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ORIGINAL ARTICLE

# Geochemistry analysis and evolution of a bolson aquifer, basin and range province in the southwestern united states

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**Abstract** This paper expands significantly on the major-ion geochemical characterization, evolution, and differentiation of groundwater in the Presidio-Redford Bolson (PRB) Aquifer of Texas as presented in Chowdhury et al. (2008). For 19 groundwater samples from the PRB Aquifer, the author calculated major cation–anion balance errors, equilibrium carbon dioxide partial pressure values and saturation indices for selected minerals. Comparison of major-ion analyses for groundwater from basin margin wells with those for basin center wells is documented and illustrated with ion-concentration maps and Piper and Stiff diagrams and reveals significant increases in concentrations of chloride, sulfate and sodium coupled with notable decrease of calcium in bolson-center well samples. These geochemical changes suggest dissolution of aquifer minerals and cation exchange as groundwater migrates downgradient to the bolson center. The US Geological Survey (USGS) computer code, NETPATH, was used to interpret probable net geochemical mass-balance reactions that potentially have occurred within the PRB Aquifer along groundwater flowpaths from bolson margin to bolson center. For all four upgradient–downgradient well pairs studied, at least three NETPATH models contain cation exchange values; calcium is being exchanged for sodium. The Rio Grande Alluvium Aquifer and Rio Grande River are notably minor sources of recharge to the PRB Aquifer, based on Chowdhury et al. (2008) and geochemical evaluations of this study.

**Keywords** Aqueous geochemistry · Geochemistry and trace elements · Hydrogeology · Surface water · Rio grande river · Texas · USA

## Introduction

The study area is the fault-bounded Presidio-Redford Bolson (PRB) in west Texas (Fig. 1; Chowdhury et al. 2008). The Presidio Bolson is much larger than the Redford Bolson, which is south of Presidio. The PRB (basin surrounded by mountains), approximately 97 km long, lies in the Basin and Range Province. The study area is characterized by a hot desert climate. The average annual rainfall ranges from about 20 cm in the basin center to about 46 cm at the highest elevations (about 2,300 m) in the adjacent mountains (Chowdhury et al. 2008).

The geochemical study of aquifers and surface water within the PRB conducted by Chowdhury et al. (2006, 2008) was broad in scope and focused on groundwater recharge. It, however, did not fully address equilibrium calcium carbonate chemistry. Specifically for this study, cation–anion balance errors, carbon dioxide ($CO_2$) partial pressure values, and saturation indices for selected minerals, missing from Chowdhury et al. (2008), were calculated for the PRB Aquifer and for the Rio Grande Alluvium Aquifer. Additionally, geochemical diagrams and maps were prepared for numerous groundwater and Rio Grande River samples to compare and contrast major ion chemistry. PRB Aquifer analyses were evaluated using a US Geological Survey (USGS) computer code that identifies

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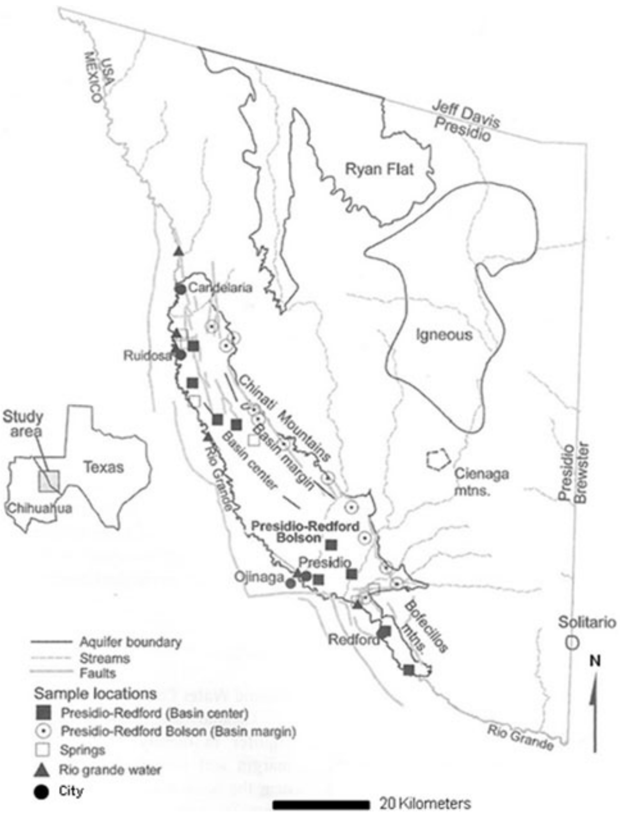


**Fig. 1** Presidio-Redford Bolson study area. Source of map is Fig. 1 in Chowdhury et al. (2008). Reprinted from Ground Water with permission of the National Ground Water Association. Copyright 2008

probable geochemical reactions along groundwater flowpaths to enhance the characterization of the PRB Aquifer, to identify probable geochemical reactions along potential groundwater flowpaths extending from the PRB basin margin to basin center, and to investigate groundwater recharge/discharge.

## Methods

The water-quality analyses and related data used to conduct the geochemical evaluation presented in Chowdhury et al. (2008) (Table 1, ESM only) were requested and received. This electronic database file contains 53 analyses, encompassing 39 groundwater samples from study area wells, eight spring-water samples and six surface-water samples. Nine samples were collected from wells tapping the PRB Aquifer, seven samples originated from springs, five samples were collected from the Rio Grande River, and the remaining sample from a tributary to the Rio Grande. These 22 groundwater and surface-water samples were collected during the time period of July 2004 through August 2005. The remaining 31 well-water and single spring-water analyses, conducted on samples collected between November 1949 and October 2001, were obtained from the Texas Water Development Board (TWDB) groundwater database.

To evaluate the quality of the 53 sample analyses and to confirm their suitability for geochemical evaluation, major ion balances were calculated and examined as a quality-assurance check of the major anion and cation analyses. Milliequivalents per liter are calculated by multiplying the concentration of the ion in millimoles per liter by the ionic charge (Bartos and Ogle 2002). The ion balance was calculated as the total dissolved-cation milliequivalents minus the total dissolved-anion milliequivalents divided by the total concentration of major ions dissolved in solution (Hem 1992). Then the USGS DOS-based computer program NETPATH (Plummer et al. 1994) was used to calculate saturation indices for selected minerals and partial pressure of carbon dioxide. For one PRB Aquifer well, PR19, however, these calculations could not be performed because no pH value was available.

