USING TRENDS AND GEOCHEMICAL ANALYSIS TO ASSESS SALINITY SOURCES ALONG THE PECOS RIVER, TEXAS

A Thesis

by

AARON JACOB HOFF

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2012

Major Subject: Water Management and Hydrological Science

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Approved by:

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Committee Members,	Kevin J. McInnes
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ABSTRACT

Using Trends and Geochemical Analysis to Assess Salinity Sources Along the Pecos River, Texas. (May 2012)

Aaron Jacob Hoff, B.S., Texas A&M University
Chair of Advisory Committee: Dr. Bradford P. Wilcox

Increasing salinity has been a growing concern for users of waters from the Pecos River and the reservoirs it feeds in the Texas portion of the River's watershed. Irrigation water diverted from the river in the northern reach of this watershed is often only suitable for a limited number of crops, reducing harvesting options for local farmers. In the south, the Pecos feeds into the International Amistad Reservoir along the border with Mexico. During the 1990s, total dissolved solids concentrations in the reservoir rose as much as 10 mg/L per year and often approached the drinking water standard for potable water (1000 mg/L). Since this time, control efforts have focused on reducing the river's salinity, requiring the identification of salt sources. Hydrologic trend analysis and geochemical identification methods were used to determine these sources for the reach of the river between Red Bluff Reservoir and Brotherton Ranch. Between Red Bluff Reservoir and Coyanosa, flow diversions remove much of the flow that carries the salts, resulting in decreased salt loads, but also making the river more sensitive to evapotranspirative concentration. This sensitivity is evident in the river between Coyanosa and Girvin, where salinity begins to increase to the highest levels within the study area. However, salt loads increase here as well, indicating external salt sources as a contributor. The most substantial increase in bromide ions and the Br^-/Cl^- ratio appears between Grandfalls and Imperial, although no conclusion could be drawn regarding the identity of the source. The ratio continues to increase up to Girvin, where it appears that evapotranspirative concentration again has a significant effect. Here, several points drifted to the right of the groundwater mixing zones, plotting at values that were uncharacteristic of these sources.

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I want to thank Mom, Dad, Emmy, Mir, and Kim for all the love and support they provided along the peaks and valleys of progress, I couldn’t have done it without you and I’m eternally grateful for the last-minute assistance that you provided.

One final measure of gratitude goes out to all of my former roommates over the past two years – I apologize for any loss of sleep that may have occurred because of my late-night tirades regarding my unending frustration with whatever computer program I was working with that night.

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NOMENCLATURE

$\boldsymbol{a}$	conversion factor for each station as described in Table 4
$\boldsymbol{\alpha}$	conversion factor for each station as described in Table 5
$\boldsymbol{\beta}$	conversion factor for each station as described in Table 5
Br^-	bromide ion
$\boldsymbol{C_1}$	concentration of bromide or chloride ions at first endpoint
$\boldsymbol{C_2}$	concentration of bromide or chloride ions at opposite endpoint
$\boldsymbol{C_{mix}}$	concentration of bromide or chloride ions in the mixture along the mixing line
Cl^-	chloride ion
CWQMN	continuous water quality monitoring network
DO	dissolved oxygen
EPA	Environmental Protection Agency
FM	Texas Farm-to-Market Road
GIS	geographic information software
IBWC	International Boundary and Water Commission
L	salt load
m^3/yr	cubic meters per year
million m^3/yr	million cubic meters per year
mg/L	milligrams per liter
pH	percent hydrogen
ppm	parts per million

PSU	practical salinity units
Q	flow rate
SC	specific conductance
SH	Texas State Highway
SO4	sulfate
SWQMIS	Surface Water Quality Monitoring Information System
TCEQ	Texas Commission on Environmental Quality
TWDB	Texas Water Development Board
TDS	Total Dissolved Solids
umhos/cm	micro mhos per centimeter
µS/cm	microsiemens per centimeter
USGS	U. S. Geological Survey
V	endpoint water volume fraction
WID	Water Improvement District

INTRODUCTION

Situated within a basin of 10 million acres, which is at some points nearly 300 miles wide (Dearen, 1996; Gregory and Hatler, 2008), the Texas portion of the Pecos River is the only perennial river feeding both the arid land and ecological heritage of the area (Miyamoto et al., 2008). The basin encompasses much of the lateral state line that separates Texas and from southern New Mexico in its northern extent, and is bound by the Rio Grande River basin to the south, of which the Pecos itself is a tributary. Pioneers crossing the river spoke of the salty taste of the river (Lingle and Linford, 1961), but frequent accounts of both early settlers and their livestock drinking from the river suggest that the water could still support a healthy ecosystem that relied on fresh water (Hoagstrom, 2009). With soil types and a growing season well-suited to crop production under irrigation, many land speculators and farmers began developing the river for use, with the heaviest activity occurring from 1884-1914 (Thompson, 2009). Continued development and anthropogenic use of the river, along with natural phenomena, have altered the river’s flow and negatively affected water quality in most cases. This has led to declines in crop production and a general shift in the types of crops grown, and has had a profoundly negative effect on the regional economy, society, and ecology (Gregory and Hatler, 2008).

Though the river has always been salty, steadily increasing salinity over the past few decades has been a growing concern for reservoirs fed by the Pecos, especially the International Amistad Reservoir (Miyamoto et al., 1995). Here, during the 1990s inflow

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This thesis follows the style and format of the *Journal of Hydrology*.

salinity increased by as much as 10 mg/L per year, often reaching a level that threatens to surpass the secondary drinking water standard of 1000 mg/L (Miyamoto et al., 2006a). Several studies have identified possible sources of this highly saline water, with most accounts identifying evapotranspirative concentration of flows and intrusion of highly saline groundwater flows as the most likely possible sources. The likelihood of either process being more prevalent in an area is highly dependent on the location along the river and the condition of the flow there. The majority of these studies have been done using available historical flow and specific conductance data from the past 50 years from several sources including the Texas Commission on Environmental Quality (TCEQ), the U. S. Geological Survey (USGS), the International Boundary and Water Commission (IBWC), and the U. S. Bureau of Reclamation. Much of this data is only available on a limited basis and may have significant data gaps. However, in the last decade, several monitoring stations capable of recording both specific conductance and flow on a much more refined temporal scale have been installed and are currently recording this data, sometimes at intervals as frequent as 15 minutes. Four of these stations are located within the Texas portion of the Pecos River in Texas, and all but one are located at sites where routine bi-monthly stream monitoring takes place.

The purpose of this study is to integrate data from multiple sources for an assessment of the most likely contributors to elevated salinity within a critical stretch of the river. Analysis of the continuous monitoring data for flow and salinity will be paired with water geochemistry constituent data from a geochemical study conducted from 2008-2010 for 5 sites in the stretch of the river between the towns of Pecos and Girvin, which is considered to be the most critical section of the river with regards to salinity concerns based on analyses of specific conductance (Hoagstrom, 2009), salt fluxes and loads isotope analysis (Yuan and Miyamoto, 2008), hydrochemical processes (Yuan and Miyamoto, 2005), and biological effects imposed by invasive plant species (Hart et al., 2005). This combined dataset will be analyzed to obtain a better understanding of the water quality trends in the river and their dependence on location, seasonality, and even time of day. This should also give some indication to which sources have the most influence on the elevated salinity, specifically evaporative concentration of salt in flows delivered from upstream, re-entry of percolated water from upstream locations traveling as lateral flow, and from deeper saline groundwater intrusion arising from aquifer seeps. A comparison of the results from both the flow monitoring and water geochemistry datasets should provide a clearer perspective of processes within the watershed, and potentially pinpoint any obvious salinity sources within the monitored area.

Literature review

Continuous water quality monitoring

In 2001, the Texas Legislature tasked the TCEQ with monitoring water quality more rigorously in the Bosque River watershed. TCEQ responded by installing two continuous water quality monitoring network (CWQMN) stations in the Bosque River and two more in the Leon River (TCEQ, 2011b). These were the first of many similar stations to be installed in the following years, four of which were installed on the Pecos River. The first two stations were installed in Fall 2004 near the towns of Pecos and

Coyanosa. The third station was constructed in early winter 2006 near the Terrell/Val Verde County line on Brotherton Ranch and the fourth was installed near the town of Sheffield later in summer 2006 (TCEQ, 2011a). Per the elements outlined in TCEQ's Quality Assurance Project Plan currently in place for the CWQMN which covers all stations of this type which was approved in March of 2011, all four stations record data at 15-minute intervals for:

- Water temperature (surface)
- Specific conductance @ 25°C
- Dissolved Oxygen
- pH
- Gage height
- Water flow rate

The increased temporal resolution provided by this type of monitoring can provide researchers with a much more in-depth and accurate record of water quality trends than is possible with routine "grab" sampling techniques, which can take place as little as twice per year up to once a month for the Pecos basin, depending on the parameters to be monitored and the station in question. Continuous monitoring has the advantage of recording data at a much higher temporal resolution, allowing the sensors to detect exceedances of water quality criteria where typical routine sampling would have overlooked them. Examples of such situations are during extreme weather events and during nighttime hours when grab sampling done by personnel is unsafe or otherwise unfeasible. The broad scope and sheer amount of data points gained will give a much better account of water quality trends that can be used to make more applicable management decisions for the river. When maintained correctly, a network of these stations will allow regulatory and supervisory agencies to better organize and streamline their coordinated monitoring schedules (Rasmussen et al., 2003). The utility of these continuous monitoring stations, at one time also known as “automatic water quality monitoring” stations, was demonstrated even as far back as the mid-1960s when the Environmental Protection Agency (EPA) first began installing them. Many of these initial trials proved to be discouraging, due in no small part to the daunting task of recording and verifying the extensive dataset produced from such intense monitoring – a station taking data every hour for four parameters could record as many as 35,040 observations in a year (Hagan and Estes, 1975). Conversion to a computerized data collection system and advanced data sampling techniques have allowed for a much more manageable system, but stations still require frequent maintenance to prevent data “drift” caused by fouling of the sensors, corrosion in electrical components due to humidity and salt, and submersion of the sensors into the sediment bed due to siltation. Ideally, maintenance frequency should be based on a historical rate of re-failure. However, this can be difficult to standardize due to variations brought on by environmental factors. Additionally, DO, pH, and turbidity sensors are more prone to fouling than are specific conductance and temperature sensors. Some higher-end sensors come equipped with wiper or shutter mechanisms that can minimize fouling, but a maintenance window of a week or less may still be needed to ensure that the data stay as true to actual values as possible (Wagner et al., 2006).

Conductivity and specific conductance

In hydrology, conductivity is a measurement of how well water conducts electricity, which can be used as an indicator of the ionic salt content of the solution, although it cannot distinguish exactly which conductive materials are present and will instead respond to all conductive ions present in the same manner (Lehr et al., 2005). Conductivity measurements have standard SI units of Siemens/meter (S/m) and are dependent on both pressure (as a function of water depth) and air temperature (Horne and Frysinger, 1963), therefore it is important that steps are taken to ensure data comparability across large datasets that involve many sites. In order to do this, measurements are routinely taken at 1 ft, or 0.3 m, and conductivity is automatically adjusted to what the sample would be at a temperature of 25°C by the measuring instrument. This is known as temperature compensated conductivity, or specific conductance and is the basis for which conductivity is routinely reported in most water quality data (Ahmed, 2006). Field measurements of specific conductance are the most common means of collection, but laboratory analysis is also used, especially when done in conjunction with other water constituent tests. Instruments used in the laboratory may or may not standardize conductivity to 25°C, so if the instrument does not do so automatically, it is important that the samples are allowed to come to room temperature (23°C-27°C) before analysis or the appropriate temperature correction is made afterwards (USEPA, 2007).

Total dissolved salts and salt load determination

With regard to water quality, the conventional method of reporting salinity is normally practical salinity units (PSUs) or in terms of total dissolved solids (TDS), regularly reported in mg/L. However, specific conductance is by far the simplest, and consequently most common, means of measuring salinity within a waterbody. Therefore it is often necessary to convert conductivity to a concentration basis, such as the aforementioned TDS basis in mg/L, in order to maintain comparability with other studies. Whereas methods of measuring specific conductance in the field or in the laboratory are fairly similar, methods of measuring TDS differ between analysis types. Generally, a determination of total dissolved solids is done within a lab setting by first passing the sample through a very fine filter to remove suspended particulates. Then, the filtrate is heated to 180°C until evaporated, and the residue weighed with units usually reported as a concentration in mg/L (Eaton et al., 2005; USEPA, 1999). For this reason TDS was once known more commonly as total filterable residue, which is still occasionally used to indicate the parameter (USBR, 2009). TDS can also be determined in-field, but the measurement is often done with a conductivity meter and a suitable conversion factor, which in most meters is calculated by multiplying the conductivity (in µS/cm) by a factor of 0.65 to get TDS (in mg/L). However, this conversion factor is only a general estimation, and can vary widely in natural systems, normally within 0.3 and 1.00. It is highly dependent on ion variability and concentration, and an accurate estimation of a water body’s actual conversion factor can be determined more accurately by comparing conductivity and TDS readings from the same laboratory sample (Ahmed, 2006). This site-specific conversion factor is needed due to limitations on making the conversion based solely on conductivity and a “standard” conversion factor. If certain considerations are not made, an inaccurate estimation of TDS may occur. For instance, at concentrations lower than 10 µS/cm, the relationship between conductivity and concentration can be fairly linear. At these low concentrations, ions tend to behave independently and the overall conductivity should be equal to the sum of all the individual conductivities of the separate ions. As concentration increases above the 10 µS/cm threshold, so does ion-ion interaction. This interaction results in a relationship that becomes more and more non-linear with increases in concentration (Down and Lehr, 2004). Another reason that this conversion factor is needed is that conductivity measurements only detect charged ions that are mobile, whereas TDS measurements can contain neutrally charged particulates such as sugars, pesticide residues, and bacteria. Conductivity meters also cannot detect macroscopic particulates that are too large to move within the field (Ahmed, 2006). Inaccurate TDS readings can also occur if the solution reaches a maximum conductivity in the percent by weight concentration range. When this happens, conductivity will begin to decrease, even as TDS continues to rise, giving an underestimated field reading (Down and Lehr, 2004). Conditions like this may be why some inland lakes have TDS concentrations that exceed their conductivity (Mitchell and Prepas, 1990), which could yield theoretically possible conversion factors greater than 1.00.

Once the concentration data has been converted as needed, salt loads are then calculated as the product of flow and salt concentration (Biswas et al., 2008; Chafin and

Butler, 2002). Salt load values differ from concentration in that they provide an estimate of mass for salts within a river. This type of information is useful for situations where multiple inputs of salts are known to affect the river, and are instrumental to an understanding of the river's dynamics with regard to management decisions regarding mitigation of salt delivered to a specific location along the river. Knowing the salinity may be more important at this point of concern, but being aware of the conditions that led to that concentration require an analysis of the salt loads from several sources upstream of this point, so data for both concentration and salt loads can be equally important. Limitations for the calculation of loads can arise where flow is measured continuously but only infrequent instantaneous grab samples are available for salt concentration (Isidoro et al., 2003). This can be overcome buy the use of regression analysis methods, similar to those outlined by Hall (1970) and Kronvang and Bruhn (1996). These methods use the limited data from grab samples to estimate an empirical relationship between either flow and concentration or flow and salt load that can be used to fill in the gaps where continuous flow data do not have corresponding concentration or load data.

Ground water/surface water interactions and brine intrusion

Saline formations left from the Permian Sea lie underneath most of the land occupied by the present Pecos River Basin (USNRPB, 1942). When this inland sea evaporated, the remaining halite (NaCl) and gypsum ($CaSO_4 \cdot 2H_2O$)salts precipitated into the underlying bed, sometimes to depths reaching 300 m (Miyamoto et al., 2006b).

These formations can be linked to a number of brine aquifers in the region, and consequently the saline springs that result from upwellings of these stores of water (Hoagstrom, 2009). In the stretch of the river below the town of Coyanosa, intrusion of this saline water is believed to be the main reason that salinity levels increase so dramatically. Here, groundwater reports from the Texas Water Development Board (TWDB) show an increase in flow of 0.074 m^3/s between the station near the town of Pecos and the Grandfalls-Big Valley diversion dam, despite a lack of apparent irrigation return flow or visible creek inflow. A year later, from May 10-12, 1965, another low-flow study that also lacked noticeable surface water contributions was conducted with similar results. From FM 1053 to Buenavista the flow increased from 0.154 to 0.163 m^3/s, increased to 0.317 m^3/s as the river reached Horse Head Crossing, and then showed a slight increase to 0.326 m^3/s as it passed Girvin. Considering the lack of surface flow in both situations, the increase in flow was attributed to additions of groundwater through the river alluvium (Grozier et al., 1966). While evidence from these initial studies supports that there is in fact a strong link between brine intrusion and elevated salinity levels based simply on the flow data, additional studies were conducted soon after where other factors were explored. In a subsequent water delivery study conducted from April 17-19, 1967, researchers discovered that chloride concentration increased from 4420 to 6340 ppm between the FM 11 and FM 1053, despite a loss of 2.83×10^{-3} m^3/s in flow. This indicates that gains nearly equaled losses in the reach, but that incoming flows contained much higher concentrations of chloride than did the existing river waters. Though not as pronounced, this trend continued in the stretch from

Buenavista to Girvin, where gains equaled losses but chloride concentration increased from 5,450 to 5,820 ppm (Grozier et al., 1968). Though these studies support the theory that saline water intrusion is a significant salinity input, the sources of these intrusions are yet to be differentiated. One hypothesis is that the saline source present below Coyanosa is in fact the river itself. Further upstream, water seeps into the river bed where it is transported laterally through the soil strata, which eventually seeps back into the river bed further downstream below the town of Pecos (Belzer and Hart, 2007; Gregory and Hatler, 2008; Miyamoto et al., 2006b). When the second study was conducted in 1965 (Grozier et al., 1966), research participants observed no surface flow from Salt Creek, a Pecos tributary located just below the Red Bluff Dam known to contribute highly saline flows. The source of the incoming salts is believed to be a spring that originates from the Rustler Formation (Miyamoto et al., 2008). Seepage escaping the reservoir initially had a salinity of 7,200 mg/L, but was elevated to 13,860 mg/L by the time the flow reached the next monitoring station. Using only the limited subsurface

Table 1. Salt Creek water quality analysis

Sampling Event	Station	Chloride (mg/L)	Sulfate (mg/L)	SO_4/Cl^- Ratio	TDS (mg/L)
3/8/2005	Red Bluff	1887	1411	0.748	5187
	Salt Creek	4311	1965	0.456	10711
	Orla	4914	2335	0.475	11358
7/12/2005	Red Bluff	1689	1336	0.791	5320
	Salt Creek	5451	2966	0.544	14520
	Orla	1764	1429	0.81	5430

Data from Belzer and Hart (2007).

data provided by the study for this area and assuming subsurface flow from Salt Creek as the single external source of this increase, it can be estimated that about half of the resulting salt load at this point was generated from this intrusion, though as previously stated more information would be needed before any confidence in this hypothesis is credited (Miyamoto et al., 2006b).

The focus on Salt Creek continues in yet another study, done by Belzer and Hart (2007), which focused on tributaries and springs in the Texas stretch of the Pecos. The study consisted of two sampling events on March 8th and July 12th of 2005. In July, salinity in the main stem only rose slightly after the confluence with Salt Creek, but data from March showed the opposite with the main stem having a higher salinity after the convergence (Table 1). Since concentration is independent of both flow volumes, the lower concentration inflow from Salt Creek could not have been the only contributor to the increased salinity, and here again, intrusion of highly saline groundwater from other sources is suspected (Belzer and Hart, 2007).

Characterizing salt sources using geochemical relationships

Bromide ions, normally referred to by their periodic table designation Br^-, are a naturally occurring constituent that is present in very low concentrations in virtually all waters throughout the world. Bromide ion concentrations in water depend primarily on the geochemistry of the materials in which the water has come into contact, with most episodes of freshwater contamination leading to increased salinity probably occurring with a concomitant increase in bromide ions (Magazinovic et al., 2004).Though use of

Br^- analyses is becoming more prevalent, traditionally their use has been limited. This is likely due to the detection difficulties presented by naturally low concentrations and the absence of major health concerns associated with its presence (Davis et al., 1998). Br^- is often used in conjunction with chloride, or Cl^-, in analyses since both possess several traits that are characteristic of good water quality indicators. Both ions are chemically conservative inorganic constituents found naturally in water, where they are not affected by adsorption on organic and mineral surfaces, do not form insoluble precipitates in minerals, and do not participate in oxidation-reduction reactions (Fetter, 1993; Whittemore, 1988). In addition, both ions have been observed moving freely within the subsurface (Andreasen and Fleck, 1997). However, the conservative nature of Br^- does not hold true for all situations. Other studies have shown that the presence of clays and argillites can affect the Br^-/Cl^- ratio due to sorption of Br^- on these finer particles, and that that the presence of significant organic matter can also affect the ratio when Br^- is released as a product of the decomposition process (Fabryka-Martin et al., 1991).

