TEXAS A&M UNIVERSITY

Texas Water Resources Institute
make every drop count

Hydrochemical Connectivity of the Allende-Piedras Negras Transboundary Aquifer

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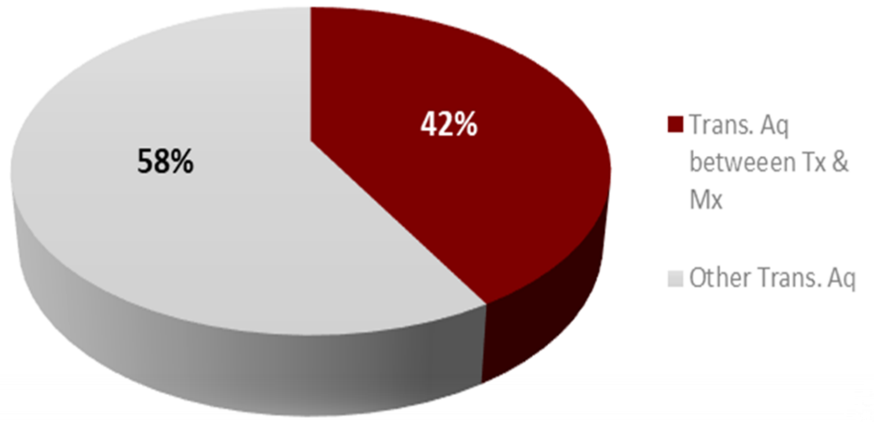
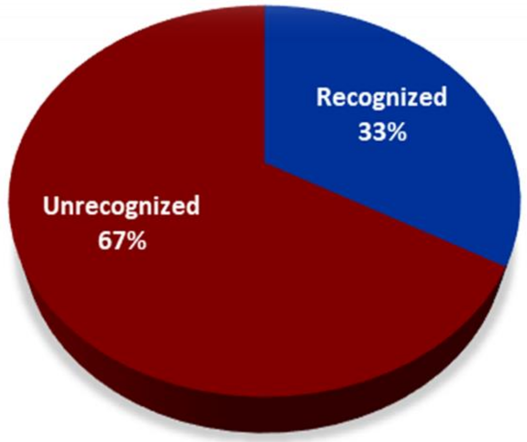
Motivation (Why this aquifer?)

- Arid to semiarid climate in the Del Rio/Ciudad Acuña área *(Boghici,2002)*
- Potential of GW over exhausted SW future source of freshwater *(Albrecht et al., 2017).*
- Intense competition over the adequate availability of water.
- Intensive water consumption. (agriculture, industries, mining)
- 1944 Treaty between Mexico and the United States for the Utilisation of Waters
- Officially not recognized as 'transboundary' aquifer *(Sanchez et al., 2016).*





Approach

Aim: To establish inter-aquifer mixing/connectivity in the APN aquifer hydro-chemically

Data Collection

Specific Aim1: *Characterization of Major Ion Chemistry (Hoffman & Cartwright, 2013)*

Identification of hydrochemical facies

- No. of classes= No. of depth ranges (Witcher,2004)
- Piper plot for each class

Specific Aim2: *Identification of chemical processes influencing the major ion chemistry (Hoffman & Cartwright, 2013)*

Identification of hydrochemical processes

- Predict from piper plots
- Statistical Analysis

Specific Aim3: *Visualization & Verification of Connectivity*

Establishing and Verification of transboundary connectivity

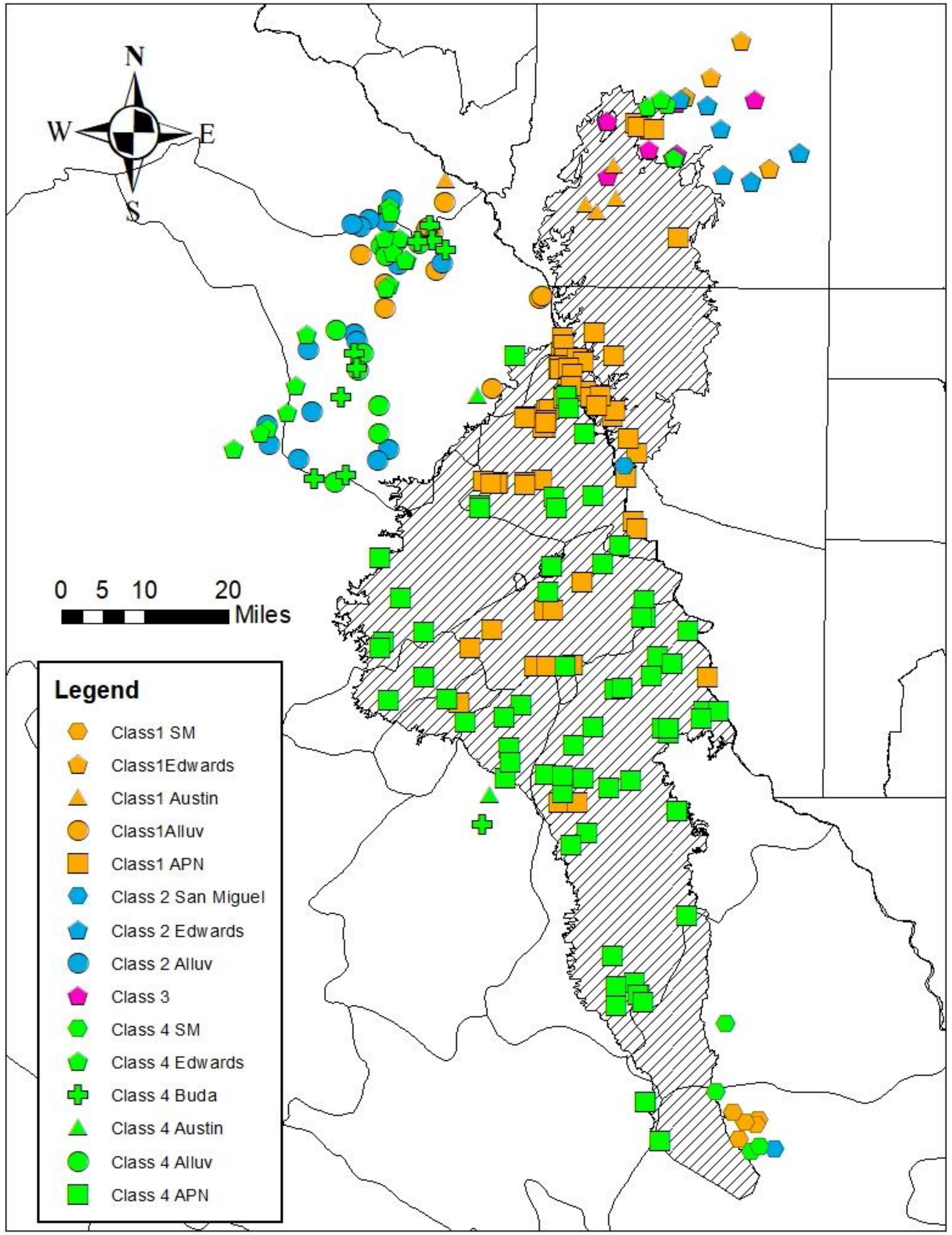
- Spatial Variablity of chemical processes
- Correlation between ionic ratios

Data Collection

- Data collection sources: TWDB, EPA, CONAGUA, private industries, Lesser & Associates
- Technical studies in the area: Boghici,2002; Castillo,2000; Lesser,2008
- Limitation of Data: (Heterogenous data sources)
  - *Missing Depth* (125/289 wells) ; (geologic information was determined by the location of the wells corresponding to the surrounding formation)
  - *Temporality* spans ~20 years or more.

Identification of Hydrochemical Facies

Step 1: No. of depth ranges= No. of Classes



Legend

- Class1 SM
- Class1Edwards
- Class1 Austin
- Class1Alluv
- Class1 APN
- Class 2 San Miguel
- Class 2 Edwards
- Class 2 Alluv
- Class 3
- Class 4 SM
- Class 4 Edwards
- Class 4 Buda
- Class 4 Austin
- Class 4 Alluv
- Class 4 APN

Orange: <u>Class 1:</u> Depth<65m

Blue: <u>Class2:</u> 66<Depth<200m

Magenta: <u>Class3:</u> 201<Depth<400m

Green: <u>Class 4:</u> Depth unknown

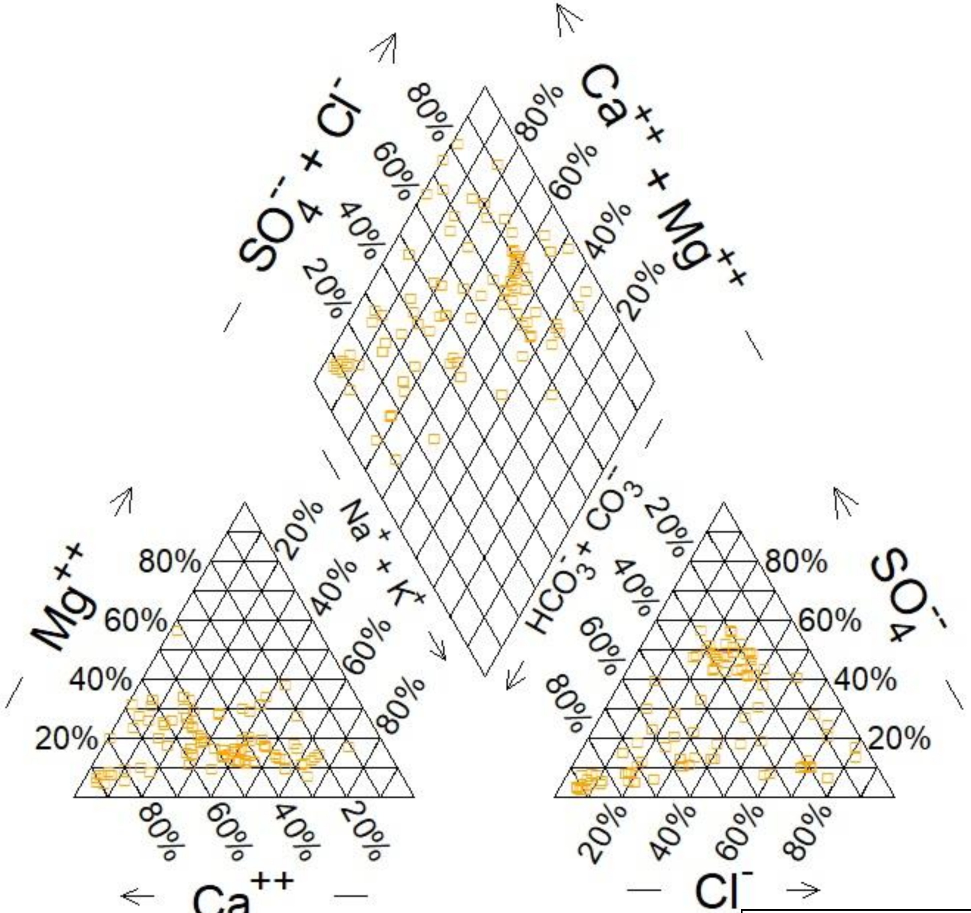
	APN	Alluvium	Austin	Edwards	San Migue	Total
Class 1	93	12	5	6	5	121
Class 2	0	18	0	10	2	30
Class 3	0	0	0	13	0	13
Class 4	77	11	2	20	4	125
			Tx	Mx		
Total		289	89	200		
Within the Boundary		174	59	115		