Stiff diagrams depict major ion as composition (as mEq/L) and indirectly, the total dissolved solids (TDS) concentration. Stiff diagrams (Stiff 1951) for selected sample analyses were prepared using HC-Gram, freeware provided by the U.S. Office of Surface Mining Reclamation and Enforcement (OSM 2005). To evaluate potential geochemical evolution of young groundwater at the bolson margin as it migrates toward the basin center and the Rio Grande, NETPATH was used to identify geochemical interactions along probable PRB Aquifer flowpaths comprised of a basin margin well and a basin center well. A code based on three USGS geochemical computer codes (WATEQ, WATEQF, and WATEQ4F), NETPATH also was employed to calculate aqueous mineral saturation indices. Additionally, a common suite of geochemical phases for a specific aquifer (e.g., $CO_2$ dissolution or outgassing, cation exchange) was used as input for the mass balance reaction scenarios.

## Geology and hydrogeology

The geologic–hydrogeologic setting of the PRB is described in significant detail in Groat (1972), Gates et al. (1980), and Chowdhury et al. (2008). A standard page-size map depicting the aquifers of Texas (Bureau of Economic Geology 2004) shows the PRB as the Bolson (Hueco-Mesilla and West Texas) aquifer (map abbreviation Bn).

The Presidio Bolson, formed by middle Tertiary normal faulting, is typical of Basin and Range Province tectonic activity. Over geologic time, the basin was filled with sediment eroded from the surrounding mountains. At least 300 m of bolson fill comprise basin margin- and basin-center facies (Groat 1972).

The most reliable groundwater supplies are obtained from the Rio Grande Alluvium aquifer south of a point along the Rio Grande River approximately 5 km north of Presidio (Groat 1972). Groundwater stored in bolson-fill sediments potentially comprises the most important aquifer; however, the large body of relatively impermeable, gypsum-rich mudstone contained in the PRB Aquifer results in small yields of poor-quality water over much of the bolson.

The Presidio Bolson is structurally and stratigraphically similar to other Basin and Range Province basins. Permeable coarse-grained deposits (basin-margin facies) overlap onto the bordering mountains where rainfall is typically concentrated. Groundwater would be expected in the bolson-fill sediments; however, two factors exert a strong influence. First, the bolson deposits have been dissected by the Rio Grande and its tributaries; and second, a large part of the basin fill, especially in the bolson center, consists of relatively impermeable mudstones (Groat 1972; Chowdhury et al. 2008).

Groundwater occurs mainly under unconfined conditions near the bolson margins and becomes semiconfined to confined as the sediments become more impermeable (predominantly mudstone) as the basin center is approached (Groat 1972; Chowdhury et al. 2008). Groundwater resides at depths of about 91 m below land surface near the basin margin and decreases to depths of less than 30 m in the basin center (Chowdhury et al. 2008). Numerous springs, encompassing those sampled for this study, are associated with faults and facies changes and discharge groundwater originating from the bolson fill of the PRB Aquifer (Groat 1972).

The Rio Grande River above Presidio typically has low discharge or is dry for much of the year. Below the confluence of the Rio Conchos with the Rio Grande, about 5 km above (north of) Presidio, the stream becomes a perennial or gaining river (Gates et al. 1980). Chowdhury et al. (2008) conclude that the Rio Grande is mainly a losing (ephemeral) stream in the PRB.

## Bolson-fill mineralogy

Gypsum is common in the basin-center deposits; it occurs as (1) disseminated crystals and subhedral grains; (2) lenses and thin beds in a clay matrix; (3) distinct beds of massive, pure gypsum; and (4) as cement in relatively mud-free sandstone. Knobby calcium carbonate nodules occur in sandstone and mudstone throughout the bolson fill. Tube-like calcite forms a network in muddy sandstone in parts of the Redford Bolson fill. Quartz and feldspar are the most abundant minerals comprising the bolson-fill sandstone and siltstone. Much of the feldspar is orthoclase (K spar) that shows little evidence of weathering. Clay mineralogy of the mudstone and sandstone is dominated by montmorillonite; illite and kaolinite are second and third, respectively, in abundance (Groat 1972). Chowdhury et al. (2008) postulate the occurrence of evaporate deposits (e.g., halite) in bolson-center sediments based on higher sodium (Na), chloride (Cl), and sulfate ($SO_4$) concentrations in groundwater in the center of the Presidio Bolson.

## Results and discussion

Nine samples were collected by Chowdhury et al. (2008) from the PRB Aquifer. Based on analytical results for these and an additional 11 well analyses residing in the TWDB database for this aquifer, cation–anion charge imbalance ranged from −5.4 (well PR4) to 11.9% for well PR15. The USGS considers ion balances within the ±6% range to indicate major-ion analyses of good quality; however, ion balances up to 12% are considered acceptable (Bartos and Ogle 2002). The significant imbalance for well PR15 was reduced to near zero using an algorithm in NETPATH. As an aqueous geochemistry overview, pH values for these 20 wells ranged from 7.16 to 9.15 and averaged 7.90. TDS results ranged from 255 to 1364 mg/L, with a median value of 472 mg/L. Calculated partial pressure values for $CO_2$ ranged from 1.7E−04 to 1.7E−02 atm, with a geometric mean of 3.0E−03 atm.

Groundwater from the PRB Aquifer is mainly a Na–Ca–$HCO_3$ type near the fault-bounded basin margin and becomes predominantly a Na–$HCO_3$–$SO_4$ hydrochemical facies down flowpaths near the bolson center. In contrast, Chowdhury et al. (2008) describe the bolson center hydrochemistry primarily as a Na–$SO_4$–Cl type. This somewhat subtle hydrochemical facies difference is graphically displayed on a Piper trilinear diagram (Piper 1944) and is especially apparent on the diagram's diamond (Fig. 2). Groundwater in the basin margin areas has low TDS, sulfate, chloride, and sodium concentrations that increase toward the bolson-center areas near the Rio Grande River. These groundwater geochemistry differences reflect the varying rock and mineral composition from conglomerate nearest the mountain front grading through sandstone into claystone near the basin center (Groat 1972).

