

GROUNDWATER SALINITY OF POSSIBLE
OILFIELD ORIGIN IN THE SHALLOW
GULF COAST AQUIFER, COLETO CREEK
WATERSHED, SOUTHEAST TEXAS



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Purpose

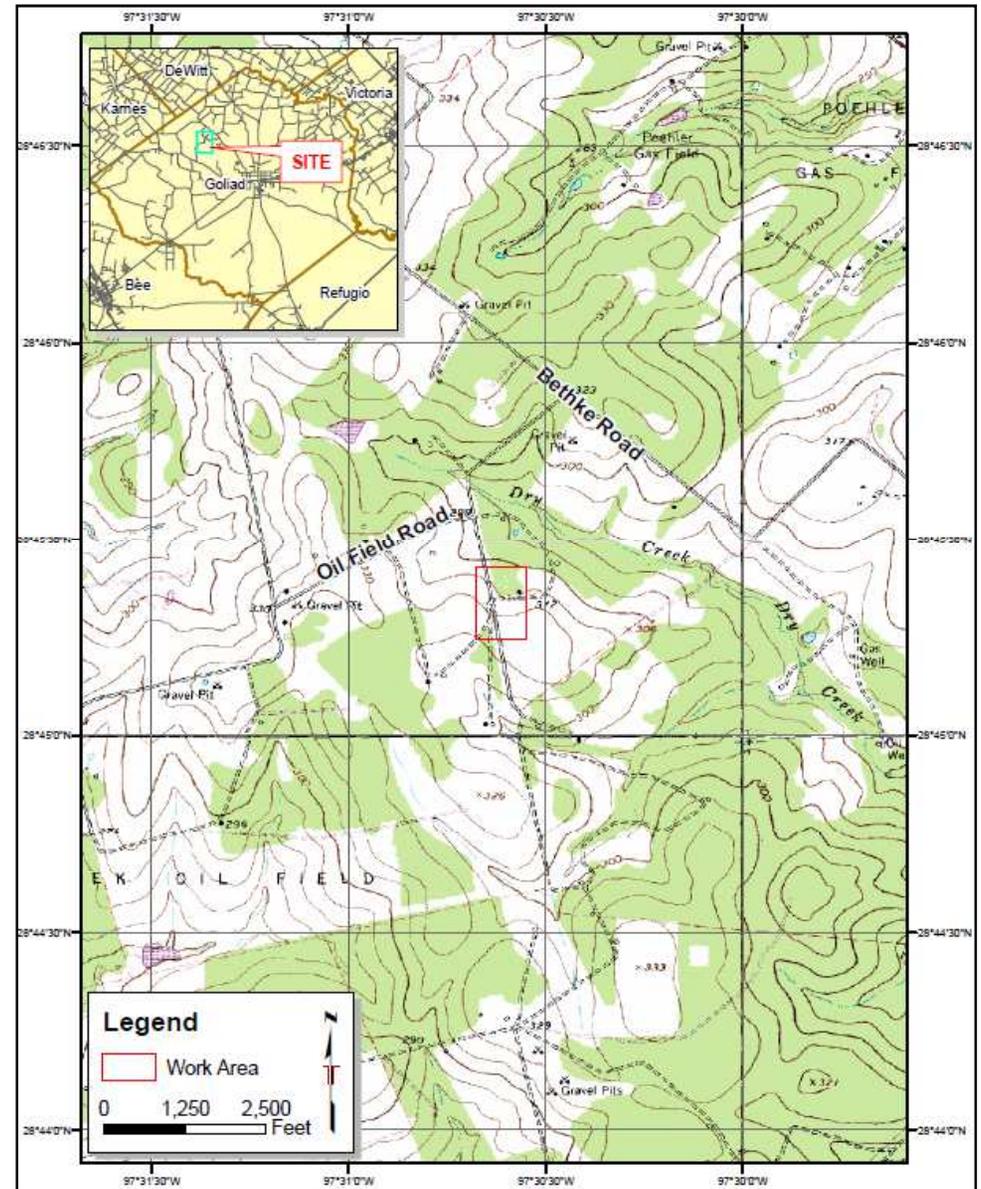
- ▶ Characterize the source(s) of elevated groundwater salinity detected in a residential water well in Goliad County



Area of Interest

Residential Well

- ▶ Residential water supply well is located in the Cabeza Creek south oil field, east of Oil Field Road in Goliad County, TX
 - Site is relatively flat
 - Surface water drains north
 - Land is used for agricultural purposes
 - Water well depth is 180 ft bgs



Background

- ▶ Examined historical aerial photographs near residential well
 - Discovered evidence of historic* earthen pits
 - Six saltwater reserve pits, approx. 10 ft in depth
 - Tank battery
 - Approx. 1,000 feet northeast of the water supply well
 - Proximity of the pits led to RRC's Site Remediation Department to evaluate the pits as possible sources of elevated groundwater salinity in the shallow Gulf Coast Aquifer

* Existing since ~1958

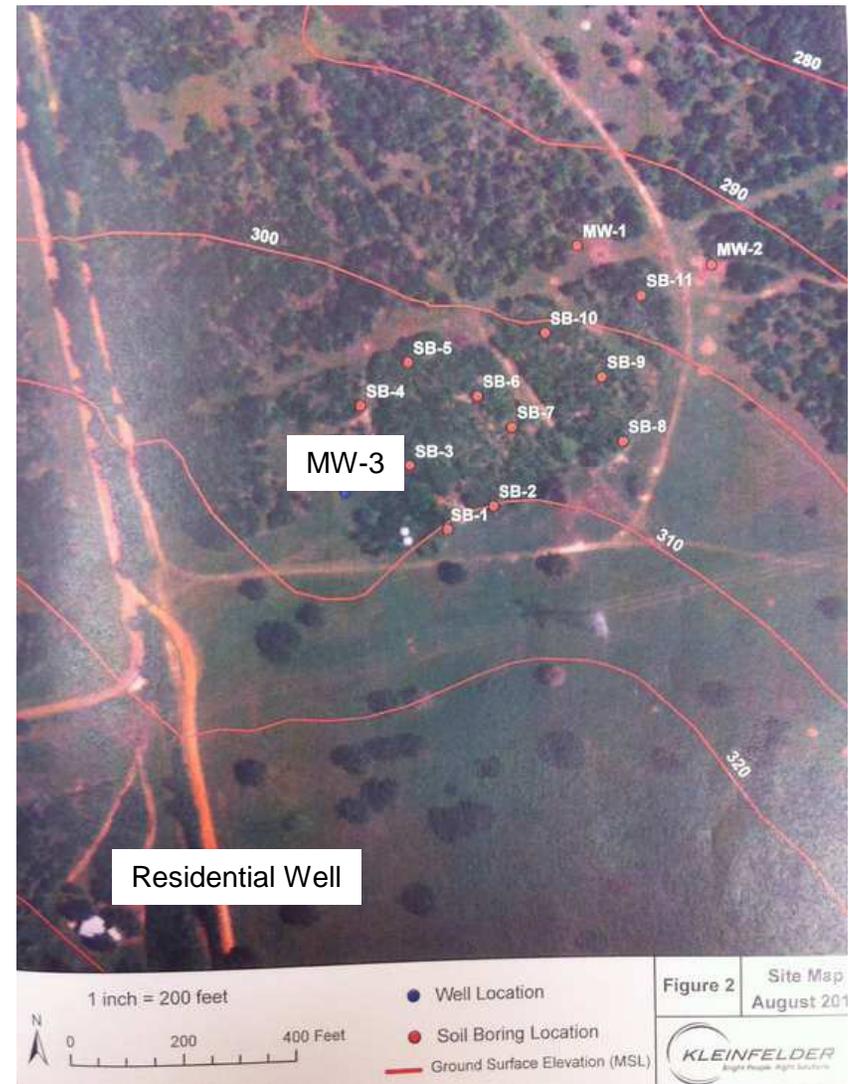
Initial Limited Environmental Site Assessment

August, 2012

by Kleinfelder/Corrigan Consulting

- ▶ Soil Analysis - no definitive results
 - No BTEX, low TPH (< 10,000 mg/Kg*), no NORM, low Chlorides

