alter the SO_4/Cl ratio prior to gypsum saturation). Sulfate to chloride ratios are plotted versus Ca/Sr (Figure 12 B) to determine if there is a relationship between SO_4/Cl ratios and residence times (as indicated by Ca/Sr ratios). Groundwaters in the confined aquifer have the highest SO_4/Cl ratios potentially due to increased dissolution of gypsum or pyrite oxidation; as both reactions produce SO_4 in groundwaters, it is necessary to use sulfur isotopes to distinguish sulfate sources (discussed below). Fracture system and unconfined aquifer waters have low SO_4/Cl ratios suggesting limited inputs of SO_4. The floodplain aquifer contains low Ca/Sr ratios, yet high SO_4/Cl values. Previous studies in the Upper San Pedro Basin have shown that these elevated SO_4/Cl values arose in the mountain system and likely stem from a change of sulfate into the system due to anthropogenic activities over time (Baillie, 2005).

Sulfur isotopes of dissolved sulfate were used to determine the sources of high sulfate waters (e.g. gypsum dissolution or pyrite oxidation) and potential mixing between the different water groups. Sulfur isotope values of groundwaters in the Middle San Pedro Basin displayed a large range (Fig. 13 A) and show a mixing trend between three end members, river water, rain water, and gypsum dissoluation. River water is represented by floodplain aquifer samples and river water samples, falling around 5‰ and having low $1/SO_4$ values; this sulfur signature may potentially indicate anthropogenic sources of sulfate, such as mining to the south of the study area. Gypsum dissolution is represented by values of reworked Permian gypsum (14‰; Gu, 2005). Samples from the confined aquifer with low sulfate concentrations and $\delta^{34}S$ values of 10‰ represent dilute rain water (potentially paleo-recharge). Most samples fall within these three end-members and show that sources of sulfate in groundwater in the basin are from gypsum dissolution, atmospheric deposition of sulfate through rain water, and modern deposition of sulfate from anthropogenic sources through the San Pedro River.

Four samples have negative sulfur isotope values (-10.7 to -8.2‰) and indicate sulfate reduction within the system. Bacterial sulfate reduction is a common phenomenon within the confined aquifer of the San Pedro Basin in areas of organic-rich sediment (Eastoe, personal communication, 2009) and is commonly associated with bacterial reduction of iron in freshwater aquifers (Bethke et al., 2008).

Sulfur isotopes are plotted with SO_4/Cl ratios in Figure 13 B; this plot shows similar end member mixing as Figure 13 A but does not indicate the source of high sources of sulfate in the groundwater system.

Fluoride also tends to be elevated in groundwaters with increased residence time and increased water-rock interaction. Fluoride can be detrimental to human health at concentrations above 1.5 mg/L (Fordyce et al., 2007) and can cause fluorosis of the bones and teeth as well as brain damage or even death. Figure 14 shows fluorine concentration plotted against carbon-14 to evaluate the relationship between fluoride and groundwater residence times. Fluoride is released to solution via weathering of fluorite-rich minerals, common in granitic bedrock and basin-fill sediments of the San Pedro Basin (Usunoff, 1984; Robertson, 1992), and can be removed from solution via adsorption onto calcite surfaces. Therefore, fluoride concentrations in groundwaters are typically inversely correlated with calcium concentrations (Jacks et al., 2005).

Many groundwaters in the basin have fluoride concentrations that exceed the EPA maximum contaminant level (4 mg/L) and secondary contaminant level (2 mg/L). Although not all data are plotted on Figure 14 due to lack of carbon-14 information, trends in fluoride concentrations with carbon-14 contents were observed. The highest levels of fluoride (up to 7.4 mg/L) are found in the confined aquifer and correspond to lower carbon-14 values (older ages), indicating that high fluoride levels may be derived from increased water-rock interaction. High levels of fluoride are also found in some fracture system wells, indicating that geologic sources of fluoride may exist in the fracture system and/or that these wells have longer residence times than other fracture system wells. Waters from the floodplain aquifer, fracture system, and unconfined aquifer have lower amounts of fluoride (below the secondary detection limit), which correspond to higher carbon-14 contents (shorter residence times). Two anomalous wells

from the floodplain aquifer have high fluoride concentrations, potentially indicating

interaction with deep wells or increased residence time. These two floodplain wells (F5,