TDS levels for sampled PRB Aquifer wells and springs (Chowdhury et al. 2008) tend to increase from the basin margin area, where recharge is occurring, to the margin center. Along the eastern extent of the bolson (on the U.S. side), TDS ranges from about 300 to 500 mg/L; near the Rio Grande River values ranging from approximately 500–1,000 mg/L are typical.

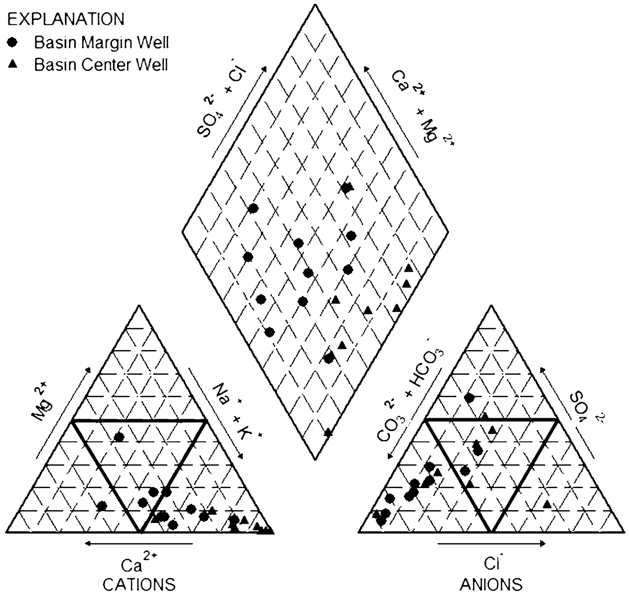


**Fig. 2** Piper trilinear diagram for 20 water-quality analyses for the Presidio-Redford Bolson Aquifer. Ion concentrations are represented as percentages of total milliequivalents per liter

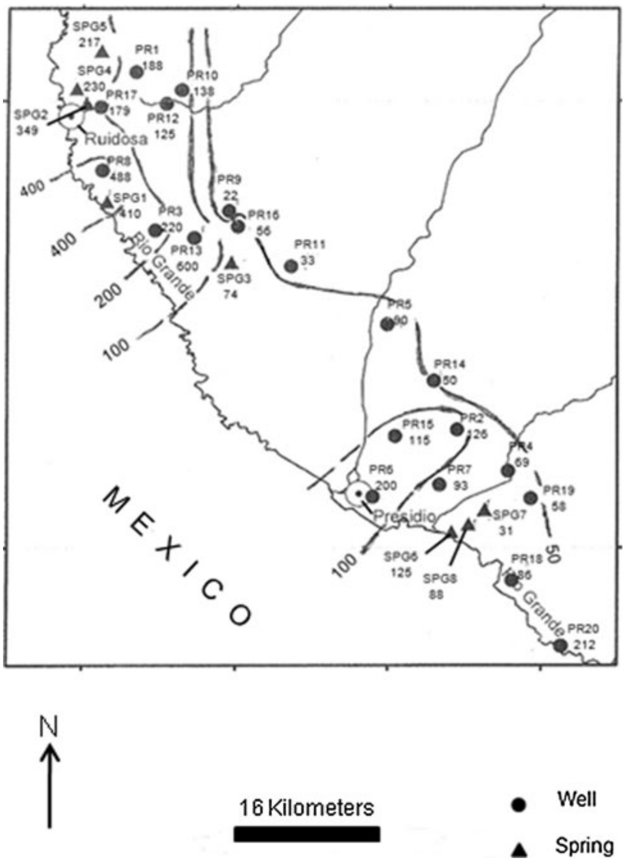


**Fig. 3** Distribution of sodium concentration (mg/L) in the Presidio-Redford Bolson Aquifer

Sodium and chloride concentrations recorded for bolson aquifer wells and springs (Figs. 3, 4, respectively) show a similar pattern as that for TDS—generally increasing levels from bolson margin westward to the center. Sodium values typically range from 30 to 60 mg/L at the margin of the bolson to approximately 100–400 mg/L at the center. For chloride, concentrations at the bolson margin approximate 20 mg/L and range from about 50 to 150 mg/L at bolson center wells and springs.

The areal distribution of calcium in the PRB Aquifer (Fig. 5) is significantly distinct from distribution patterns for TDS, sodium, and chloride. As a general rule, calcium concentration decreases downgradient from bolson margin to center area. A typical calcium level at the bolson margin is 50 mg/L; whereas calcium concentration commonly ranges from about 20 to 30 mg/L at the bolson center. A probable explanation for this distribution is presented below.

Eleven of the sampled wells tapping the PRB Aquifer are characterized as basin margin wells. The median TDS for these bolson-margin wells is 376 mg/L (Table 1). For nine basin-center wells, the median TDS value is 676 mg/L, nearly double that for the margin wells. Median values for sodium, chloride, bicarbonate ($HCO_3$), and sulfate for the basin center wells are higher than those for basin margin wells. The median basin-center concentration for calcium, however, is lower than that for the bolson margin wells. NETPATH-calculated $CO_2$ partial pressures ($pCO_2$) for 19 PRB Aquifer groundwater samples ranged from 1.7E−04 to 1.7E−02 atm. For comparison purposes, $pCO_2$ for the present-day atmosphere is 3.16E−04 atm (Appelo and Postma 1994). Foster (1950), however, notes that the $pCO_2$ for soil air typically is much higher than for atmosphere air. This increased $pCO_2$ results primarily from the microbial and plant-root respiration of organic matter in soils and aquifer deposits. The median for $pCO_2$ in basin-margin wells is 6.6E−03 atm and for basin-center wells is 1.5E−03 atm. This equates to a basin center to basin margin $pCO_2$ ratio of 0.22:1. The similarity of this ratio to that for Ca, 0.29:1, conforms with the Foster (1950) finding that $pCO_2$ increases with increasing concentrations of dissolved calcium carbonate and with Plummer et al. (1976) who provided text and a figure which demonstrate total calcium in solution as a function of $pCO_2$.