- ▶ Groundwater analysis: 3 monitor wells (MW-1, MW-2, MW-3)
 - Groundwater only detected in MW-3
 - No sand present in MW-1 and MW-2, dry holes
 - MW-3 and residential well tested for TPH, BTEX, major cations and anions
 - Cl⁻ concentration 12,400 mg/L in MW-3
 - Cl⁻ concentration 4,700 mg/L in Residential Water Well



* RRC standard for crude oil spills

Limited Environmental Site Assessment

December, 2012

by Terracon

- ▶ Site soil description beneath and around the pits
 - Permeable sand and sandstone to a depth of 79 ft
 - Low permeable plastic clay below 79 ft in MW-6
 - Residential Well Report (#192124) specifies a clay layer from 77 ft to 175 ft

- ▶ Groundwater Analysis: 3 additional monitor wells (MW-4, MW-5, MW-6)
 - Groundwater gradient is nearly flat
 - Moves north-northwest at 0.0013 ft/ft
 - Directed away from the Residential water well
 - Exceedances
 - Chloride concentrations in all wells ¹
 - Boron and strontium concentrations in all wells ²
 - Low concentration of benzene found in MW-5 ³
 - TDS concentrations for all wells ⁴

¹ Exceed TCEQ secondary standard for Cl⁻ of 250 mg/L

² Exceed TCEQ action levels for Class 1 groundwater

³ Exceeds TCEQ Class 1 action level

⁴ Exceed TCEQ criteria for Class 1 and 2 groundwater (10,000 mg/L)

Limited Environmental Site Assessment

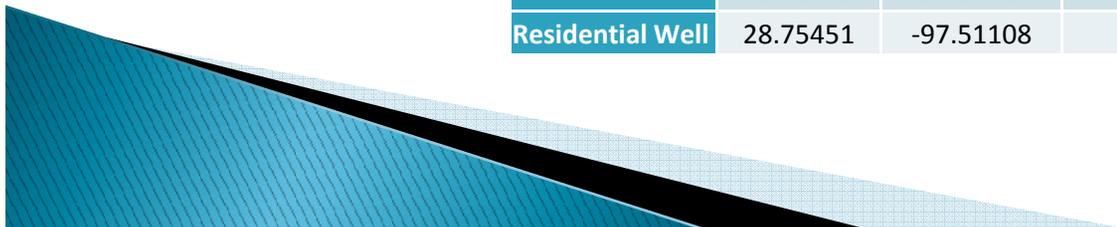
July, 2013

by Terracon

- ▶ 5 additional soil borings were converted to monitoring wells (MW-7 to MW-11)
 - MW-11 was placed between the pits and residential water well (~100 ft NE of residential well)
 - MW-11 may not have a static GW level; it recharges slowly

Monitoring Well and Groundwater Depths

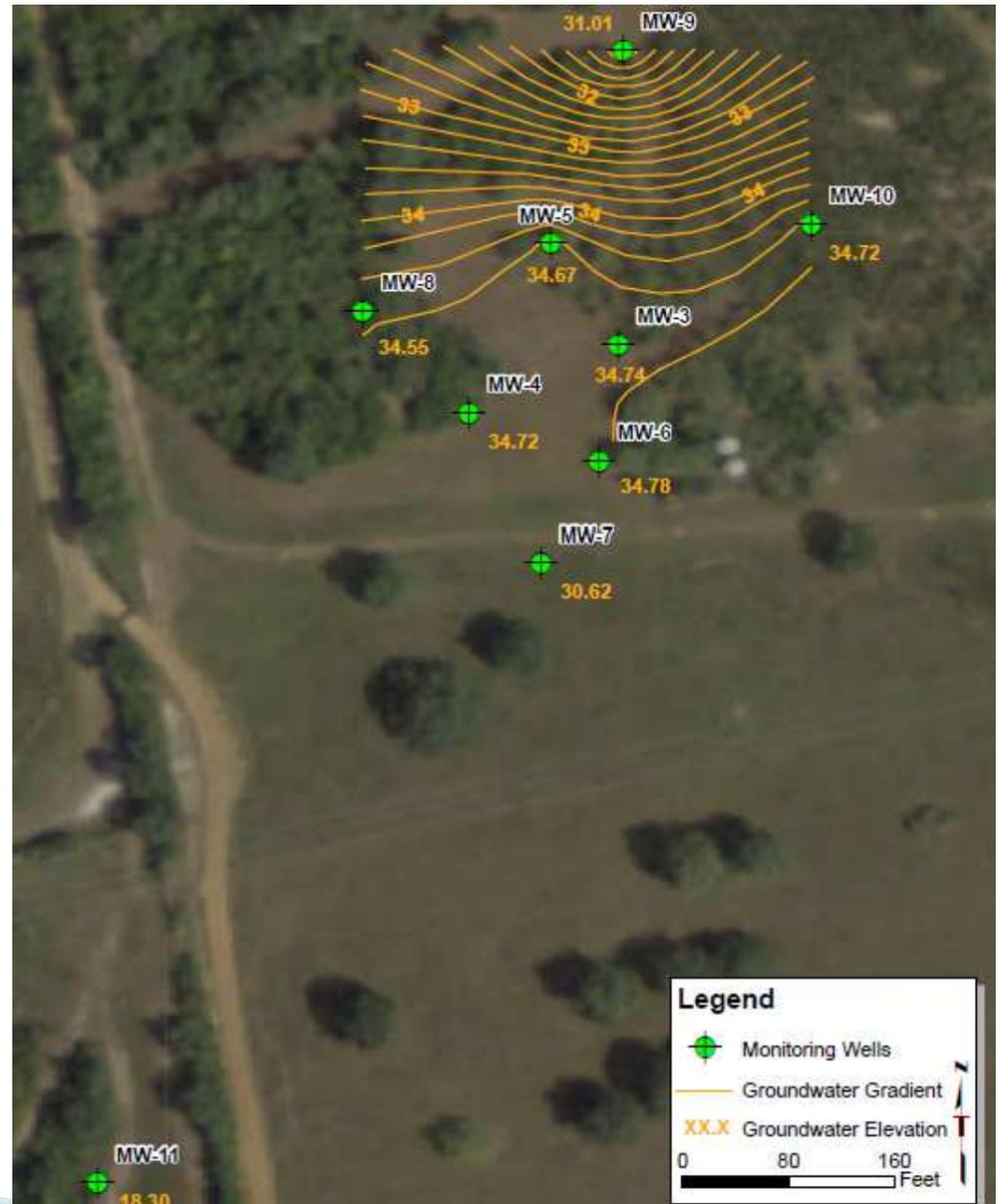
Monitoring Well No.	Latitude	Longitude	Relative TOC Elevation (ft)	Adjusted TOC Elevation (ft)	Depth to Water from TOC (ft)	Ground Water Elevation (ft)
MW-3	28.75652	-97.50994	0	95.11	60.37	34.74
MW-4	28.75638	-97.51025	1.68	96.79	62.07	34.72
MW-5	28.75673	-97.51008	-2.54	92.57	57.9	34.67
MW-6	28.75628	-97.50998	2.99	98.1	63.32	34.78
MW-7	28.75607	-97.5101	4.55	99.66	69.04	30.62
MW-8	28.75659	-97.51047	0.88	95.99	61.44	34.55
MW-9	28.75713	-97.50993	-6.12	88.99	57.98	31.01
MW-10	28.75677	-97.50954	-4.26	90.85	56.13	34.72
MW-11	28.75479	-97.51102	14.02	109.13	90.83	18.3
Residential Well	28.75451	-97.51108			180	-71.7



Groundwater Gradient Map

with groundwater elevation

- ▶ Difference in groundwater elevation between MWs and Residential Well
 - Separate hydrostratigraphic units
- ▶ GW gradient 0.026 ft/ft north
- ▶ Low permeable clay encountered beneath 93 ft bgs