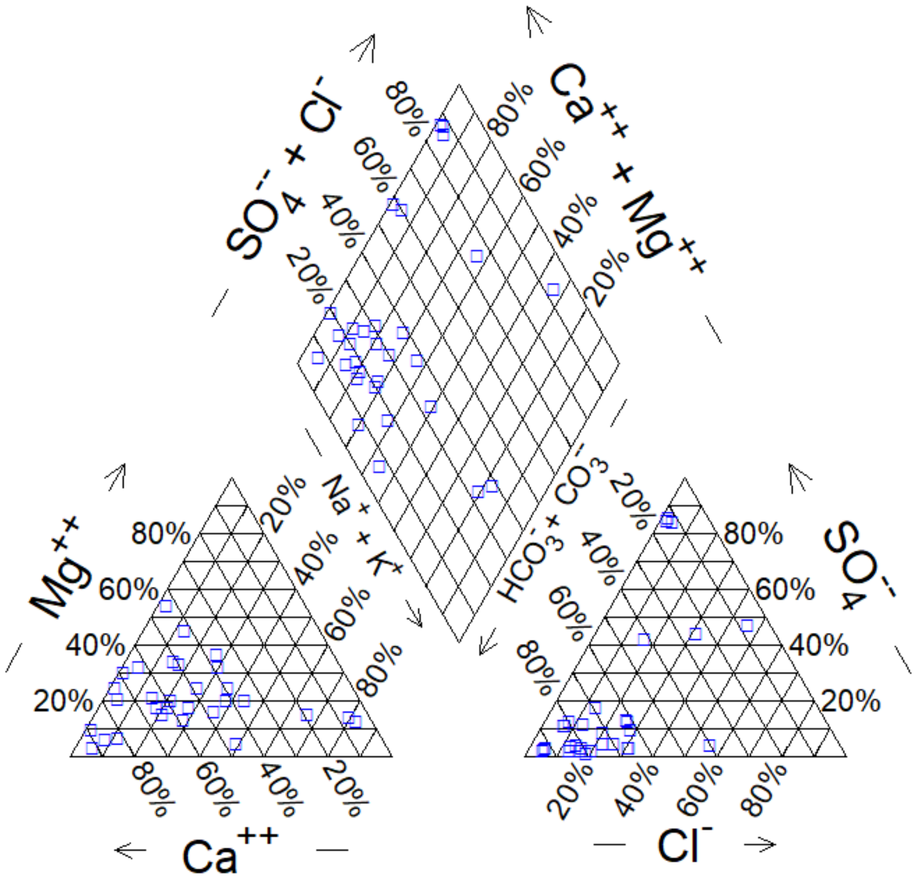
Identification of Hydrochemical Processes

Step 1: Piper plots for each class

Step 2: Prediction of chemical processes from piper plots

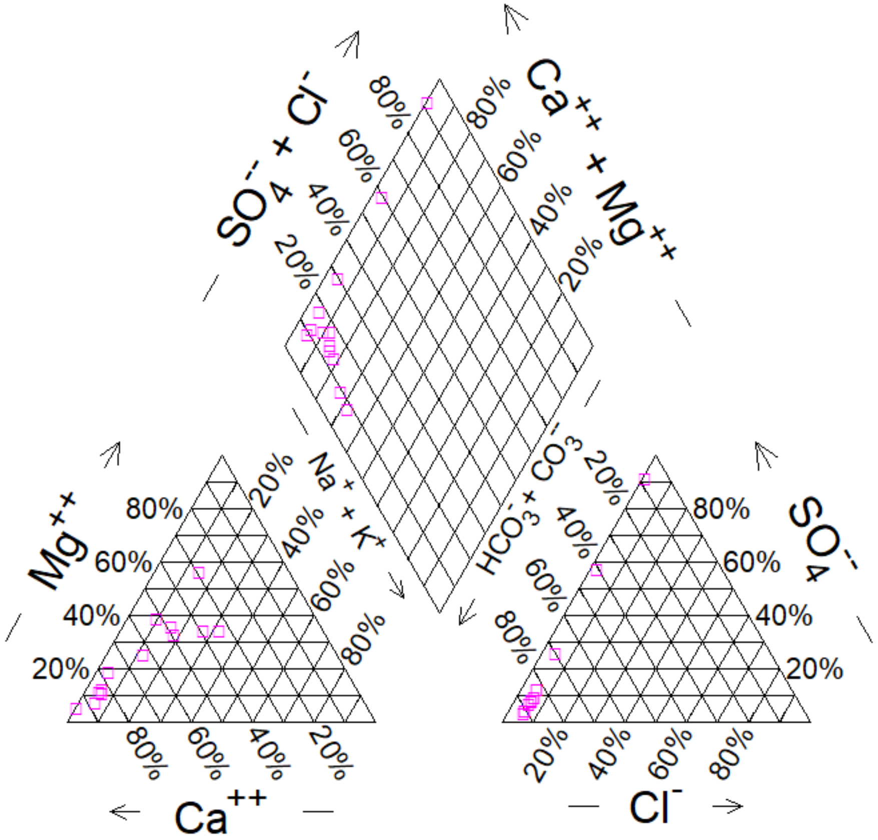
Step 3: Statistical plots of ionic ratios to identify chemical processes

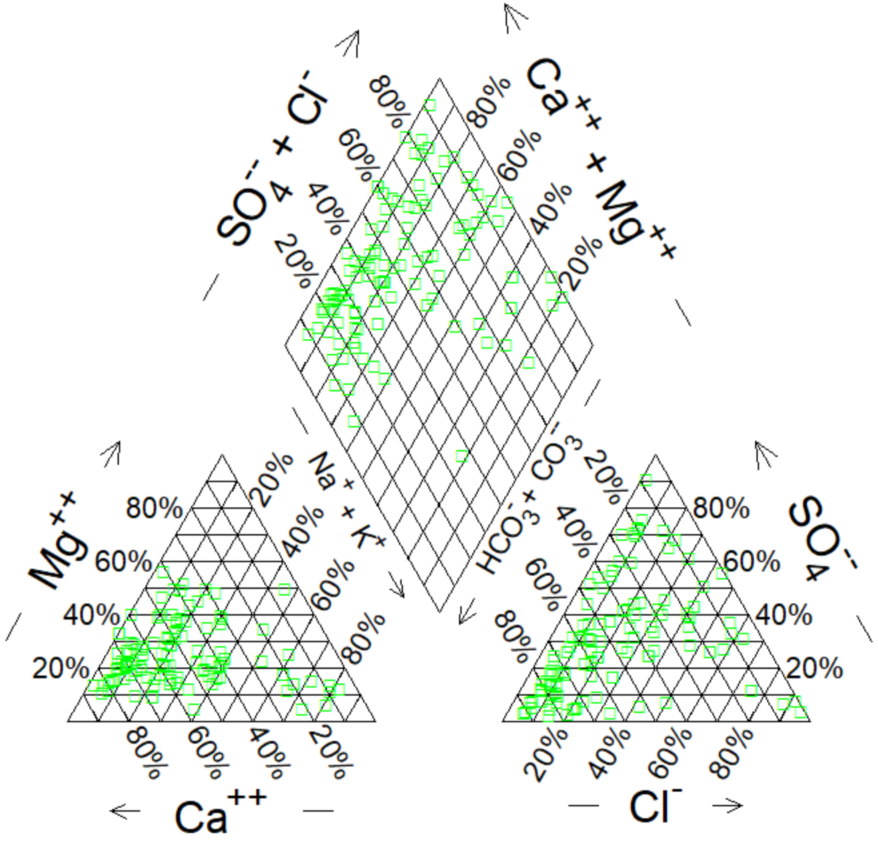




Orange: Class 1: Depth<65m
Blue: Class2: 66<Depth<200m

Class 1 (d<65m)	Class 2 (65<d<200)
• Ca-HCO3, Ca-Na-HCO3, Ca-SO4, Ca-Na-SO4 • Calcite/dolomite/gypsum/halite dissolution • Cation Exchange • Mixing	• Ca-HCO3, Na-HCO3, Ca-SO4, Ca-Na-SO4 • Calcite/dolomite/gypsum dissolution • Silicate weathering • Cation Exchange • Mixing





Magenta: Class3: 201<Depth<400m

Green: Class 4: Depth unknown

Class 3 (201<d<460m)	Class 4 (d=unknown)
• Ca-HCO3, Ca-SO4 • Calcite/dolomite dissolution • No mixing	• Ca-HCO3, Na-HCO3, Ca-SO4, Ca-Na-SO4, Ca-Na-HCO3 • Calcite/dolomite/gypsum dissolution • Silicate weathering • Cation Exchange • Mixing

Class 1 (d<65m)

- Ca-HCO_3, Ca-Na-HCO_3, Ca-SO_4, Ca-Na-SO_4
- Calcite/dolomite/gypsum dissolution
- Cation Exchange
- Mixing

Class 2 (65<d<200)

- Ca-HCO_3, Na-HCO_3, Ca-SO_4, Ca-Na-SO_4
- Calcite/dolomite/gypsum dissolution
- Silicate weathering
- Cation Exchange
- Mixing

Class 3 (201<d<460m)

- Ca-HCO_3, Ca-SO_4
- Calcite/dolomite dissolution
- No mixing

Class 4 (d=unknown)

- Ca-HCO_3, Na-HCO_3, Ca-SO_4, Ca-Na-SO_4, Ca-Na-HCO_3
- Calcite/dolomite/gypsum dissolution
- Silicate weathering
- Cation Exchange
- Mixing

Major processes:

- Source of Sodium:
  - Silicate weathering
- Source of Ca-Mg:
  - Calcite/Dolomite/Gypsum dissolution
- Source of HCO_3:
  - Calcite/Dolomite dissolution
  - Silicate weathering
- Source of SO_4:
  - Gypsum Dissolution
- Source of Chloride
  - Irrigation outflows