Saturation indices were calculated for five common minerals. Median saturation indices for aragonite, dolomite, gypsum, and halite are slightly to moderately negative, indicative of mildly to moderately undersaturated (dissolving) conditions (Table 2). For calcite, median indices are very slightly positive, documenting notably mild supersaturated (precipitating) conditions. Except for halite, median saturation indices for basin margin well analyses are quite similar to those for basin center wells.

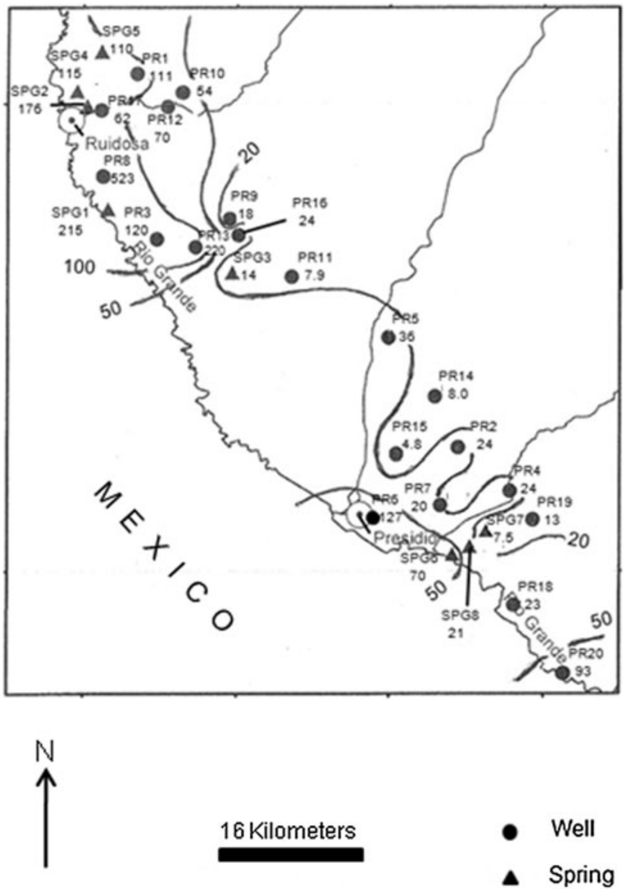


Fig. 4 Distribution of chloride concentration (mg/L) in the Presidio-Redford Bolson Aquifer

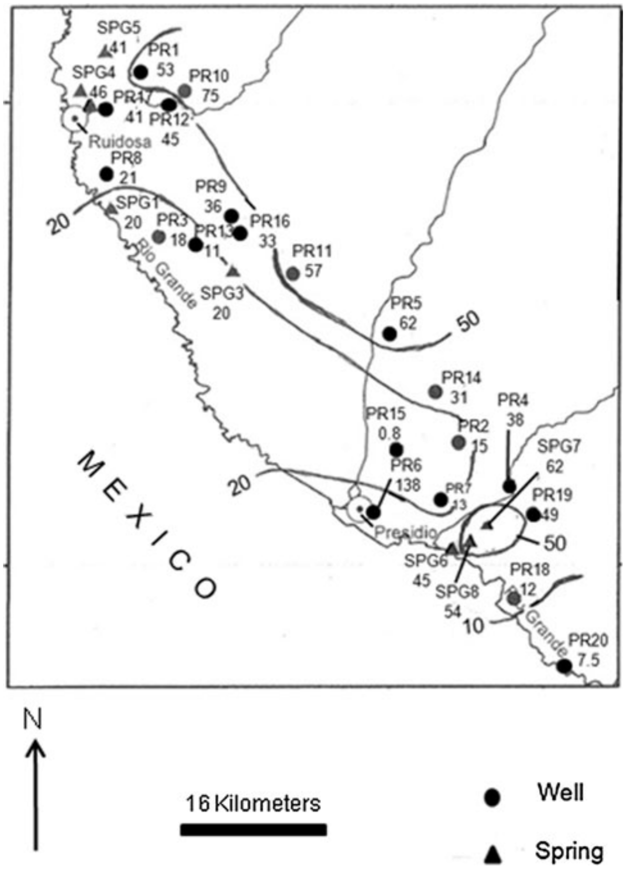


Fig. 5 Distribution of calcium concentration (mg/L) in the Presidio-Redford Bolson Aquifer

For halite, the relative percent difference between the median saturation index values for basin margin wells (−7.18) and basin center wells (−6.26) is almost 14%. Longer residence times for basin center groundwater and evaporite deposits possibly account for this calculated saturation difference, a potentially less undersaturated environment for the basin center.

Chowdhury et al. (2008) note that basin-margin wells have chloride/bromide (Cl/Br) ratios of <200; whereas basin center wells have Cl/Br ratios of about 200–800. For the 11 basin-margin wells, this ratio ranges from 40 to 252, with a median value of 130 (Table 1). The Cl/Br ratios for the nine basin-center wells range from 96 to 594, with a median value of 374. The rejection of bromide from the halite lattice as the evaporite minerals form most likely accounts for notably high Cl/Br ratios in bolson-center well samples. Comparing median Cl/Br ratios for basin center with basin margin wells yields a median ratio of 2.88.

Groundwater flow through the PRB Aquifer is relatively slow as it moves through increasingly fine-grained material toward the basin center. Chowdhury et al. (2008) note that isotopic chemistry of this bolson aquifer characterizes groundwater with a long residence time, subsequent reaction with the aquifer matrix, and lack of significant mixing with water from a different source. Carbon-14 data suggest that groundwater in the PRB Aquifer possesses apparent ages of up to 18,000 years (Chowdhury et al. 2005). As groundwater flows from recharge areas at the basin margin to the bolson center and discharges to the Rio Grande (Gates et al. 1980), it dissolves significant quantities of Na, Cl, and $SO_4$. The notable decrease in calcium content (Table 1), with exception of well PR6, suggests cation exchange of Ca by Na as asserted by Chowdhury et al. (2008). The relatively unchanged median $HCO_3$ concentration may reflect a dearth of carbonate minerals in the basin-center portion of the PRB Aquifer.