F7) are located south of the town of St. David, near a gaining area of the river (wet during

the summer solstice). These high fluoride concentrations and low tritium values may

possibly indicate that water from the confined aquifer is leaking into the floodplain

aquifer here. This may also indicate that the confined aquifer is providing the river with

baseflow near this point; further researched would need to be conducted to test this

assumption.

7.3 Geochemical evidence for compartmentalization and/or mixing of basin

groundwaters

Unlike the Upper San Pedro Basin, the Middle San Pedro Basin contains a thick

clay confining unit, the St. David Formation, in the center of the basin that extends for a

significant distance (~70 km) along the basin axis (Figure 4 B). This clay confining unit

may inhibit interaction of groundwaters in the confined aquifer with overlying

unconfined aquifer waters and the San Pedro River. With increased groundwater

development due to projected population growth in the region it is important to determine

how effective the St. David Formation is as a barrier to groundwater flow and

contaminant transport. It is also important to determine the contribution of confined

aquifer water to the San Pedro River system to more fully understand the potential effects

of pumping from the confined aquifer. Solute and isotope geochemistry was used to

determine if there are geochemical differences between aquifer units above and below the

clay confining layer, which would imply that the confining unit inhibits fluid migration and mixing.

The majority of wells sampled in the confined aquifer system have distinct isotopic and solute chemistries from the overlying unconfined aquifer and floodplain aquifer. They have much lower Ca/Sr ratios, high SO_4/Cl ratios, relatively long residence times (low carbon-14 and tritium contents), and low $\delta^{18}O$ values indicative of winter precipitation recharge from high elevation fracture systems along long flowpaths. These waters are likely out of communication with the unconfined aquifer, suggesting that the clay confining unit is an effective barrier to groundwater migration in these regions. Hydraulic head data confirm these results, showing artesian conditions in many confined aquifer wells, which suggests the clay confining unit is relatively impermeable. However, there are a few wells in the confined aquifer with anomalous geochemistries that may represent areas of potential mixing or leakage of waters between the confined aquifer system and overlying unconfined aquifer. Five water samples from the confined aquifer (C4, C6, C9, C23, C25) have $\delta^{18}O$ values within the range of the river system and floodplain aquifer. In addition, two samples from the floodplain aquifer (F10, F11) have $\delta^{18}O$ values significantly lower than the majority of the samples, suggesting potential input of deeper confined aquifer waters. Neither of these samples plot distinctly away from floodplain aquifer samples except with respect to oxygen isotopes. Two other samples from the floodplain aquifer (F5, F7), discussed above, had high fluoride and tritium below detection limits and may signal contribution of confined aquifer water into the floodplain aquifer or river region. However, due to the fact that there were limited

confined aquifer samples collected in the region of these anomalous floodplain aquifer wells, more samples would need to be collected to test these hypotheses.

7.4 Comparing geochemical and numerical model results

In order to best manage groundwater resources of the Middle San Pedro Basin it is necessary to develop groundwater flow models that can be used to evaluate future groundwater pumping stresses on the aquifer system. The numerical model constructed by Goode and Maddock (2000) for the San Pedro Basin is capable of simulating the effects of groundwater pumping and other alternate futures. While this model provides insight into the hydrologic setting of the basin, the Middle San Pedro Basin portion of the model could be improved with a more refined conceptualization of basin hydrogeology and geochemistry using results from this study. The Middle San Pedro Basin contains a thick, regionally-extensive clay confining unit in the central basin (Figure 4B), which is absent in the Upper San Pedro Basin and in the Goode and Maddock (2000) model hydrostratigraphy (Figure 5). Incorporation of the clay confining unit into future numerical models may help to improve assumptions and more accurately simulate basinal groundwater flow.