Establishing and Verification of transboundary connectivity

Step 1: Developing GIS based SQL equations for each chemical process

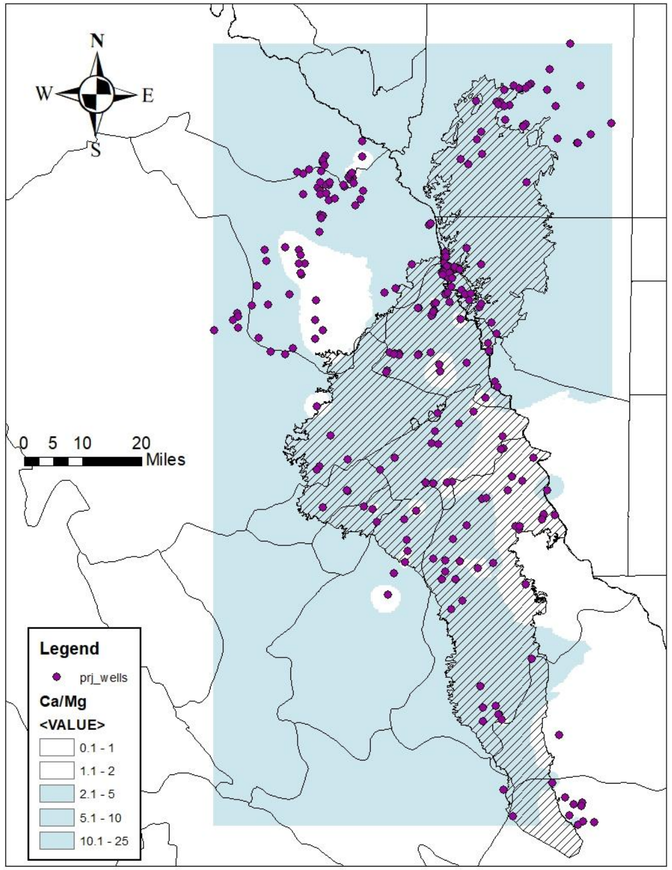
Step 2: Spatial variability of ionic ratios relevant for each chemical process

Step 3: Correlation between ionic ratios across border

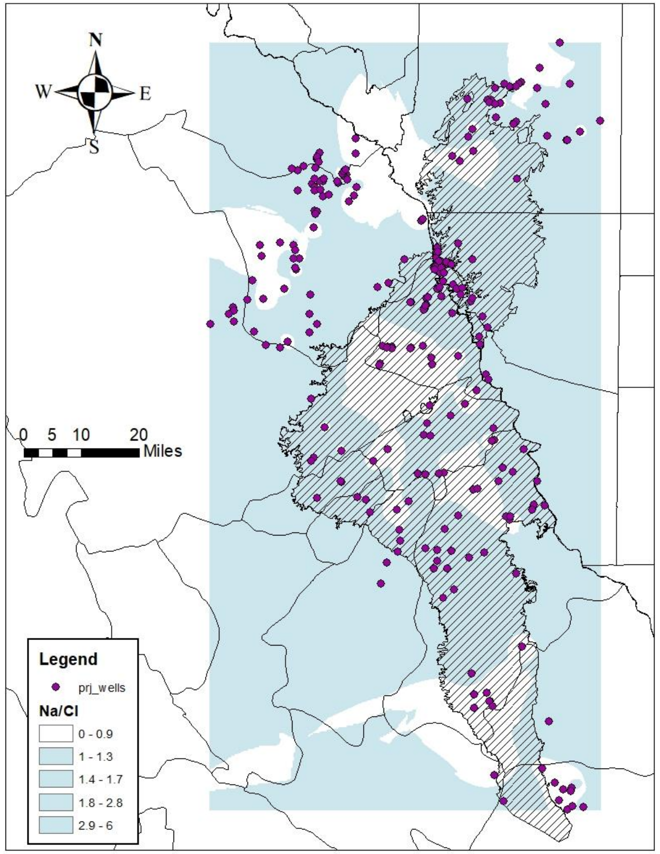
Silicate weathering: Source of Sodium

[Ca/Mg > 2 AND Na/Cl >1 AND Na>Ca] *(Reddy & Kumar, 2010)*

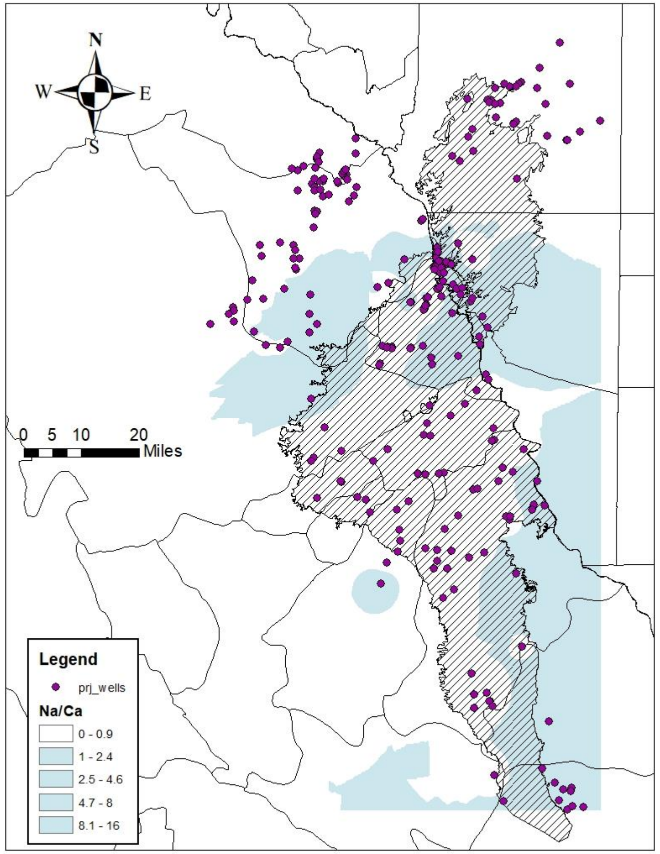
Ca/Mg > 2



Na/Cl >1



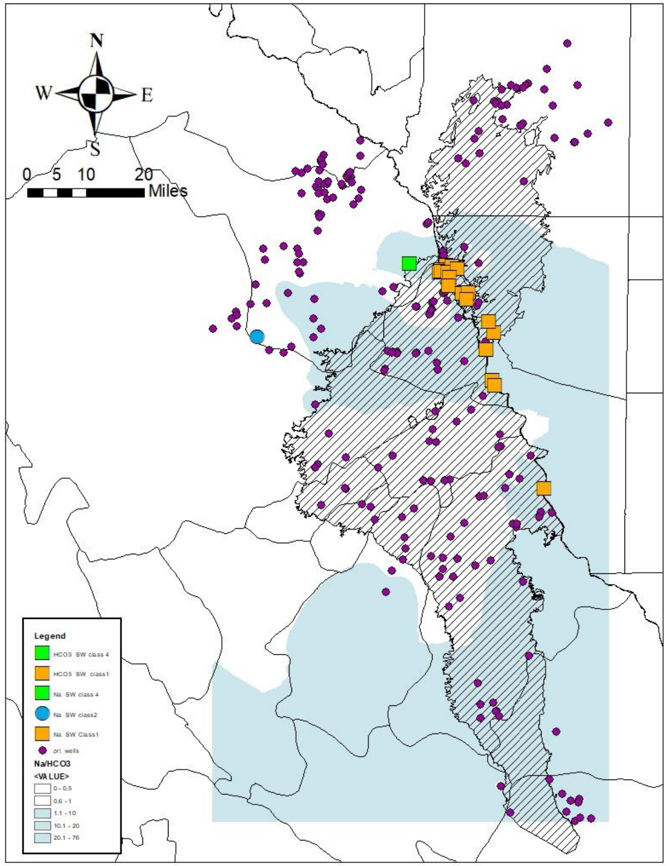
Na>Ca



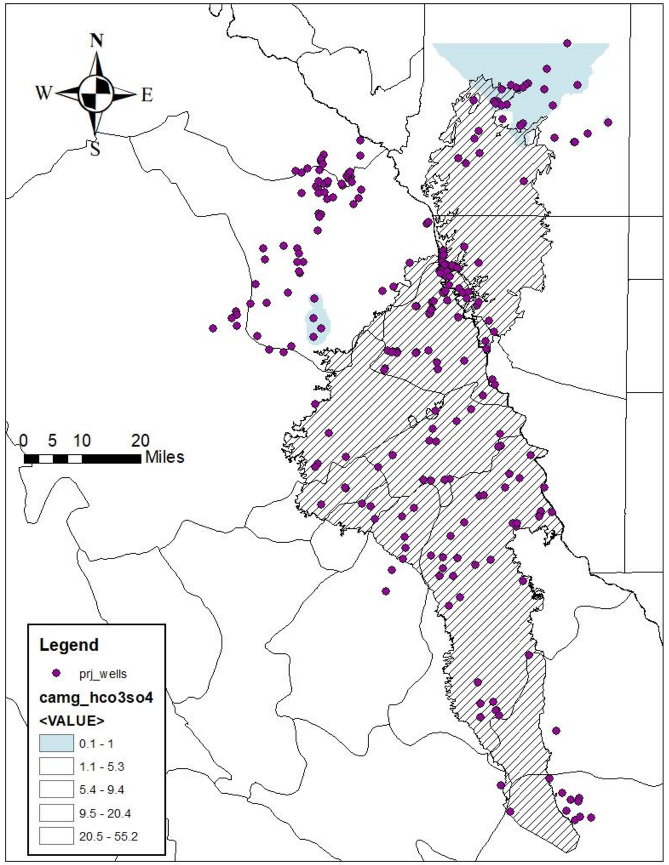
Silicate weathering: Source of Bicarbonate

[Ca/Mg > 2 AND Na/HCO3 >=1 AND (Ca+Mg/HCO3+SO4 <1 OR Ca+Mg/HCO3 <1)] *(Reddy & Kumar, 2010)*