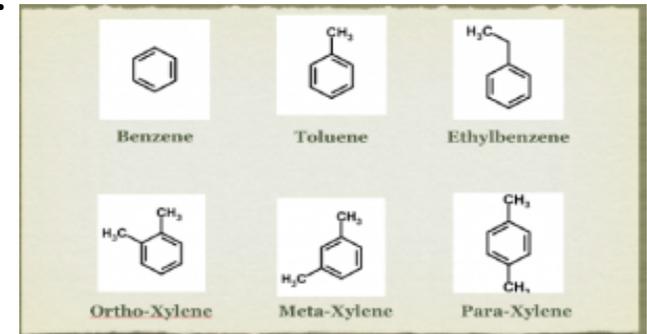


Terracon Analytical Methods

Second Site Assessment

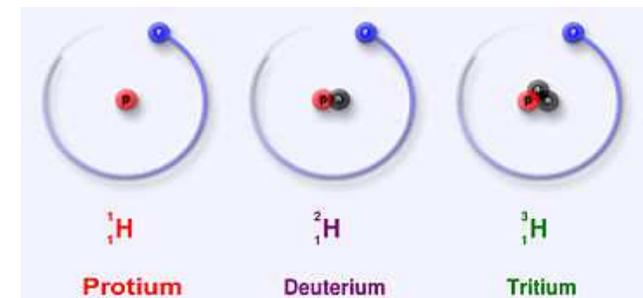
- All MW samples were analyzed for the following parameters:

- TPH (Texas 1005)
- BTEX (EPA method 8260C)
- B^{3+} , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Sr^{2+} (EPA Method 6010b)
- Br^- , Cl^- , SO_4^{2-} , HCO_3^- , I^- , pH (EPA Method 9040C)
- TDS (EPA SM2540 C)



- Isotopic Analyses of MW-3, MW-4, MW-5, MW-6 and MW-11:

- **Radioactive isotopes used for age dating of water:**
 - **Carbon Isotope Analysis** (^{14}C and ^{13}C) (by accelerator mass spectrometry)
 - **Tritium** (3H) (with electrolytic enrichment)
- **Isotopic tracers used to pinpoint and fingerprint sources of groundwater**
 - **Stable isotopes for hydrogen and oxygen** (2H and ^{18}O) from precipitation measured relative to Vienna Standard Mean Ocean Water (VSMOW) (Method RSKSOP 296, Revision No. 1)
 - **Strontium Isotopes** ($^{87}Sr/^{86}Sr$) from weathering (by thermal ionization mass spectrometry)
 - **Inorganic Chlorine Isotope** (^{37}Cl) from diffusion of salts (by continuous flow isotope ratio mass spectrometry)
- Beneficial for oilfield contamination studies



Analytical Results

October, 2013

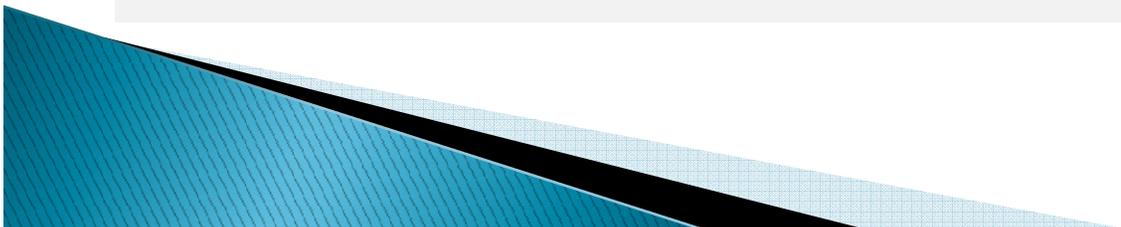
- ▶ Elevated chloride concentrations in the wells
 - Average of 9,355 mg/L in MW 1 thru 10
 - 572 mg/L in MW-11
 - 3,620 mg/L in residential well

- ▶ High boron (naturally occurring in the regional groundwater) and strontium concentrations in MW 1 thru 10

- ▶ High concentrations of total dissolved solids in 7 of 9 monitoring wells
 - MW are above 10,000 mg/L except MW-7 and MW-11
 - 7,720 mg/L in the residential well

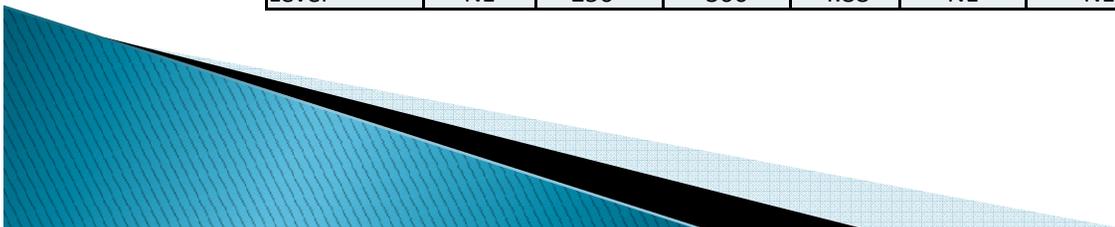
- ▶ BTEX constituents:
 - Presence of benzene in MW-6 in 2013 and MW-5 in 2012
 - Low Dissolved Oxygen in MW-5 and MW-6

- ▶ Isotopic analyses described with graphs



Basic Chemistry: Cations and Anions

Sample Designation	Anions (EPA 9056)			Cations (EPA 6010C)						TDS
	Bromide	Chloride	Sulfate	Boron	Calcium	Magnesium	Potassium	Sodium	Strontium	
July 2013 Sampling Event										
MW-3	79.5	9850	2.79	15.5	855	127	79.4	5880	66.1	19700
MW-4	59.8	7030	2.11	12.7	678	100	56.9	4540	52	15400
MW-5	35	10700	9.32	11.6	1060	156	39.5	5700	50	19900
MW-6	63.2	9330	2.7	14.9	758	114	51.9	5470	57	18800
MW-7	39	5150	8.07	14.3	304	48.7	25.8	3400	17.3	9340
MW-8	34.3	9530	1.31	11.7	790	126	76.2	4880	61.2	18200
MW-9	34.3	7890	90.7	2.01	2000	281	26.6	2090	12.5	14700
MW-10	52.2	14500	12.1	11.6	1460	198	35.7	7700	46.4	28600
MW-11	2.33	572	64	0.243	253	36.1	32	152	0.9	1450
December 2012 Sampling Event										
MW-3	51.5	12300	2.58	15.7	883	126	86.7	6090	72.9	17800
MW-4	36.4	8370	4.99	15	834	116	68.6	5200	59.2	16300
MW-5	38.1	8310	9.64	11.5	833	125	35.7	4820	40.3	11000
MW-6	40.6	9300	9.94	15.9	730	104	58.6	4880	49.7	16000
Residential Well	15	3620	34.6	2.77	971	122	27.1	1400	5.67	7720
TCEQ Action Level	NE	250 ¹	300	4.88	NE	NE	NE	NE	14.6	10000