Intrusion of seawater or other saline water is also a factor, as is dissolution in beds of evaporated seawater in areas once covered by ancient seas where the river passes through where the ratio may fall below that of seawater (Vengosh and Pankratov, 1998). As this seawater first began to evaporate from these seas, the residual water becomes saturated with halites (NaCl) causing them to precipitate, leaving residual brine that is concentrated with bromide ions and thus having a higher ratio of bromide to chloride ions. This is the case with the fossilized water often found in deep aquifers where water became trapped during rock deposition (Whittemore, 1995). These interactions can drastically alter the constituent concentrations and/or their respective ratios, as shown in Figure 1. Precipitation can also introduce new salts into a river basin, and analysis of this phenomenon has been included in several studies (Duce et al., 1965; Fabryka-Martin et al., 1998; Junge and Werby, 1958; Kennedy et al., 1979; Sollars et al., 1982). As water evaporates from the earth's surface (i.e., from open water, soil, surface interception, or through transpiration), the dissolved solids in solution are left behind, although it is possible for trace amounts of salts to exist within the evaporated portion. As the water vapor travels through the atmosphere towards its land destination, it takes with it any particulate salts that may be present in the air. These additions can come from

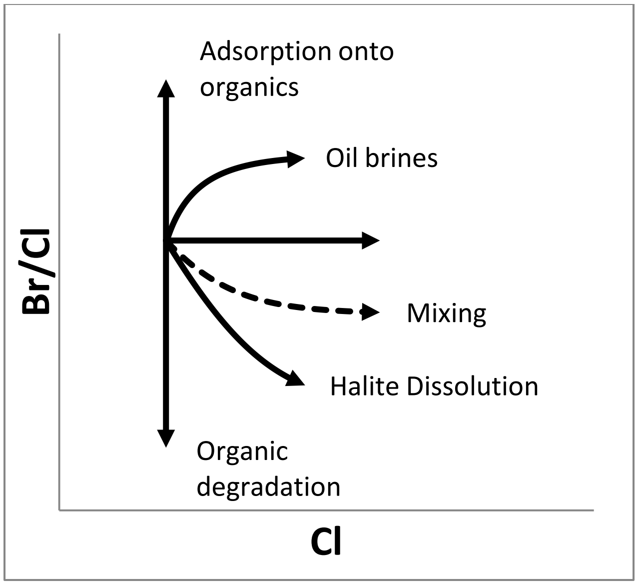

Figure 1. Conceptual depiction of the effects of various geophysical processes affecting constituent concentrations in surface waters and groundwaters in the Pecos Basin.

airborne concentrations present in the air above ocean water, or can come from Cl^- and Br^--enriched particulate matter such as dust from dry lake beds (Wood and Sanford, 1995). This can alter both the concentrations of specific ions and their ratios, the extent of which varies by location (Alcalá and Custodio, 2008). In general, availability of salt ions like Cl^- and Br^- in rainfall decrease with distance from the ocean, so deposition rates for the ions will be higher in coastal areas and lower as winds carry precipitation formations inland (Davis et al., 1998).

Though found in nature as components of ionic compounds, if only the ions themselves are numbered, chloride is the much more prevalent of the two, often by a factor of 300:1 (Stumm and Morgan, 1981). Though an older phenol red technique is still viable and sometimes used in analysis, ion chromatography is now the most common method used to detect bromide and chloride ions in collected water samples. This process separates the bromide and chloride anions using an array consisting of a guard and analytical column, a suppressor device, and conductivity detection equipment. Typically, a 2-3 mL partition of the original water sample is forced through the columns by a high-pressure pump. The constituents pass through the analytical column at different rates, which allows the detector to identify them as they pass by at different times (Haddad and Jackson, 1990; Pfaff, 1993).

A review of the literature on Br^- geochemistry offers several typical concentrations and Br^-/Cl^- or Cl^-/Br^- ratios of waters in various regions and substrates, but several studies have found that plotting a water source's Br^-/Cl^- ratio at a given Cl^- concentration is much more useful as a method of identification (Davis et al., 1998; Vengosh and Pankratov, 1998; Whittemore, 1984; Whittemore and Savage, 1980; Whittemore et al., 1980), mostly due to the large amount of variation present in measured values of bromide and their associated ratios that vary by location (Whittemore, 1988). This method can be used to identify several different sources of increased salinity within a watershed, including differentiating between shallow and deep basin brines (Nordstrom et al., 1989), oil field brines (Whittemore, 2007), failing septic systems (Katz et al., 2011), landfill leachates, animal wastes, and fertilizers (Mullaney et al., 2009).

In some cases where minor constituent data is scare or unavailable, relationships using ratios of major constituents may be used to supplement the analysis for further verification of sources. Another useful constituent used for comparison is sulfate (SO_4). Though not as conservative as bromide and chloride ions are when dissolved in water, sulfate ions are still relatively conservative alongside chloride ions and may also prove to be useful indicators where bromide ion data are scarce. However, if evapotranspirative concentration is likely a significant contributor to salt concentration increases for the study area, then the effects of calcium sulfate (anhydrite, or $CaSO_4$) precipitation/dissolution should be considered. Fractionation of sulfate begins when waters subject to evapotranspirative concentration begin to exceed the solubility of gypsum ($CaSO_4.2H_2O$), at which point the anhydrite precipitates while chloride ion concentrations continue to increase. The result of this process is a decrease in the SO_4/Cl^- ratio even as concentrations continue to rise (Whittemore, 1995). Though published values for this solubility limit plot within the range of 2000-2200 mg/L @

25 C, it is worth noting that these values are temperature-dependent. This is due to a loss of water molecules that evaporate from within the crystal lattice when heated, hardening the substance and making it less soluble (Bock, 1961). Limitations on the amount of calcium in the system that is available for use in the formation of anhydrite or gypsum can limit the amount of anhydrite or gypsum formation that occurs, but even when calcium is available, sulfate values can continue to escalate due to mineral processes like incongruent dissolution of anhydrite, sometimes as high as 12,500 mg/L when chloride ion levels in brines originating from evaporite dissolution beds reach concentrations approaching 45,000 mg/L (Whittemore, 1993).The presence of strong electrolytes in saline waters, namely NaCl, can also increase the solubility limit due to the ionic strength effect (Jurinak and Suarez, 1990). As electrolyte contents increase to more closely reflect those in seawater, solubility limits can be three times that of fresh waters (Shternina, 1960). Precipitated soluble chloride salts left behind in soils during dryer periods will be rapidly dissolved by infiltrating rainfall, which is likely to result in a spike in the SO_4/Cl^- ratio of the remaining salts after the rest have been carried away by runoff or percolated to groundwater (Whittemore, 1995).

Purpose

The purpose of this study was to determine where increased salinity in the Pecos River between towns of Pecos, TX and Girvin, TX is most greatly affected by evapotranspirative concentration within the river’s flow, and if there is also significant influence from groundwater entering the river, where this process dominated the increases from evapotranspirative concentration. This will be accomplished by using these methods:

1) Evaluate continuous and routine monitoring data to determine if TDS, flow, and salt loads can be used effectively to indicate potential salt sources.
2) Evaluate bromide, chloride, and sulfate ion relationships from the geochemical study sites to determine their viability as indicators of groundwater influence on salinity within a critical segment of the Pecos River.

The intent of this study is that its findings will be used to assist local officials, citizens and the scientific community in making informed management decisions on how best to manage and control salinity sources within the Pecos River basin so that both current and future users of this resource may be provided with a reliable water source that is of acceptable quality for their needs.

STUDY AREA

The Pecos River enters Texas from its border with New Mexico along the 32° N parallel, where the river feeds into Red Bluff reservoir. From here, the river winds through Texas for 640 km, forming a boundary for seven Texas counties before cutting through Val Verde County and feeding into the Rio Grande near the town of Langtry. Along the way, the river encounters several different landscapes, including semi-arid grasslands, irrigated croplands, and sparsely vegetated desert. Once the river passes Interstate Highway 10 (I-10), the cut of the river begins to run deeper, eventually making its way through deep canyons as it approaches the Rio Grande. Below Red Bluff, the Pecos River has a drainage area of 45,505 km^2, with the majority of its tributaries

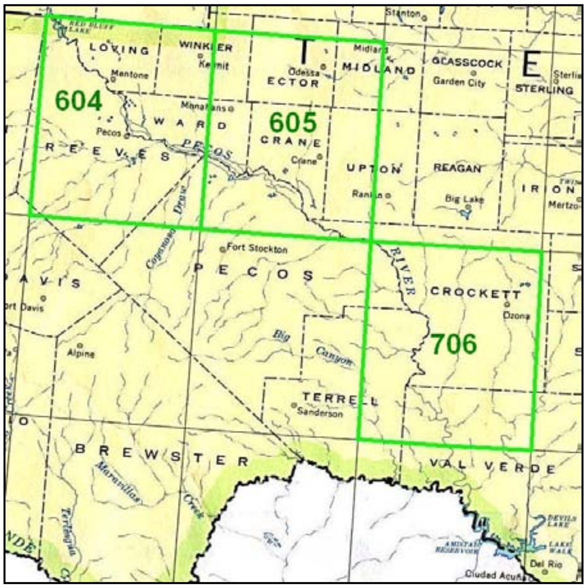

Figure 2. Location of three latitude-longitude quadrants surrounding the Pecos River used by the Texas Freshwater Inflows Program for generation of climatic data presented in Table 2.

feeding in from the western banks. These tributaries flow from the most mountainous region of Texas, known as the Trans-Pecos (Hayter, 2001; Miyamoto et al., 2006b). There is only one perennial stream feeding the Pecos River between Red Bluff and Girvin, known as Salt Creek (or Screwbean Creek). Less frequent flows from tributaries like Salt Draw, Barilla Draw, and Toyah Creek enter the river below the town of Pecos. Coyanosa Draw is the most significant tributary between Red Bluff and Girvin. Though flow is normally minimal or even nonexistent, heavy storm events can produce flows as high as 5 m^3/s. Comanche Creek is a spring-fed tributary that flows into the Pecos River just north of the town of Girvin. Before heavy pumping from wells began, flows from these springs helped Comanche springs contribute as much as 35 million m^3 of water per year, but this has been reduced to less than 2 million m^3/year since the 1950s (Brune, 2002; Miyamoto et al., 2008).

Climate

Climatic data for the Texas Portion of the Pecos River Basin were obtained from the Texas Freshwater Inflows Program, which is managed by the TWBD and analyzes climatic data in quadrants formed by one-degree changes in latitude and longitude. Quadrants in the study area spanned from 30°N to 32°N and from 101°W to 104°W (Figure 2), with an average annual rainfall of 25 cm from Red Bluff Reservoir to the Pecos County line (Quadrant 604) from 2008-2010. Annual rainfall increases to about 45 cm in Crockett and northern Val Verde Counties (Quadrant 706) (Table 3). Rainfall is

Table 2. Annual precipitation and lake evaporation for three quadrants surrounding the Pecos River between Red Bluff Reservoir and Brotherton Ranch, 2008-2010.

Quadrant	**604**	**605**	**706**	**604**	**605**	**706**
	Precipitation (cm)			Lake Evaporation (cm)		
Jan	0.94	1.30	2.57	8.14	8.26	8.64
Feb	1.03	0.98	1.78	10.29	10.97	13.26
Mar	0.58	0.92	3.32	13.81	14.34	15.32
Apr	0.97	1.63	4.96	15.42	17.20	17.98
May	1.18	2.34	3.84	17.34	19.47	19.88
Jun	3.67	7.73	6.69	16.86	20.65	20.71
Jul	8.03	7.63	6.99	12.19	16.29	19.45
Aug	2.96	4.91	3.58	11.55	15.37	24.11
Sep	3.65	4.55	5.52	8.91	13.05	16.67
Oct	1.80	2.42	3.97	11.68	14.84	13.32
Nov	0.08	0.04	0.46	9.03	10.21	9.39
Dec	0.43	0.63	1.07	9.33	10.68	10.12
Annual:	**25.33**	**35.08**	**44.75**	**144.55**	**171.35**	**188.84**

Texas Freshwater Inflows Program data, 2008-2010 (TWDB).

highest from May to September, which coincides with the Southwest United States Monsoon Season, also known as the Mexico Monsoon. Increased flow from the monsoonal rainfall is further supplemented by snowmelt from the Pecos' mountainous headwaters in May and June (Yuan and Miyamoto, 2008). Lake evaporation in this part of the basin is much higher than precipitation, totaling to 145 cm for the year in Quadrant 604 and increasing to 189 cm annually in Quadrant 706. The deficit between precipitation and evaporation creates a high potential for evaporative losses in the basin that are a source of increased salt concentrations in the river.

Geology

Soils along the Pecos River are alluvial deposits from the Pecos, Patrole, Toyah, Gila, and Arno series. All have textures ranging from silty to loamy, except for the Arno series, which is montmorillonitic clayey and has low permeability. Near Red Bluff Reservoir, the soil strata close to the river consist of well-drained gypsic soils, usually of the Reeves and Holloman series. Downstream from Red Bluff, soils on the east riverbank are mostly calcareous soils formed over caliche. These moderately permeable soils are from the Simona and Sharvana series. On the opposite side of the river in Pecos and Reeves Counties, soils near the river are predominantly Aridisols like the Del Norte, Nikel, and Reakor series or calcareous silty clay loams like the Hoban series. Overall, soil permeability is high throughout the watershed, with percolation losses as high as 40% according to studies done by Grozier (1966), with similar results reported by a field study done by Clayton (2002). High percolation losses and low rainfall within the watershed means that surface runoff received by the river is very low. Once the river enters Texas, USGS flow stations estimate flow gains of about 175 million m^3/yr, according to historic records before 1937. This amounts to about 1.4% of the total precipitation in the basin at that time (Miyamoto et al., 2006b).

Groundwater

The principal aquifer in the region is the Cenozoic Pecos Alluvium aquifer (Figure 3), formed from infiltration of runoff within the basin. Roughly 90% of groundwater used within Pecos, Ward, and Reeves counties comes from this aquifer

(Miyamoto et al., 2008). According to information from the groundwater database managed by TWDB, average depth to the water table near the river (within 5000 m) south of Red Bluff was about 9 m, but that average decreased to 4.5 m near Coyanosa, sometimes decreasing to 3 m at times. The Rustler Formation rests below the Cenozoic Pecos Alluvium in its southernmost extent into Texas (Figure 4). The northernmost extent of this aquifer resides in New Mexico, where it is believed at least a portion of the halite dissolution brine affecting high salinities in the Pecos River is coming from (Richter and Kreitler, 1991). One location where these brines are entering the river is

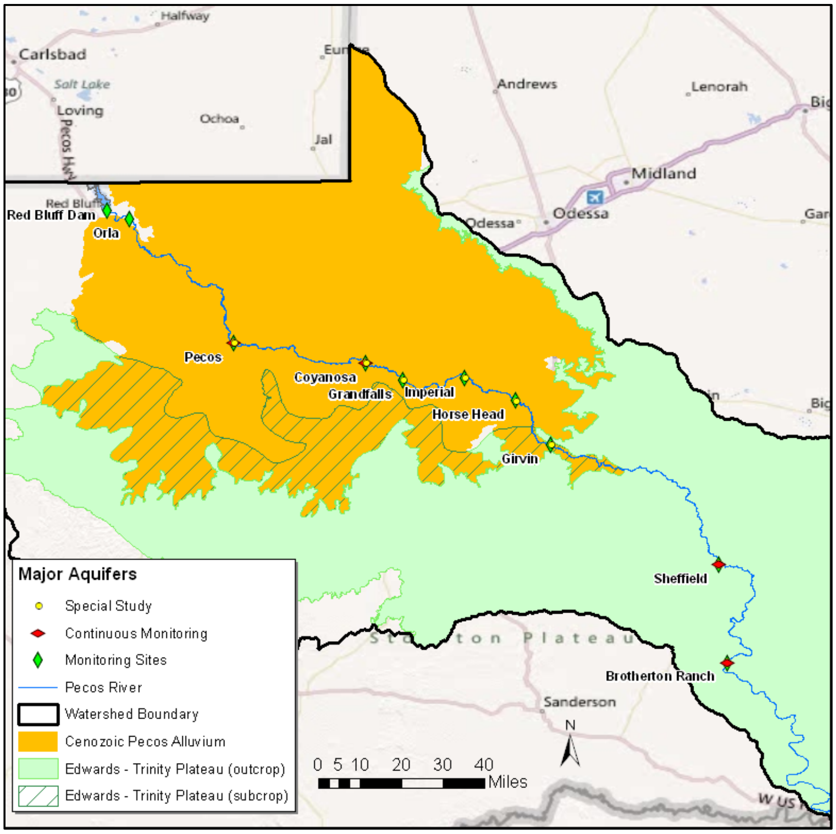

Figure 3. Locations of major aquifers underlying the Pecos River.

near Malaga Bend, where it was identified as the main source of salts to springs in the area. Here, an upward movement of saturated brine between the boundary between the Salado Formation and the Rustler Formation is thought to be the cause of high salt contents in the springs (Havens and Wilkins, 1979). The Capitan Reef Complex exists about 730-1100 m below the surface and intersects the river between the Coyanosa and Imperial monitoring stations in Pecos and Ward Counties. Due to high salinities, water from wells drilled into the Complex is rarely used for drinking, instead being used for oil recovery operations. The Dockum Group underlies Ward, eastern Reeves, and Northern

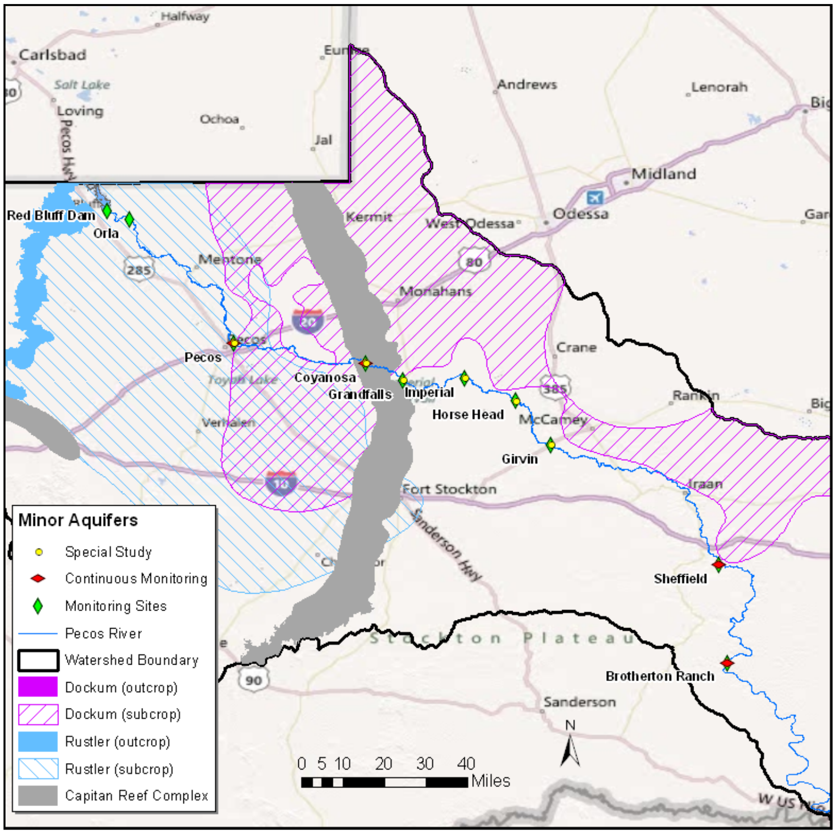

Figure 4. Location of minor aquifers underlying the Pecos River.

Pecos Counties. Waters produced from the aquifer are fresh to moderately saline and are often interconnected with waters from the Pecos Alluvium.

Development, use, and impacts

Evaporative losses from Red Bluff to Girvin are supplemented by high groundwater recharge potential and surface diversions for irrigation water (Grozier et al., 1966; Slade et al., 2002). Several of these diversions projects date back to the late 1800s and early 1900s, and those that were not abandoned eventually evolved into seven irrigation districts that managed how water was delivered to farmers. To supply this irrigation water to these projects, a series of small dams were installed, most of which were in place before construction on Red Bluff Dam began in 1934 (Jensen et al., 2006; USNRPB, 1942). It is also believed that introduction of saltcedar into the Pecos River basin is also contributing to flow reduction. Because of their dense root system, these plants were ideal for stream bank stabilization and were introduced by early settlers of the region with this intent (Jensen et al., 2006; Nagihara and Hart, 2007). Within a few decades, it became clear that these plants were more detrimental to the watershed than beneficial. Saltcedar is capable of growing in very dense stands - 700-1000 plants per hectare under optimum conditions – which can choke out natural vegetation. The plant is also capable of pulling salts from subsurface layers, which it then delivers to the surface through leaf litter. Storm runoff from this litter and direct deposition of the litter into the river will increase salt loading, negatively impacting the river even further. Early pioneers that traveled through the basin described the river as being dangerous to cross due to its swift current and sandy substrate (Leftwich, 1957), and was even navigable by boat from its confluence with the Rio Grande to a point somewhere near the New Mexico state line (Pope, 1854). However, the combined effects of flow impounding, irrigation diversions, groundwater overdraft, and invasive plant introduction have reduced flows to the point where navigability in this reach is no longer possible (except for south of the city of Sheffield), and crossing the river is no longer much of an issue (Dearen, 1996).