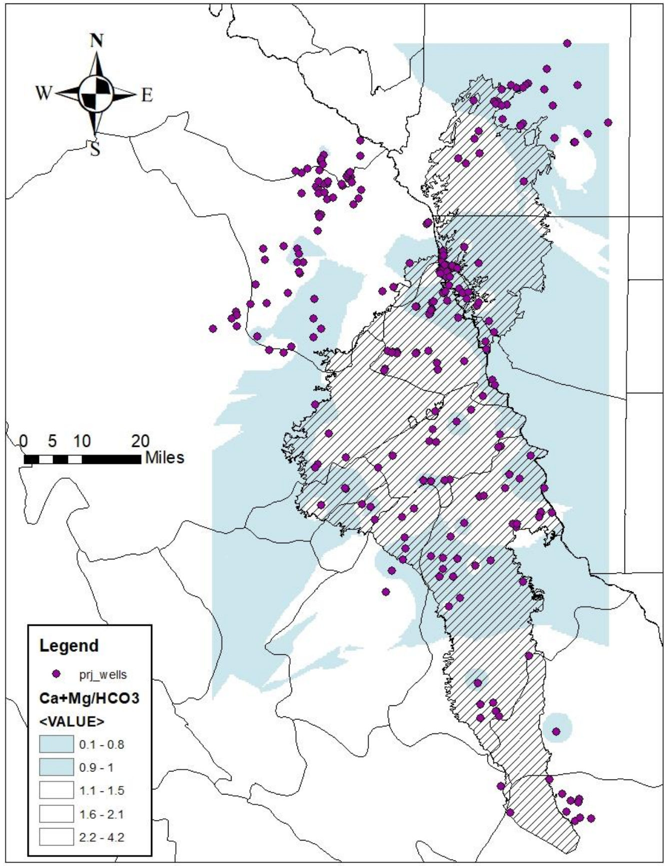
Na/HCO3 >=1



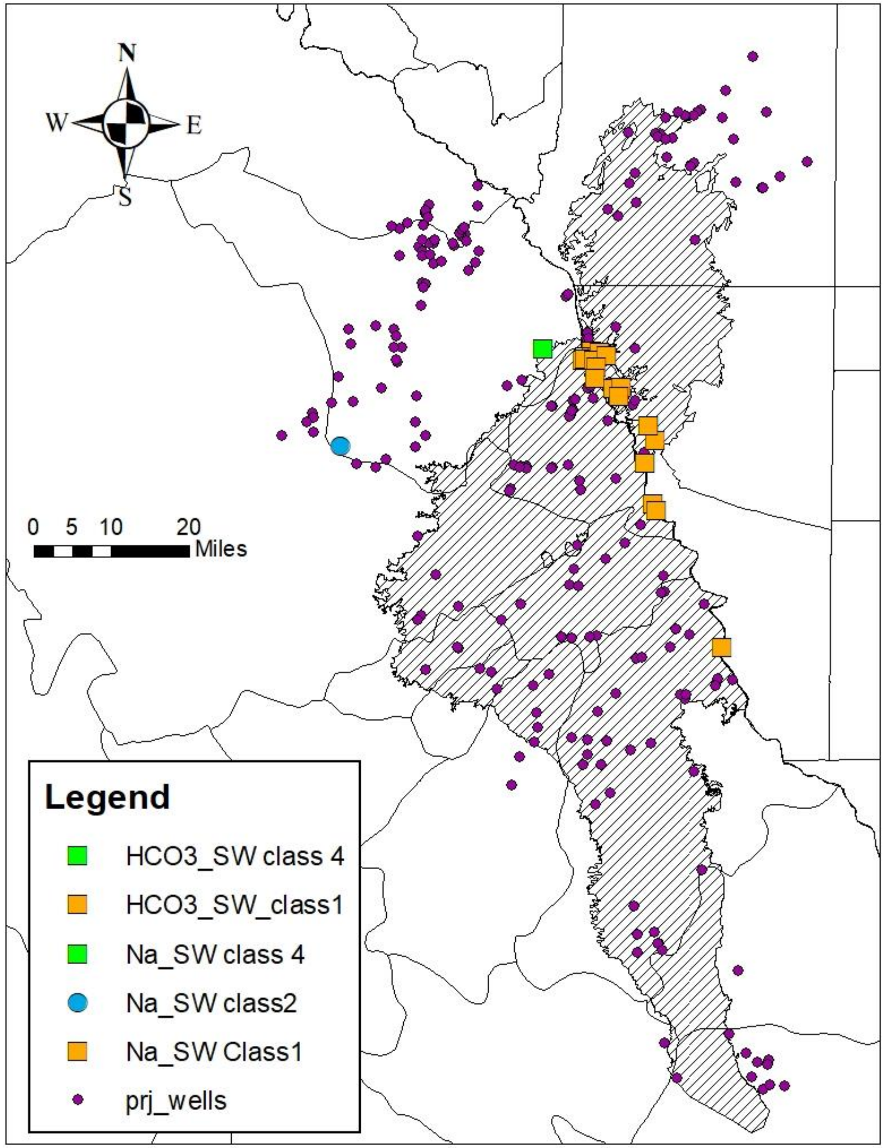
Ca+Mg/HCO3+SO4 <1



Ca+Mg/HCO3 <1



Silicate Weathering



Uvalde Gravels:

- Clusters with 70% limestone and 30% fragments of volcanic rocks (rhyolite, trachyte). *[Escalante et al., (2002)]*

Alluvial Deposits:

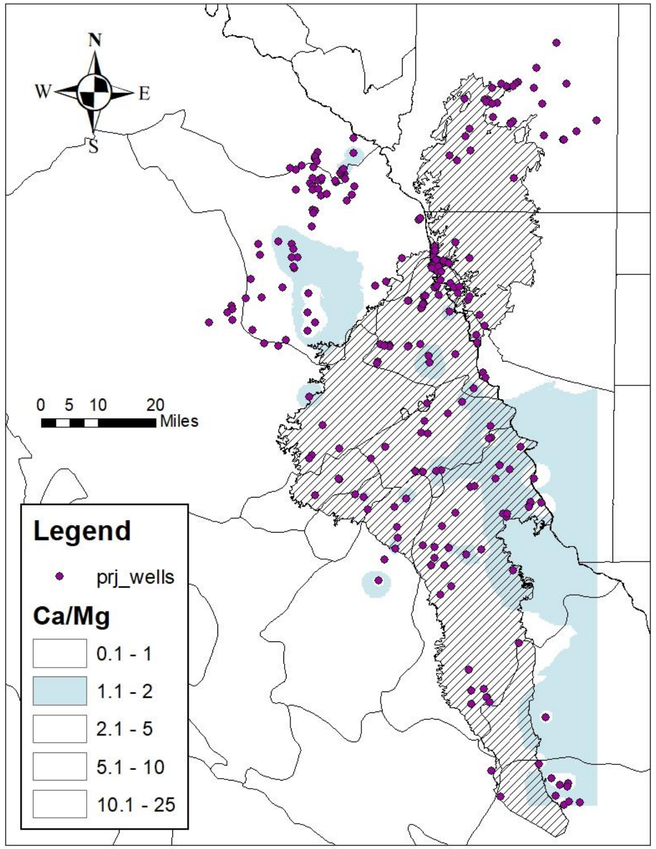
- Holocene Quaternary alluvium fills the valley streams in the APN region
- Contains: silt, sand, clay, and gravel (weathering of the adjacent formations) *[Boghici,2002].*

Limestone Dissolution: Source of Bicarbonate

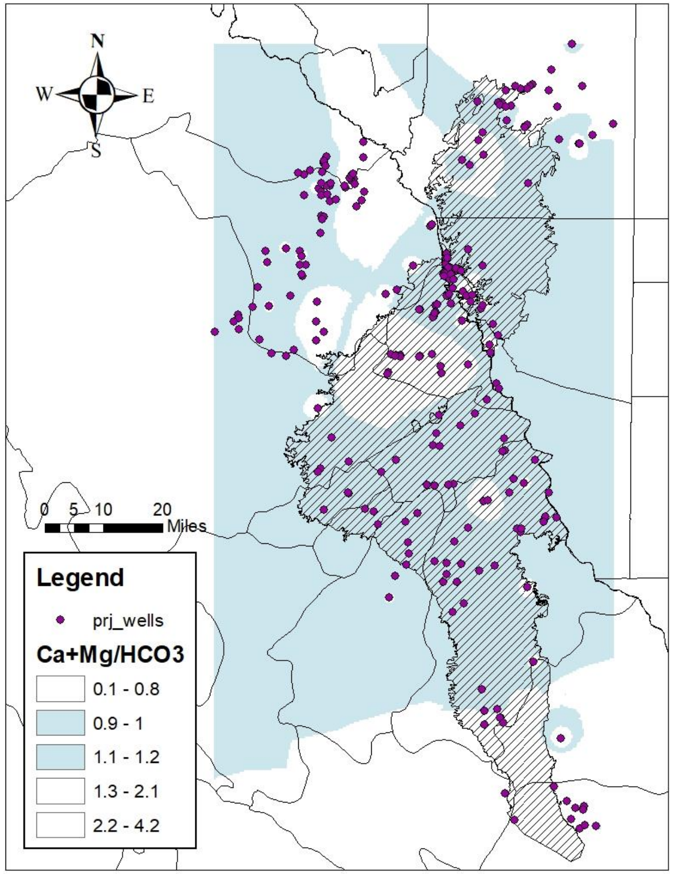
[Ca/Mg >=1 AND Ca/Mg < 2 AND (Ca/HCO3 <1.2 AND Ca/HCO3 >0.8) OR (Ca+Mg/HCO3 <0.8 AND Ca+Mg/HCO3 > 0.3)]

(Boghici,2002; Narany et al., 2014)