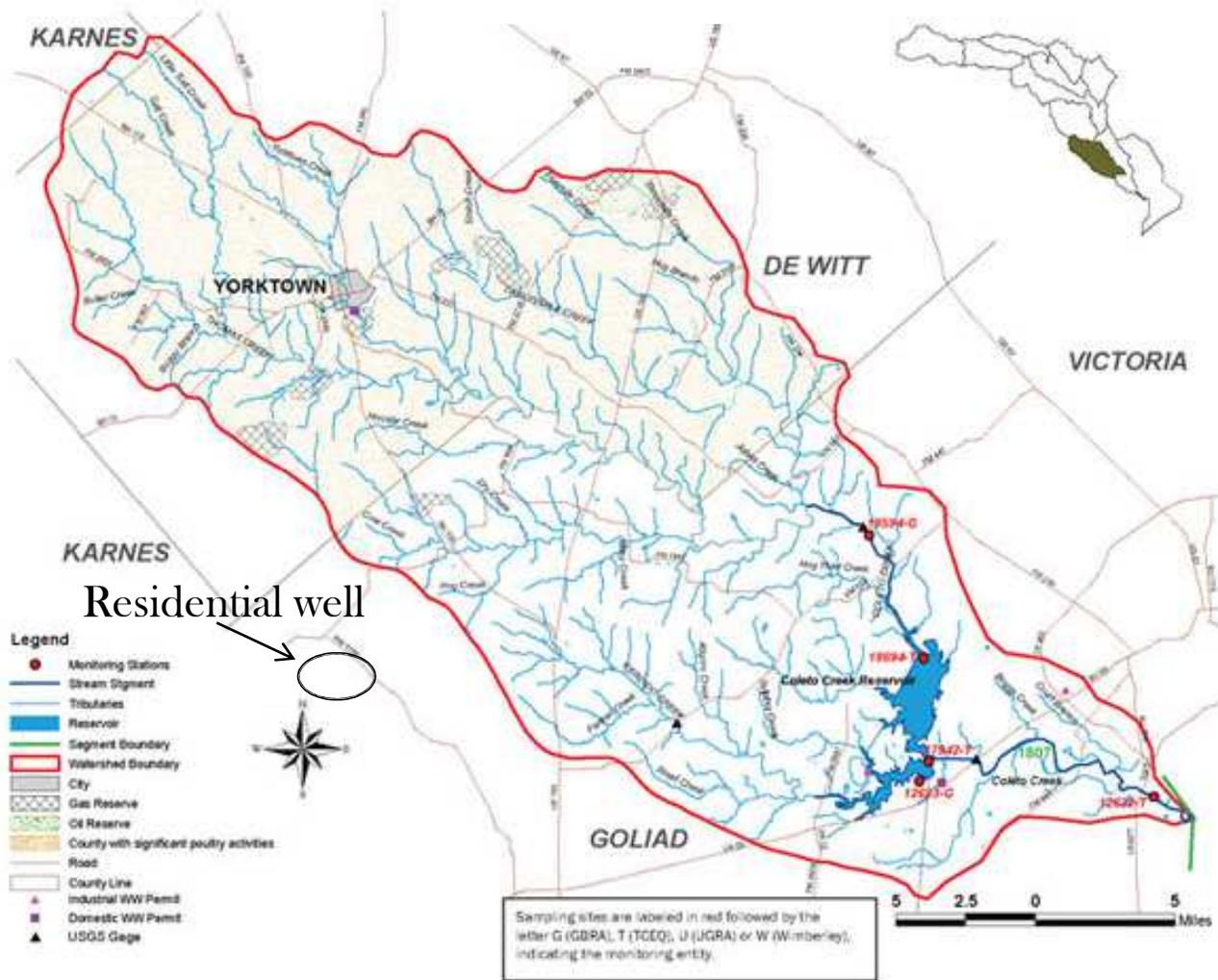


Discussion

- ▶ Monitoring Well data was compared to regional water sources from the Coleta Creek Watershed
 - 9 monitoring wells (MW-7 thru MW-10 compared for example below)
 - 1 Residential water well
 - 34 groundwater samples from the Texas Water Development Board (TWDB)
 - 9 surface water samples from TWDB

Parameters	Monitor Wells		Residential Water Well	Groundwater		Surface Water	
	Average	Std Dev	Average	Average	Std Dev	Average	Std Dev
Br	40	5.9	15	0.5	0.2	0.54	0.2
Cl	9570	1624	3620	133	66	148	44
SO4	7	3.1	15	167	11	36	11
B	15	1.8	3	167	45	174	71
Ca	820	56	971	99	17	99	11
Mg	117	8.8	122	13	3.1	12	3.2
K	62.9	18	27	3	0.79	4.7	2
Na	5247	507	1400	85	34	85	32
Sr	55	12	6	0.5	0.22	0.42	0.09
I	5	1	0.3				
TDS	15275	2561	7720	599	129	604	101
Ratios							
Ca/Mg	7	0.2	8	8.9	1.9	8.6	1.9
Sr/Ca	0.07	0.01	0.01	0.006	0.003	0.004	0.0007
SO4/Cl	0.0008	0.0004	0.01	0.23	0.11	0.25	0.06
(Ca+Mg)/Na	0.18	0.013	0.78	1.53	0.68	1.44	0.42
Br/Cl	0.0044	0.00014	0.0041	0.0038	0.0014	0.0036	0.0002

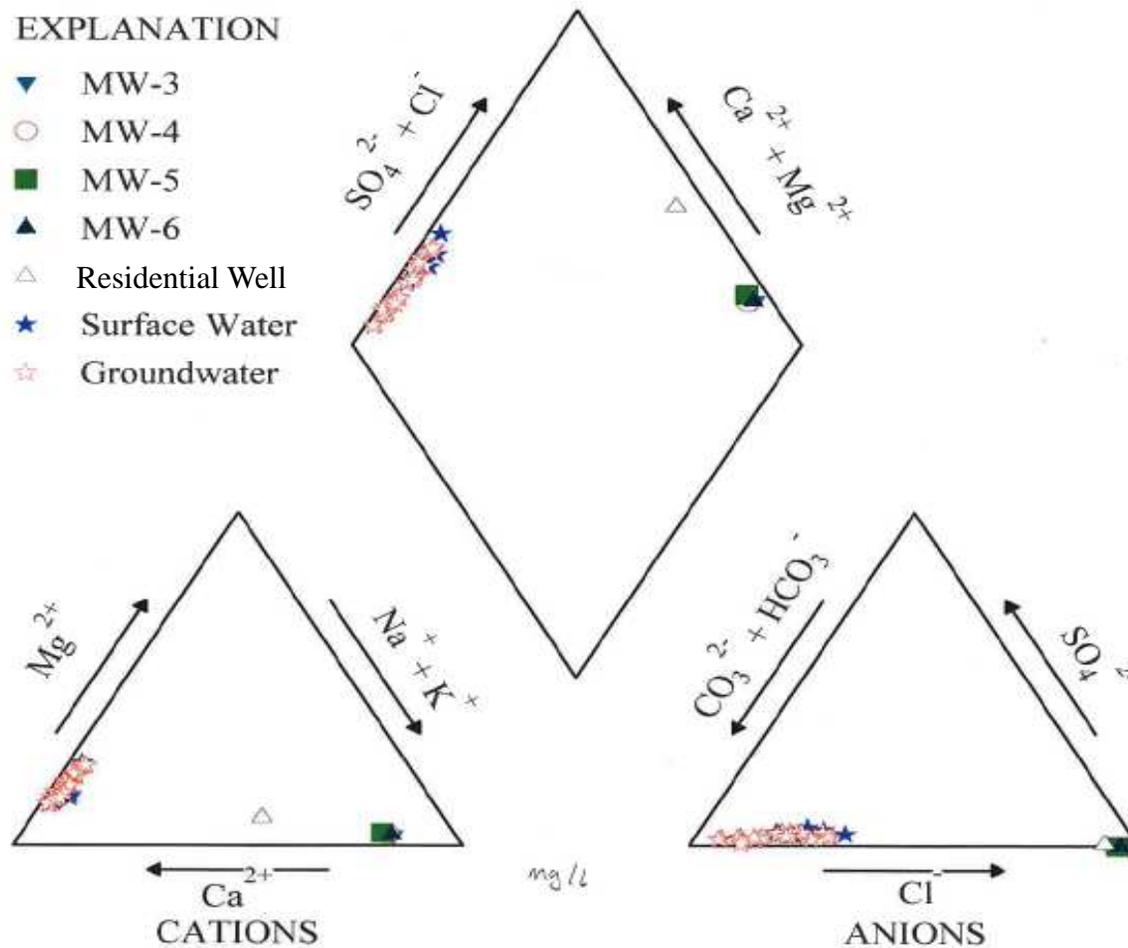
Coletto Creek Watershed



- Best available data comes from the Coletto Creek investigation (Braun and Lambert, 2011)
- The residential well is actually in the Lower San Antonio Watershed

Piper Diagram:

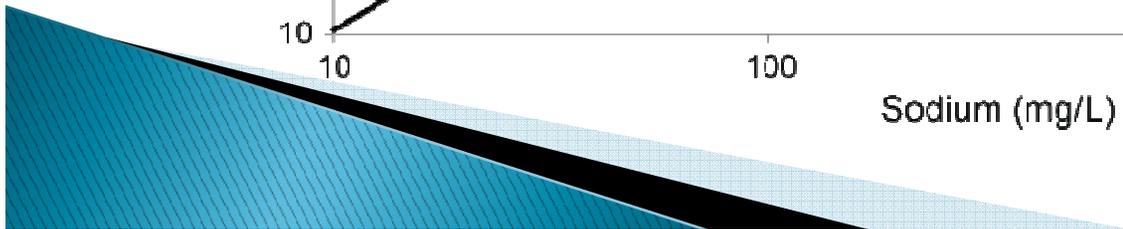
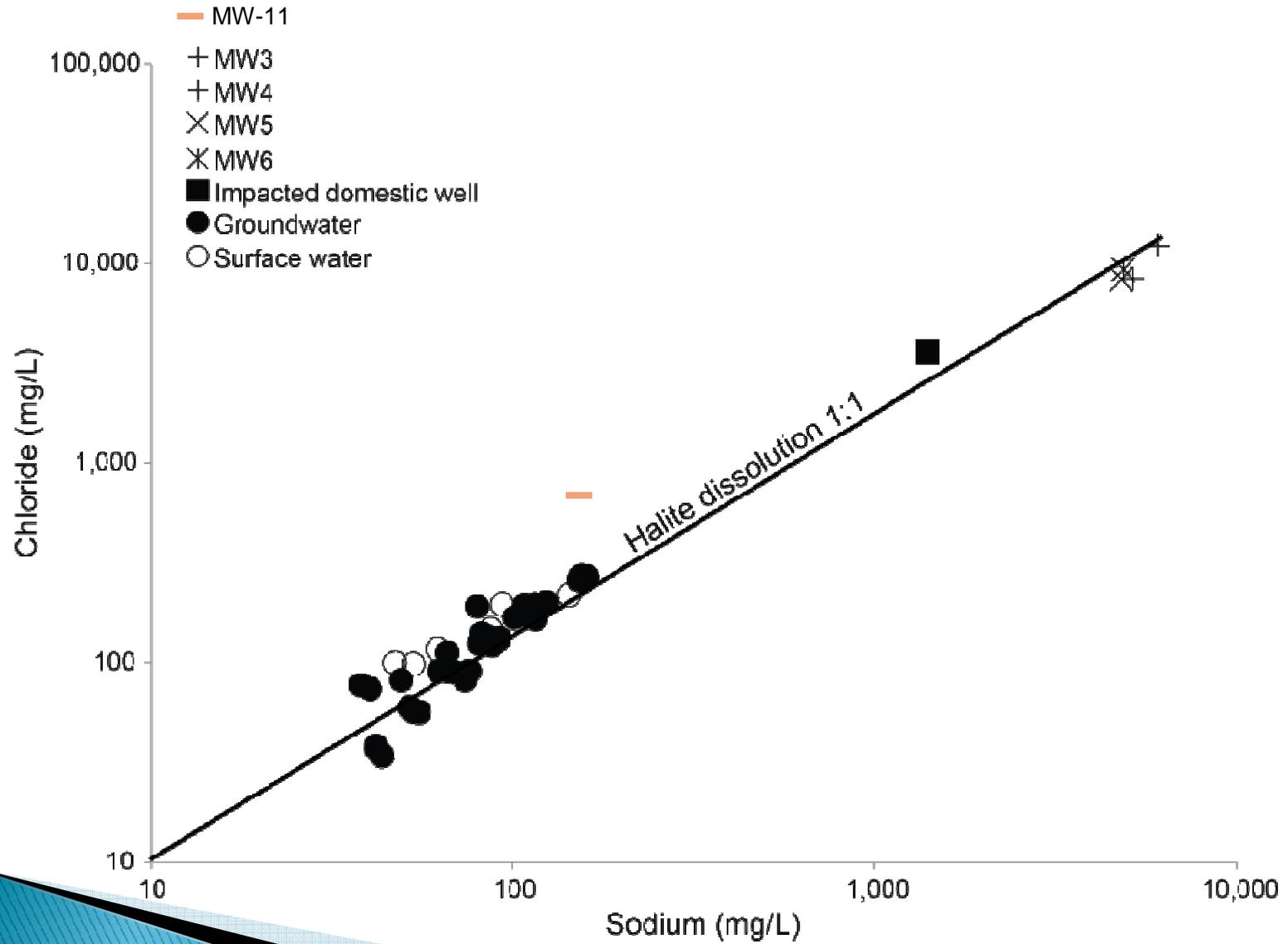
Illustrates the chemical compositions of water from regional sources and monitoring wells



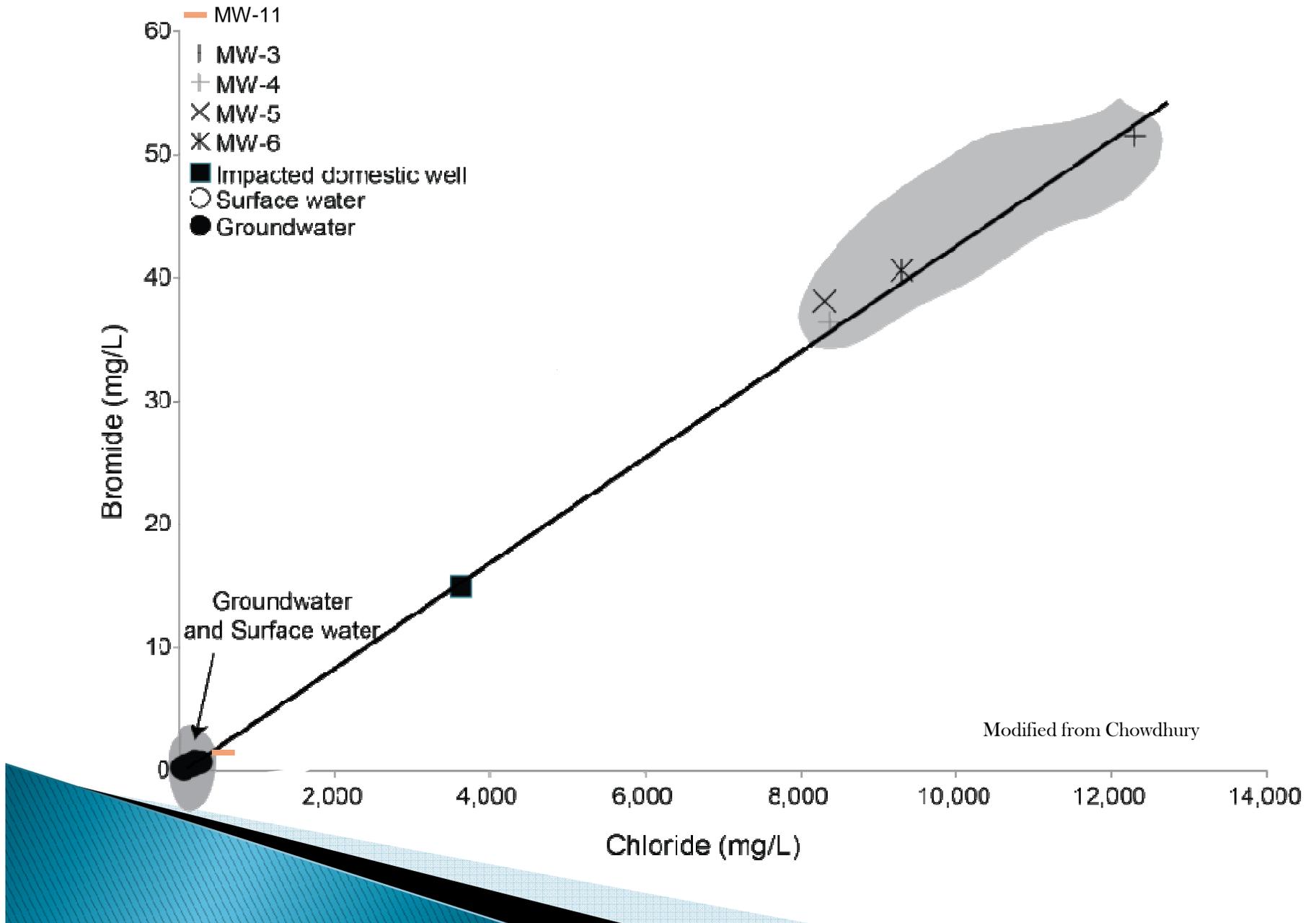
Braun and Lambert, 2011

- ▶ Residential and monitoring wells: high Na-Cl concentrations
- ▶ Regional groundwater and surface water: predominantly calcium-bicarbonate ($Ca-HCO_3$)