These geochemical changes along four discrete basin margin-to-center flowpaths (Fig. 6) were evaluated using a common graphical method and a geochemical equilibrium speciation computer model (NETPATH). Major anion and cation concentrations were compared and graphically illustrated by preparing Stiff diagrams for four well pairs (Figs. 7, 8, and 9). The size of the polygon comprising the Stiff diagram is a relative indication of the dissolved-solid concentration (Bartos and Ogle 2002). Significant

**Table 1** Presidio-Redford Bolson well statistics, comparing basin margin to basin center

| Well ID | Concentrations in mg/L | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | TDS | Na | Cl | $HCO_3$ | Ca | $pCO_2$ | $SO_4$ | Cl:Br |
| Basin margin wells | | | | | | | | |
| PR01 | 712 | 188 | 111 | 329 | 53 | 1.68E−02 | 153 | 252 |
| PR02 | 414 | 126 | 24 | 269 | 15 | 2.06E−03 | 46.6 | 113 |
| PR04 | 344 | 69 | 24 | 235 | 36 | 2.79E−03 | 47 | 192 |
| PR05 | 526 | 90 | 36 | 289 | 62 | 1.66E−02 | 112 | 68 |
| PR09 | 299 | 22 | 18 | 195 | 36 | 5.11E−04 | 47.9 | 105 |
| PR10 | 806 | 138 | 54 | 215 | 75 | 1.08E−02 | 351 | 130 |
| PR11 | 376 | 33 | 7.9 | 228 | 57 | 9.71E−03 | 33.1 | 68 |
| PR12 | 674 | 125 | 70 | 283 | 45 | 1.36E−02 | 124 | 229 |
| PR14 | 255 | 50 | 8.0 | 198 | 31 | 3.56E−03 | 9.0 | 40 |
| PR16 | 297 | 56 | 24 | 164 | 33 | 1.26E−03 | 48 | 158 |
| PR19 | 372 | 58 | 13 | 290 | 49 | – | 22.6 | 154 |
| Median values | 376 | 69 | 24 | 235 | 45 | 6.64E−03 | 48 | 130 |
| Basin center wells | | | | | | | | |
| PR17 | 709 | 179 | 62 | 366 | 41 | 1.27E−02 | 132 | 222 |
| PR08 | 1360 | 488 | 523 | 320 | 21 | 3.81E−03 | 130 | 594 |
| PR03 | 676 | 220 | 120 | 316 | 18 | 1.49E−03 | 110 | 462 |
| PR13 | 1610 | 600 | 220 | 552 | 11 | 1.24E−03 | 460 | 478 |
| PR15 | 417 | 115 | 5.4 | 274 | 0.75 | 1.71E−04 | 18.6 | 96 |
| PR07 | 374 | 93 | 20 | 221 | 13 | 2.31E−03 | 43.7 | 113 |
| PR06 | 1070 | 200 | 127 | 267 | 138 | 1.58E−02 | 391 | 374 |
| PR18 | 309 | 86 | 23 | 179 | 12 | 1.26E−03 | 45.5 | 189 |
| PR20 | 674 | 212 | 93 | 154 | 7.5 | 3.78E−04 | 199 | 583 |
| Median value | 676 | 200 | 93 | 274 | 13 | 1.49E−03 | 130 | 374 |
| Basin center to basin margin ratios using median values | | | | | | | | |
| | 1.80 | 2.90 | 3.88 | 1.17 | 0.29 | 0.22 | 2.71 | 2.88 |

mineralization occurs for all four potential flowpaths described by the well pairs (in downgradient order: PR9-PR3, PR16-PR13, PR14-PR15, and PR2-PR6). Increases in sodium concentration are especially obvious on the Stiff diagrams and suggest geochemical evolution of young basin-margin groundwater moving downgradient toward the Rio Grande River. Figures 7 and 8 support the thesis that cation exchange (Ca exchanged for Na) occurs in bolson-center groundwater. The geochemistry of the bolson-margin PR9 sample (Fig. 7) is unique in that Mg is the predominant cation. Comparing the polygons for PR2 and PR6 (Fig. 9), gypsum dissolution may largely explain the significant change in shape and axial elongation of the Stiff diagram for PR6 and validates the premise of measurable mineralization as groundwater migrates from bolson margin to bolson center. Finally, examination of the Stiff diagrams generally confirms the predominant Na–$HCO_3$–$SO_4$ hydrochemical facies of bolson-center groundwater.

The public-domain computer code NETPATH was used to examine the possible geochemical evolution of groundwater flow along the above-described four basin-margin-to-basin-center flowpaths. Based largely on the mineralogy of the geologic units encompassing clays as described above, eight common minerals were chosen for simulation: calcite, dolomite, gypsum, halite, illite, montmorillinite (Na and Ca), and carbon dioxide. Halite was chosen partly because Chowdhury et al. (2008) hypothesize that the high chloride/bromide ratio and chloride values in basin-center wells suggest minor to moderate halite dissolution. Additionally, cation exchange was simulated, primarily because Chowdhury et al. (2008) conclude that ion exchange is occurring in bolson center deposits. For all well pairs, dissolution of modeled minerals for all simulated mass reactions exceeds precipitation. Net dissolution ranged from a low of 0.83 mmol/L for a model simulation for well pair PR14–PR15 to 71.0 mmol/L for a simulation for pair PR16–PR13 (Table 3). Median net dissolution values for the two downstream well pairs (PR14–15 and PR2–6), 5.05 and 5.18 mmol/L, respectively, are significantly lower than those for upgradient well pairs PR9–PR3