METHODS

Sampling sources and data management

A survey of previously collected data and conducted studies were synthesized to plot the most recent trends in salinity on the Pecos, with the study focusing on the critical area between the towns of Pecos and Girvin. Previous studies were reviewed for background information on perceived salinity sources, and what sorts of efforts have already been conducted in order to identify specific sources or their locations. The

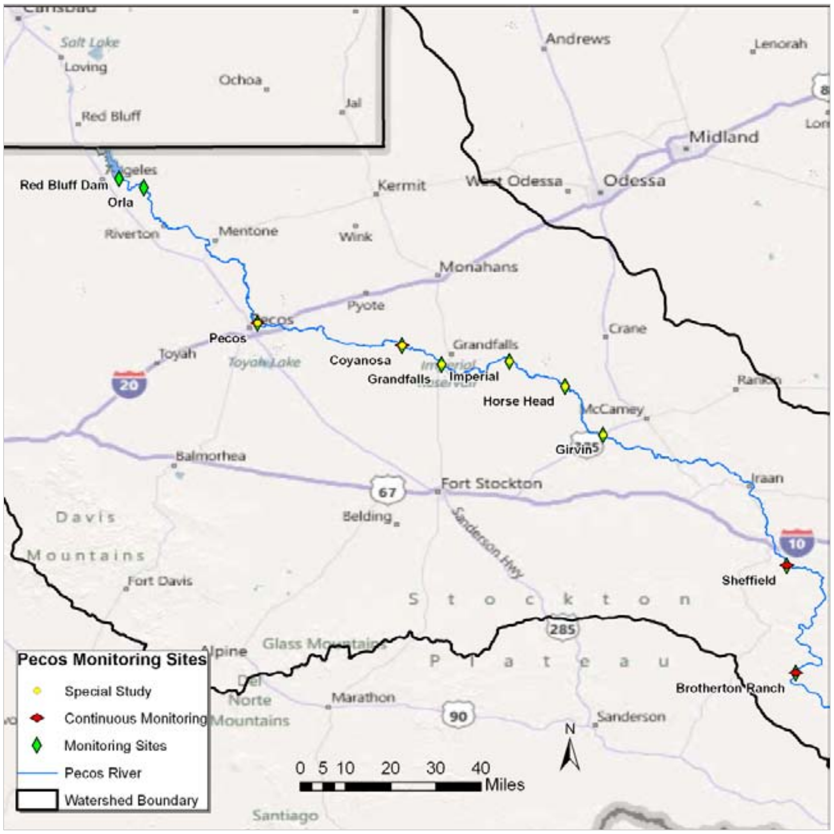

Figure 5. Monitoring stations on the Pecos River. These 10 stations provided various forms of surface water quality data for the salt load and geochemical analyses.

principal data source that was used came from 10 stations (Figure 5) maintained by the Surface Water Quality Monitoring Information System (SWQMIS), which is operated under the jurisdiction of the Texas Commission on Environmental Quality through EPA's Clean Water Act funding. Sampling done during a routine monitoring trip to a SWQMIS station consists of both on-site and laboratory measurements. The in-stream measurements are taken with a sonde, which is a submersible sensor that gives real-time measurements of water quality parameters such as temperature, conductivity, dissolved oxygen, pH, and turbidity. The remaining water quality parameters are usually determined by "grab" samples. The collector fills sample containers with water from the perceived "centroid of flow" (the geometric center of the river's cross-section) in the middle of the river. At least four different containers are filled, with additional containers added as needed, depending on the analysis required by each project's sampling plan. As mentioned earlier, this project utilizes data from several sources, each with their own set of sampling needs, so there is no set sampling plan particular to this analysis. For the sake of accessibility, samples are taken where the river crosses or at least comes near to a public access point whenever possible, usually at a bridge or low-water crossing where a public road intersects the river. Where this is not possible, agreements with private landowners are sought in order to allow samplers access to critical points along the river where public access in not available. In the case of road bridges, upstream sampling is preferred, if at all possible, to avoid any direct interference that may result from any anthropogenic activity (i.e., illegal dumping), as well as from any avian or other wildlife that use the bridge as refuge and deposits fecal material in and around the creek on a regular basis (TCEQ, 2008). All of the stations used in this analysis are taken at such bridges, with exceptions being the Red Bluff Reservoir sites and the stations at Horse Head Crossing and Brotherton Ranch, where access is gained from roads that pass near these points in the river, but do not cross. All but two of the stations exist north of the Girvin station, and are displayed sequentially, along with significant stream inputs and irrigation diversion canals in Figure 6. Records from the routine monitoring visits coordinated under this monitoring effort supplied all of the specific conductance, TDS, bromide, sulfate, and chloride ion data as well as the majority of the surface water flow data. Surface flow data was not recorded by TCEQ at the Pecos station, so data from the USGS flow gauge (located 90 m downstream) were used in lieu of the TCEQ flow data and were considered comparable after a side-by-side analysis of data where both entities recorded flow. Flow data was obtained for Red

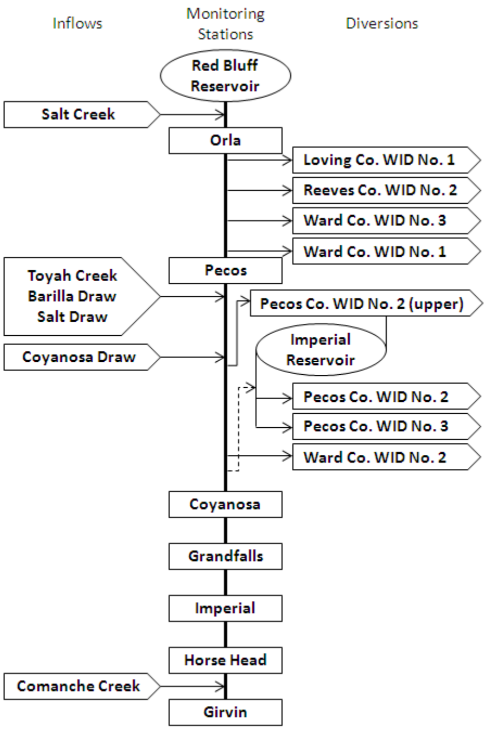

Figure 6. Inflows, outflows and stations along the Pecos from Red Bluff Reservoir to Girvin. Inflows and diversions occur sequentially as indicated by their position on the main stem. The dotted line indicates a "cut-around canal" that bypasses Imperial Reservoir as an alternative means of routing water to Pecos Co. WID Nos. 2 and 3 (adapted from Thompson (2009) and Miyamoto (2008)).

Bluff Reservoir in the form of daily release records from the Red Bluff Water Power Control District. Flow data for the seven active irrigation diversion canals is also maintained by the District, but the latest available data details average yearly flow volumes from 1991-2001 (Table 3). Two of these irrigation diversions, known as Pecos Co. Water Improvement District (WID) Nos. 2 and 3, are fed by water flowing from Imperial Reservoir, which receives water from an upstream diversion north of Ward Co. WID No. 2. Although the diversion point is technically north of the Pecos/Reeves county line and located in Reeves County, it is traditionally referred to as “Pecos WID No. 2 (upper)." Any attempts to accurately measure diversions are further complicated by a “cut-around canal” that bypasses Imperial Reservoir completely to provide an alternative source of inflow for Pecos Co. WID Nos. 2 and 3 that is not governed by reservoir release. This diversion is located below Ward Co. WID No. 2, as indicated by the dashed line in Figure 6. Due to this complex series of canals with alternative diversion points and a storage basin, attempting to use the diversion flow data in water balance equation calculations may produce inaccuracies from station to station. Table 3 also lists the contributions of tributaries that exist between Red Bluff and Girvin. The data for many of these annual mean flows are estimated from USGS observations made during the mid-

Table 3. Annual mean flows for tributaries of and diversions from the Pecos River between the towns of Pecos and Girvin.

a) Annual mean flow from tributaries to the Pecos between Red Bluff and Girvin.			b) Average diverted flow for irrigation canals along the Pecos, 1991-2001).	
Tributary	Collection Period	Flow (million m3/yr)	Irrigation Canal	Flow (million m3/yr)
Salt Creek	1939-1957	3.30	Loving Co. WID No. 1	0.01
Salt Draw	1939-1945	3.94	Reeves Co. WID No. 2	0.65
Toyah Creek	1939-1945	4.25	Ward Co. WID No. 3	3.44
Barilla Draw	1924-2010	0.69	Ward Co. WID No. 1	12.92
Coyanosa Draw	1964-1977	9.30	Ward Co. WID No. 2	7.27
Comanche Creek	1956-1964	1.65	Pecos Co. WID No. 2	3.67
			Pecos Co. WID No. 3	3.92

Source: USGS and Red Bluff Water and Power Control District data, adapted from Miyamoto et al.(2006b)

1900s, with the exception of the flow at Barilla Draw, where monitoring resumed in 2002.

A portion of the constituent analysis requires groundwater data, so well water data for bromide, chloride, and sulfate ions was obtained from the groundwater database maintained by the TWDB. A useable dataset was created combining the database entries for the constituents of interest with well location files plotted with ArcGIS, which is a geographic information software (GIS) package. Consideration of interaction with deeper basin waters was taken into account by using well readings from the underlying aquifer. Based on the results of multiple geologic surveys compiled by Ashworth (1990) and Boghichi (1999), the Cenozoic Pecos Alluvium Aquifer is the most likely candidate for exchange with the river within the study area, and thus is the focus of the groundwater analysis in this study. While previous studies have used comparative data from other sites anywhere as far as 8 km to 19 km away (Whittemore, 1995), selection of wells for proximity in this analysis was restricted to wells drilled into the Pecos Alluvium within 3.5 km of the river (Figure 7). Each of these well sites is given its own

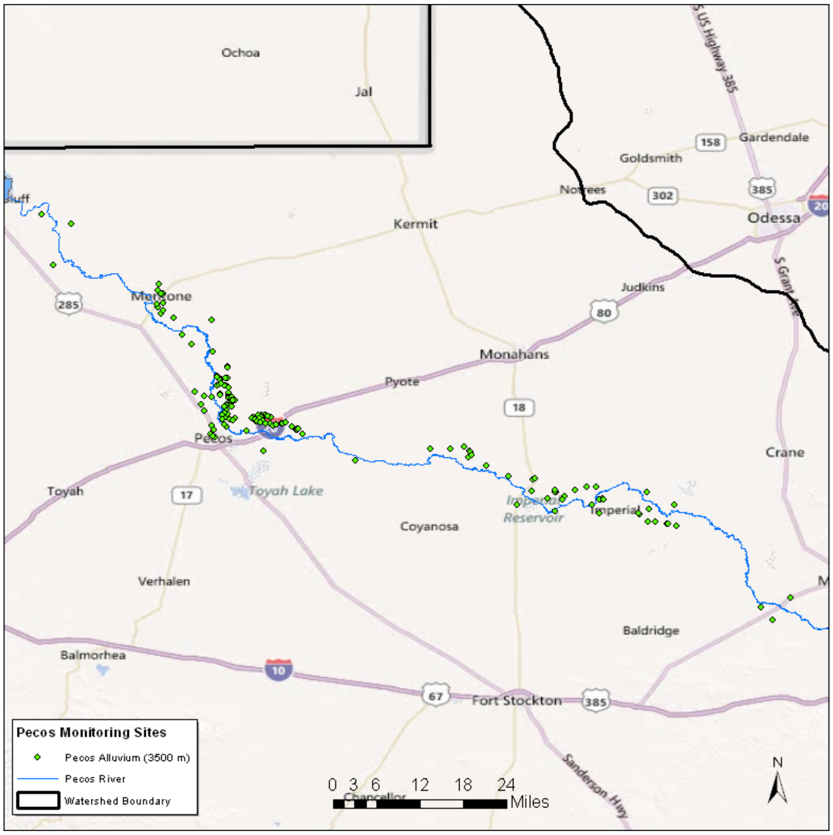

Figure 7. Groundwater data used in geochemical analysis. Brown dots identify wells within 3500 m of the Pecos River that represent intrusion from deeper basin water flowing from the Pecos Alluvium Aquifer.

unique well number in the statewide database, and this was used to link the well's spatial information to its respective constituent data from two databases maintained by the TWDB. The first database holds the more commonly measured constituent data that are routinely measured when a well water sample is retrieved, such as conductivity, TDS, chloride ion, sulfate ion, bicarbonate, fluoride ion, etc. The second database includes data that is not routinely collected, as in this case where bromide ion samples were needed as part of the 2008-2010 geochemical study. Chloride and sulfate ion entries from the common constituent database that linked up to an entry from the spatial dataset were isolated in a new table. This link is established by the TWDB-designated well number, and the two tables are merged using the table joining functions provided in ArcGIS. This process was repeated for the bromide ion data in the infrequent constituent table. The two constituent tables were then combined and simplified within Excel to create a comprehensive dataset that includes all the relevant bromide, chloride, and sulfate ion data for each of the wells represented in the spatial dataset.

Flow, salinity, and salt load dynamics

Fluctuations in flow and salt load values, along with changes in salinity, can be used to help make broad conceptual determinations of salt sources in the river. This is

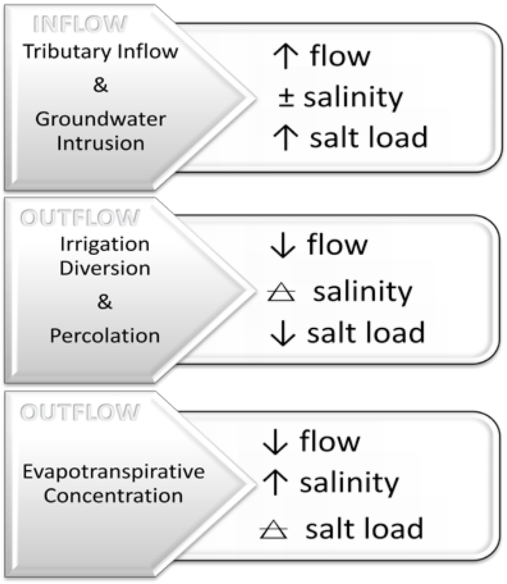

Figure 8. Conceptual outlay of river processes and their effect on trends. Directional arrows indicate increases (↑) or decreases (↓), ± symbols indicate that the change is dependent on the nature of the inflow, and △ indicates no change.

accomplished by analyzing the trend changes and referencing them to the stream processes described in Figure 8. Several of the processes have similar effects on trends, such as inflow processes from river tributaries and intrusion from saline groundwater seeps and springs. While these two processes will always contribute to increases to the flow and salt load, their effect on the concentration of salts depends on the inflow's concentration with respect to that of the Pecos itself. As inflow volumes get larger, the salinity of the Pecos will have a corresponding larger increase or decrease if the inflow is more or less saline, respectively. This process may also include return flows related to municipal treated wastewater and septic system outflows to the river via surface and groundwater, but due to the low population of the area this was not a major consideration of the study. Where water is taken from the river, the trend dynamics tend to differ based on the specific process, and fall into two categories. First, there are terrestrial outputs, which include water diverted for irrigation and percolation of water through the bed and banks of the river into shallow groundwater or deeper aquifer storage. These "takes" from the river will always result in a decrease in flow and salt load, but will normally have no corresponding change in salinity, unless heavily influenced by differences between the passing waters and the underlying soils that either limit or accelerate the exchange. This is especially important with regard to SO_4 exchange, which was discussed earlier in the text. Atmospheric draws on river resources related to evapotranspirative concentration, however, remove only water from the river. This means that there will be no impacts to the actual salt load, but the salt concentration will continue to increase as evapotranspiration utilizes more water within the system.

To ensure comparability with salinity information in existing studies, the conductivity data was converted to a concentration basis. This is also necessary for calculations of salt loads, which will be covered in the next section. In order to make this conversion, a conversion factor for each station was calculated using data from days where measurements for both conductivity and TDS were taken at the same time during routine sampling trips. Each station yielded approximately 9-30 data points during the 5-year assessment period from 2006-2010 (Table 4). Due to the small sample size found at many of the sites, a regression analysis was used to check for statistical validity and significance. The strength of the relationship is shown by the correlation coefficient, ***r***. This relationship was established using regression analysis on the conductance vs. TDS relationship with zero as the y-intercept. Correlation coefficient values were >0.9 in most cases, with the Pecos station being the only exception, reporting at ***r*** = 0.89. At the Pecos station, the specific conductance data used for the relationship was taken from the

Table 4. Correlation between specific conductance (@ 25˚C) readings and total dissolved salts (TDS) at Pecos River gauging stations.

Station	**a**	**n**	**r**
Red Bluff	0.69	11	0.97
Orla	0.70	22	0.97
Pecos	0.73	22	0.89
Coyanosa	0.70	21	0.99
Girvin	0.71	21	0.98
Sheffield	0.69	9	0.92
Brotherton Ranch	0.63	9	0.97

a = EC to TDS conversion factor
n = number of samples
r = coefficient of correlation

continuous monitoring station because no manual gathering of specific conductance data was recorded during the routine monitoring visit when the water sample used for TDS analysis was taken. After a review of values for both the routine and continuous conductance measurements at all other Pecos River stations, it was discovered that the data from the CWQM was consistently lower than the routine readings, sometimes differing as much as 1000-2000 uS/cm when readings crept into the > 15,000 uS/cm ranges. Upon closer analysis, it was discovered that this effect was cyclical, corresponding with the bi-weekly maintenance visits when the sondes were exchanged. This indicates that sensor fouling is occurring between maintenance visits, which was previously only thought to affect biological sensors like those used for detection of dissolved oxygen. Table 4 indicates that the conversion factor for the Pecos station is

Table 5. Empirical coefficients used to describe the relationship between flow and salt loads.

Station	α	β	n	r
Red Bluff	20.85	0.98	1826	0.99
Orla	22.25	0.97	18	1.00
Pecos	20.16	1.00	926	0.99
Coyanosa	21.78	1.00	1336	0.92
Girvin	79.12	0.76	20	0.97
Sheffield	21.53	1.03	883	0.96
Brotherton Ranch	4.01	1.18	698	0.86

α and β = salt load prediction equation coefficients
n = number of samples
r = coefficient of correlation

0.73, which is higher than the factors for the adjacent upstream and downstream stations. The higher value here acts a calibration to account for the use of the continuous collection specific conductance values in the analysis since they tend to be lower than in-stream routine analysis values. TDS was calculated from the specific conductance using the following equation:

$$TDS_1 = a \cdot SC \tag{1}$$

where

a = conversion factor for each station as described in Table 4

SC = original specific conductance value from SWQMIS data (uS/cm)

TDS_1 = resulting daily total dissolved solids concentration from SWQMIS data (mg/L)

The factor converts the conductivity data into a concentration-basis measurement, mg/L, allowing for calculation of salt loads when flow data is available. The calculation here is nearly as simple:

$$L_1 = TDS_1 \cdot Q_1 \tag{2}$$

where

TDS_1 = daily total dissolved salts concentration from SWQMIS data (mg/L)

Q_1 = daily flow value from SWQMIS data(cfs)

L_1 = daily salt load produced by SWQMIS data (tons/day) with unit conversions for liters to cubic feet (1 ft^3 = 28.3168466 L) and for milligrams to tons (1 short ton = 907,184,740 mg) and then multiply 86,400 seconds/day in order to arrive at a daily salt load in tons (tons/day).

Once corresponding daily flow and salt load values were calculated from the SWQMIS data, these data were used to develop a second site-specific relationship for predicting salt load based on flow, which will be used to develop yearly estimates for flow and salt loads at each station. This allows for calculation of salt loads at times when records of flow exist, but concentration data may not be available. This occurs often at many of the stations along the Pecos River, as is the case with the more complete flow records found at several USGS flow stations. For the Pecos River, most USGS flow measurements are taken near the same road crossings as SWQMIS stations, many of which are less than 40 m of one another. The two notable exceptions are the Pecos stations which are separated by 90 m and at Girvin, where the USGS flow gauge is located 6580 m north of the SWQMIS station at the road crossing. Flow is not monitored by the USGS at Horse Head Crossing, but is analyzed at the same location as SWQMIS is on Brotherton Ranch. Though these stations have been monitoring continuous flow with limited interruption from August 2007 to present at most stations, only data from 2008-2010 were used to calculate the daily flow volumes and salt loads because they were the only solid years of data from January to December. The relationship used to relate this flow data to salt loads is as follows:

$$\boldsymbol{L_2 = \alpha \cdot Q_2^{\beta}} \qquad \textbf{(3)}$$

where

Q_2 = daily flow value from USGS data (million m^3/day)

α, β = conversion factors for each station as described in Table 5

L_2 = daily salt load estimated from USGS flow data and conversion factors (tons/day)

The equation effectively takes the flow and salt load trends, sets them as equal, and then uses the TDS concentration to explain the difference. The variation between flow and salt load induced by the TDS concentration values is represented by two conversion factors of a power function. This function can be applied to flow data with no accompanying salt concentration data to obtain an estimated salt load. This approach was used because each site possessed valuable data that the other did not. SWQMIS stations had many flow data gaps, but the USGS stations did not record the conductivity or concentration data needed for salt load calculation. By applying the relationship developed from SWQMIS flow and salt load data to the more complete flow data from the USGS stations, the positive aspects of both datasets were taken advantage of, providing a more useful composite as the result. Strong correlation (>0.80) was observed at all stations, but was lowest at Brotherton Ranch. This station is near the stretch of the Pecos where water quality begins to improve, so freshwater inputs such as the influx of freshwater from Independence Creek may be destabilizing the flow-salt load relationship. Once the daily values were obtained for the daily flow and salt loads at each station, estimation of yearly values for each was calculated by summation of the daily values. Understanding the effects of the value of β coefficient can provide additional insight into the flow-salt load relationship. When salt loads increase proportionally alongside increasing flow, the coefficient $\boldsymbol{\beta}$ is equal to one, indicating a relationship with the salt load that is linear. A $\boldsymbol{\beta}$ -value less than one at a station indicates that at that point in the river, increases in salt loads are suppressed with respect to increases in flow, so salt loads increase at a slower rate than flow during high flow events. At stations where $\boldsymbol{\beta}$-values are greater than one, the salt load is amplified as flows increase, and salt loads increase faster than flow during high flow events.

Analysis of geochemical relationships

As was the case with the methods used in the flow/salinity/salt load analysis, both trending and correlation/regression analyses were used to develop the results of the geochemical analysis. Some relatively straightforward downstream trends were first developed to provide an account of individual constituent concentrations for bromide, chloride, and sulfate ions and their corresponding ratios as they varied from station to station downstream. Values used in the determination of average values for the constituents at each station were estimated using all available data. For the routine monitoring stations, the 2008-2010 data from the geochemical study was used. The bromide, chloride and sulfate ion data found for Red Bluff Reservoir were not analyzed as part of this study. Bromide ion values were collected in 2004 and 2005, but sulfate ion data for the reservoir have been recorded since 1972 with some frequency. Once average values were calculated for each station, they were plotted together to observe any corresponding changes between individual constituents and their corresponding ratios. Using this method, trends can be analyzed for effects of evapotranspirative concentration, especially with respect to sulfate and chloride ion relationships where precipitation and dissolution processes come into play. Whereas the SO_4/Cl^- relationship is most useful for identifying where increasing concentrations caused primarily by evapotranspiration processes are prevalent, the relationship between bromide and chloride ions will prove more useful for identifying areas where additional inputs of salts from either river return flow or seepage from the Pecos Alluvium aquifer is occurring.