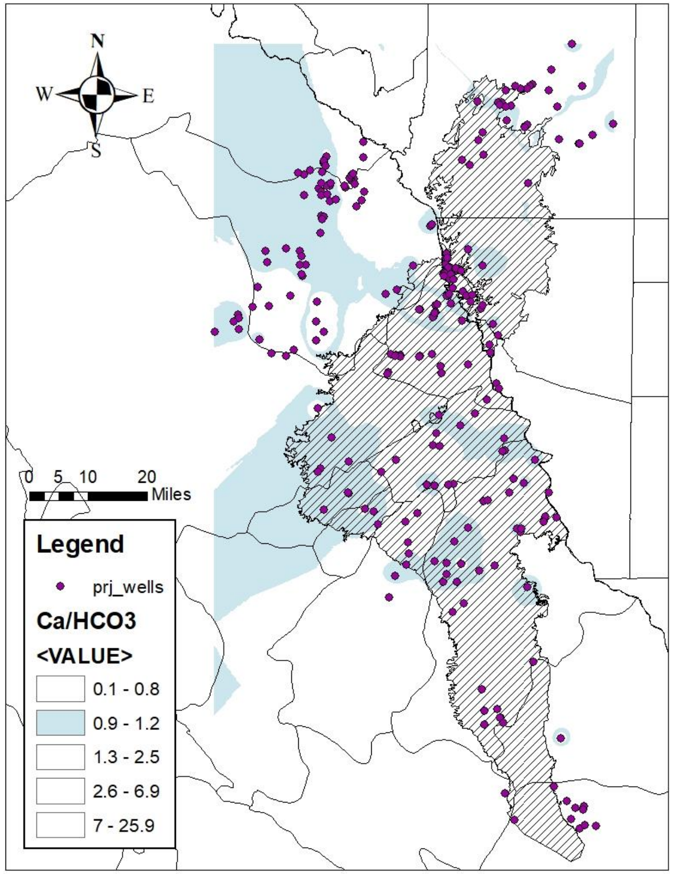
1<=Ca/Mg<2



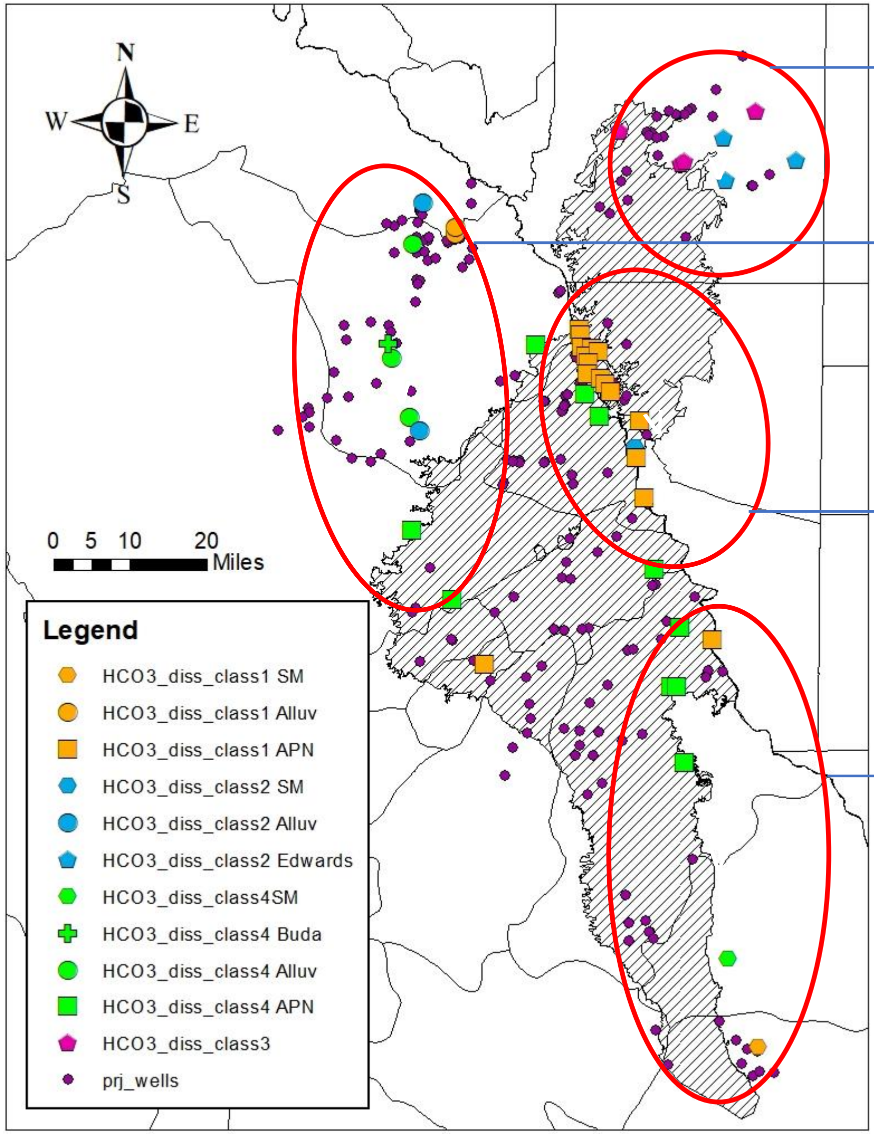
0.3<Ca+Mg/HCO3 <0.8



0.8< Ca/HCO3 <1.2



Bicarbonate Dissolution



Austin Chalk Fm:

- Massive in outcrop.
- Altering thin limestone, chalk, and marl
- Produces large yields from shallow wells near Uvalde, Texas [Boghici,2002].

Uvalde Gravels:

- Clusters with 70% limestone and 30% volcanic rocks. [Escalante et al., (2002)]

San Miguel:

- Overlies the Upson Clay
- Hard calcareous sandstone and sandy limestone [Boghici,2002].

Buda Fm:

- light-gray to pale-orange, fine-grained, bioclastic, and fossiliferrous limestone.
- outcrops border the northern edge of the APN aquifer in Texas south of the Balcones fault zone. [Boghici,2002].

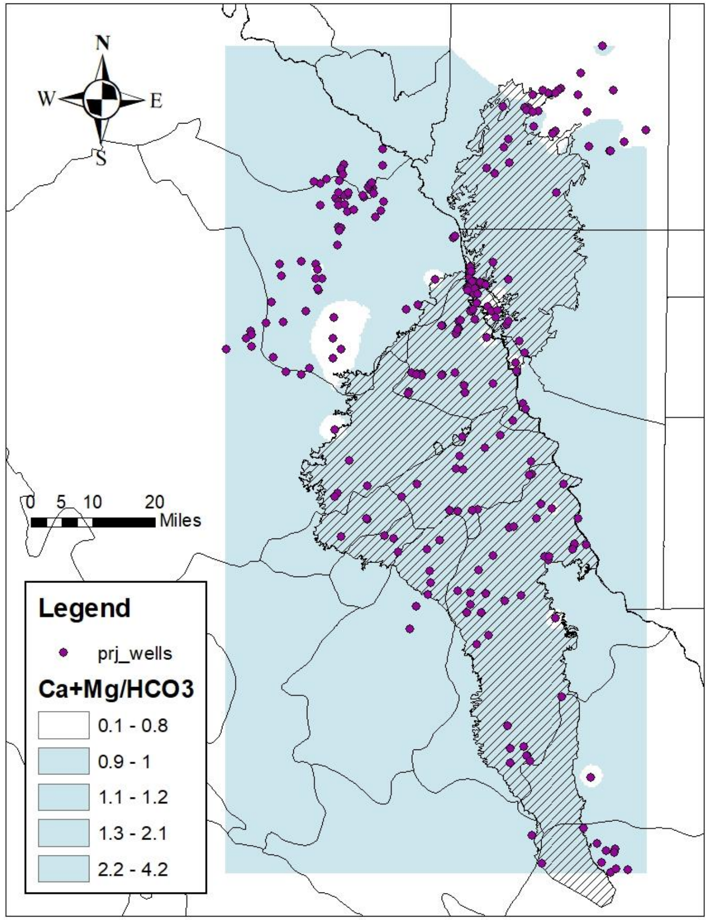
Edwards Fm:

- Carbonate dissolution/precipitation and gypsum dissolution - main chemical processes in Edwards-Trinity groundwater. [Boghici,2002].

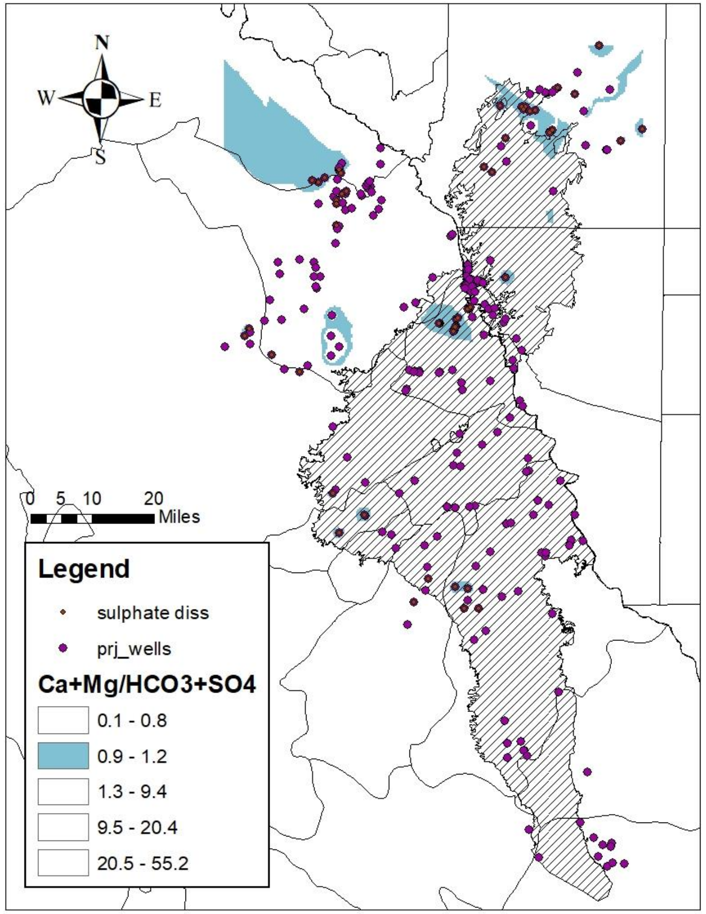
Gypsum Dissolution: Source of Sulphate

[Ca+Mg/HCO3 >0.8 AND Ca+Mg/HCO3+SO4 < 1.2 AND Ca+Mg/HCO3+SO4 >0.8] *(Boghici,2002; Narany et al., 2014)*