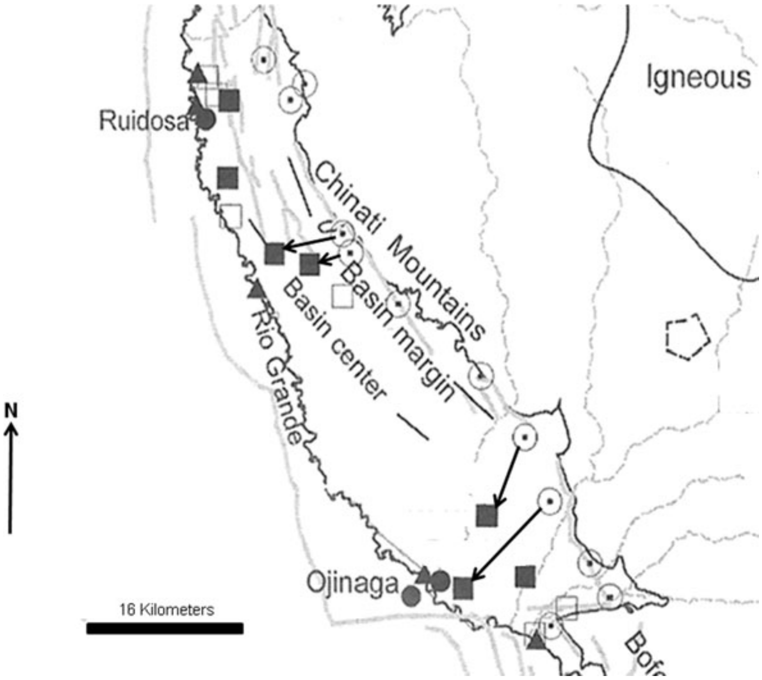
**Table 2** Saturation indices for Presidio-Redford Bolson Aquifer

| Well ID | Calcite | Aragonite | Dolomite | Gypsum | Halite |
|---|---|---|---|---|---|
| Basin margin wells | | | | | |
| PR1 | −0.009 | −0.152 | −0.358 | −1.626 | −6.257 |
| PR2 | 0.221 | 0.077 | 0.259 | −2.541 | −7.055 |
| PR4 | 0.332 | 0.187 | −0.245 | −2.147 | −7.315 |
| PR5 | 0.006 | −0.136 | −0.137 | −1.664 | −7.052 |
| PR9 | 0.949 | 0.809 | 2.152 | −2.199 | −7.948 |
| PR10 | −0.039 | −0.179 | −0.146 | −1.199 | −6.721 |
| PR11 | 0.016 | −0.128 | −0.538 | −2.120 | −8.126 |
| PR12 | −0.032 | −0.172 | −0.272 | −1.748 | −6.630 |
| PR14 | 0.199 | 0.059 | −0.155 | −2.881 | −7.937 |
| PR16 | 0.373 | 0.230 | 0.146 | −2.160 | −7.405 |
| Median | 0.108 | −0.035 | −0.151 | −2.134 | −7.185 |
| Basin center wells | | | | | |
| PR3 | 0.502 | 0.359 | 0.965 | −2.199 | −6.146 |
| PR6 | 0.016 | −0.132 | −0.786 | −0.929 | −6.177 |
| PR7 | 0.032 | −0.109 | −0.345 | −2.59 | −7.269 |
| PR8 | 0.105 | −0.038 | 0.075 | −2.181 | −5.196 |
| PR13 | 0.658 | 0.517 | 0.848 | −2.046 | −5.504 |
| PR15 | −0.111 | −0.252 | −0.402 | −4.282 | −7.750 |
| PR17 | 0.043 | −0.102 | −0.096 | −1.780 | −6.519 |
| PR18 | 0.066 | −0.075 | −0.544 | −2.606 | −7.248 |
| PR20 | 0.016 | −0.129 | −0.774 | −2.305 | −6.263 |
| Median | 0.043 | −0.102 | −0.345 | −2.199 | −6.263 |

and PR16–PR13, 21.6 and 41.8 mmol/L, respectively. For all five models, gypsum, halite, and illite are dissolving for the most upgradient well pair, PR9–PR3. For two of these models, sodium montmorillinite is dissolving at high concentrations. For the last model, calcium montmorillinite is dissolving at a high concentration. All five models for well pair PR16–PR13 simulate gypsum and halite to be dissolving and dolomite and illite to be precipitating. One model simulates sodium montmorillinite to be dissolving at high concentrations. Additionally, one model predicts dissolution of calcium at a high concentration. For well pair PR14–PR15, dolomite, halite, and illite are precipitating at low concentrations for all five models. For well pair PR2–PR6, the most downgradient well pair, NETPATH identified four geochemically feasible mass-balance reactions (see Table 3). In all models for this well pair, dolomite, gypsum, halite, and illite are dissolving. For all four well pairs, at least three models contain cation exchange values; calcium is being exchanged for sodium (release of sodium into solution, commonly referred to as water softening).

Eight spring samples were collected in the PRB and analyzed for general inorganic parameters. The hydrochemical facies type is Na–$HCO_3$–$SO_4$, corresponding to the predominant hydrochemical facies of the bolson center well samples. This commonality of hydrochemical facies substantiates the assertion by Groat (1972) that the Bolson's springs originate from the PRB Aquifer. Summarizing the analytical results, pH ranged from 7.35 to 8.49 and averaged 7.73. Cation–anion charge imbalance ranged from −1.7 to 2.6. For TDS, results ranged from 289 to 1155 mg/L, with a median of 756 mg/L. Calculated partial pressure values for $CO_2$ ranged from 1.1E−03 to 1.6E−02 atm, with a geometric mean of 5.8E−03 atm. Saturation

**Fig. 6** Presidio-Redford Bolson depicting four groundwater flowpaths defined by well pairs discussed in the text. Map is modified from Fig. 1 in Chowdhury et al. (2008)