The second portion of the geochemical analysis focuses on using Br^-, SO_4 and Cl to characterize sources of saltwater intrusion at each of the five special studies sites between Pecos and Girvin. These concentrated saltwater sources may be from halite dissolution beds within aquifers, waters under intense evapotranspiration pressure, or from anthropogenic sources such as oil field brines from mismanaged or forgotten drill sites with failing well casings, all of which exhibit different geochemical ratio patterns. These patterns were depicted previously in Figure 1. When values for Br^- and SO_4 constituents are available, preferably from as many of the previously mentioned sources as possible in addition to the data from the geochemical study, a ratio is calculated and plotted with respect to each value's corresponding Cl^- concentration. Once plotted, mixing curves that bound the data of interest can be developed using the following equation:

$$C_{mix} = C_1 V + C_2 (1-V) \tag{4}$$

where

C_1 = concentration of bromide or chloride ions at first endpoint
C_2 = concentration of bromide or chloride ions at opposite endpoint
C_{mix} = concentration of bromide or chloride ions in the mixture along the mixing line
V = volume fraction of first endpoint water

This formula incorporates the observed chloride ion values here for the C_1 and C_2 values, forming the list of x-values for plotting the comparative analysis. Corresponding y-values are calculated in a similar manner, but both the bromide and chloride ion (or sulfate and chloride ion) data are used for the $\boldsymbol{C_1}$ and $\boldsymbol{C_2}$ values to plot the points since the y-axis represents the ratio (either Br^-/Cl^- or SO_4/Cl^-) between the two. The x-y calculation process is done twice to form the upper and lower bounding areas or mixing curves, essentially connecting four points: 1) high and 2) low ratio values at a low Cl^- value for the fresh water endpoints, and 3) high and 4) low ratio values at a Cl^- value on the high chloride ion end of the graph representing the source of brine concentration. These two mixing curves create a “mixing zone” bound on the top and bottom by the curves and on the left and right by horizontal limits (Figure 9). The upper and lower limits represent the end members at varying chloride ion contents as described previously, while the left and right limits represent the end members with the same chloride ion content, to some degree limited by water chemistry. This mixing zone

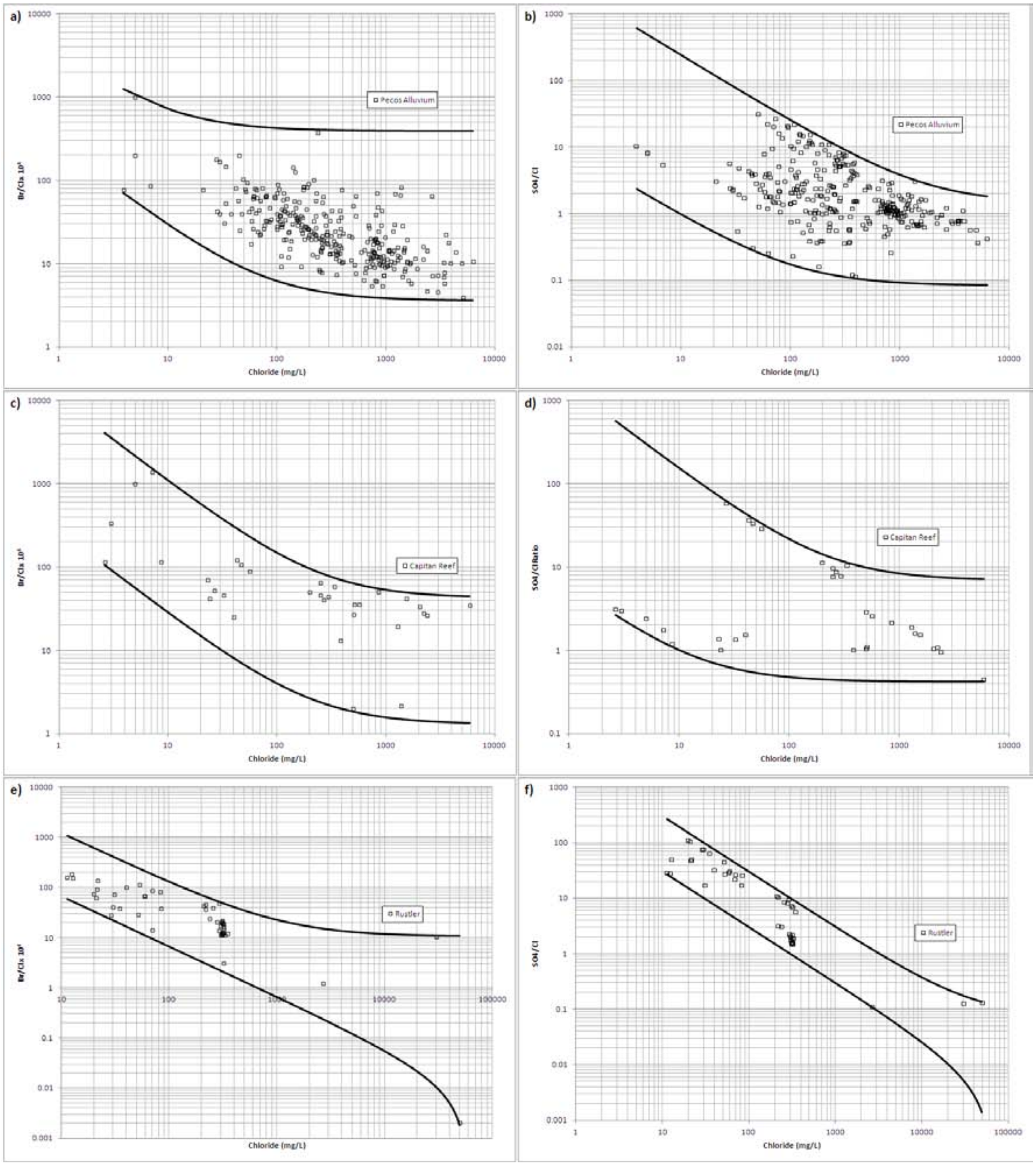

Figure 9. Geochemical mixing curves for three aquifers that underlie the Pecos River. Br$^-$/Cl$^-$ vs. Cl$^-$ graphs are in the left column, SO$_4$/Cl$^-$ on the right for the Pecos Alluvium aquifer [a) and b)], Capitan Reef Complex [c) and d)], and the Rustler Formation [e) and f)].

represents all possible values for either ratio at a given Cl$^-$ concentration that arise from sample variation and error (Knuth et al., 1990; Whittemore, 1988). For this study, accepted values for total analytical error are used, with 3% for chloride ions, 4% for sulfate ions, and 5% for bromide ions. According to Whittemore (2004), these values were determined through the use of periodic sampling where samples were spiked with a known standard and then analyzed. This was done in cooperation with the U.S. Geological Survey as part of their Standard Reference Water Program. These percentages were added to each of the two endpoints of the upper curve and subtracted from the two endpoints on the lower curve to account for the additional area on the graph. Once they have been fully developed and plotted along with the river measurements, the mixing zones can be used to compare data from site to site to see where they may overlap with corresponding well data from any of the three aquifers. If values plot within the zone delineating values for the Pecos Alluvium aquifer, then it is likely that the river has a strong hydrologic connection with the aquifer and likely exchanges water with it through interconnections between subsurface river flows and shallow groundwater. If points fall outside of the Pecos Alluvium mixing zone, then it can be assumed that other drivers of increased salinity are active within that reach of the river, such as deeper basin brines from the Rustler or Capitan Reef formations. If values maintain a constant ratio at increasing concentrations and do not diverge from the point pattern displayed by the station immediately upstream, it can be determined that processes related to evaporative concentration are prevalent. The influences will be evaluated on a site-by-site basis to assess the dominant processes affecting the river between each station. These results will then be compared to results from the trend analysis to establish any overlapping or contradicting indications of increased salinity.

RESULTS AND DISCUSSION

Flow, salinity, and salt load dynamics

The graphs presented in Figure 10 compare salt load values observed in the river at each station to the daily salt loads that were predicted using the relationship and coefficients described in Table 5. Overall, the equations were able to accurately depict the series of summer peaks and the winter low-flow periods reflected in the observed values from the four continuous stations. For these continuous stations, the site-specific equations yielded very similar visual results, with mean percent error between predicted and observed loads shown in Table 6. Predicted loads at the Pecos station had a mean arithmetic error of 15.63%, despite having nearly identical trends and rarely over- or under- predicted the salt load when compared to the observed values. A closer look at the data revealed that much of this error was attributed to differences at extreme values, so an analysis of the geometric mean was also carried out. This reduces the bias from extreme high and low values, which tend to inflate error measurements. Using this method, the geometric mean error at Pecos was reduced to 7.87%. Equations for the other three stations (Coyanosa, Sheffield, and Brotherton Ranch) were very reliable when predicting most high load peaks and their immediate troughs, but had some difficulty with predicting peak loads at the Sheffield and Coyanosa stations during the summer of 2009, usually resulting in an over-approximation of the peak value. In contrast, the equations also tended to under-predict values during extended periods of lower salt loads, as seen during month of December 2007 at all three stations as well as in the Spring of 2009 at the Coyanosa station. Mean error estimates for Coyanosa were

16.06% and 16.6% respectively, while geometric mean error values for Coyanosa and Sheffield stations were both near 10.37%. Downstream at Brotherton Ranch, mean error rose to 18.55% while geometric mean error fell to 9.19%. The comparison of the downstream increase in mean error values to the mid-stream peak in geometric mean error values indicate that error at extreme values was more prevalent at Brotherton Ranch. However, this may be attributed to the larger data gaps present in the Brotherton Ranch dataset. In the case of the standard routine stations, mean error tended to increase downstream. At Red Bluff, mean error was only 9.77% but quickly increased to 17.94% just downstream at Orla. The Girvin site had the highest mean error for the study area at 20.22%. Geometric mean error values for the three stations were 4.54%, 10.67%, and 14.99% respectively, also indicating increasing error with distance downstream. For the routine sites, most errors were under-predictions at peak values, specifically at all stations in the summer of 2010. Overall, the equations for all stations were able to predict the peaks and troughs from high salt load events at each station uniformly from one end of the project area to the other even when no observed values were available, as seen in the predicted salt load peaks from the late summer to winter in 2010.

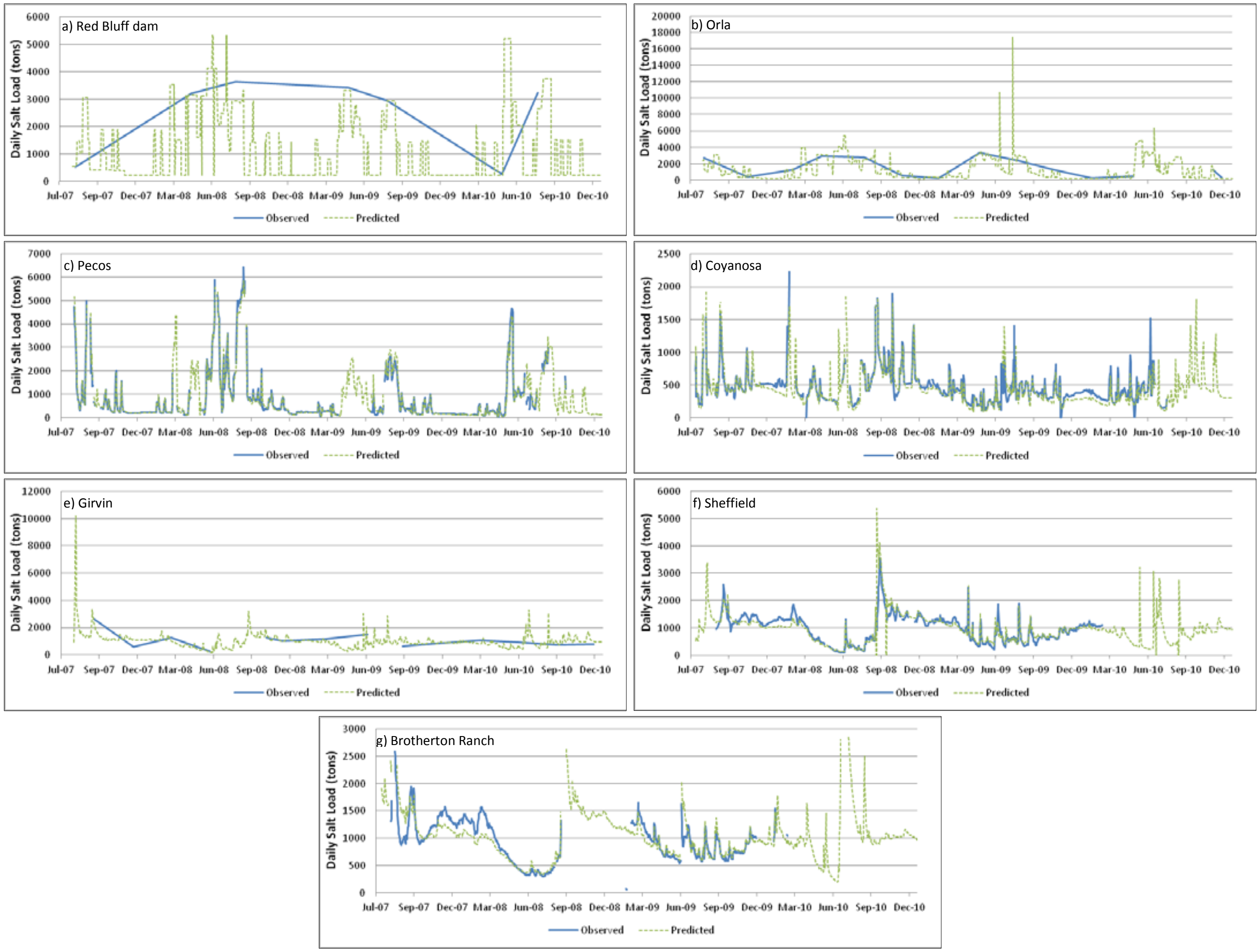

Figure 10. Plots of daily salt loads observed in-stream vs. salt loads predicted via the flow-salt load relationship from July 2007-December 2010.

Figure 11 shows the average yearly trends for flow, salinity (in terms of TDS), and salt load for the seven stations included in this part of the study for the years 2008-2010. These were the three years of continuous streamflow that had very few or no interruptions at all in the USGS flow analysis used. The significant decreases in both net flow (70%) and the salt loads (65%) from Red Bluff Reservoir to Coyanosa can be explained by water diversions to the seven active irrigation canals operated between the two locations, in addition to the losses to evapotranspiration and percolation.

Table 6. Average percent error between observed and estimated salt loads for stations on the Pecos River in Texas.

		Mean % error	
Station	n	Aritmetic	Geometric
Red Bluff	10	9.77%	4.54%
Orla	13	17.94%	10.67%
Pecos	796	15.63%	7.87%
Coyanosa	854	16.06%	10.37%
Girvin	12	20.22%	14.99%
Sheffield	758	16.60%	10.37%
Brotherton Ranch	553	18.81%	9.19%

n = number of samples. Stations with low-n values indicate standard routine collection rates, high-n (>500) indicated continuous collection stations.

Some early estimates of percolation losses indicate that as much as 40% of the water released from the Red Bluff infiltrates into shallow groundwater stores between the reservoir and Pecos, with an additional 12% being lost to percolation from Pecos to Grandfalls (Grozier et al., 1966). This percolation loss does not occur immediately, however. As indicated earlier in the study done by Grozier (1966), the river seems to be receiving a significant amount of seepage water from the reservoir, which may partly explain the increase in flow volumes from Red Bluff to Orla in Figure 11, an average yearly increase of 3.65 million m^3/yr. The majority of this may be coming from

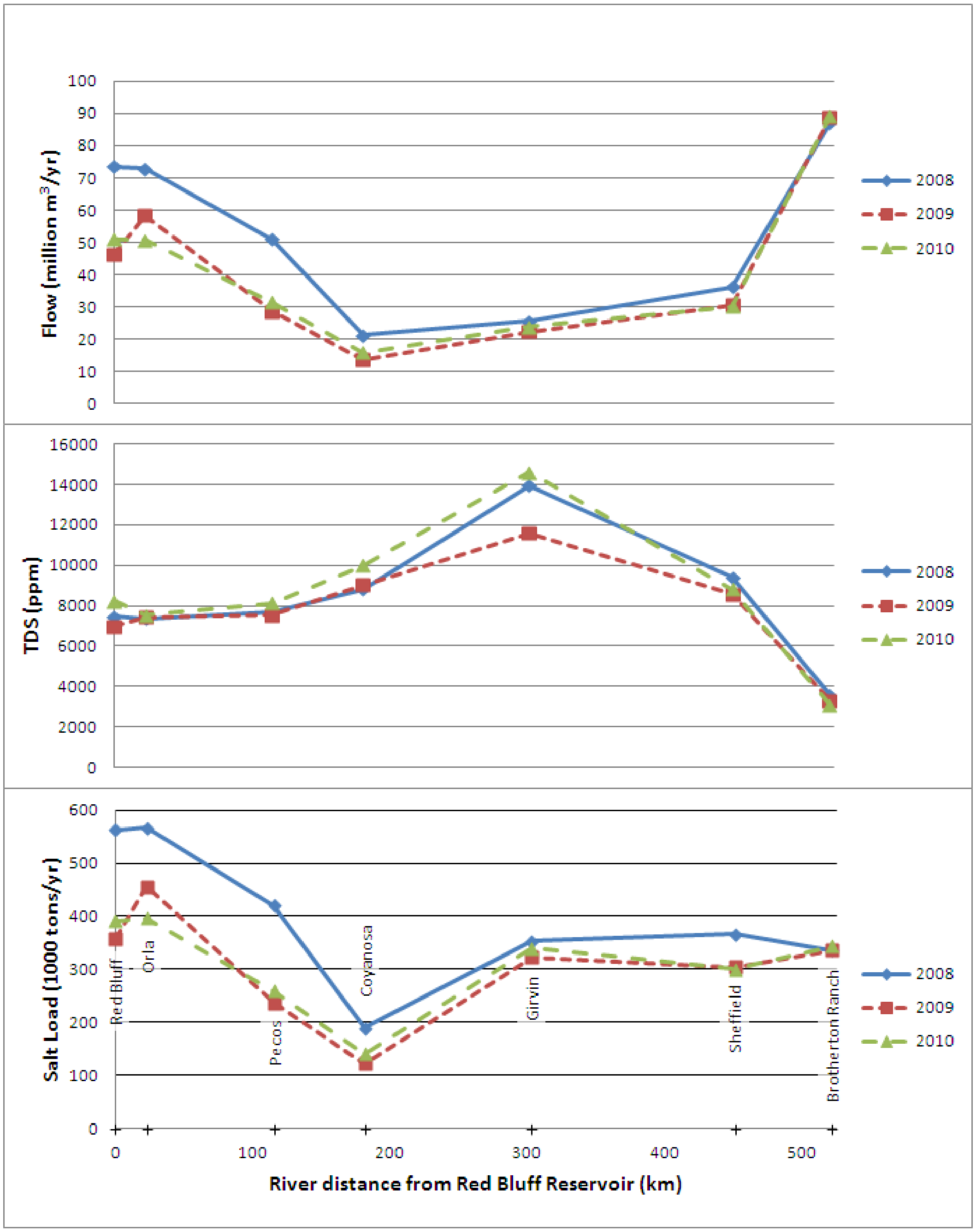

Figure 11. Flow, Salinity, and salt load trends for stations on the Pecos River in Texas.

Salt Creek, which contributes about 3.3 million m^3/yr, as estimated by Miyamoto et al. (2008). However, it is admitted that this estimate is very “crude” since the USGS data used to make the estimate is from 1939-1957. The net effect of diversion and continued percolation on flow increases the river’s sensitivity to evapotranspiration. Therefore, the net decrease for both flow and salt load suggests that the salinity increase between the Red Bluff Reservoir and Coyanosa is mostly driven by evapotranspirative concentration, recalling the process dynamics outlined earlier in Figure 8. This is not the case for the river between Coyanosa and Girvin. Here, an average net increase of 7 million m^3/yr, which is equal to about 12% of the initial discharge from Red Bluff, brings with it a 43% increase in salinity from 7,776 to 13,370 ppm (Table 7). This net increase includes diversions to two more irrigation canals in this reach, which route away a combined 7.59 million m^3/yr from the river, and according to estimates made by Miyamoto et al. (2008), the only surface water inflow is from Comanche Creek, with a yearly input of 1.65 million m^3/yr. This change signals the highest salinity increase for the entire Texas portion of the Pecos, and is likely due to a combined effect of continued evapotranspirative concentration and the river’s increased sensitivity to any intruding groundwater due to the low flow through this area.As a result of this highly saline intrusion, salinity finally peaks at Girvin before significant freshwater inputs begin to have a dilution effect on the trend soon thereafter. The largest of these freshwater

Table 7. Average values for flow, salinity, and salt load for stations along the Pecos, 2008-2010.

Station	Flow (million m^3/yr)	Change in Flow (million m3/yr)	TDS (ppm)	Salt Load (1000 tons/yr)	Change in Salt Load (1000 tons/yr)
Red Bluff	57		7568	437	
Orla	61	4	7447	473	36
Pecos	37	(24)	7776	306	(167)
Coyanosa	17	(20)	9286	151	(155)
Girvin	24	7	13370	339	188
Sheffield	32	8	8928	324	(15)
Brotherton Ranch	88	56	3339	339	15

inputs is from Independence Creek and the Caroline Springs that are its source, which occur 21 km (17 miles) south of the Sheffield Station. However, significant dilution occurs upstream of the confluence with Independence Creek, indicating that waters with much lower salt concentrations are entering the river between Girvin and Sheffield as well. As indicated in Figure 11, salt loads tend to remain stable from that Girvin onward. As salinity falls once the river passes this station, the higher flow brings with it a greater amount of salt (though at a lower concentration), so the salt loads begin to stabilize to around 300,000-350,000 tons/yr from Girvin to Brotherton Ranch.