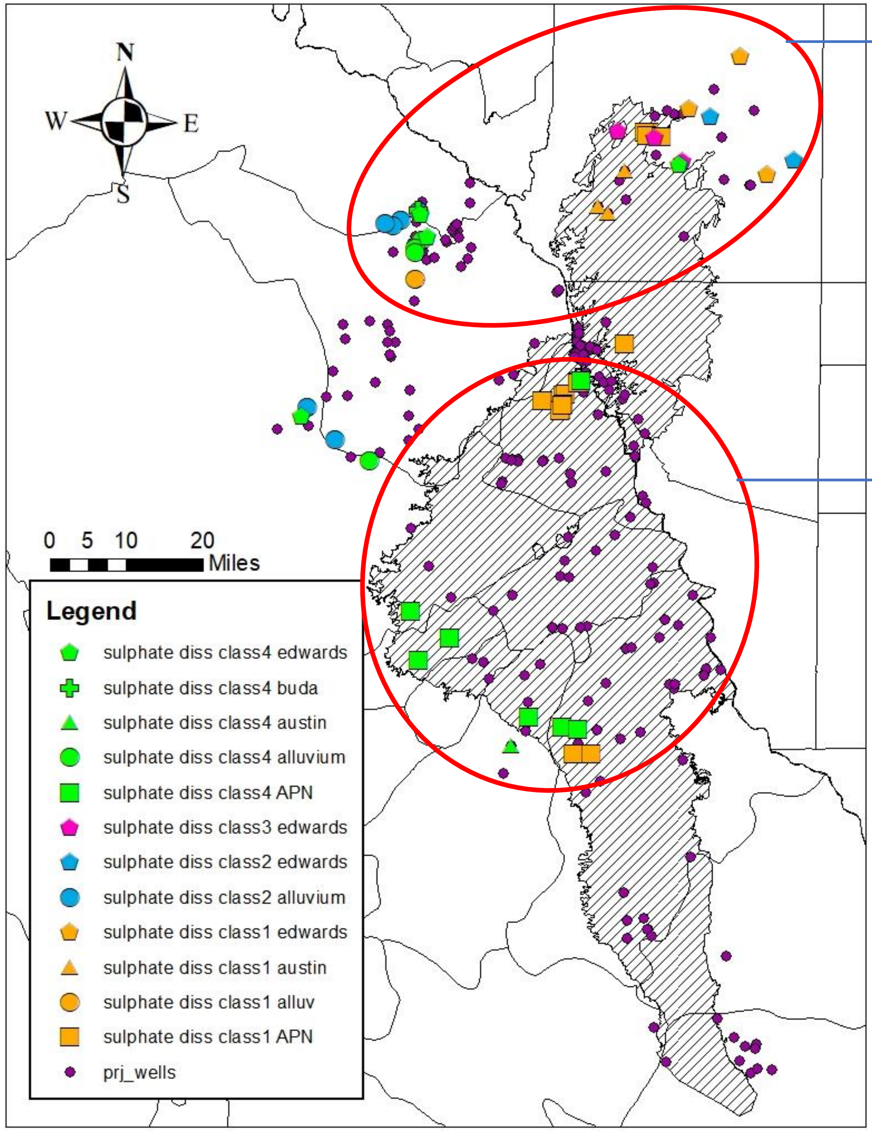
Ca+Mg/HCO3 >0.8



0.8< Ca+Mg/HCO3+SO4 <1.2



Gypsum Dissolution



Sulphate dissolution from Edwards Fmn

Sulphate dissolution from Olmos Fmn

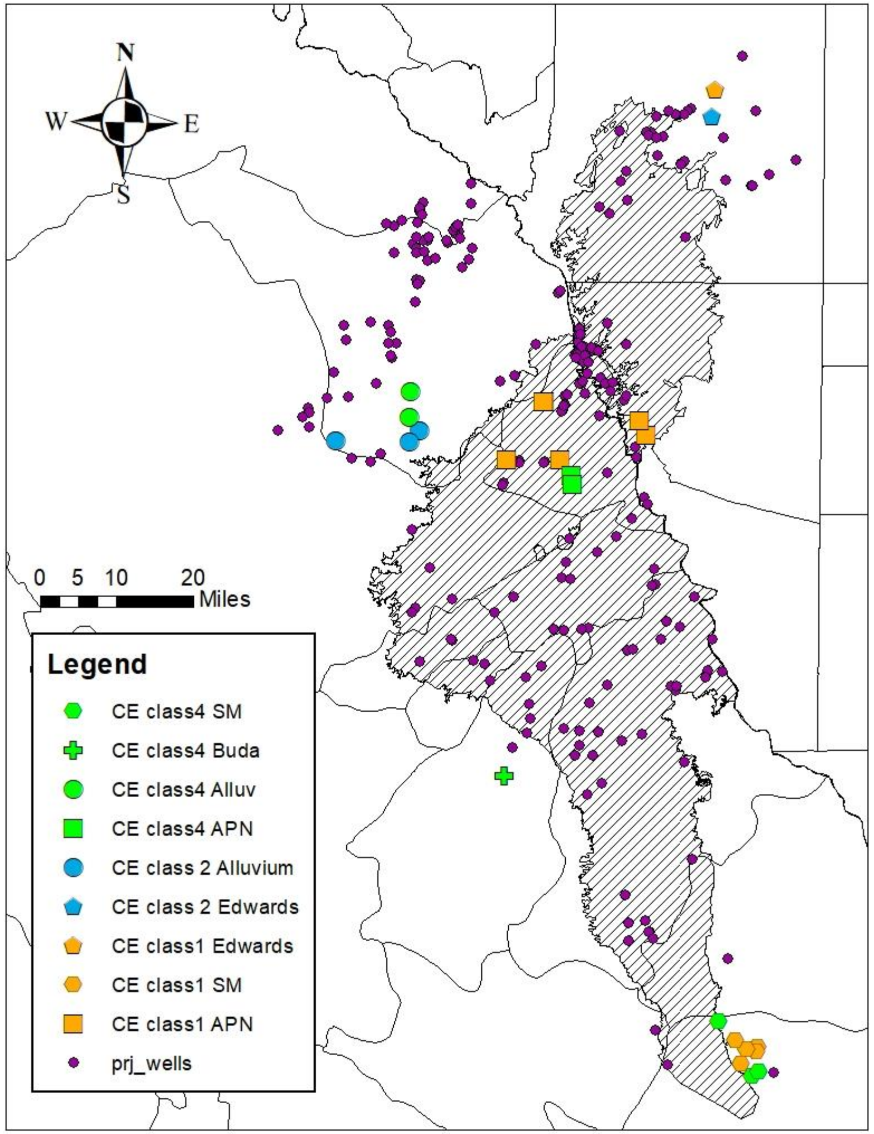
Edwards Fmn:

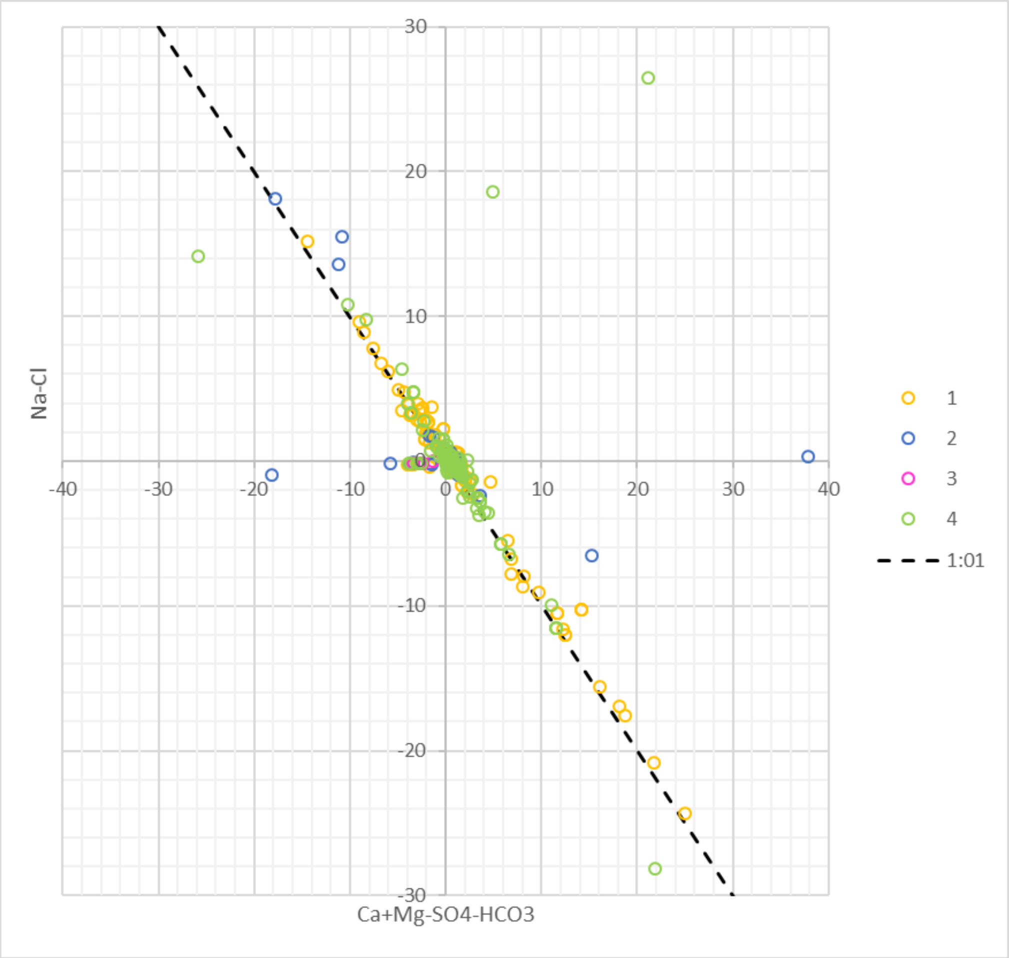
- Carbonate dissolution/precipitation and gypsum dissolution - main chemical processes in the Edwards-Trinity groundwater. [Boghici,2002].

Olmos Fmn:

- Deposited in a deltaic-front environment
- Dark gray carbonaceous shales interrupted by sandstone layers.
- Seams of coal and lignite (<=2m thick) . [Boghici, 2002; Castillo,2000]