Results from this geochemical study indicate that the St. David Formation is an important confining unit that prevents mixing of waters between the confined and unconfined aquifer systems. Including this clay confining unit in future model simulations would likely lengthen basin groundwater travel times, as confined groundwaters would be inhibited from discharging into near-surface systems, which

would increase water-rock reactions and travel times to more closely match those observed in the water geochemistry.

Groundwater travel times as calculated by NETPATH varied throughout the basin, from less than 50 years to up to 34,600 ybp. Four flowpaths that were modeled by MODPATH agreed with the indicated flowpaths from the initial to final well (Figure 16) as modeled by NETPATH. Travel times calculated by NETPATH differ from travel times calculated by particle tracking based on the Goode and Maddock (2000) model (Table 4). Travel times calculated using particle tracking depend on groundwater velocity and flowpath distance. To calculate velocity, MODFLOW uses a user-defined porosity input value (0.1 was applied to the Goode and Maddock model) and calculates a flux (q). Travel times calculated using particle tracking for four flowpaths that corresponded to modeled flowpaths using NETPATH for this study, ranged from 200 to 2,750 years. NETPATH travel times for these same flowpaths ranged from 1,700 to 6,660 years. This difference in travel times could be due to a number of factors, including assumptions about the basin hydrostratigraphy (i.e. exclusion of clay confining unit) or hydrologic properties (i.e. porosity of aquifer materials) used in the MODPATH model, or assumptions about important geochemical reactions (e.g. calcite dissolution or proton exchange) used in the NETPATH model.

This study has shown that future groundwater flow modeling efforts for the Middle San Pedro Basin, and other basins world-wide, could incorporate geochemical results as one way of improving assumptions of physical systems and conceptual models of fluid flow.

8. CONCLUSION

Groundwater within the Basin and Range Province is an important but limited resource. It is essential to understand groundwater resources for future development of the semi-arid Southwest. In this study, solute and isotope geochemistry were coupled to geochemical and particle track modeling to test and improve conceptual models of groundwater flow in the Middle San Pedro Basin, Arizona by demonstrating that groundwater chemistry varies in relation to a confining unit, suggesting compartmentalization of water in the aquifer system.

Geochemical results show evidence for focused recharge of recent waters (<50 years old) in fracture systems in high elevation mountain blocks bounding the western and eastern margins of the basin. Groundwaters migrate downgradient into the confined aquifer system, as evidenced by relatively depleted oxygen isotope values (indicating high elevation, mixed season recharge), increasing groundwaters ages (decreasing ^{14}C and ^{3}H contents) and increased amounts of F, SO_4 and Sr (relative to Ca) due to increased water-rock reactions.

Differences in the seasonality (i.e. winter rains versus summer monsoons) and elevation of precipitation helped to explain large variations in the d18O values of groundwaters throughout the basin. Groundwaters in the fracture system and unconfined aquifers were primarily recharged by winter precipitation, as indicated by their low $\delta^{18}O$ values (< -9.5 ‰). Groundwater in the confined aquifer demonstrated a large range of $\delta^{18}O$ ratios, indicating recharge from both summer and winter precipitation. Relatively

positive $\delta^{18}O$ values and elevated tritium and carbon-14 contents in floodplain aquifers and select unconfined aquifer waters suggest that these areas have experienced recent recharge (<50 years) with a strong summer precipitation component. The majority of these wells have distinct geochemistries from underlying confined aquifer waters, pointing to limited mixing, if any across the clay confining unit. However, high amounts of fluoride and sulfate in select floodplain wells may suggest localized areas of upward leakage of confined aquifer waters into the floodplain system.