Analysis of geochemical relationships

Trends for average values of the separate constituents and their ratios are displayed in Figure 12. All three constituents of interest continued to increase downstream through the study area, although at different rates, as depicted by their

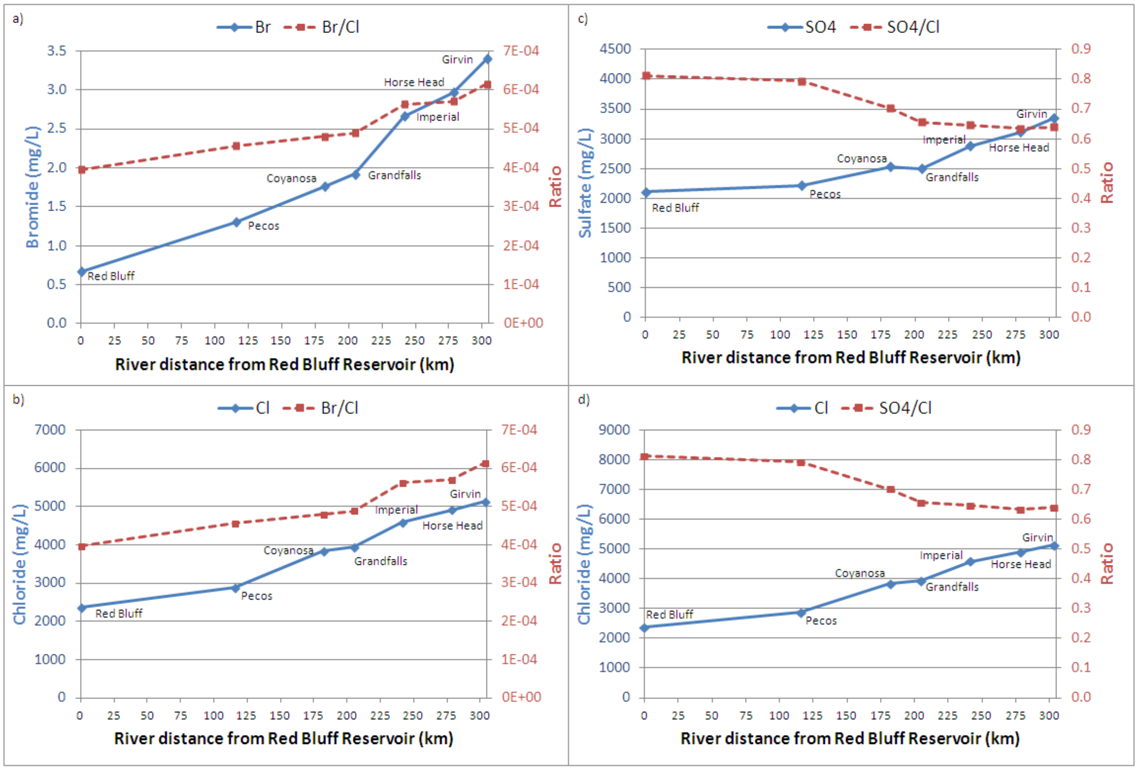

Figure 12. Average trends for geochemical relationships from data collected through 2010. Constituent (Br$^-$, SO4, and Cl$^-$) are represented by solid lines with values read from the left axis, while the ratios (Br$^-$/Cl$^-$, SO4/Cl$^-$) follow the dashed lines with values read from the right axis. All trends progress downstream from left to right as indicated by the station names on the x-axis.

respective ratios. The relationship between bromide and chloride ions was a direct relationship, as was the relationship of the Br$^-$/Cl$^-$ ratio to the amount of chloride ions in solution. Though both bromide and chloride ions rose continuously from station to station, bromide ions tended to increase at a faster rate proportional to chloride ions. This causes an increase in the Br$^-$/Cl$^-$ ratio, as seen in Figure 12, where the Br$^-$/Cl$^-$ ratio rose steadily from one end of the study area to the other. This indicates additions of water from an outside source with different levels of chloride and bromide ions (tributary inflow or groundwater intrusion) almost throughout the entire course of the river. The greatest increase in the ratio corresponds with the highest increase in bromide ions relative to chloride ions, which occurs between Grandfalls and Imperial. As mentioned earlier in the text, higher bromide ion contents are often associated with deeper basin brines left behind when inland seas begin to evaporate. Should these brines find a way to get closer to the surface and mix with the waters of the Pecos, the Br^-/Cl^- ratio would increase. This is likely the case for the stretch of the river between Grandfalls and Imperial, indicating a greater influence from another salt source, which may likely be from deep basin sources. This hypothesis falls in line with one made by Armstrong and McMillion (1961), citing the possibility of a geologic fault near the intersection of Texas SH-18 and FM 1450, which is located between the two stations. No further details about the fault's orientation, length, or depth are given in the text. The suspected fault line is depicted by the black marker in Figure 13. It is here that

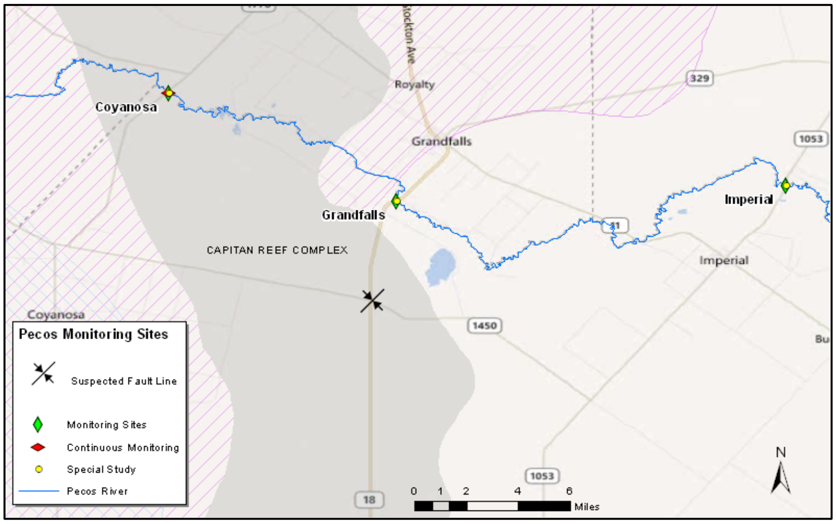

Figure 13. Location of suspected fault line near town of Grandfalls.

Armstrong and McMillion suggest that the higher TDS content present may be from brines upwelling from deeper aquifers such as those from the Capitan Reef and mixing with waters from upper formations that frequently interact with the river. This possibility is further explored in later sections of this study. Another possibility is that the increases came from surface runoff and additions from tributaries. This is a certainly a possibility, but as discussed earlier, historically only about 1.4% of precipitation ever contributes to flow gains in the part of the basin that sits in Texas (Miyamoto et al., 2006b). Therefore it is unclear to what extent tributary inflow may play in these contributions, considering that Barilla Draw was the only tributary being monitored north of Girvin during the course of this study. Another conclusion would be to assume that evapotranspirative concentration was the sole source of the increase in Br^-, Cl^-, and SO_4, and no new sources were entering the river. If that were the case, the Br^-/Cl^- ratio would not fluctuate significantly and, in theory, would graph as a flat line if analyzed from station to station. However, depending on how sampling is conducted, differences in time of sample retrieval, uneven mixing within the water flow, and due to analytical error, there will likely always be some fluctuation from station to station even if no new salt source is affecting the river. The only section of the river where this occurred was between the Imperial and Horse Head stations, where the average ratio stabilizes between 5.66×10^4 and 5.72×10^4 as depicted in graphs (a) and (b).

Whereas Br^-/Cl^- values are an important tool in determining external salt sources, the SO_4/Cl^- ratio is particularly useful for determining where evapotranspiration is having a significant effect on the river. Here, there was also a direct relationship between the base constituents, but in this case the SO_4/Cl^- ratio declined with increasing chloride ion concentration. In graph (c) of Figure 12, the SO_4/Cl^- ratio is already on a slight decline south of Red Bluff, even as sulfate values increase from 2105 mg/L to 2215 mg/L as the river reaches the town of Pecos. This is succeeded by a steeper decline in the SO_4/Cl^- ratio observed between Pecos and Grandfalls, where sulfate increases to 2503 mg/L. This decline corresponds with increases past critical concentrations for sulfate, at approximately 2000-2200 mg/L where the solubility of gypsum has been exceeded and sulfate begins to precipitate from solution, which is the river in this case. This slows addition of new sulfate into the stream as chloride continues to increase unabated, resulting in a dramatic decrease in the SO_4/Cl^- ratio. Despite the inhibitive nature of this reaction, addition of new sulfate is not completely deterred, as shown in graphs (c) and (d) in Figure 12 where sulfate concentrations continue to rise to an average value of 3345 mg/L at Girvin. This is due in part to limitations on the amount of calcium in the system that is available for use in the formation of anhydrite or gypsum, but incongruent dissolution is likely occurring as well. Both of these phenomena allow sulfate values to continue to escalate. Ionic strength effects related to high levels of halite dissolution salts (NaCl-) may also play a role, but since this is not likely to affect waters until they reach concentrations closer to that of seawater, any influence from this is not as likely as from the other reactions.

With the basic trends established for the constituents at each station, there is now an opportunity to learn more about the behavior of the constituents on an event basis, which may provide more clues about where certain salinity sources have the most influence. Using the same symbol to represent one sampling event, the fluctuations in Cl^- and the Br^-/Cl^- ratio can be observed as they progress further downstream. Data points at the upstream stations displaying much more erratic and non-linear patterns than those of the downstream stations, as shown in the graph analysis in Figure 14. Aside from a few straying values, observations from the Pecos station had much more similar chloride ion contents clustered within a thinner horizontal range, but showed much more range with respect to the Br^-/Cl^- ratios. The result was a more vertical distribution, shown as the cluster of points seen at the center of the graph for the first station. With progression downstream, behavior from station to station began to change. At first glance, it would appear that the consolidation of points that occurs at Coyanosa gave way to a linear transition with a slow upward drift of each point towards both higher Cl^- and Br^-/Cl^- values (from the center left of the graph towards the upper right). However, a closer look at each value's movement reveals that this shift may not be the same for all sampling events. Many of the outlying values seen at the Pecos station shifted to the cluster at Coyanosa (points E, H, and N) while others moved to the opposite side of the plot (points B, M and Q). After Coyanosa, this behavior was still displayed by most of the points even as the range for Br^-/Cl^- values was reduced from $1.42 \times 10^4$and 10.2×10^4 to $4.8 \times 10^4$and 7.96×10^4 and chloride ion range expanded from 670 mg/L and 3780 mg/L to 2080 mg/L and 8050 mg/L. The end effect can be described as a moving "cloud" of points with varying individual movement within, but an overall shift towards higher chloride ion contents and Br^-/Cl^- ratios at Girvin as the cloud spread to the right along the x-axis. The erratic behavior of the points from station to station, especially from

Pecos to Coyanosa, may be linked to the three irrigation diversions present between the two stations. Yearly flow decreases by 54% from 37 to 17 million m^3/yr (Table 7), of which 14.86 million m^3/yr (40%) is diverted to irrigation, based on 1991-2001 data (Table 3). Halving the flow leaves the remaining water roughly twice as sensitive to concentration changes incurred from incoming subsurface salt sources due to proportionality. In other words, it is assumed that the rate of inflow from the subsurface source would not differ under either high or low flow conditions. This may explain why point movements decrease as flows increase, even as ratios and chloride ion concentrations increase downstream.

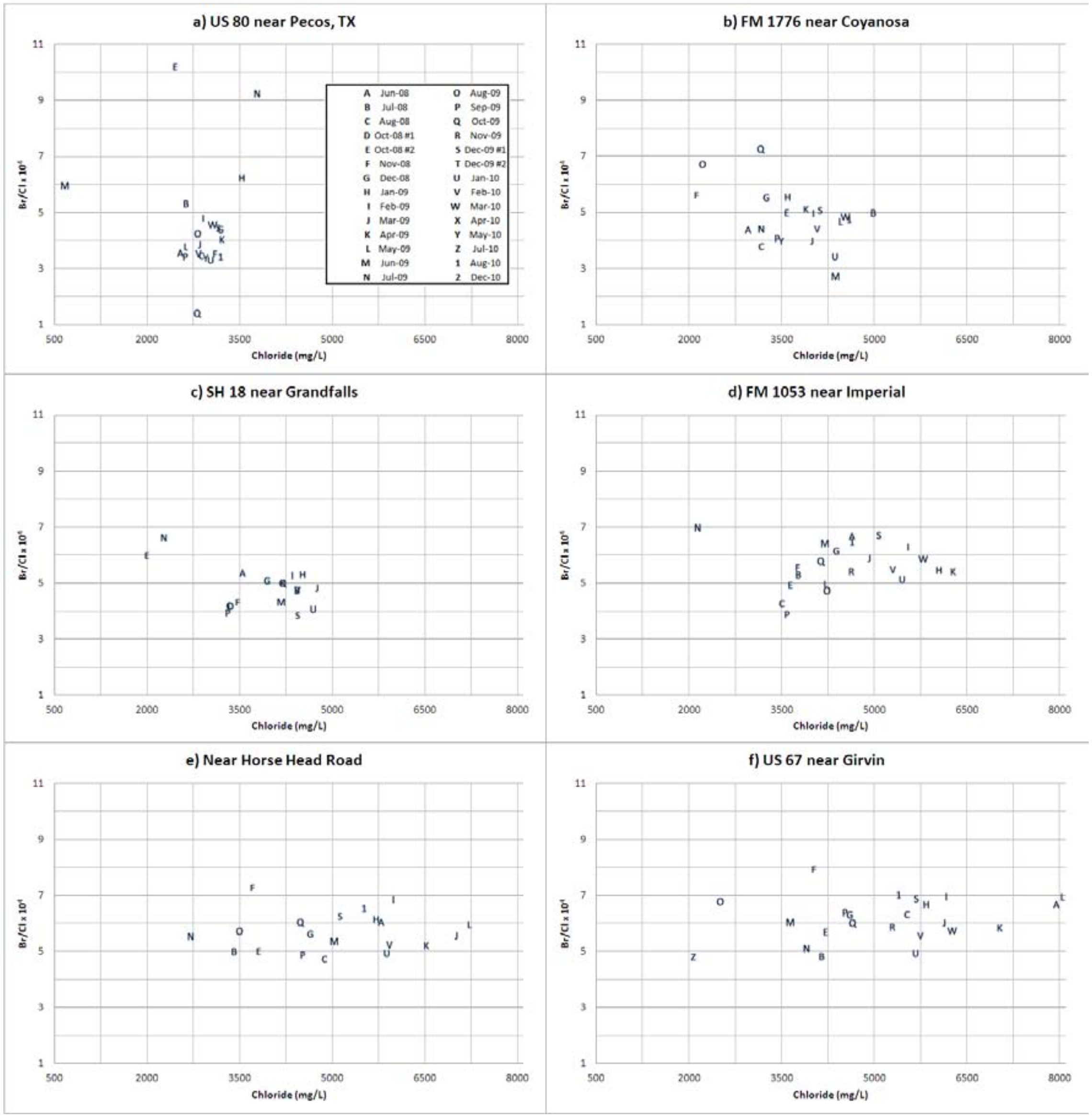

Figure 14. Comparison of Br$^-$/Cl$^-$ ratio at different chloride contents at the six surface water monitoring stations on the Pecos River. The Pecos station near US 80 is the furthest upstream, with downstream stations noted alphabetically. Each capital letter (or number) within the body of the graph represents a series of samples taken at the 6 stations within 24 hours.

Some of the same point pattern characteristics were observed in the SO$_4$/Cl$^-$ data. A cluster of points (ratios ranging from 0.72 to 0.84, Cl$^-$ from 2450 to 3530 mg/L) was again present at Pecos along with a few stray values (M and N), which expanded at

Coyanosa before becoming more linear with progression downstream (Figure 15). However, SO_4/Cl- ratio values began to trend downward with increasing chloride ion contents as flows progress downstream. By the time flows reach Girvin, the range of ratios has dropped to 0.54 to 0.75, at the same chloride ion content range shown earlier at Girvin for Br^-/Cl^- in Figure 14 (2080-8050 mg/L). The SO_4/Cl^- station graphs are also unique in that they show a clearer negative association between SO_4/Cl^- values and increasing chloride ion contents until flows reach the lower three stations and point patterns begin to flatten out. This shows that the effects of sulfate solubility limitations can be seen on a temporal scale at each station so that analysts need not rely solely on station-to station trends to make decisions. The ability to view trends such as this is the main advantage of analyzing data with this method, but it is not without limitations. One such constraint is that samples at different stations can be taken as much as 24 hours apart, which may introduce some uncertainty with respect to differences in the values if these differences are more time-dependent instead of location-dependent. This method is also not designed to discriminate between different groundwater sources. The ability to do this is useful in basins where multiple aquifers and shallow groundwater recharge may all be potential salt sources. This can be accomplished by comparing the station data to mixing zones that are characteristic of other salt sources, which is the focus of the next section of this study.

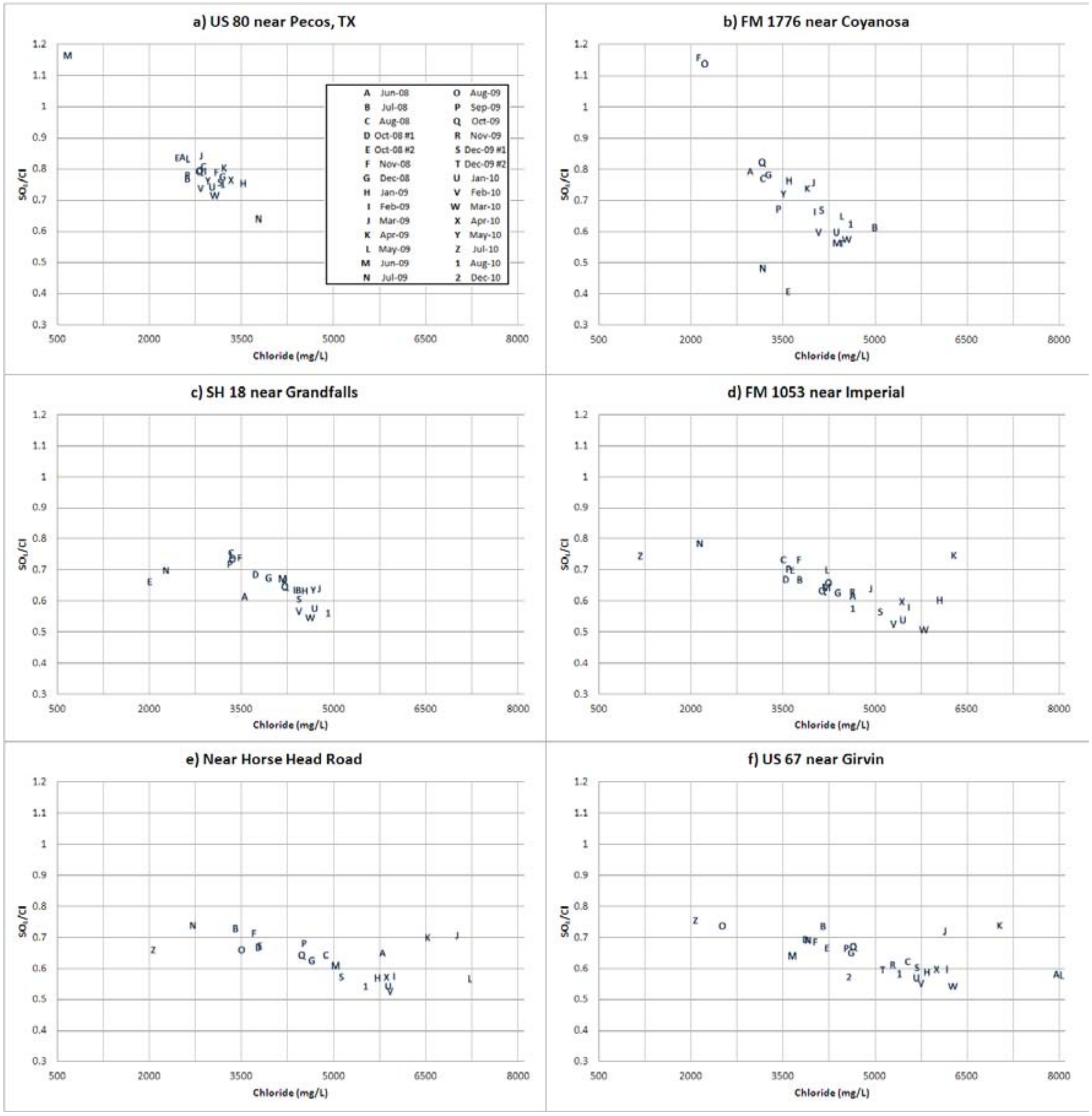

Figure 15. Comparison of SO_4/Cl^- ratio at different chloride contents at the six surface water monitoring stations on the Pecos River. The Pecos station near US 80 is the furthest upstream, with downstream stations noted alphabetically. Each letter (or number) represents a series of samples taken at the 6 stations within 24 hours.

For this portion of the analysis, data from all six stations show in Figure 14 were overlain to create one Br^-/Cl^- – to – Cl^- plot. The SO_4/Cl^- – to – Cl^- data in Figure 15 were overlain in the same fashion. Using this format, further investigations combined the station measurements with the ground water observations identified in this study. Figure 9 shows the geochemical ranges for the groundwater data used to define the mixing boundaries for several aquifers underlying the Pecos River. Here, the process for determining the mixing boundaries that was described earlier in the methods can be more clearly seen. Figure 16 shows the plot for the data from all six stations analyzed for Br^- and Cl^- in the advanced geochemical analysis that took place from 2008-2010. The data is compared to values observed in the underlying Pecos Alluvium aquifer (Figure 9, graph (a)) with which the river is suspected to have the most interconnectivity. The mixing zone for points in the Pecos Alluvium aquifer is bounded by the solid black lines, but the points themselves have been removed so that the stream station data can be more clearly seen. The upper and lower bounding mixing curves were then added, using as many of the intermediary data points as possible as tangent points for the curves. To accomplish this, the endpoints in the formula for the mixing curve are modified to best fit as many of these tangent points as possible experimenting with different Br^- contents at the upper and lower endpoints at both ends of the graph that will allow each curve to best fit the peripheral points. This process is described by Knuth (1990) and used similarly in other works (Freeman, 2007; Nordstrom et al., 1989; Whittemore, 1997). The zone for the Pecos Alluvium depicts chloride ion values from 3.9 mg/L (representing the freshest water in the formation), and 6290 mg/L (the saltiest waters found in the formation). The observations in between are the result of mixing of these two waters at varying percentages. Several points from the Pecos and Coyanosa have much lower bromide ion contents than can be found in the Pecos Alluvium, as indicated by group of points that fall below the mixing zone in graph (a) in Figure 16. This indicates that waters leaving the reservoir or entering the river between the reservoir and the Pecos station were heavily influenced by other sources.

Graph (c) of Figure 16 shows the mixing zone for Br^-/Cl^- in the Rustler formation, an aquifer residing below the Pecos River basin in both New Mexico and Texas. As discussed earlier in the text, the Rustler formation is believed to be the primary source of saline water entering the Pecos near Malaga Bend in New Mexico (Havens and Wilkins, 1979), and is also believed to be the source of saline water coming from Salt Creek, which contributes to flow just below Red Bluff Reservoir (Miyamoto et al., 2008). The mixing zone for the Rustler formation comfortably encompasses all observations made along the Pecos at the monitoring stations, including those not bound by the mixing zone for the Pecos Alluvium. This indicates that it is very likely that waters from the Rustler may in fact be a major source of salt contribution to Red Bluff, and that the Formation is also an equally likely source feeding Salt Creek. Unfortunately, no bromide ion data is available for Salt Creek, so an in-depth geochemical analysis cannot be done to determine if there is any similarity.