Cation Exchange

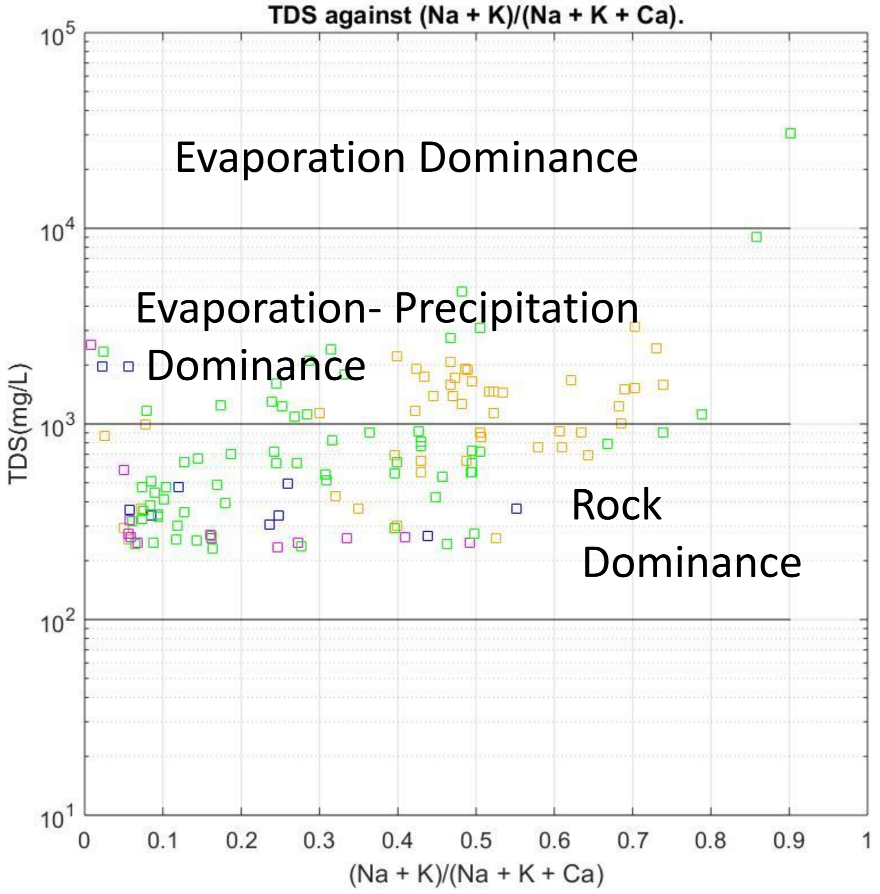


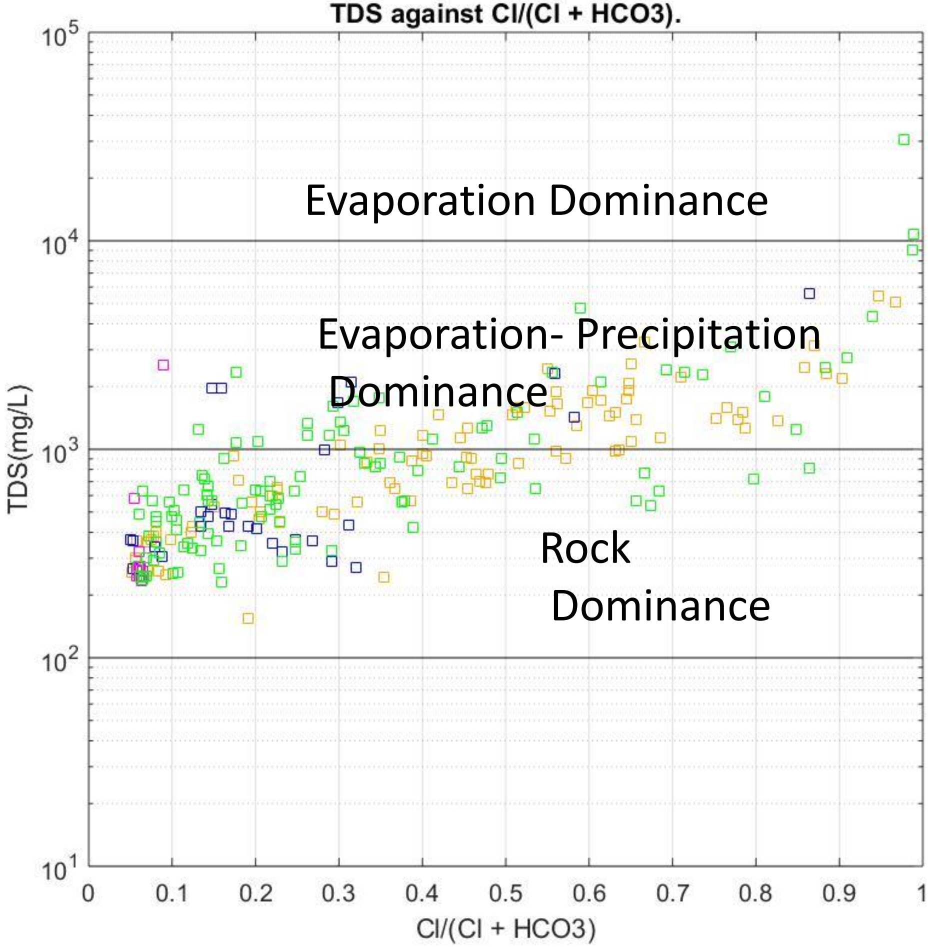


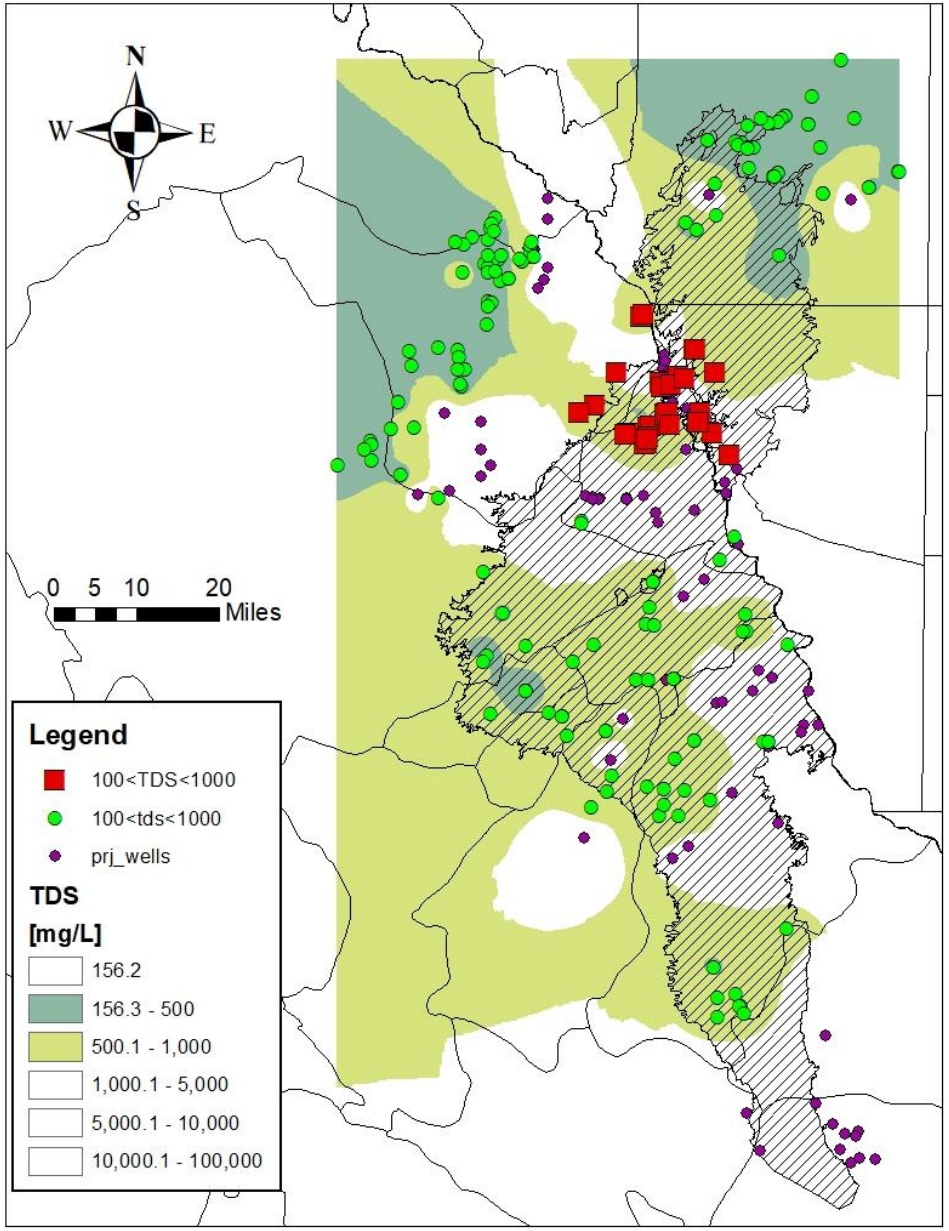
- linearity indicates a highly correlated relationship between the increase of sodium and the loss of the Ca2+ and Mg2+ ions by cation exchange.
- But dominant ion in the region is Ca.
- Thus, cation exchange is not a dominant process here [Boghici, 2002].

Correlation between ionic ratios across border [Gibb's Diagram]

Orange: Class 1: Depth<65m
Blue: Class2: 66<Depth<200m
Magenta: Class3: 201<Depth<400m
Green: Class 4: Depth unknown



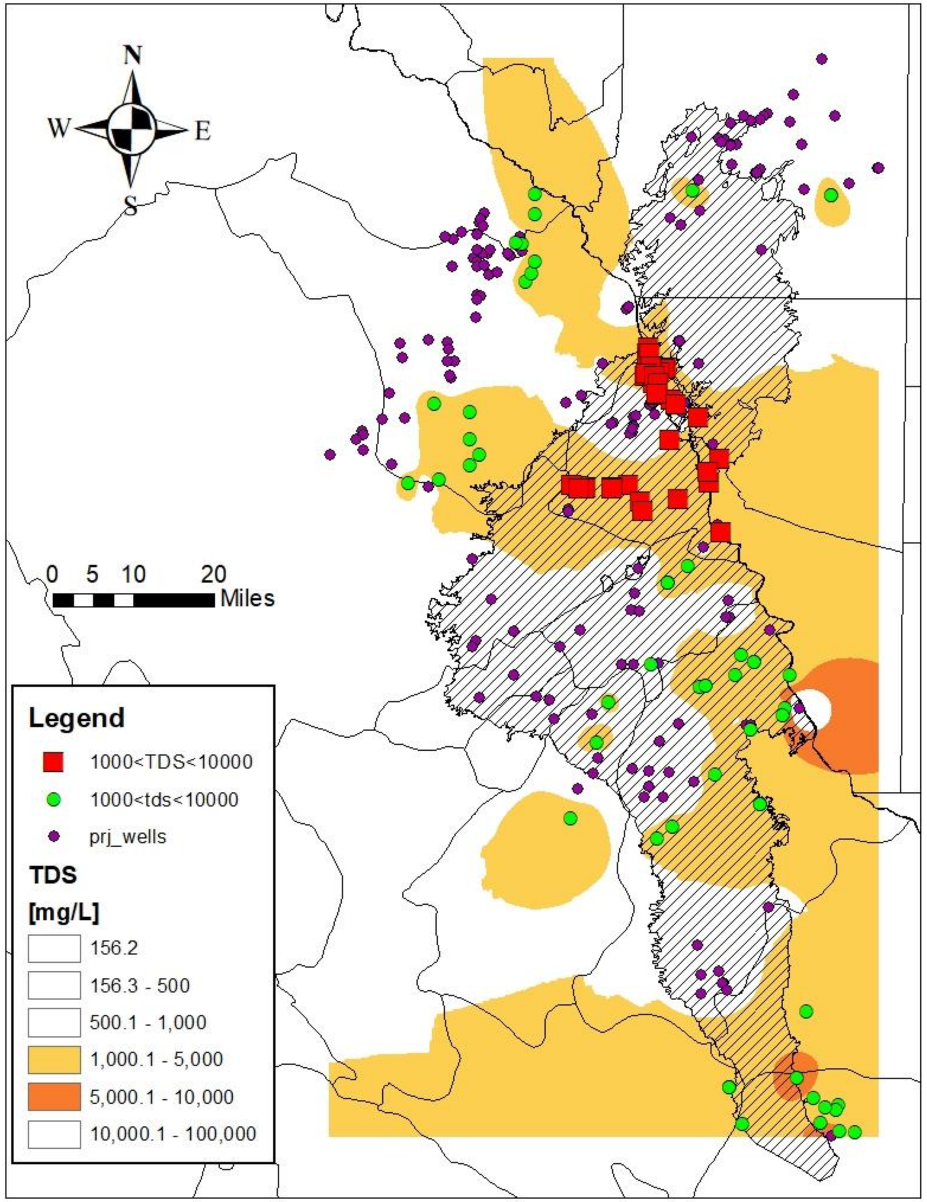




Areas connected by the process of rock-water interaction:
The TDS of these areas is decided by the chemical process of rock-water interaction (Gibbs Plot)
[Narany et al., 2014]

