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Dominant processes controlling water chemistry of the Pecos River in American southwest

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[1] Here we show an analysis of river flow and water chemistry data from eleven gauging stations along the Pecos River in eastern New Mexico and western Texas, with time spanning 1959–2002. Analysis of spatial relationship between the long-term average flow and total dissolved solids (TDS) concentration allows us to illuminate four major processes controlling river chemistry, namely saline water addition, evaporative concentration with salt gain or loss, dilution with salt gain or loss, and salt storage. Of the 10 river reaches studied, six reaches exhibit the process dominated by evaporative concentration or freshwater dilution with little change in salt load. Four reaches show considerable salt gains or losses that are induced by surface-ground water interactions. This analysis suggests that the evaporative concentration and freshwater dilution are the prevailing mechanisms, but local processes (e.g., variations in hydrologic flowpath and lithologic formation) also play an important role in regulating the hydrochemistry of the Pecos River. **Citation:** Yuan, F., and S. Miyamoto (2005), Dominant processes controlling water chemistry of the Pecos River in American southwest, *Geophys. Res. Lett.*, 32, L17406, doi:10.1029/2005GL023359.

1. Introduction

[2] There is an increasing indication that salinity of water supply has become a critical issue in the American southwest, as well as in the Middle East and elsewhere in arid regions of the world [Allison *et al.*, 1990; Farber *et al.*, 2004; Yuan and Miyamoto, 2004]. Nevertheless, controlling mechanisms for river chemistry of watersheds in arid-semiarid regions have not been sufficiently assessed [Phillips *et al.*, 2003]. The chemical composition of natural river water is derived mostly from weathering parent rocks and soils [Lasaga *et al.*, 1994], as the airborne component (i.e., atmospheric deposition) is relatively insignificant in interior watersheds [Van Denburgh and Feth, 1965]. However, water chemistry of many rivers in arid-semiarid regions changes substantially from reach to reach [Livingstone, 1963; Farber *et al.*, 2004; Yuan and Miyamoto, 2004]. Most of the observed variations are attributable to climatic, hydrologic, and lithologic heterogeneities, as well as anthropogenic perturbations, but the exact causes or processes may differ from site to site.

[3] There are presumably three major mechanisms controlling the chemistry of surface waters, namely atmospheric precipitation, rock dominance, and evaporation-crystallization process [Clarke, 1924; Gibbs, 1970]. An existing

model relies on the relationship between the TDS and Na/(Na + Ca) ratio to assess the relative significance of the three major mechanisms [Gibbs, 1970]. The Gibbs model is presented in many geochemistry and limnology textbooks [Wetzel, 1975; Faure, 1998] but flawed [Feth, 1971], as a significant portion of the world surface waters reside outside of the boomerang envelope [Kilham, 1990; Eilers *et al.*, 1992], where atmospheric precipitation dominance falls within the lower right arm, evaporation-crystallization dominance falls within the upper right arm, and rock dominance falls within the middle base area. The flaw may be attributed to the facts that the model exaggerates the significance of the atmospheric component [Kilham, 1990] and overlooks the dynamic nature of surface waters. With respect to river water, its chemical composition alone may be insufficient to determine the hydrochemical processes that affected it [Faure, 1998]. There is a clear need to develop a more effective approach to illuminate dominant processes controlling the chemistry of the dynamic surface waters. Here we present a hydrochemical model to differentiate the dominant processes through its application to the Pecos River.

2. Study Area

[4] The Pecos River is a major tributary of the Rio Grande, which accounts for 20% of the entire drainage area of the Rio Grande Basin. In contrast, the Pecos River yields less than 10% of water but more than 20% salts for the lower Rio Grande [Yuan and Miyamoto, 2004]. The headwaters of the Pecos River are in the southern Sangre de Cristo Mountains of northern New Mexico. The river flows southward through eastern New Mexico and western Texas and joins the Rio Grande at the international border with Coahuila, Mexico. It traverses several climatological zones from the alpine tundra to the Chihuahuan desert to the Mexican monsoon. Annual precipitation changes from 65 cm in the headwaters region to 28 cm in Red Bluff. The hydrologic regime of the Pecos changes substantially from the mountainous headwaters region to the lower Pecos valley. The upper Pecos receives runoff mainly from snowmelt of the mountains with high elevations (1000 to 3600 m). The middle Pecos near the Roswell Basin receives runoff from springs [Fiedler and Nye, 1933]. The lower end of the Pecos receives base flow from the Edwards-Trinity aquifer consisting of warm season monsoonal rainfall. There are several relatively small-scale dams constructed on the river, such as Santa Rosa, Sumner, Brantley, and Red Bluff. The Sumner and Red Bluff dams were completed in 1937 and 1936, whereas the Santa Rosa and Brantley dams were completed in