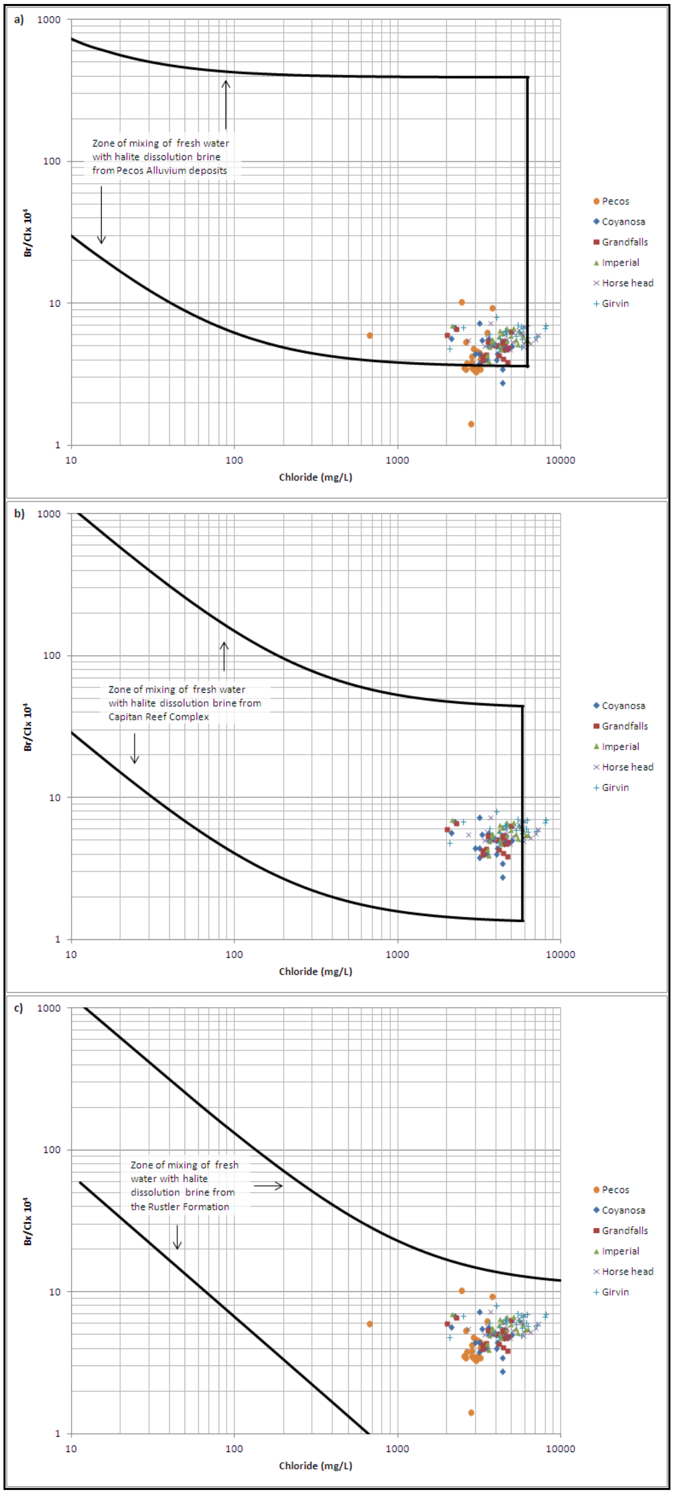

Figure 16. Br$^-$/Cl$^-$ mass ratio vs. Cl$^-$ concentration for surface water samples taken at 6 locations along the Pecos River compared to mixing zones for 3 aquifers suspected of having interconnectivity with the river.

Another suspected source, identified in the Grozier study (1966) cites possible influence along a fault line that may exist near the town of Grandfalls (Figure 13). This fault may allow saline water from the Capitan Reef Complex to intermingle with upper formations that have interconnectivity with the Pecos River. This possibility is analyzed in graph (b) of Figure 14, where stations that could be influenced by the Complex as well as those downstream were observed. This includes the Coyanosa station and all downstream locations. Results of the analysis show that interaction with waters from the Capitan Reef Complex could be the source for the samples with low Br^-/Cl^- ratios at Coyanosa that could not be explained by the mixing zone for the Pecos Alluvium. However, the results still fail to explain the source responsible for the samples with high chloride ion content that exist to the right of the chloride ion limit in both the Pecos Alluvium (a) and Capitan Reef (b) graphs. This indicates that influence shifted to other sources with progression downstream. Based on the graphs in Figure 16, an easy answer to this would be that the source is the Rustler formation, since samples are encompassed by the mixing zone for halite dissolution brine from that aquifer. Unfortunately, this may or may not be true. This phenomenon highlights a shortfall presented by using this type of analysis for progressive downstream geochemical studies, since the chloride ion range at the Pecos station reached a maximum of 3780 mg/L and the values for the samples in question range from 6520 to 8050 mg/L. Based on the point patterns shown for Horse

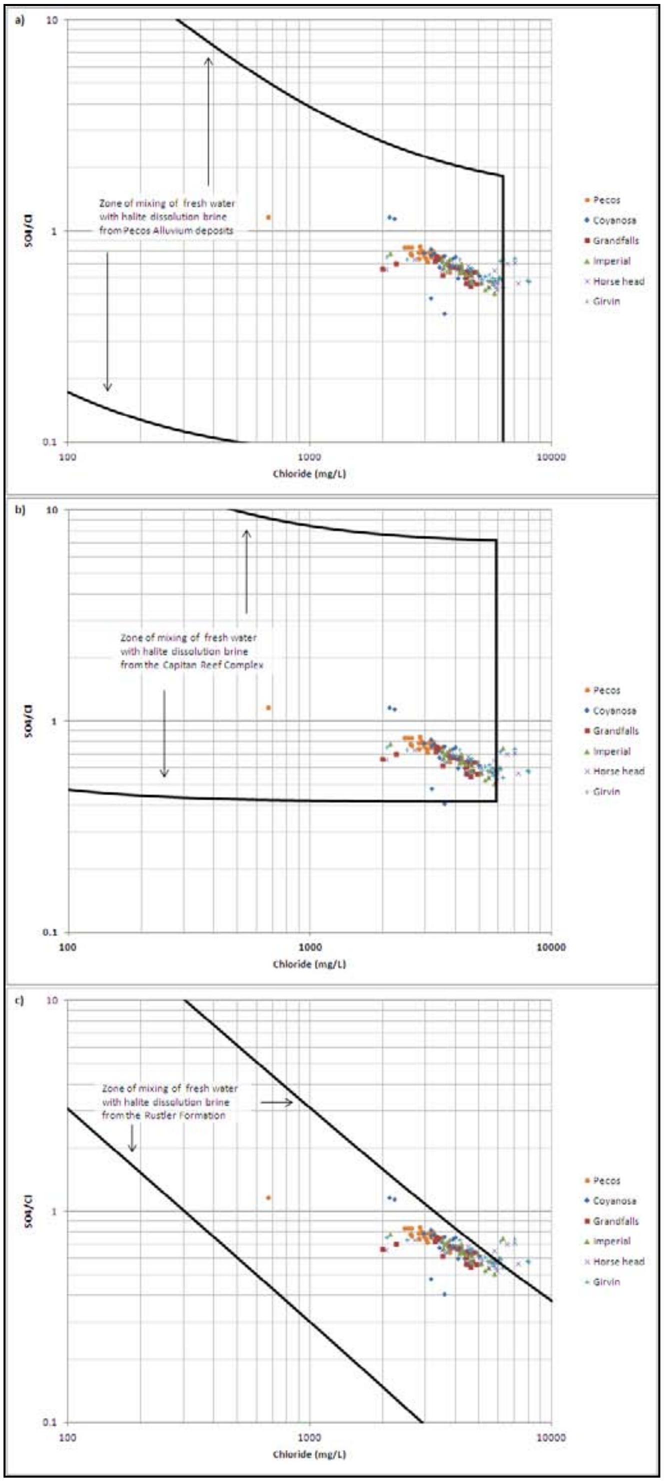

Figure 17. SO_4/Cl^- mass ratio vs. Cl^- concentration for surface water samples taken at 6 locations along the Pecos River compared to mixing zones for 3 aquifers suspected of having interconnectivity with the river.

Head and Girvin stations in Figure 14 and the conceptual diagram seen in Figure 1, the most likely source is evapotranspirative concentration of salts within the flow of the river. To supplement this hypothesis, an analysis of Cl^- vs. SO_4/Cl^- was also conducted. Figure 17 shows that the samples with chloride ion concentrations above 6000 mg/L had Br^-/Cl^- ratios that were uncharacteristic of all three aquifers. Construction here is similar to the Br^-/Cl^- graph, with lines representing mixing lines for the upper and lower bounds of the mixing zone and vertical lines representing the limits bounding the highest and lowest chloride ion concentrations for the dataset .It is worth noting that SO_4/Cl^- relationships are unique in that they are particularly useful for identifying areas where evapotranspiration plays a significant role in the increased solids concentration, as explained earlier, although its ability to distinguish between groundwater sources is undocumented. Studies using this ratio usually only compared suspected evapotranspirative concentration influences to one groundwater source, which was usually oil field brine (Whittemore, 1995; Whittemore, 2004). Oil brines may also be affecting the groundwater and surface water in the basin, but their influence is beyond the scope of this study, so it is unclear if it may be a contributing source.

CONCLUSIONS

The main objective of this study was to identify the processes that affect salinity within the Pecos River watershed using flow and salt load trends as well as geochemical analysis. This study differs from earlier studies in the Pecos since it takes advantage of the opportunity afforded by the new continuous water quality monitoring stations' ability to record high resolution temporal data. The daily values were used to form empirical relationships for flow and concentration that were much more sensitive to changes in flow rate and concentration. This is a significant advantage over previous studies where monthly values had to be relied upon for estimates adjusted to actual flow for the yearly flow and load values.

This study also takes advantage of the addition of a bromide ion analysis that proved to be very useful for targeting where specific sources were more prevalent between the towns of Pecos and Girvin. Assuming that the waters leaving Red Bluff Reservoir are heavily influenced by waters originating in the Rustler Foundation, this would explain why waters at Pecos and Coyanosa most resemble the mixing zone characteristics from that aquifer. Diversions from Orla to Coyanosa remove much of this water (an average of 32 million m^3/yr), which in turn causes the remaining low flow to be more susceptible to evapotranspirative concentration. As the diversions remove more than half of the water that typically leaves Red Bluff, it takes the Rustler-characteristic salts with it. This makes the remaining flow more sensitive to changes from incoming flows, such as those from tributary surface flow and other aquifers. It is here where other studies hypothesize that subsurface return flow from the river is re-emerging. If this is occurring, then it is likely that the return flow would be the most geochemically similar to the samples analyzed at the Pecos Station. This is a plausible hypothesis, since the Pecos geochemical points had the widest Br^-/Cl^- range. This wide range manages to contain all downstream points, even though unique sampling events may not have identical ratios as they progress downstream.

A second hypothesis is that subsurface flow from the river is intermingling with shallow groundwaters of the Pecos Alluvium. Given the shift in the geochemical patterns away from the lower geochemical ratios characteristic of the Rustler Formation towards the higher ratios found in the Pecos Alluvium, this is also plausible. These hypotheses become complicated when attempting to account for the diversions that lower the flow and salt loads from Orla to Coyanosa. Diversions may also buffer any additions from springs within this reach that are responsible for the TDS increases that occur downstream of the Pecos station. If diversions were the only process affecting in this reach, the point pattern seen at the Pecos station would not have changed. However, the pattern condensed and shifted, indicating that other sources were entering the river and affecting the geochemical ratios of the river flow at least as far upriver as the Pecos Station.

For the length of river between Coyanosa and Horse Head Crossing, the river gains flow and salts, and the geochemical patterns continue to shift. This occurs despite having no significant surface tributaries that could contribute to flow and salt loads, which indicates that additions from outside sources are prevalent throughout this reach as well. If a fault allowing upwelling brines from the Capitan Reef Complex does exist, it could explain some of the low-ratio Br^-/Cl^- points at the Coyanosa station that are outside of the Pecos Alluvium mixing zone, However, the points also fall within the mixing zone for the Rustler Formation, so the low points could just as easily be retaining their source properties. Therefore, although it is readily apparent that saline groundwater is the source of the pronounced increase in both bromide ions and the Br^-/Cl^- ratio for the area in this reach between Grandfalls and Imperial, a definite assertion cannot be made on which aquifer it is coming from.

From Horse Head Crossing to Girvin, the geochemical patterns stabilize along a similar range for the geochemical ratios while chloride ion concentrations increase. This indicates that additions from outside sources, while they are a factor, are not as prevalent for this reach and evapotranspirative concentration is the dominant force behind salinity increases.

Thereafter, dilution becomes the dominant process, resulting in salt concentration decreases from Girvin as the river winds its way down past the Sheffield and Brotherton Ranch stations, gaining flow from several freshwater inflows along the way. The trends in flow, salinity, and salt load were useful in making broad generalizations about the sources and the locations where they were likely to occur, which, in most cases were confirmed by the geochemical analysis. Interpretation of these results and the different sources driving salinity increases in each reach will be critical for river managers, local officials, and citizens as they attempt to manage salinity levels within the river. Decision makers must make logical choices regarding the best options for salt control based on the origin of the increase.

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APPENDIX A

Flow, Salinity, and Salt Load Data

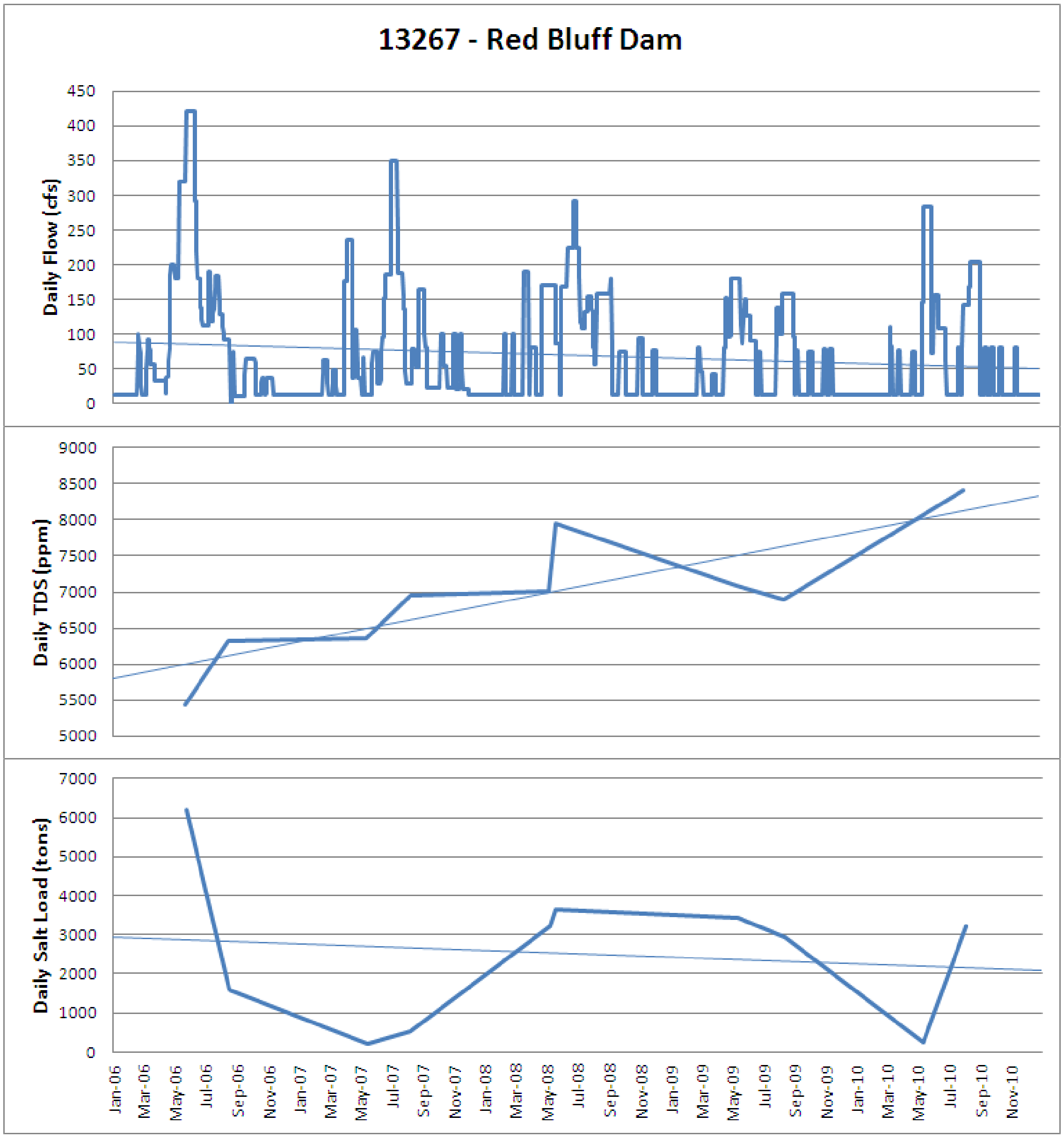

Figure A-1. Flow, salinity and salt loads for the station at the outlet of Red Bluff Reservoir, 2006-2010. Linear trend for each dataset is characterized by the straight blue line.

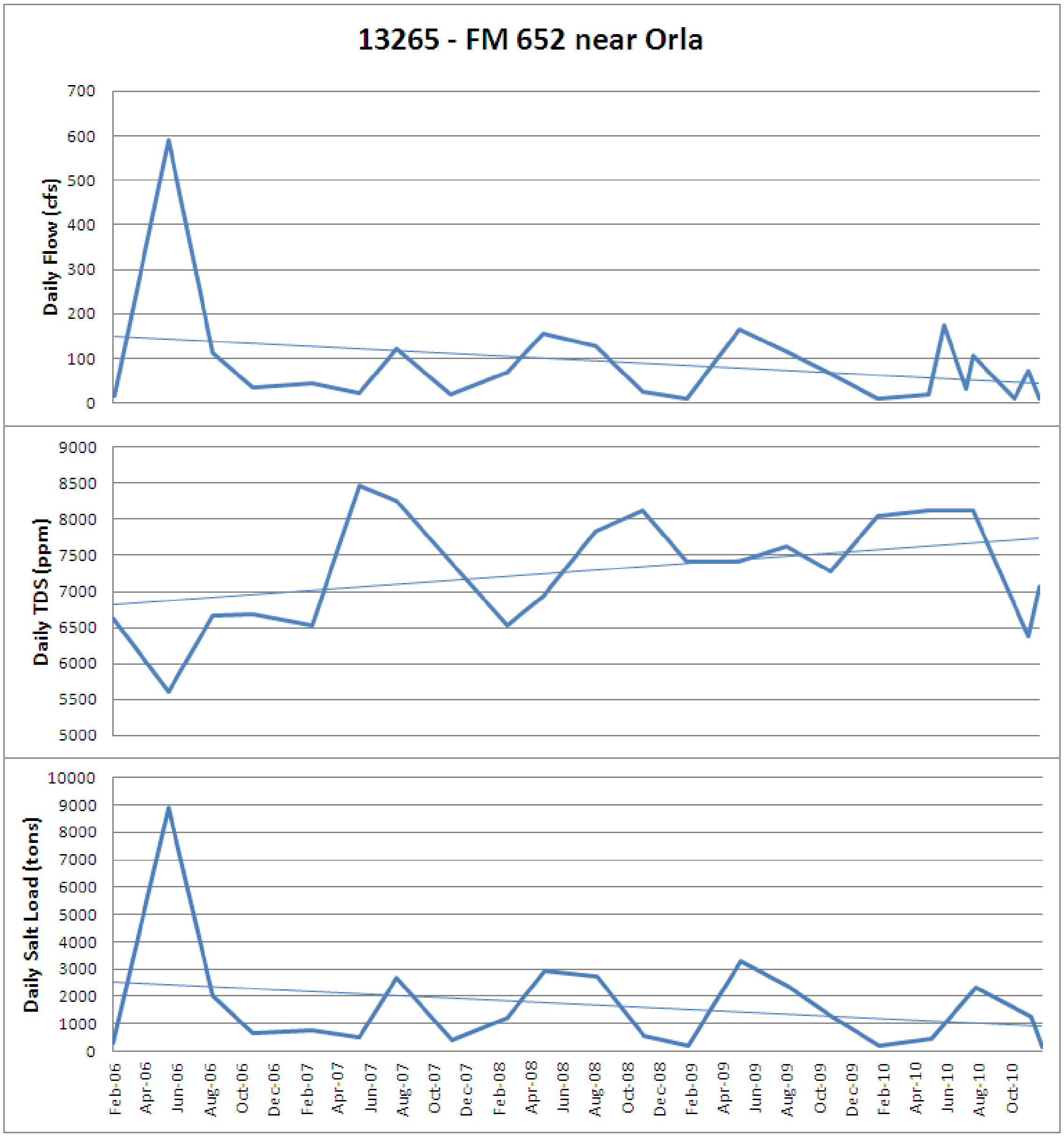

Figure A-2. Flow, salinity and salt loads for the station near Orla, TX, 2006-2010. Linear trend for each dataset is characterized by the straight blue line.