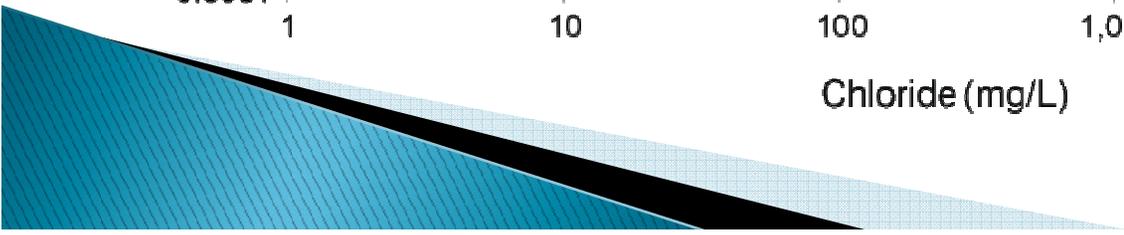
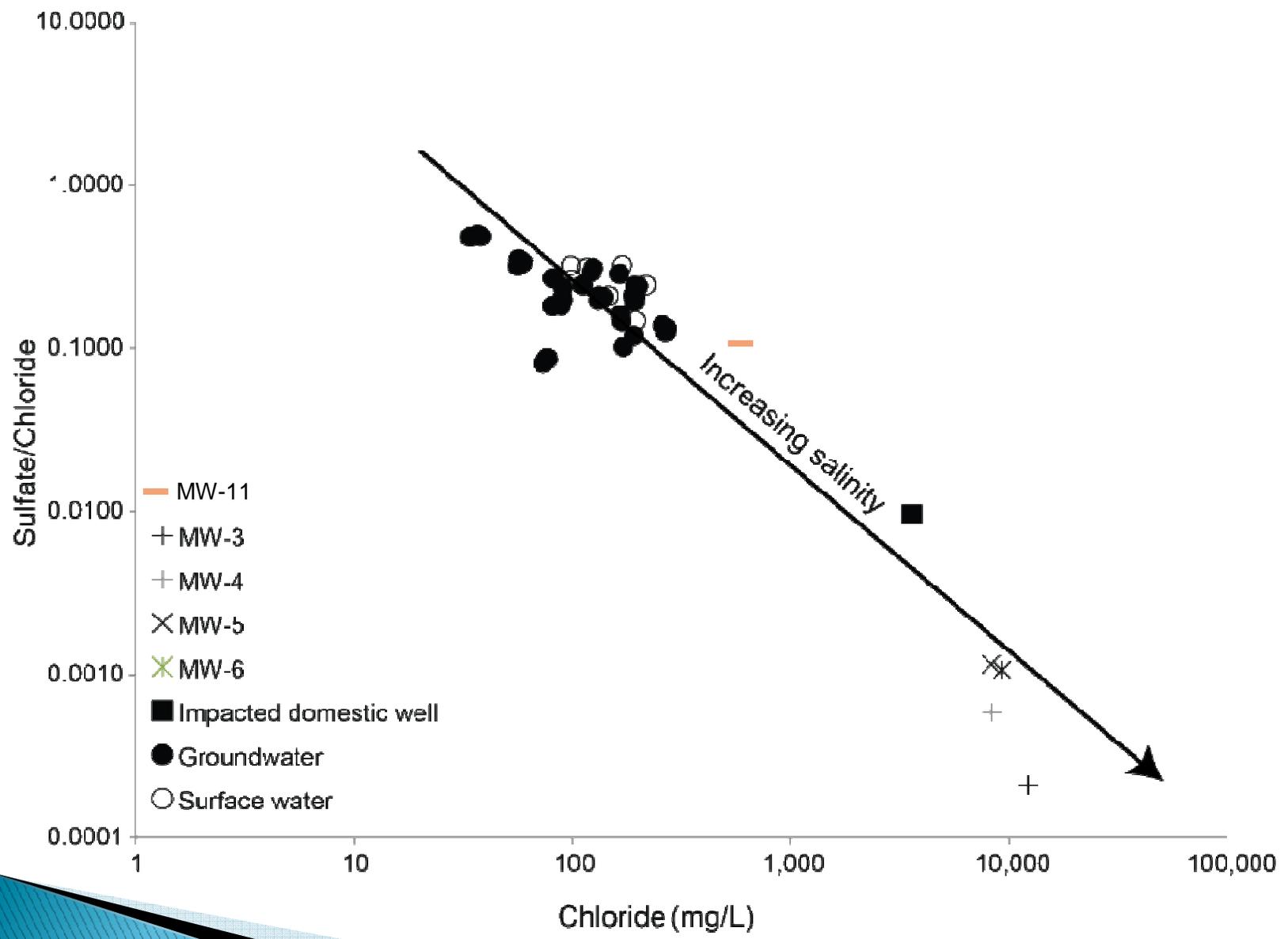
Cross-Plot of Sodium and Chloride



Cross-Plot of Bromide and Chloride

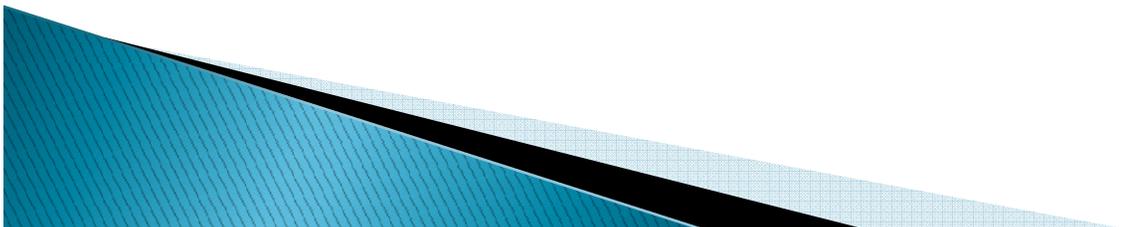


Cross-Plot of Sulfate/Chloride and Chloride



Isotopic Analytical Results

- Oxygen and deuterium isotopes of groundwater
 - Monitor wells are considerably more enriched than fresh meteoric water observed in the Texas Gulf Coast Aquifer System (Chowdhury, 2008)
 - $\delta^{18}\text{O}$ value range:
 - Fresh meteoric water - between -4.5 and -5.7 ‰ (SMOW)
 - Observed monitoring wells - 0.88 to -0.89 ‰ (SMOW)
 - MW-11 has stable isotope concentrations characteristic of regional groundwater
 - $\delta^{18}\text{O} = -4.08$ ‰ and $\delta^2\text{H} = -26$ ‰
 - Insignificant amount, if any, of contaminant present in MW-11 nearest to residential well
- Strontium Isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$)
 - MWs are also enriched and suggest involvement from the contaminated brine pits encountered in the Gulf Coast
 - ^{87}Sr isotope values of groundwater from the residential well are less enriched with much greater contribution from aquifer recharge



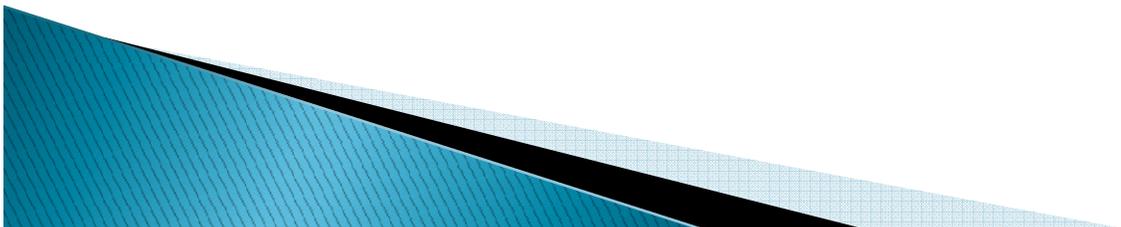
Isotopic Analytical Results

- ^{37}Cl
 - Values in the MWs are characteristic of salt-water interaction
 - Minor differences caused by diffusional processes
- ^{14}C
 - MW concentrations range from 43 to 51 pmC* (approx. 6,000 years old)
 - Residential water well contains 70 pmC (approx. 2,950 years old)
 - Indicates shallow groundwater above the deeper residential well is older
 - Residential well may have a separate water source that recharges quicker
 - Values can be diluted by dissolution of carbonate sediment