Table 1. Mean Flow and Major Element Hydrochemistry of the Pecos River^a

Gaging Station	Flow, m ³ /s	pH, S.U.	Ca, mg/l	Mg, mg/l	Na, mg/l	K, mg/l	HCO ₃ , mg/l	SO ₄ , mg/l	Cl, mg/l	SiO ₂ , mg/l	TDS, mg/l	Salt Load, 10 ⁶ kg/yr
Santa Rosa	2.75	8.0	99	13	12	2.2	132	214	9	7	488	42
Puerto De Luna	5.34	7.8	286	34	46	2.2	144	726	62	12	1312	221
Sumner Dam	5.13	7.7	298	34	51	2.7	123	759	64	13	1345	218
Acme	4.39	7.7	311	48	117	3.3	115	890	150	14	1649	228
Artesia	4.99	7.6	374	78	319	5.3	140	1086	489	14	2506	394
Brantley Dam	4.13	8.0	395	99	388	6.0	121	1230	630	10	2879	375
Malaga	2.55	7.7	323	99	450	10.3	131	1006	743	12	2773	223
P. C. Crossing ^b	2.56	7.7	363	127	1107	31.7	139	1209	1793	11	4780	385
Red Bluff	2.67	7.6	312	104	977	25.3	127	914	1614	11	4083	344
Girvin	0.93	7.4	610	327	2781	44.4	118	2593	4254	4	10730	314
Langtry	7.43	7.9	121	48	311	7.4	176	304	515	12	1494	350

^aFlow-weighted mean of the chemical data at each station during the period from 1959 to 2002.

^bPierce Canyon Crossing, New Mexico.

1981 and 1988. Because of upstream impoundments and increased irrigation demands, water export from the Pecos River into the Rio Grande has reduced considerably (40%) since 1945 [*International Boundary and Water Commission, United States and Mexico*, 2001].

3. Data and Methods

[5] We analyzed the stream flow and water quality data from eleven gauging stations along the main channel of the Pecos River over the last four decades. Most of the data used are from the U.S. Geological Survey database containing continuous daily flow readings and nearly monthly-resolved water quality records at major gauging stations during this time interval. The data was retrieved and screened through crosschecking by comparing the TDS concentration with the electrical conductivity. The relationship of streamflow discharge with major ion fluxes can be best described by log-linear regression models [Yuan and Miyamoto, 2004], and major ions are highly inter-correlated with each other in the stations studied. Because sampling frequency for chemical analysis varies from station to station, we interpolated daily ion fluxes between observations through the log-linear regression models using the continuous daily stream flow data [Crawford, 1991; Hooper et al., 2001] to estimate the long-term average of ion fluxes and TDS loads. Flow-weighted averages of the major ion concentrations were then calculated for the eleven gauging stations along the Pecos River during the period 1959–2002 (Table 1).

4. Results and Discussion

[6] Figure 1 shows relationship between stream discharge and TDS of river water at the eleven gauging stations. Arrows designate flow pathways from the upper basin downward. The most striking feature is that half of these arrowed lines (i.e., 2, 3, 5, 9, and 10) have nearly the same orientation, which is interpreted to reflect the evaporative concentration and/or freshwater dilution processes. In contrast, there are concurring increases in stream discharge and TDS in reaches 1 and 4. In reach 7, TDS increases considerably but stream flow remains almost unchanged. This suggests occurrences of saline water addition and even displacement besides evaporation/dilution processes in these reaches.

[7] To elucidate major mechanisms controlling the Pecos hydrochemistry, we projected the 10 vectors (i.e., arrowed lines) on the polar coordinates (Figure 2). Each coordinate has distinctive hydrology/hydrochemistry indication. The horizontal orientation (W-E axis) reflects hydrological processes like stream gain/loss. The vertical orientation (N-S axis) represents the scenario that stream gain is balanced by stream loss, implying the occurrence of either saline or fresh groundwater displacement. Saline groundwater is readily displaced by agricultural drains in the Rio Grande basin [*National Resource Committee*, 1938]. The NW-SE orientation represents processes dominated by evaporative concentration or freshwater dilution, in which no net salt gain/loss occurs. It is inferred from equation A3 in Appendix A that the upper hemisphere (above the evaporation/dilution line) is a region with salt gain and the lower hemisphere is a region with salt loss. Overall, there are four major areas designating four major processes, namely saline water addition, evaporative concentration, freshwater dilution, and salt storage. Salt storage is likely to occur when river water passes through dry porous media (e.g., water-depleted aquifer). The areas of evaporative concentration and freshwater dilution are subject to subdivision depending on net salt gain or loss. For each point, its distance from the zero