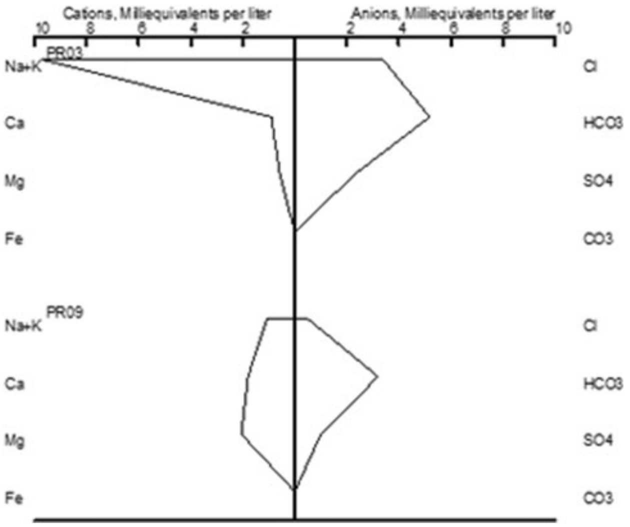


**Fig. 7** Stiff diagrams for well pair PR9 and PR3

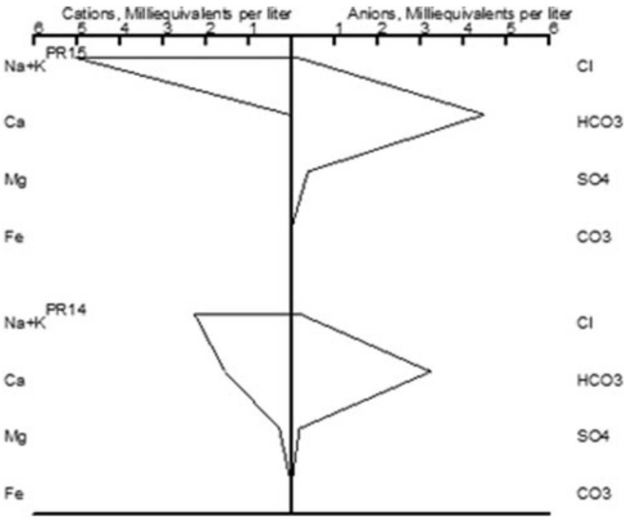


**Fig. 8** Stiff diagrams for well pair PR14 and PR15

indices for calcite range from −0.15 to 0.82; and for gypsum fall within the range of −2.53 to −1.61.

Chowdhury et al. (2008) evaluated nineteen TWDB database analyses for wells tapping the Rio Grande Alluvium Aquifer. The water type is predominantly Na–Cl–$SO_4$ based on 16 samples with complete major anion and cation analyses. Groundwater from the Rio Grande Alluvium and surface water from the Rio Grande are geochemically similar and predominantly consist of mixed cation (Na–Ca)-mixed anion ($SO_4$–Cl) hydrochemical facies.

Stiff diagrams were prepared for five water samples collected from the Rio Grande River for the Chowdhury et al. (2008) study (Fig. 1). These diagrams show a wider range in mineralization than do the PRB Aquifer margin and center sample pairs. Similar to the PRB Aquifer aqueous

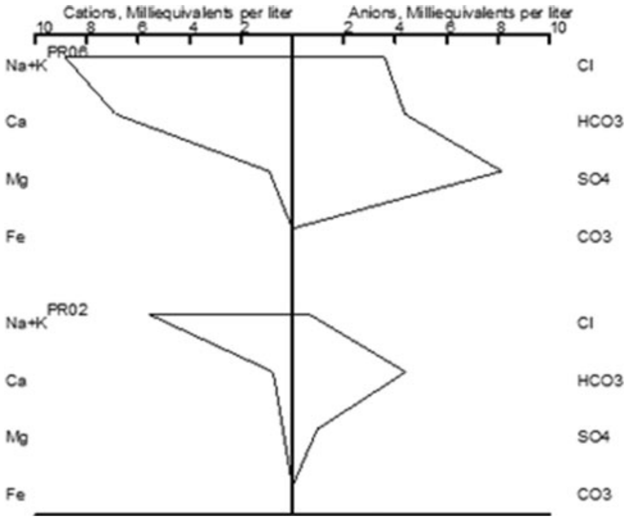


**Fig. 9** Stiff diagrams for well pair PR2 and PR6

geochemistry, the primary cation is sodium. The primary anion is predominantly chloride, whereas the predominant anion for the PRB Aquifer typically is bicarbonate. This dissimilarity in the anion half of the Stiff diagrams suggests that direct hydrologic interaction between the PRB Aquifer and the Rio Grande is insignificant.

Only a preliminary assessment of the aqueous geochemistry of the Rio Grande Alluvium Aquifer is possible. To date, researchers have not described or substantiated any appreciable recharge of the PRB Aquifer by this alluvial aquifer. Rather, the converse appears to be true; the PRB Aquifer is a source of recharge to the Rio Grande Alluvium Aquifer. Chowdhury et al. (2008) assert that the Rio Grande Alluvium potentially receives recharge from four sources: (1) precipitation; (2) flow in the Rio Grande; (3) seepage from the PRB Aquifer; and (4) upward flow from the deeper subsurface. Based on stable isotope results, Chowdhury et al. (2008) further state that the Rio Grande Alluvium receives recharge from lateral discharges of the PRB Aquifer.

Modern recharge to the PRB Aquifer is probably very low and localized. Chowdhury et al. (2008) conclude that this ongoing recharge mainly occurs through the broad, exposed stream channel beds containing coarse sand and gravels based on increased levels of selected isotopes.