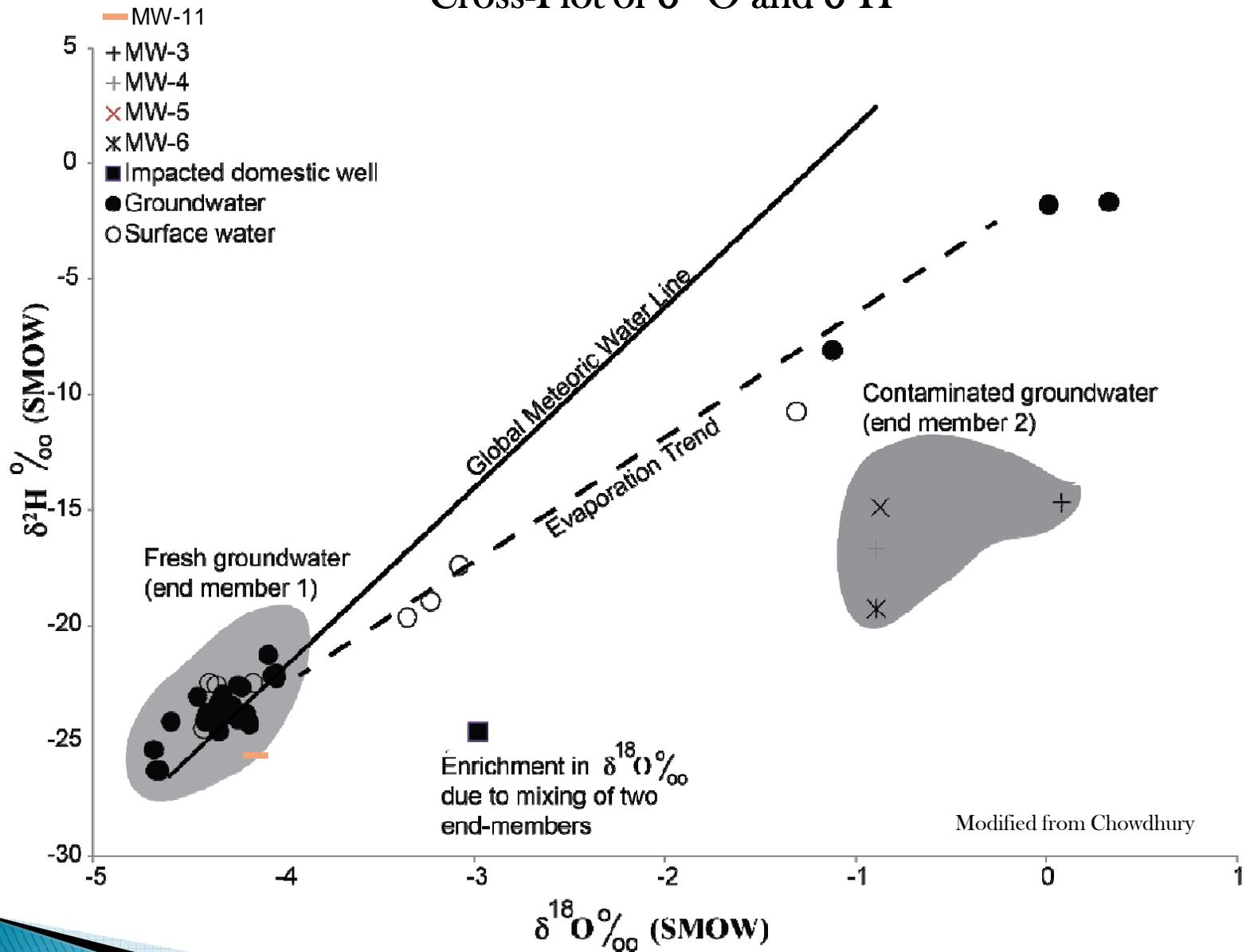
* pmC - Percent Modern Carbon

Isotopic Analytical Results

- Tritium
 - Detected in the MWs around the pit but not the residential well
 - GW in the MWs is modern - between 1 and 2 TU (less than 50 years)
 - Water from the pits influenced by atmospheric tritium
 - GW in the residential well is a mixture of modern and sub-modern waters - <1 TU
 - Suggests that a fraction of the water in the shallow zone must have recharged in the last 50 years
 - If contaminated water reached the residential well, no traces of tritium are present
 - Migration was not lateral thru the contaminated zone

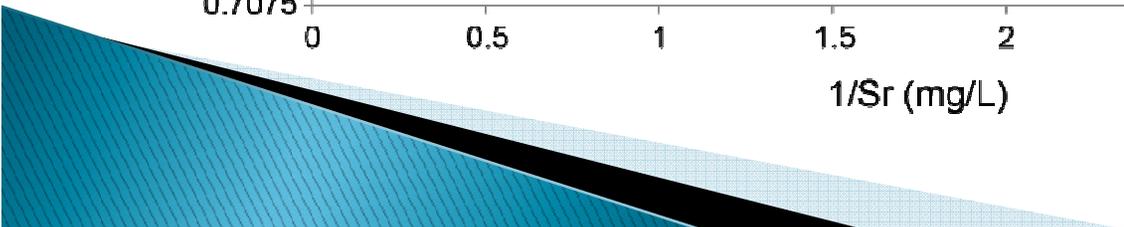
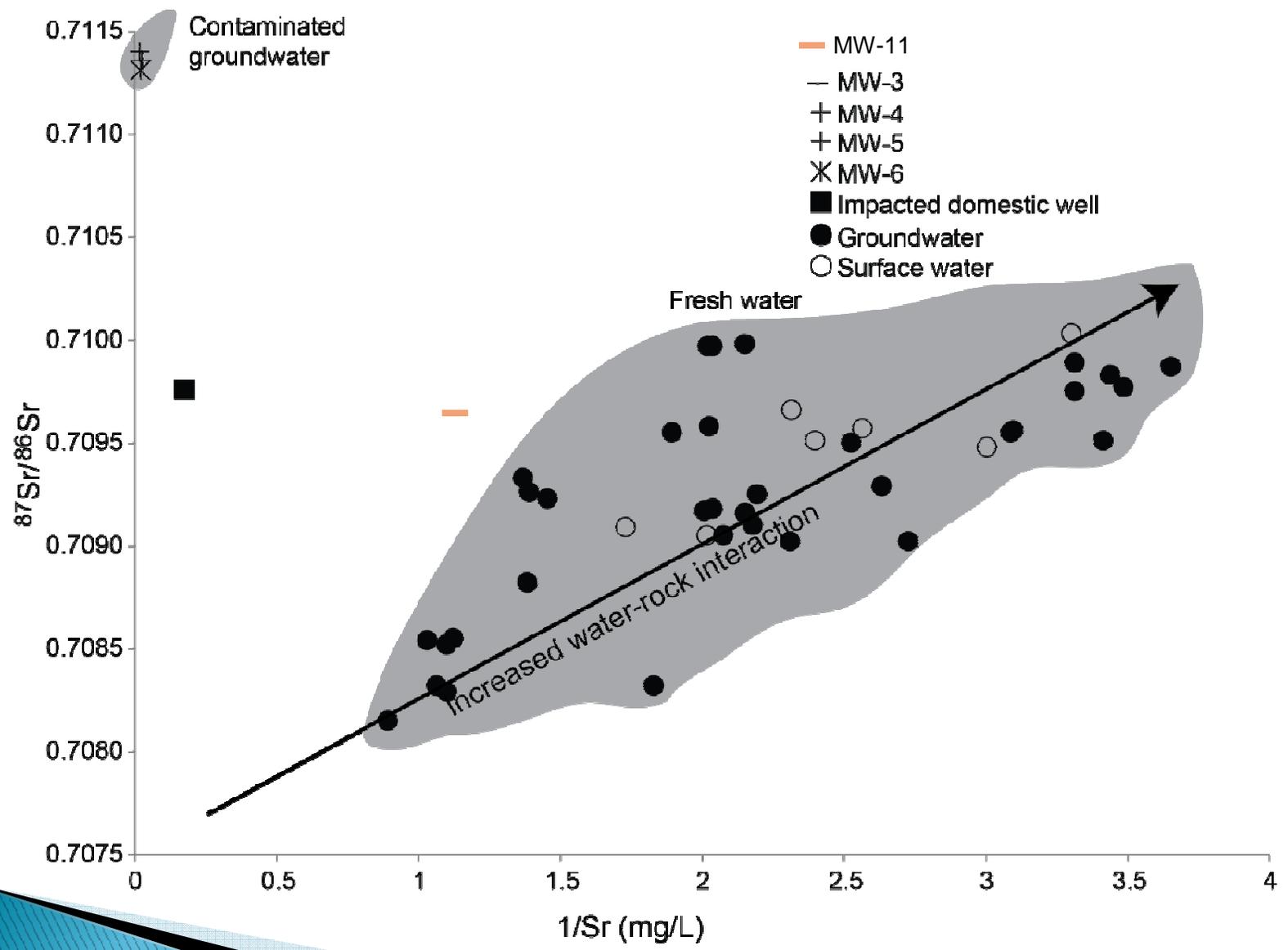