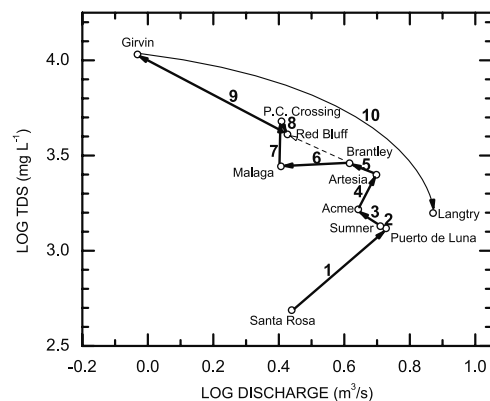


Figure 1. Logarithmic relationships of the total dissolved salts (TDS) concentration with streamflow discharge of the Pecos River at the eleven gauging stations. Arrows denote flow direction from the upper basin downward. Open arrowed, dashed line represents a hydrochemical “short cut” of reaches 6, 7, and 8.

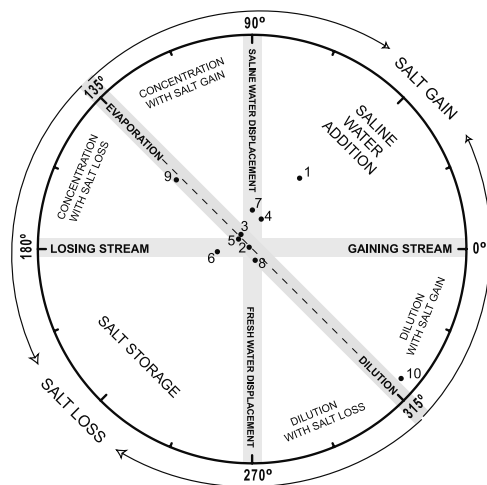


Figure 2. Polar projections of the 10 points showing dominant processes that are associated with their reaches. Numbers 1 to 10 denote the reaches tagged in Figure 1. The data used here is the same as presented in Figure 1, but the polar coordinate system is adopted. Conversion from Cartesian to polar coordinates is described in Appendix A.

point represents the relative significance of corresponding process occurring in its associated reach over the entire reaches studied.

[8] Of the 10 reach points studied, six of them are nearly aligned with the evaporation/dilution line, two fall in the area of saline water addition, one lies on the axis of saline water displacement, and one is close to the axis of losing stream (Figure 2). Points 1 and 4 fall within the area of saline water addition, probably due to the interaction of ground and surface waters. Increase in salt load in reach 1 (between Santa Rosa and Puerto de Luna) is probably related to the upper Triassic Santa Rosa formation, which consists of conglomerates, mudstones, and sandstones with gypsum pellets [Sidwell and Warn, 1953; Bodine and Jones, 1990]. The water chemistry of reaches 2 and 3 appears to be controlled primarily by the evaporative concentration process. Reach 3 shows more water loss than reach 2. However, the former gains slight salt while the later loses slight salt. This suggests occurrence of saline water addition in the reach between Sumner Dam and Acme. Reach 4 gains only 14% of water but 73% of salt. Most of the salt increases are ascribed to increases in sodium and chloride (Table 1). This reach (between Acme and Artesia) lies in the eastern margin of the Roswell Basin that consists of Quaternary alluvial deposits, Grayburg formation, and underlying San Andres limestones of Permian age [Fiedler and Nye, 1933; Bean, 1949]. The early evidence indicates a considerable amount ($\sim 5 \text{ m}^3/\text{s}$) of spring flow at Roswell [Fiedler and Nye, 1933; Theis, 1965]. In the vicinity of the Malaga Bend about 20 miles southeast of Carlsbad, the river chemistry appears to be modified by local hydrological flowpaths. There are about 40% of stream water and salt losses with a 4% decrease in TDS between Brantley Dam and Malaga. This indicates that stream flow loses primarily through discharge into groundwater aquifers instead of evaporation. It is interesting to note that the salt loss of reach 6 is nearly compensated by the salt gain in reach 7 (between Malaga and Pierce Canyon Crossing) without noticeable flow gain.

This indicates that saline groundwater is displaced by the less saline surface water upstream. Reach 8 falls in the area of dilution with salt loss while reach 9 falls in the area of evaporative concentration with salt loss. Some of the salt losses in the reach between Red Bluff and Girvin are probably due to water loss into the Pecos Alluvium Aquifer in the two reaches [Slade *et al.*, 2002], but most may be attributed to the evaporation-crystallization process [Gibbs, 1970, 1971]. This reach shows a considerable (32%) reduction in calcium flux with little change in other ion fluxes, which is probably removed via carbonate precipitation. The water chemistry of the reach between Girvin and Langtry is affected by the freshwater dilution process with slight salt gain. The freshwater is mostly from the Cretaceous Edwards-Trinity Aquifer receiving local monsoonal rainfall [Slade *et al.*, 2002].