Groundwater travel times (calculated using carbon-14 data, solute and stable isotope geochemistry, and NETPATH) varied throughout the basin, from less than 50 years in recharge zones, to up to 34,600 years in the confined aquifer system. These estimated travel times vary from those calculated using particle track modeling coupled to Goode and Maddock (2000)'s MODFLOW model of the San Pedro Basin. The differences in travel times between the geochemical and numerical models may be a function of assumed basin hydrostratigraphy or basin characteristics. The geochemical results of this study show that the St. David Formation is in fact a relatively impermeable barrier to groundwater flow and should be included in future modeling efforts.

By combining solute chemistry (water type, F content, SO_4/Cl ratios), stable isotopes (O, H, C, S), age tracers (^{14}C, ^{3}H, Ca/Sr ratios), and particle track modeling this study was able to determine areas of recent recharge, groundwater flowpaths, travel times, and evidence for compartmentalization of waters in the Middle San Pedro Basin. These results are important for constructing more accurate conceptual and numerical models of basin hydrogeology aimed to better manage water resources.

APPENDIX A: FIGURE CAPTIONS

Figure 1. Map of the study area (Middle San Pedro Basin), showing towns and major roads.

Figure 2. Map of hydrologic features of the study area including USGS gages for reference. Water level contours were constructed from measurements made by the Arizona Department of Water Resources in 2005 (Arizona Department of Water Resources, 2005). Areas of wet (black) and dry (red) stretches of river are plotted on the San Pedro River as determined by The Nature Conservancy (map, 2008).

Figure 3. Geologic map of the study area, showing the Whetstone, Rincon, Santa Catalina, Galiuro, and Dragoon Mountains. Transects A-A' and B-B' were used to construct geologic cross sections in Figure 4.

Figure 4. Geologic Cross Sections A (A-A' from Figure 3) and B (B-B' from Figure 3) constructed from driller's logs. Geologic units include Upper Basin Fill, floodplain aquifer alluvium, a confining clay layer (St. David Formation), Lower Basin Fill, and fractured bedrock. The location and IDs of wells sampled along the two cross section lines are shown for reference; detailed information on these wells is listed in Table 1.

Figure 5. Cross Sections A (A-A' from Figure 3) and B (B-B' from Figure 3) used in a previous groundwater flow model of the San Pedro Basin (Goode and Maddock, 2000). Layers 1 through 4 were constructed from the Goode and Maddock (2000) model, using the elevation of the tops of each layer, for comparison to this study.

Figure 6. Map of groundwater, surface water, and precipitation sample sites in the study area.

Figure 7. Map showing spatial distribution of tritium and carbon-14 contents of groundwater samples in the study area. Locations with overlain symbols indicate sites where both tritium and carbon-14 were measured.

Figure 8. Hydrogen versus oxygen isotope values of groundwater, surface water, and precipitation samples relative to the local meteoric water line (LWML) from Baillie (2005).

Figure 9.   Altitude in meters (A) and hydrogen isotope values (B) versus oxygen isotope values for precipitation. Figure 9A shows seasonal trend lines from precipitation collected for this study. Figure 9B includes seasonal precipitation collection for this study, seasonal precipitation as calculated from Wright et al. (2001) at elevations of 1000m, 1400m, and 2600m, and seasonal precipitation values from Baillie (2005).

Groundwater isotope ranges from the fracture system and floodplain aquifer are overlain for reference.

Figure 10. Tritium versus oxygen isotope values of groundwater samples. The lower limit (0.6 TU) for tritium concentrations in modern (<50 years old) precipitation is shown for reference.

Figure 11. Carbon-14 (A) and Ca/Sr ratios (B) versus $\delta^{18}O$ values of groundwaters and surface waters. Plots indicate that more negative $\delta^{18}O$ values may be sourced by paloerecharge during a different climate regime.

Figure 12. Carbon-14 values (A) and SO_4/Cl ratios (B) of groundwater and surface water samples plotted versus Ca/Sr ratios, which are a qualitative indicator of groundwater residence times.