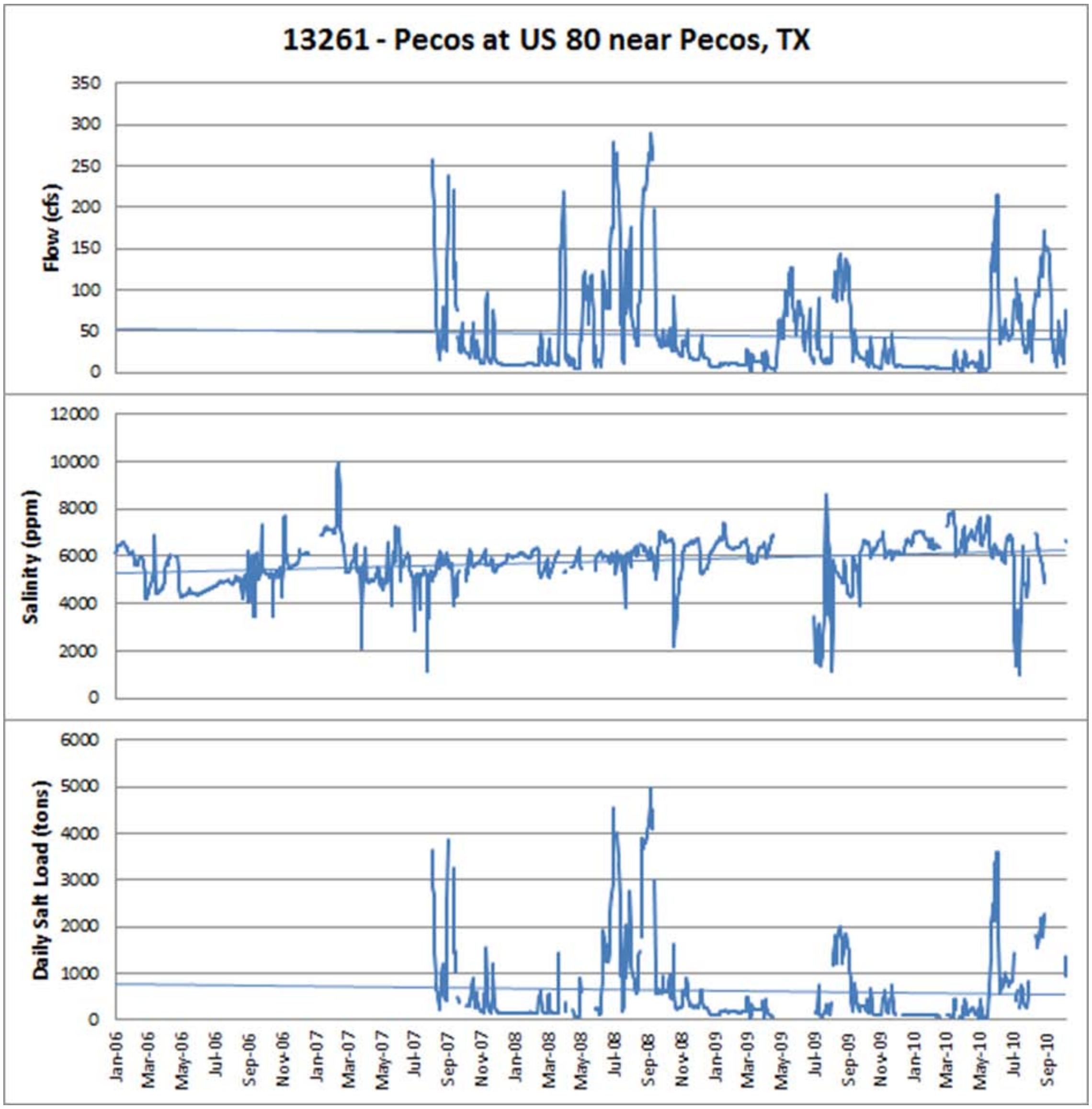

Figure A-3. Flow, salinity and salt loads for the CWQM station near Pecos, TX, 2006-2010. Linear trend for each dataset is characterized by the straight blue line.

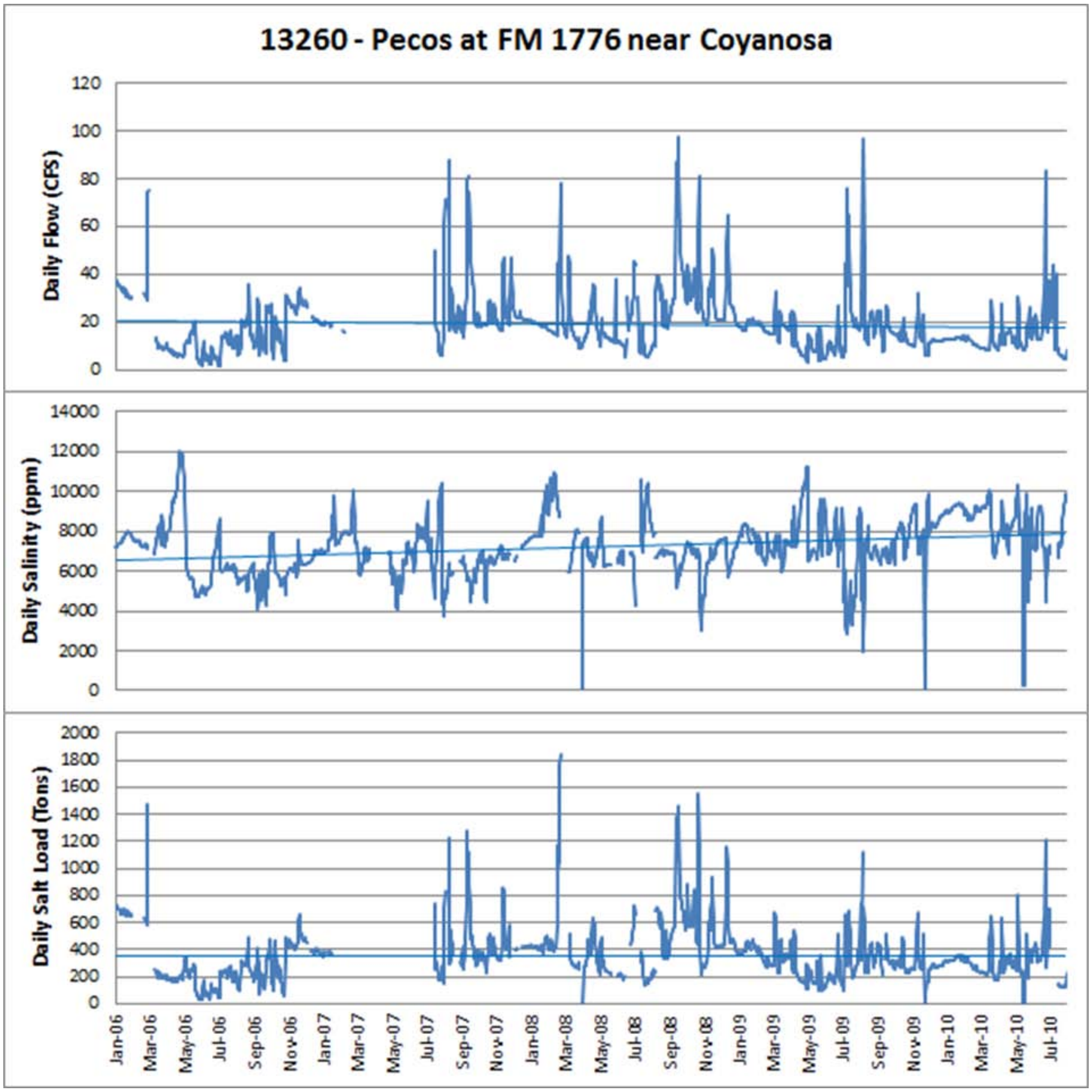

Figure A-4. Flow, salinity and salt loads for the CWQM station near Coyanosa, TX, 2006-2010. Linear trend for each dataset is characterized by the straight blue line.

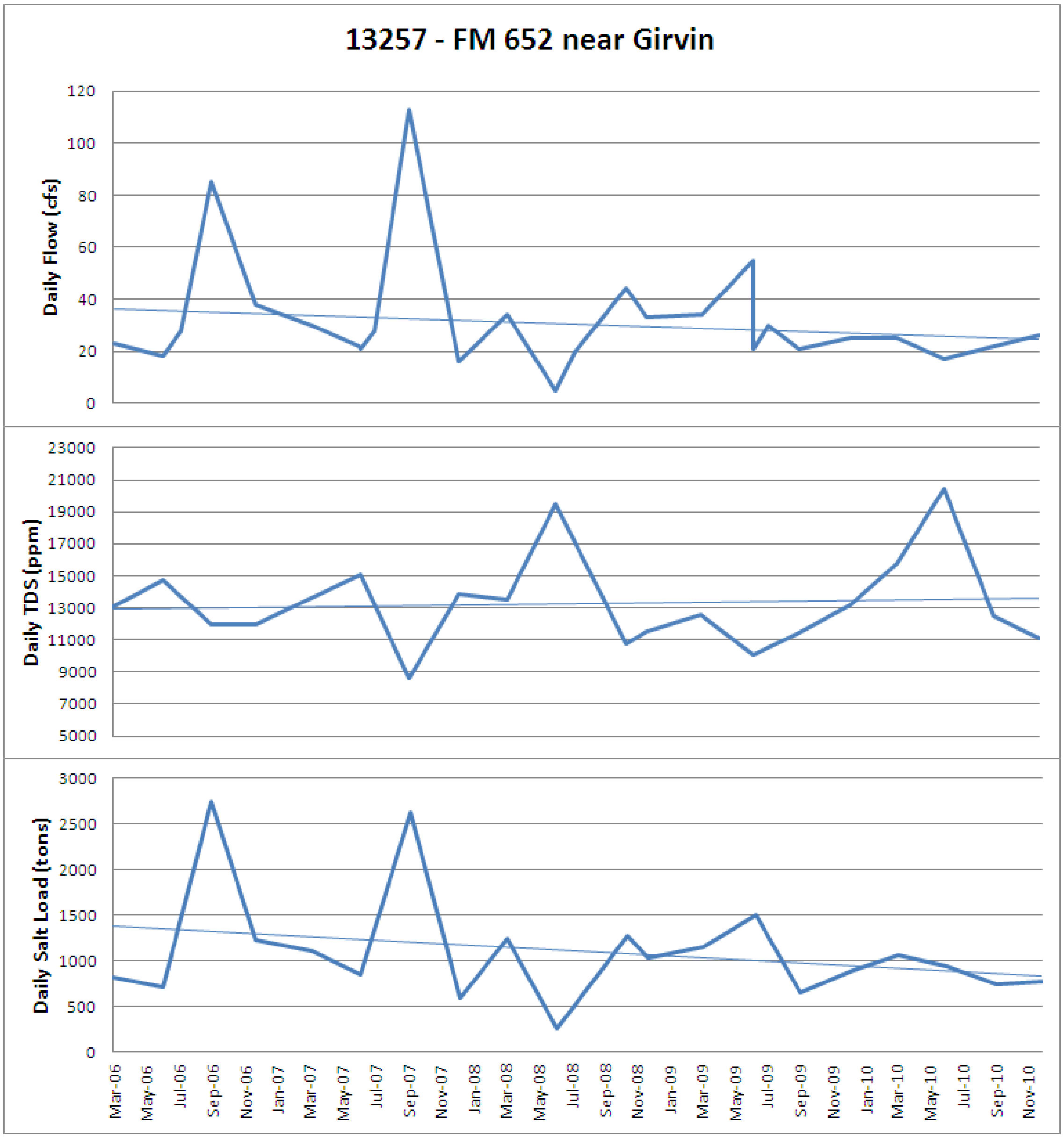

Figure A-4. Flow, salinity and salt loads for the CWQM station near Girvin, TX, 2006-2010. Linear trend for each dataset is characterized by the straight blue line.

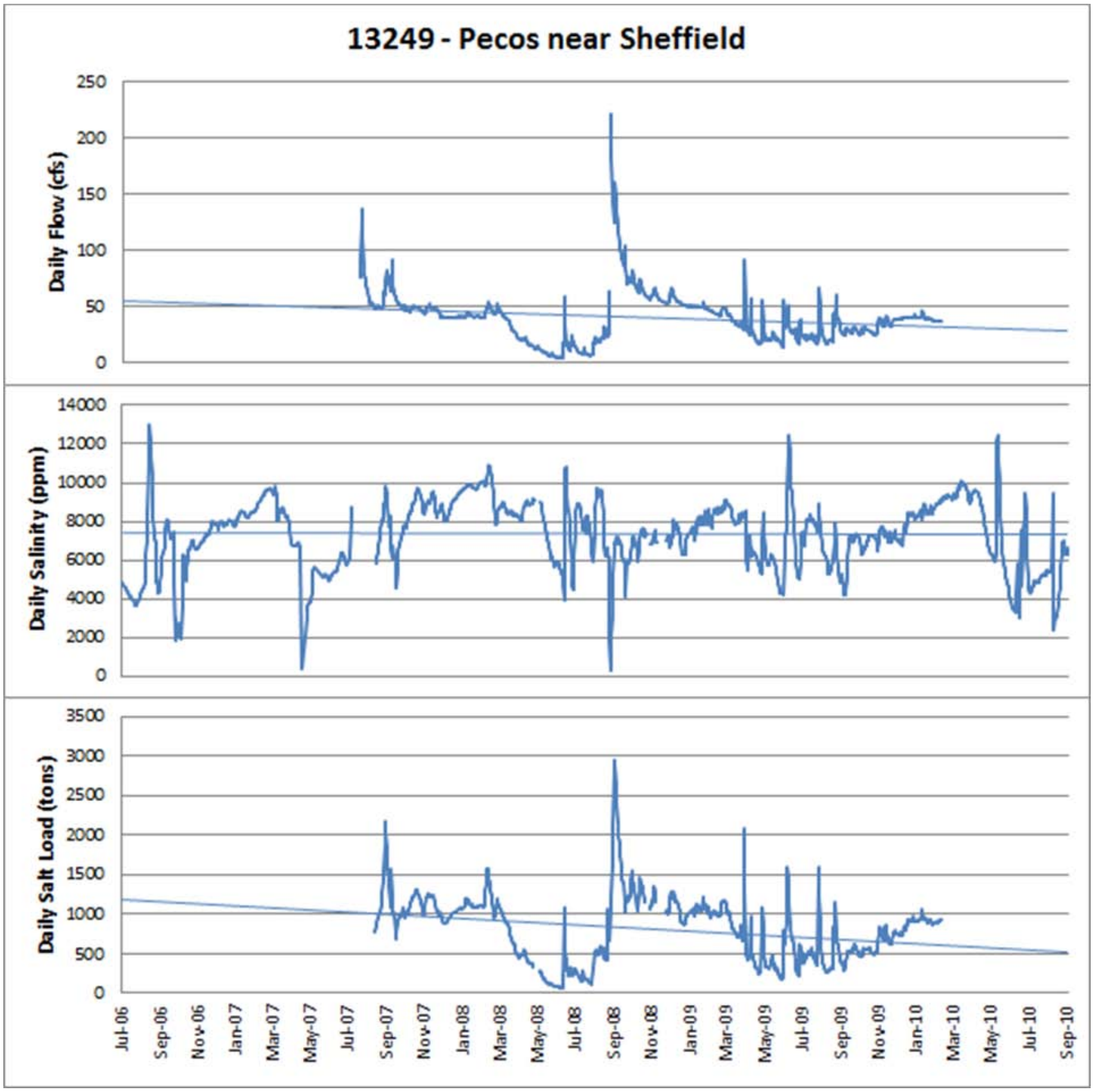

Figure A-5. Flow, salinity and salt loads for the CWQM station near Sheffield, TX, 2006-2010. Linear trend for each dataset is characterized by the straight blue line.

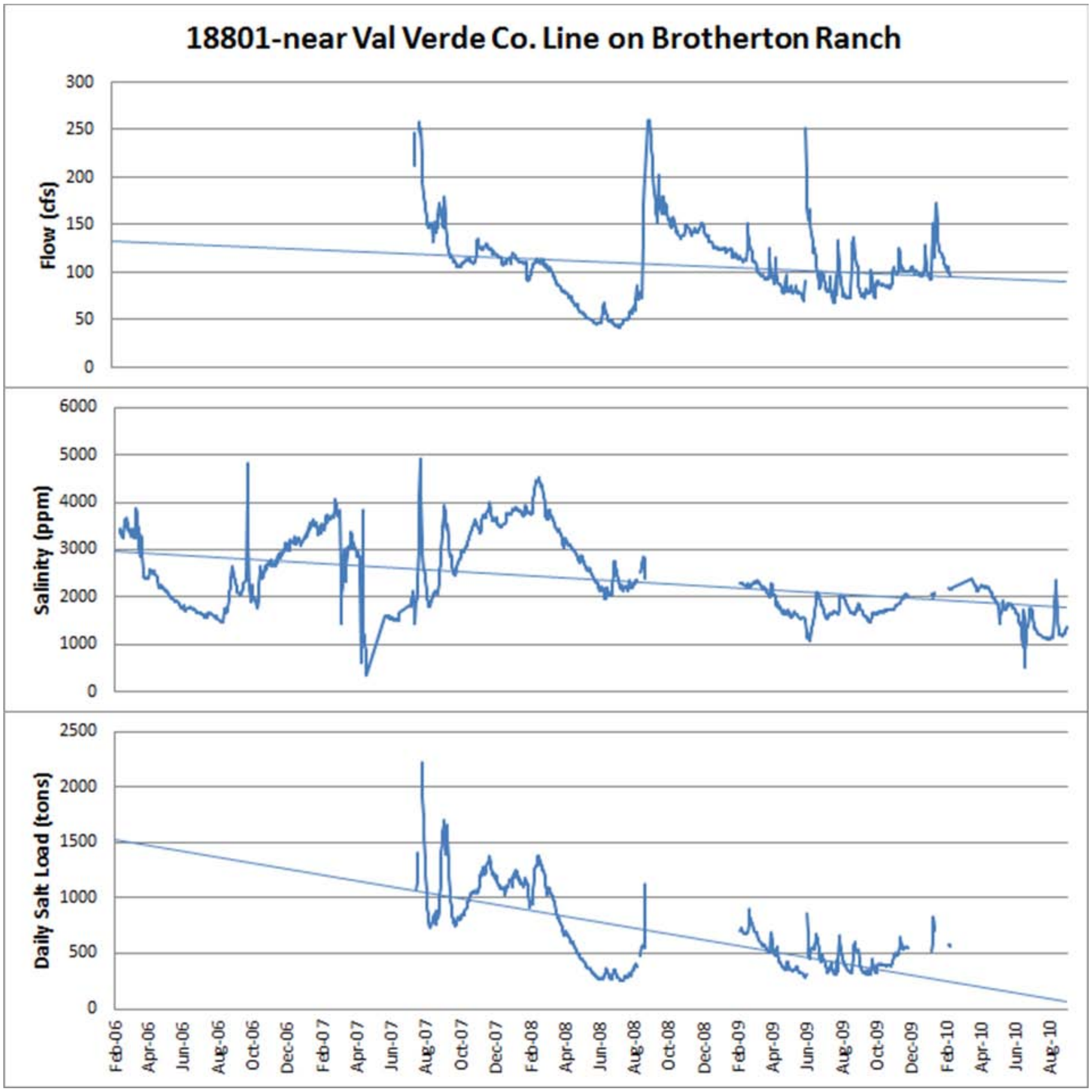

Figure A-6. Flow, salinity and salt loads for the CWQM station on Brotherton Ranch near the Val Verde/Terrell/Crockett County Line, 2006-2010. Linear trend for each dataset is characterized by the straight blue line.

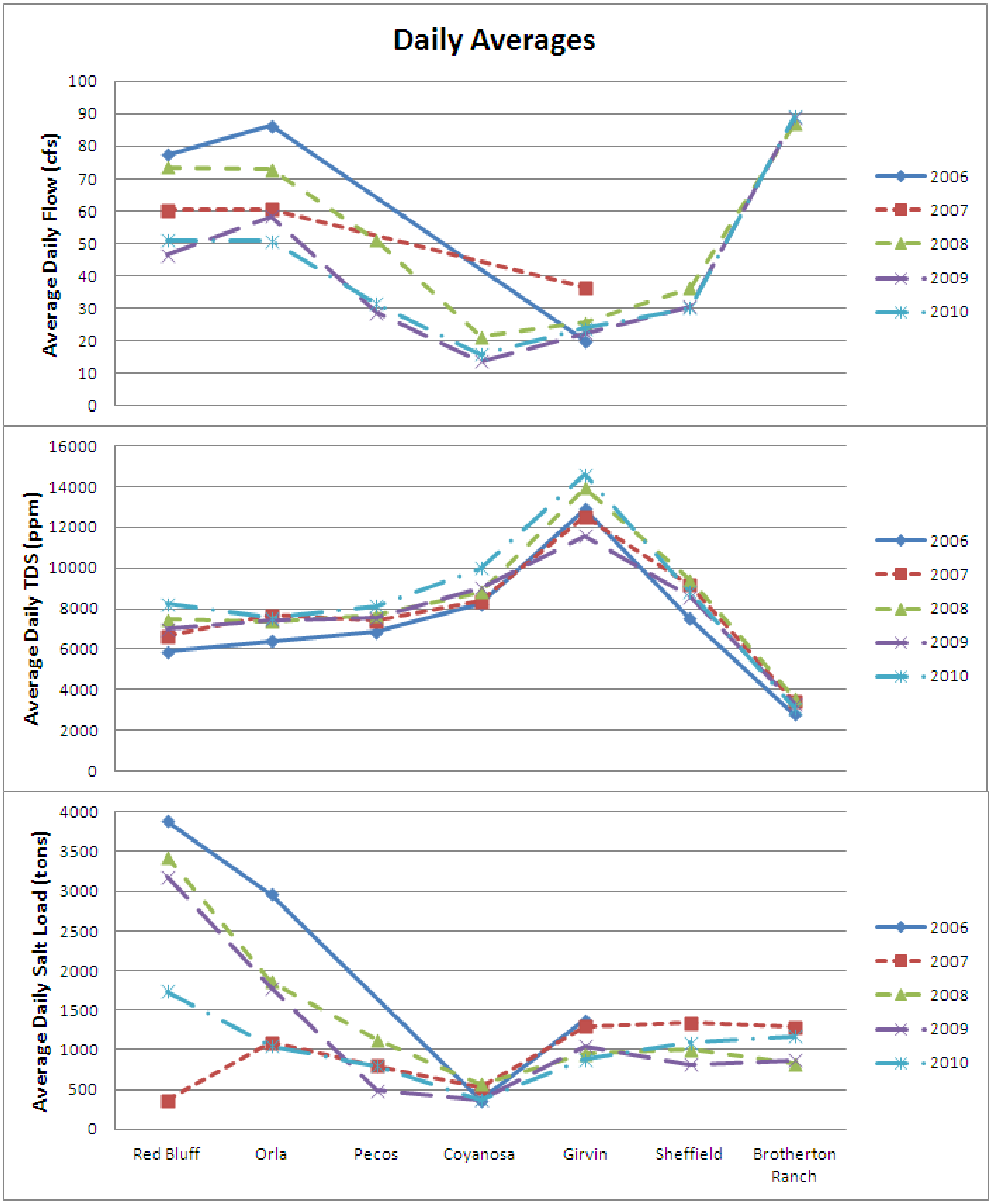

Figure A-7. Average daily flow, salinity, and salt load for stations along the Pecos River in Texas, 2006-2010

Table A-1. Observed average daily values for flow, salinity, and salt load at stations along the Pecos River in Texas, 2006-2010.