15 wells on either side

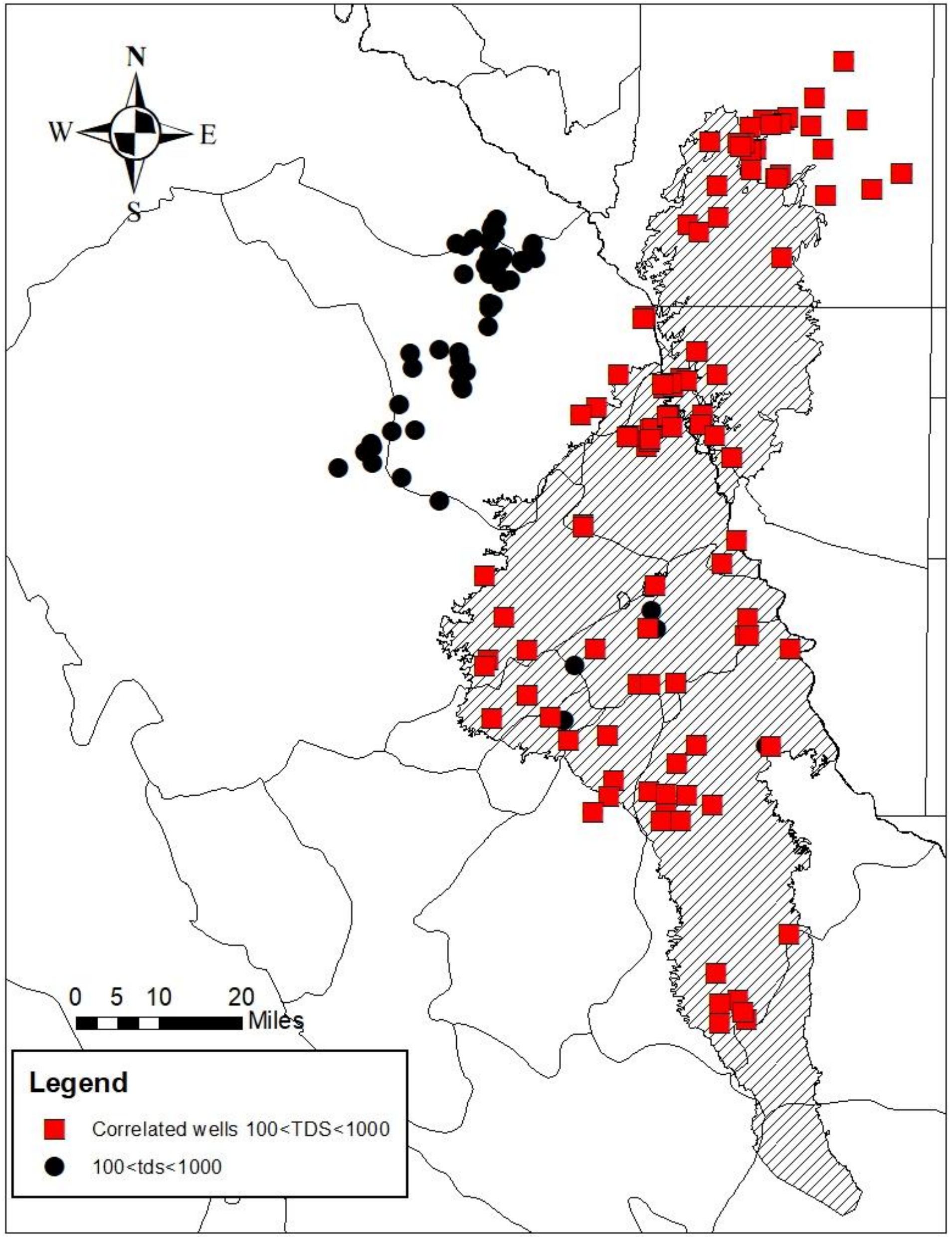
Ionic Ratio	Pearson's Correlation Coefficient
(Na+K)/(Na+K+Ca)	0.9583
Cl/(Cl+HCO3)	0.8728



Areas connected by the process of evaporation & precipitation:
The TDS of these areas is controlled by the evaporation-precipitation dominance (Gibbs Plot)
[Narany et al., 2014]

15 wells on either side

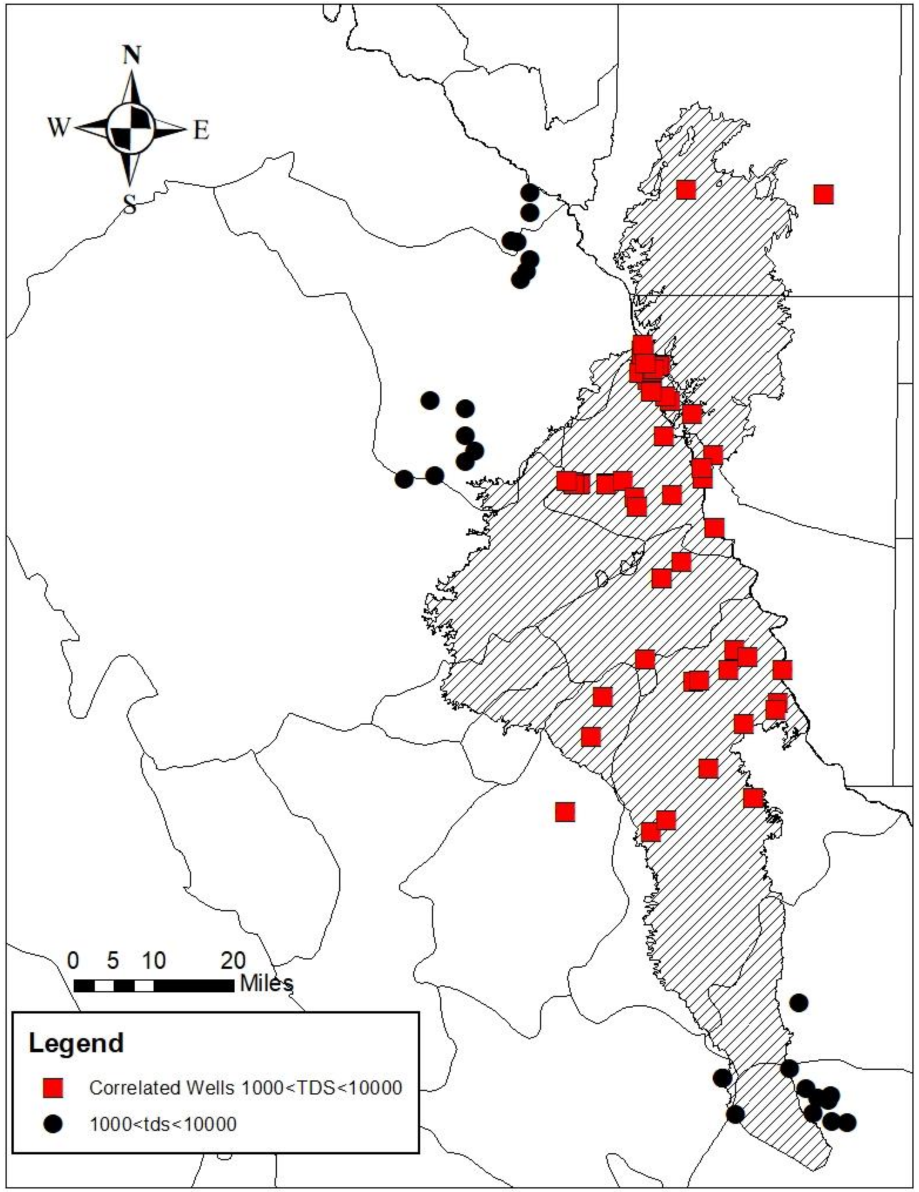
Ionic Ratio	Pearson's Correlation Coefficient
(Na+K)/(Na+K+Ca)	0.9573
Cl/(Cl+HCO3)	0.8064



Areas connected by the process of rock-water interaction:
The TDS of these areas is decided by the chemical process of rock-water interaction (Gibbs Plot)
[Narany et al., 2014]

71 wells on either side

Ionic Ratio	**Pearson's Correlation Coefficient**
(Na+K)/(Na+K+Ca)	0.987007727
Cl/(Cl+HCO3)	0.963397911



Areas connected by the process of evaporation & precipitation:
The TDS of these areas is controlled by the evaporation-precipitation dominance (Gibbs Plot)
[Narany et al., 2014]

38 wells on either side

Ionic Ratio	Pearson's Correlation Coefficient
(Na+K)/(Na+K+Ca)	0.89591874
Cl/(Cl+HCO3)	0.894134525

CONCLUSIONS

1. **Assumptions & Limitations:**
   a) Heterogenous data source
   b) Missing Depth
   c) Temporality constant
2. **Connectivity:**
   a) Areas connected by the process of rock-water interaction:
      i. Bicarbonate Dissolution
      ii. Sulphate Dissolution
      iii. Silicate Weathering
   b) Areas connected by the process of evaporation & precipitation:
   - high sulfate and chloride concentrations from irrigation wells along the Rio Grande Valley
   - Salts in irrigation water - concentrated in soils due to low atmospheric moisture and high evaporation rates.
   - Salts readily remobilized by leaching to the shallow aquifer table (Hibbs and Boghici, 1999).

   c) Rock water interaction- major process
   (Salinity of wells with depth>200m is not controlled by evaporation-precipitation)

THANK YOU