Figure 13. $1/SO_4$ concentration (A) and SO_4/Cl ratios (B) versus the sulfur isotope value of dissolved sulfate in groundwater and surface water samples. Values for pyrite in the San Pedro Basin range from -25 to 4.3‰ (Burtell, 1989), while values of reworked Permian marine gypsum are 13 to 14‰ (Gu, 2005). Most water samples plot between river water, rain water, and gypsum dissolution end members with evidence of sulfate reduction in negative isotope values (-10.7‰ to -8.2‰).

Figure 14. Carbon-14 values versus fluoride concentrations of groundwaters. The EPA maximum contamination limit (MCL, 4 mg/L) and secondary contamination limit (SCL, 2 mg/L) for fluoride are shown for reference.

Figure 15. Oxygen isotopes, tritium, carbon-14, and Ca/Sr values for groundwater and surface water samples overlain on the geologic cross-sections to determine spatial and depth relations of water chemistry and residence times.

Figure 16. Approximate flow paths modeled by NETPATH (this study) versus flowpaths modeled by particle tracking, using MODPATH coupled to MODFLOW (Goode and Maddock, 2000). Initial wells used in NETPATH and MODPATH are indicated by the start of dotted lines, while the final wells are indicated by the tip of the arrows.

APPENDIX B: EXTENDED STUDY AREA INFORMATION

In addition to its importance for groundwater resources, The San Pedro Basin is also an important ecosystem in the southwestern United States. The riparian habitat along the river supports an estimated 390 species of birds, 83 species of mammals, and 47 species of amphibians and reptiles (Glennon, 2002). Three endangered species live in the Middle San Pedro Basin: the southwestern willow flycatcher, the Huachuca water-umbel, and the jaguar. The San Pedro River has been declared as one of America's top ten last great places by the Nature Conservancy due to its magnificent beauty and variety of wildlife.

Early explorers to the San Pedro valley found many thriving Native American communities. Evidence of human settlement in the San Pedro valley extends back hundreds of years and artifacts found throughout the valley suggests that the native cultures used river water to irrigate agriculture. At the time of American explorers, the San Pedro was reported to be abundant in wildlife and was named "Beaver River" due to the abundant beaver population.   The early explorers also reported large fish thriving in the river and reported the river to be large enough that it was a burden to cross (Batman, 1984).

Major vegetation types within the San Pedro Basin include Chihuahuan desert scrub, mesquite, Cottonwood and Willow trees along riparian corridors, sacaton grasses, cienegas, and Sonoran desert vegetation (Makings, 2005). Vegetation has experienced a

directional shift since the 1870s towards more woody plants, especially mesquite, and a decline in native grasses found in Southeastern Arizona (Bahre and Shelton, 1993).

Groundwater demand in the areas is increasing with an increase in population growth. Although large-scale agriculture is no longer a large consumer of groundwater in the basin, municipal water usage was found to have the largest water demand in the basin in 2002 (at 18,800 acre-feet) and is projected to grow to over 25,000 acre-feet per year by 2030 with current population projections (Arizona Department of Water Resources, 2005). The Arizona Department of Water Resources (2005) found that 89% of water demands in the Upper San Pedro Basin in 2002 were from groundwater while 8% were from surface water.

APPENDIX C: ADDITIONAL REGIONAL CARBON ISOTOPE INFORMATION

Previous studies have demonstrated evidence of ecosystem change by using carbon isotopes of groundwaters. Plummer et al. (2004) used $\delta^{13}C$ measurements of groundwater in the Rio Grande Basin to examine a recent shift in vegetation. The $\delta^{13}C$ record of groundwater indicates the predominance of C4 over C3 plants until a rapid shift occurred in the past thousand years (Plummer et al., 2004). McPherson et al. (1993) examined carbon-13 values of soil carbonates in the San Pedro Basin and discovered a shift from grasslands (C4 plants) to woody species (C3 plants). This shift could have potentially increased carbon storage in this ecosystem (McPherson et al., 1993). Previous studies have also suggested the importance of wind-blown dust from nearby regions that also contribute sediment and soil carbonates to the basin (Naiman et al., 2000).

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