		2006	2007	2008	2009	2010
Daily Flow (cfs)	Red Bluff	87	68	82	52	57
	Orla	97	68	81	65	57
	Pecos		41	58	33	42
	Coyanosa	17	25	24	16	15
	Girvin	35	38	23	31	23
	Sheffield		55	41	34	40
	Brotherton Ranch		137	103	101	112
Daily TDS (ppm)	Red Bluff	5880	6655	7480	6995	8230
	Orla	6396	7670	7357	7438	7546
	Pecos	6841	7408	7672	7531	8126
	Coyanosa	8235	8358	8833	9029	9997
	Girvin	12898	12520	13940	11573	14598
	Sheffield	7507	9181	9402	8578	8805
	Brotherton Ranch	2797	3414	3578	3321	3119
Daily Load-TDS (tons)	Red Bluff	3888	365	3429	3181	1741
	Orla	2964	1090	1866	1783	1052
	Pecos		800	1124	490	802
	Coyanosa	364	526	573	376	375
	Girvin	1376	1294	950	1046	880
	Sheffield		1337	1003	814	1088
	Brotherton Ranch		1284	822	866	1173

APPENDIX B

Flow-Salt Load Relationships

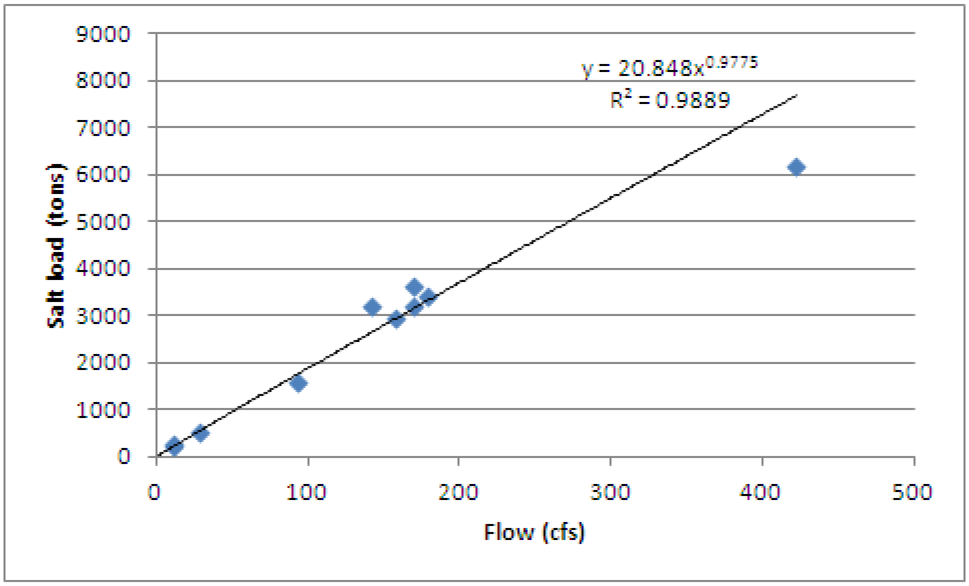

Figure B-1. Flow-salt load relationship at the outlet of Red Bluff Reservoir.

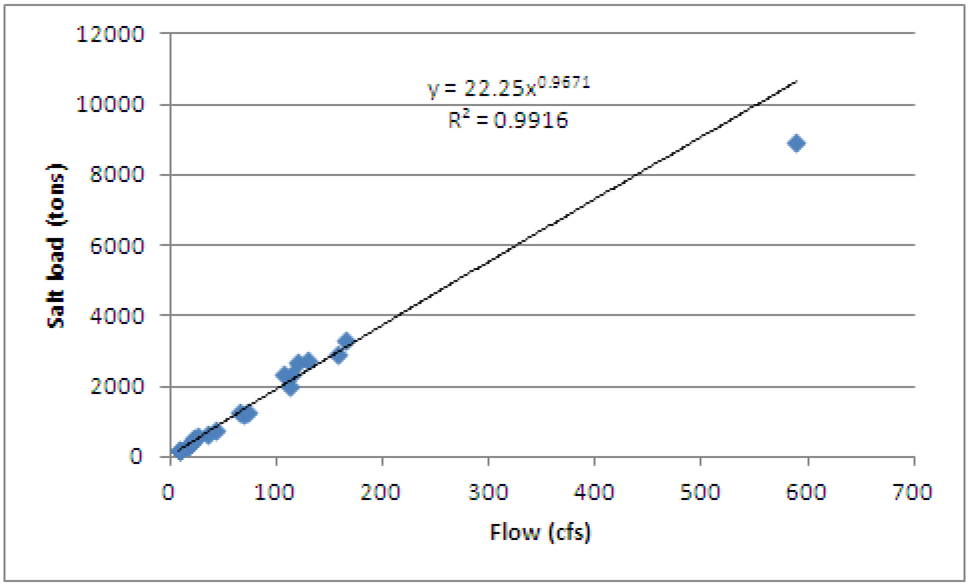

Figure B-2. Flow-salt load relationship at the station near the town of Orla.

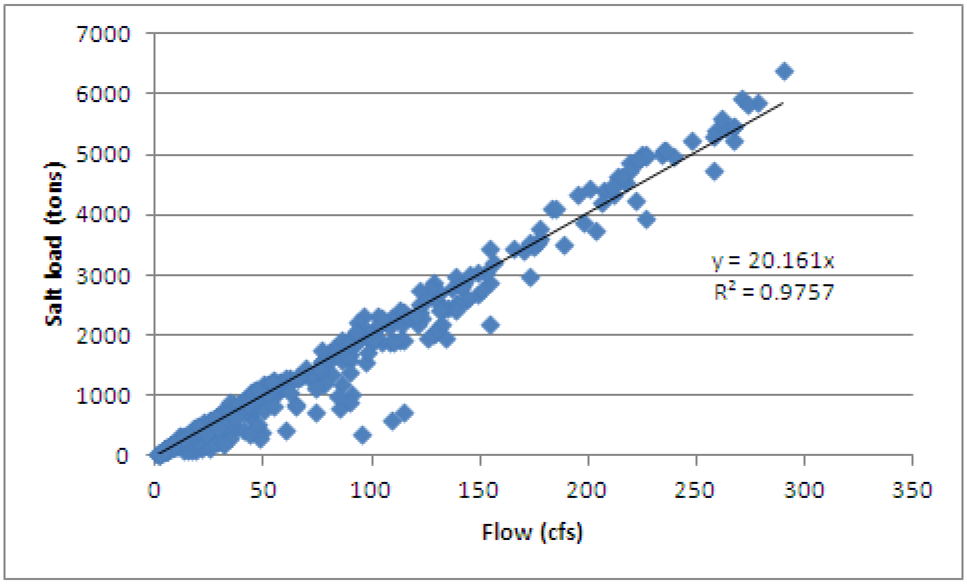

Figure B-3. Flow-salt load relationship at the station near the town of Pecos, TX.

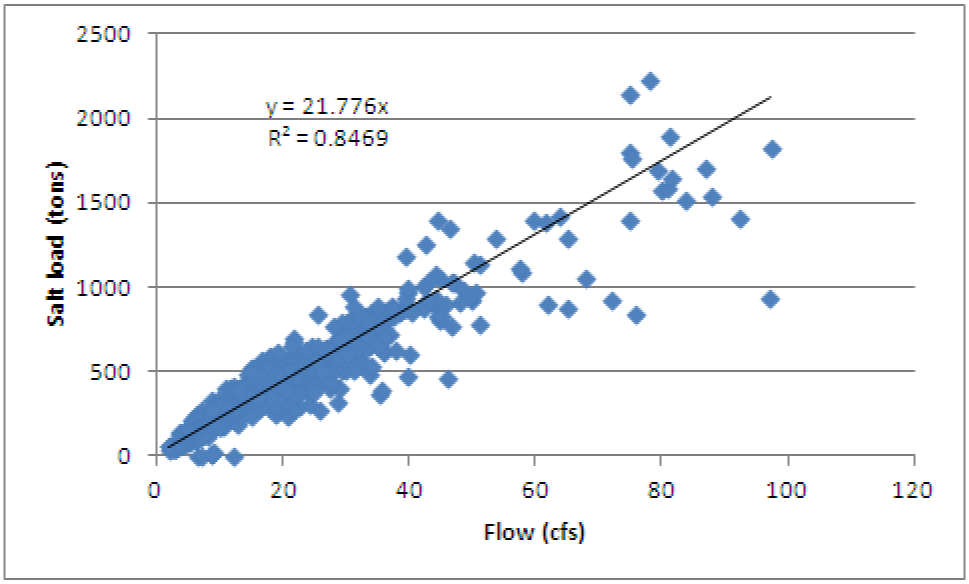

Figure B-4. Flow-salt load relationship at the station near the town of Coyanosa.

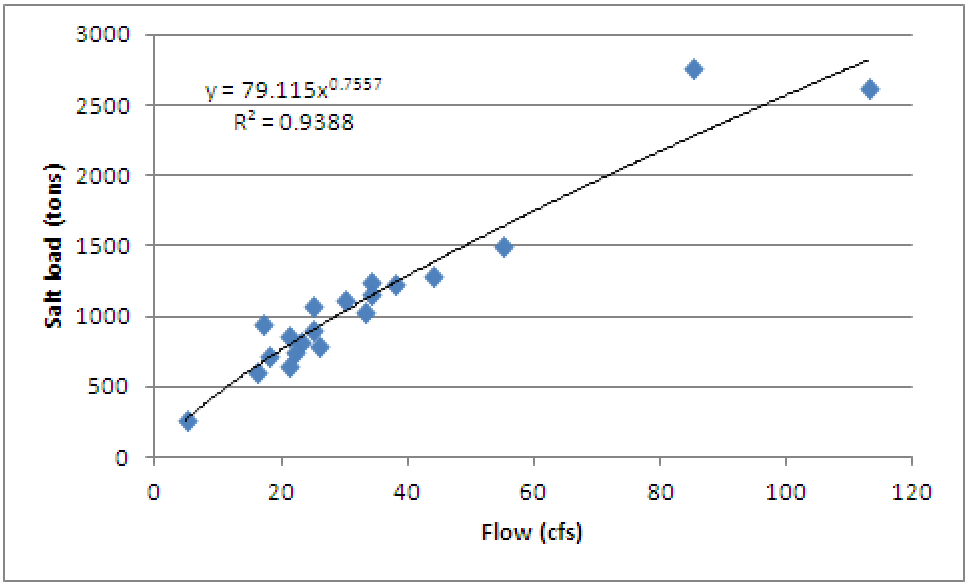

Figure B-5. Flow-salt load relationship at the station near the abandoned town of Girvin.

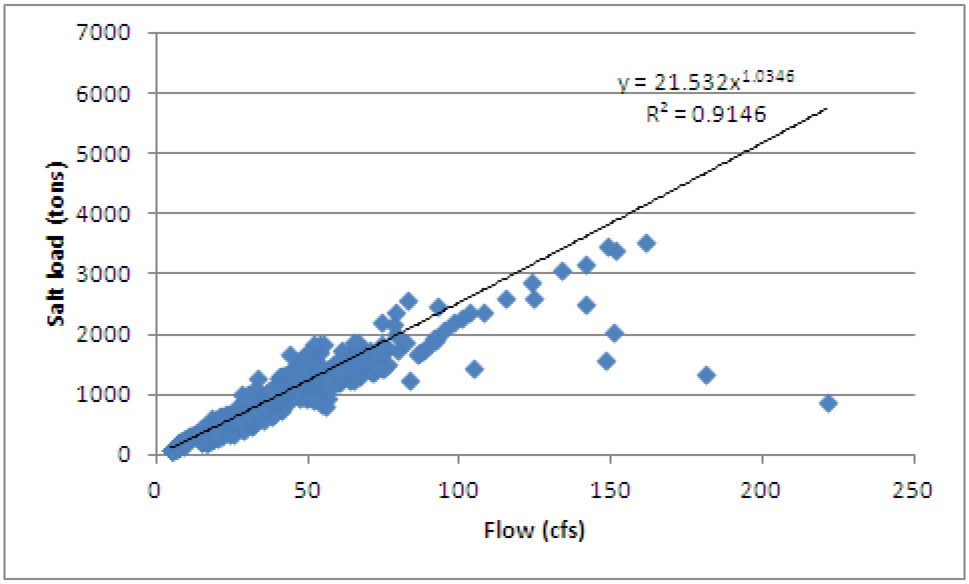

Figure B-6. Flow-salt load relationship at the station near the town of Sheffield.

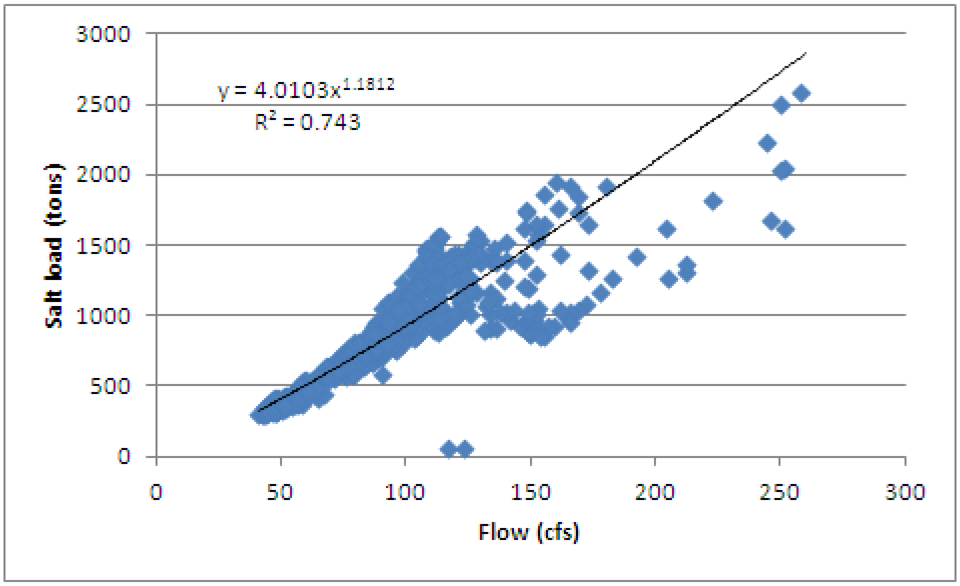

Figure B-7. Flow-salt load relationship at the station near the town of Orla.

APPENDIX C

Br$^-$/Cl$^-$ Trends

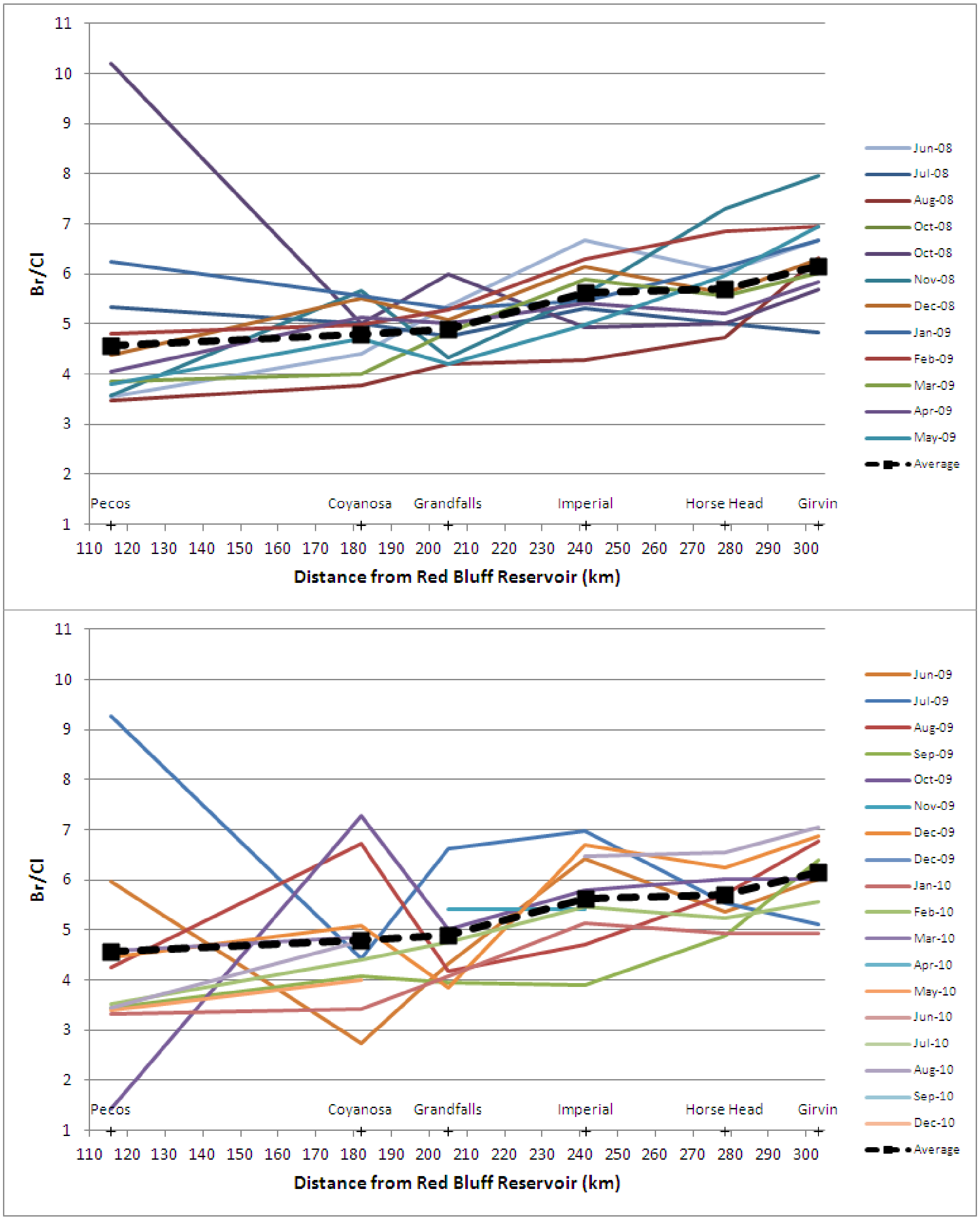

Figure C-1. Br$^-$/Cl$^-$ trends for each sampling event at sites along the Pecos River in Texas, 2008-2010.

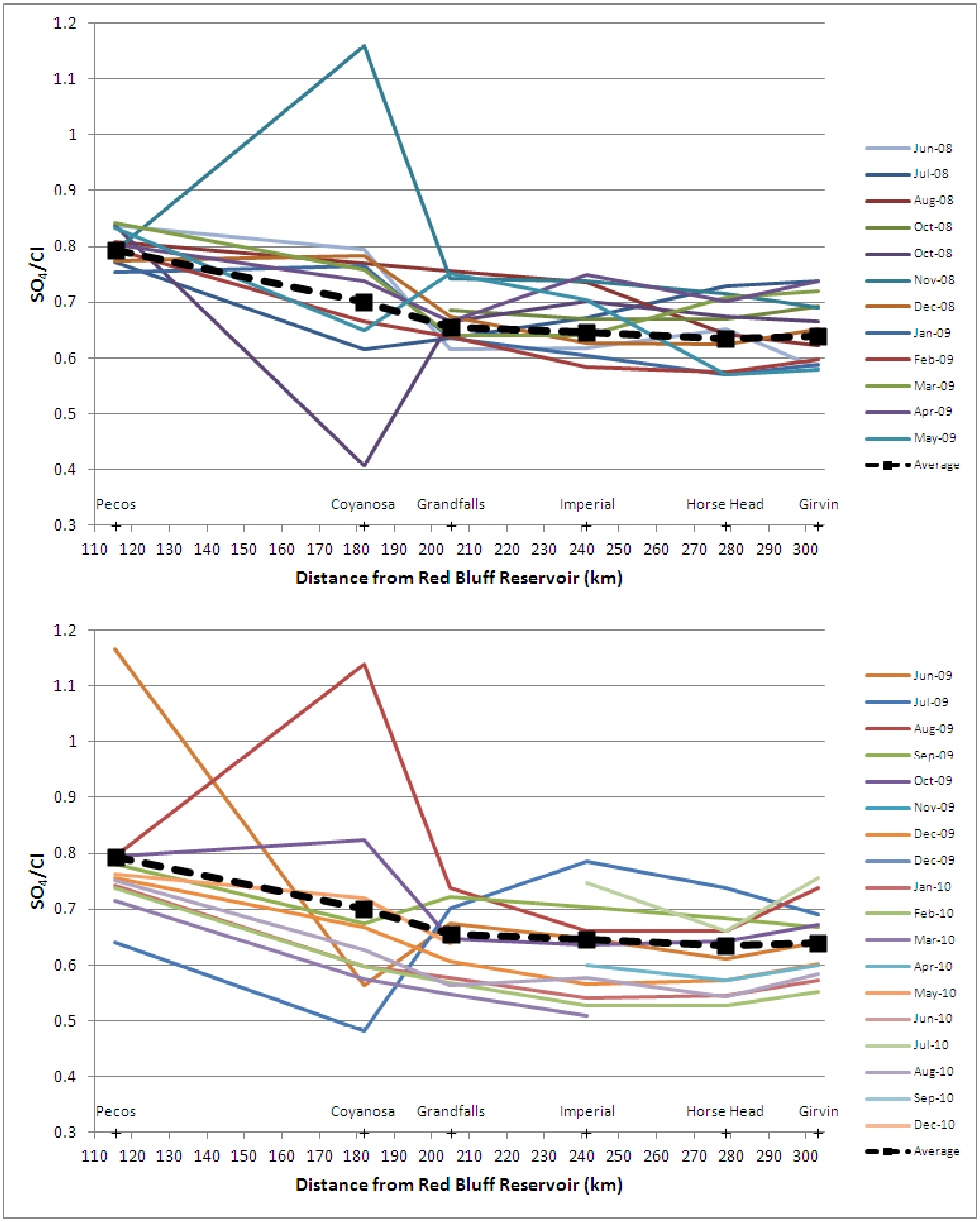

Figure C-2. SO$_4$/Cl$^-$ trends for each sampling event at sites along the Pecos River in Texas, 2008-2010.

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