## Conclusions

This geochemical study of the PRB Aquifer, located in the Basin and Range Province of southwestern Texas, evaluated equilibrium calcium carbonate chemistry to encompass calculation of $pCO_2$ values and saturation indices for selected minerals. Chemical analyses of 20 samples from

**Table 3** NETPATH simulation results for four well pairs, Presidio-Redford Bolson Aquifer

| Well pair | Model no. | Mass transfer in mmol/L | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Calcite | Dolomite | $CO_2$(g) | Gypsum | Halite | Illite | Na montm | Ca montm | Cation exchange | Net dissolution mmol/L |
| PR9–PR3 | 1 | 2.53 | −0.76 | 1.07 | 0.647 | 2.88 | 0.079 | – | – | 2.86 | 6.45 |
| PR9–PR3 | 2 | −0.336 | −0.76 | 3.94 | 0.647 | 2.88 | 0.079 | 17.4 | – | – | 23.8 |
| PR9–PR3 | 3 | 3.60 | −0.76 | – | 0.647 | 2.88 | 0.079 | −6.51 | – | 3.94 | −0.060 |
| PR9–PR3 | 4 | – | −0.76 | 3.60 | 0.647 | 2.88 | 0.079 | 15.3 | – | 0.336 | 21.8 |
| PR9–PR3 | 5 | – | −0.76 | 3.60 | 0.647 | 2.88 | 0.079 | – | 15.1 | 2.86 | 21.6 |
| | | | | | | | | | | Median | 21.6 |
| PR16–13 | 1 | 4.32 | −0.086 | 1.87 | 4.30 | 5.54 | −0.017 | – | – | 9.08 | 15.9 |
| PR16–13 | 2 | – | −0.086 | 6.19 | 4.30 | 5.54 | −0.017 | 26.2 | – | 4.76 | 42.1 |
| PR16–13 | 3 | – | −0.086 | 6.19 | 4.30 | 5.54 | −0.017 | – | 25.9 | 9.08 | 41.8 |
| PR16–13 | 4 | −4.76 | −0.086 | 10.9 | 4.30 | 5.54 | −0.017 | 55.1 | – | – | 71.0 |
| PR16–13 | 5 | 6.19 | −0.086 | – | 4.30 | 5.54 | −0.017 | −11.3 | – | 10.9 | 4.60 |
| | | | | | | | | | | Median | 41.8 |
| PR14–15 | 1 | 0.706 | −0.11 | 0.292 | 0.10 | −0.073 | −0.09 | – | – | 1.45 | 0.825 |
| PR14–15 | 2 | −0.745 | −0.11 | 1.74 | 0.10 | −0.073 | −0.09 | 8.79 | – | – | 9.62 |
| PR14–15 | 3 | 0.998 | −0.11 | – | 0.10 | −0.073 | −0.09 | −1.77 | – | 1.74 | −0.95 |
| PR14–15 | 4 | – | −0.11 | 0.998 | 0.10 | −0.073 | −0.09 | 4.28 | – | 0.745 | 5.11 |
| PR14–15 | 5 | – | −0.11 | 0.998 | 0.10 | −0.073 | −0.09 | – | 4.23 | 1.45 | 5.05 |
| | | | | | | | | | | Median | 5.05 |
| PR2–PR6 | 1 | −0.581 | 0.238 | 0.659 | 3.59 | 2.90 | 0.139 | – | – | 0.174 | 6.94 |
| PR2–PR6 | 2 | – | 0.238 | 0.079 | 3.59 | 2.90 | 0.139 | −3.52 | – | 0.755 | 3.42 |
| PR2–PR6 | 3 | −0.755 | 0.238 | 0.834 | 3.59 | 2.90 | 0.139 | 1.06 | – | – | 8.00 |
| PR2–PR6 | 4 | 0.079 | 0.238 | – | 3.59 | 2.90 | 0.139 | −4.00 | – | 0.834 | 2.95 |
| | | | | | | | | | | Median | 5.18 |

Negative number indicates amount of mineral precipitating; positive number indicates amount of mineral dissolving

Conversion of mmol/L to mg/L is obtained by multiplying by the gram formula weight

Montm, montmorillonite; –, mass-transfer result not simulated

groundwater from the PRB Aquifer were plotted on a Piper trilinear diagram, illustrating the distinct hydrochemical facies of the basin margin and basin center portions of this bolson aquifer. Stiff diagrams were prepared for numerous groundwater and Rio Grande River samples. PRB Aquifer major-ion analyses were evaluated using a USGS computer program (NETPATH) that identifies probable geochemical mass-balance reactions along groundwater flowpaths. These geochemical assessments and characterizations were used to investigate hydrochemical equilibrium conditions and probable hydrogeochemical evolution as groundwater has migrated from the bolson margins to the basin center throughout recent geologic time (approximately 18,000 years before present).

Groundwater in the basin margin areas is a Na–Ca–$HCO_3$ hydrochemical facies and has low TDS, sulfate, chloride, and sodium concentrations that increase toward the bolson-center areas near the Rio Grande River. Basin-center groundwater has a predominant Na–$HCO_3$–$SO_4$ composition. These groundwater geochemistry differences reflect the varying rock and mineral composition from conglomerate nearest the mountain front grading through sandstone into claystone rich in gypsum near the basin center as well as the increasing residence time downgradient.

NETPATH-calculated $pCO_2$ values for 19 groundwater samples from the PRB Aquifer ranged from 1.7E−04 to 1.7E−02 atm. This two-order-of-magnitude range encompasses the $pCO_2$ levels for the present-day atmosphere 3.16E−04 atm. The median for $pCO_2$ values for basin-margin wells is 6.6E−03 atm and for basin-center wells is 1.5E−03 atm. The similarity of the basin-center to basin-range ratios for $pCO_2$ and Ca, 0.22 and 0.29:1 indicate that $pCO_2$ increases with increasing concentrations of dissolved calcium carbonate and total calcium, respectively.

Eight minerals were chosen for simulation using NETPATH: calcite, dolomite, gypsum, halite, illite, montmorillinite (Na and Ca), and carbon dioxide. For all four potential PRB Aquifer flowpaths studied, significant mineralization occurs. Increases in Na concentration suggest geochemical evolution of young basin-margin groundwater moving downgradient toward the Rio Grande River. For all four well pairs, at least three NETPATH models contain cation exchange values; calcium is being exchanged for sodium (release of Na into solution).

With the exception of the fault-bounded margins, the PRB Aquifer is essentially a closed hydrologic system. Semiconfined and confined conditions prevail across most of this arid bolson. The Rio Grande Alluvium aquifer and Rio Grande are, at best, minor sources of recharge to the bolson aquifer. Modern recharge to the PRB Aquifer is probably very low and localized and occurs primarily through the broad, exposed stream channel beds containing coarse sand and gravel, based on increased levels of selected isotopes (Chowdhury et al. 2008) and on the results from this hydrogeochemical study.

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