Cross-Plot of $\delta^{18}\text{O}$ and $\delta^2\text{H}$

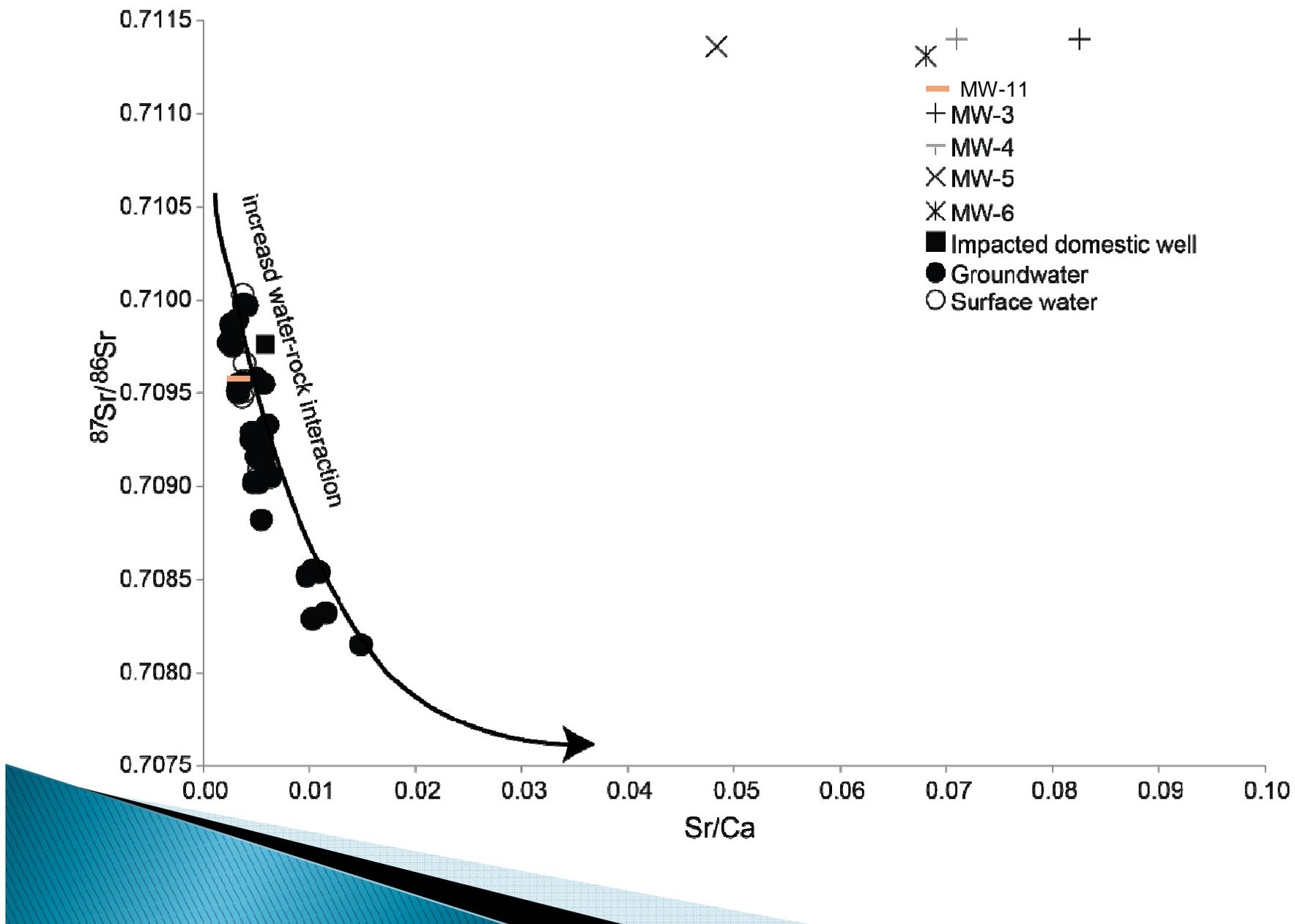


Note isotopic compositions of the groundwater from the monitor wells are similar to the formation water brine from the Gulf Coast Basin.

Cross-Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$

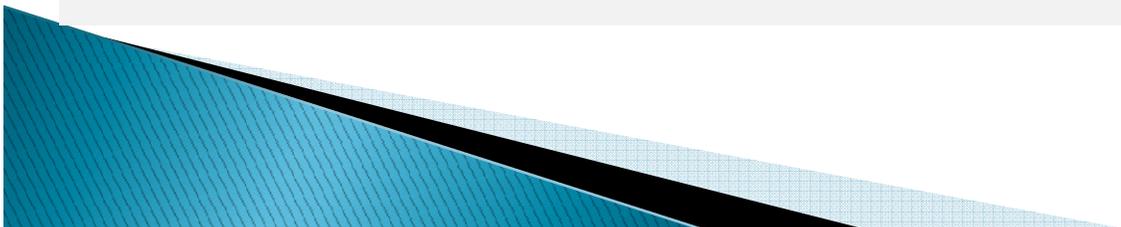


Cross-Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca



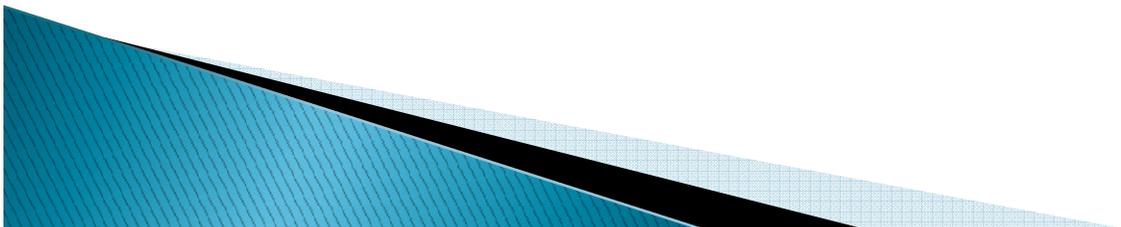
Conclusions

- Evidence of shallow groundwater contaminants from brine discharge/leakage from historic pits
 - Average TDS levels in all MWs is 17,145 mg/L (except MW-11 at 1,450 mg/L)
 - Increasing salinity trends in Na/Cl, Br/Cl, and SO₄/Cl ratios, not in MW-11
 - ⁸⁷Sr/⁸⁶Sr, oxygen and deuterium isotopes are enriched in MWs around the historic pits, less enriched in residential water supply well
- Separate stratigraphic groundwater zones
 - Groundwater depths:
 - Residential well is 180 ft bgs
 - MWs are approx. 90 ft bgs
 - Migration of contaminants is not lateral according to MW-11 and a slight gradient north
 - If migration is vertical, water would have to penetrate the 100 ft contiguous clay zone



Conclusions

- Age dating conclusions
 - ^{14}C values indicate deeper residential well is older, recharged from a different source
 - Tritium detected in MW-3 thru MW-6, not in MW-11 or the Residential Well
 - Influence of atmospheric tritium around the pits from atmospheric interaction
 - No evidence of tritium outside of the historical pit site
- Isotopic and chemical analyses suggests the deeper GW in the residential well has an alternate contamination source
 - Impacted by mixing of different, unidentified sources
 - Not the same contamination source as the MWs
- More research is needed to more definitively constrain the source(s) and extent of the saline groundwater impact at that depth



Acknowledgements

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- ▶ Department of State Health Services: Heidi Bojes
- ▶ Shell Global Solutions: Ali Chowdhury



References

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