[9] Gibbs [1970, 1971] argued the importance of the evaporation-crystallization processes relative to the other two mechanisms of rock dominance and atmospheric precipitation in controlling the Pecos hydrochemistry. This analysis suggests that the evaporative concentration and freshwater dilution are the prevailing processes that affect the river chemistry. In perspective of the entire Pecos River, however, the rock dominance is the most important mechanism controlling the water chemistry of the Pecos. Hale *et al.* [1954] estimated that saline springs and seepages at the Malaga Bend alone added about 380,000 kg salts daily into the Pecos River. This is in line with our current estimates (Table 1). However, the origin of the saline springs is probably from seepage of river water upstream, instead of upward percolation of the underlying Salado formation [Hale *et al.*, 1954]. This is because 1) the salt gain at the Malaga Bend is nearly balanced by the salt loss between Brantley Dam and Malaga, 2) there is no spectacular variation in water chemical composition in the reaches above and below the Malaga station [Gibbs, 1971], and 3) upward percolation of brines is unlikely to occur as the underlying Salado formation is below the clay aquitard of the Rustler formation. A majority of salts contributed to the Pecos River are added in reaches 1 and 4 in the upper valley with probable different origins. The added salts are dominated by CaSO_4 between Santa Rosa and Puerto de Luna, and by NaCl between Acme and Artesia (Table 1).

5. Conclusions

[10] The database analyzed contains daily to monthly resolved stream flow and water quality records at the eleven gauging stations during the period 1959–2002. This time period nearly spans the last full cycle of the Pacific Decadal Oscillation [Mantua *et al.*, 1997; Yuan and Miyamoto, 2004], allowing us to avoid short-time scale surface processes. For example, dissolved salts tend to be stored in irrigated lands during low-flow periods and be flushed out during high-flow periods after a drought [Hernandez, 1978]. Over the past 44 years, there has been no perceivable salt buildup in the entire drainage. In contrast, most of the salts contributed to the Pecos River are from the upper basin (above Artesia) through dissolution of evaporites such as gypsum, anhydrite, and halite.

[11] Transformation of TDS-discharge relationships into a polar projection plot allows us to unravel major processes

controlling river water chemistry, namely saline water addition, evaporative concentration with salt gain or loss, dilution with salt gain or loss, and salt storage. Both saline water addition and salt storage processes appear to be related to flow pathways and physical properties of subsurface porous media (e.g., hydraulic conductivity and mineralogical interactions). On the other hand, both evaporative concentration and freshwater dilution processes appear to be linked with atmospheric conditions. This work indicates that evaporative concentration and/or freshwater dilution are the prevailing processes, but changes in flow path and lithologic conditions are also important sources of variations in the water chemistry of the Pecos River.

[12] Knowledge of mechanisms controlling river chemistry is essential for water resources and land use management, in particular for arid-semiarid regions of the world. The approach developed here is useful and effective to elucidate dominant mechanisms controlling surface water chemistry. The polar plot method has the advantage of easily differentiating the dominant processes controlling river chemistry. Such approach is readily expanded to individual ions to further investigate the mechanisms that control water chemical composition, which has broad implications in water resources management and scientific research.

Appendix A

[13] Suppose two gauging stations S_1 and S_2 have streamflow discharge Q_1 and Q_2 and TDS concentration C_1 and C_2 , they can be represented by two points S_1 ($\log Q_1$, $\log C_1$) and S_2 ($\log Q_2$, $\log C_2$) in the log-scaled Cartesian coordinates. To project the vector from S_1 to S_2 in the polar coordinates, one needs to calculate the corresponding angle (α) and radius (ρ) by

$$\alpha = \begin{cases} \arctan \frac{\log C_2/C_1}{\log Q_2/Q_1} & Q_2 > Q_1 \\ \frac{\pi}{2} & Q_2 = Q_1 \\ \pi + \arctan \frac{\log C_2/C_1}{\log Q_2/Q_1} & Q_2 < Q_1 \end{cases} \quad (A1)$$

$$\rho = \sqrt{(\log C_2/C_1)^2 + (\log Q_2/Q_1)^2} \quad (A2)$$

$$\log \frac{L_2}{L_1} = \begin{cases} (1 + \tan \alpha) \log \frac{Q_2}{Q_1} & Q_2 \neq Q_1 \\ \log \frac{C_2}{C_1} & Q_2 = Q_1 \end{cases} \quad (A3)$$

where L_1 and L_2 are salt loads at stations S_1 and S_2 , respectively.

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