Historic Oilfield Arsenic Sources: Implications for Pit Groundwater Models

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Presentation Objectives

Consider issues for a pit arsenic groundwater model if a production corrosion arsenic inhibitor (1950s) was used

- Review history of arsenic corrosion inhibitors
- Reminder of oilfield chemistry & iron
- Review As pit groundwater model assumptions
- Look at probably the best example in U.S. to address questions

Author’s Use of Public Records for Her Opinions

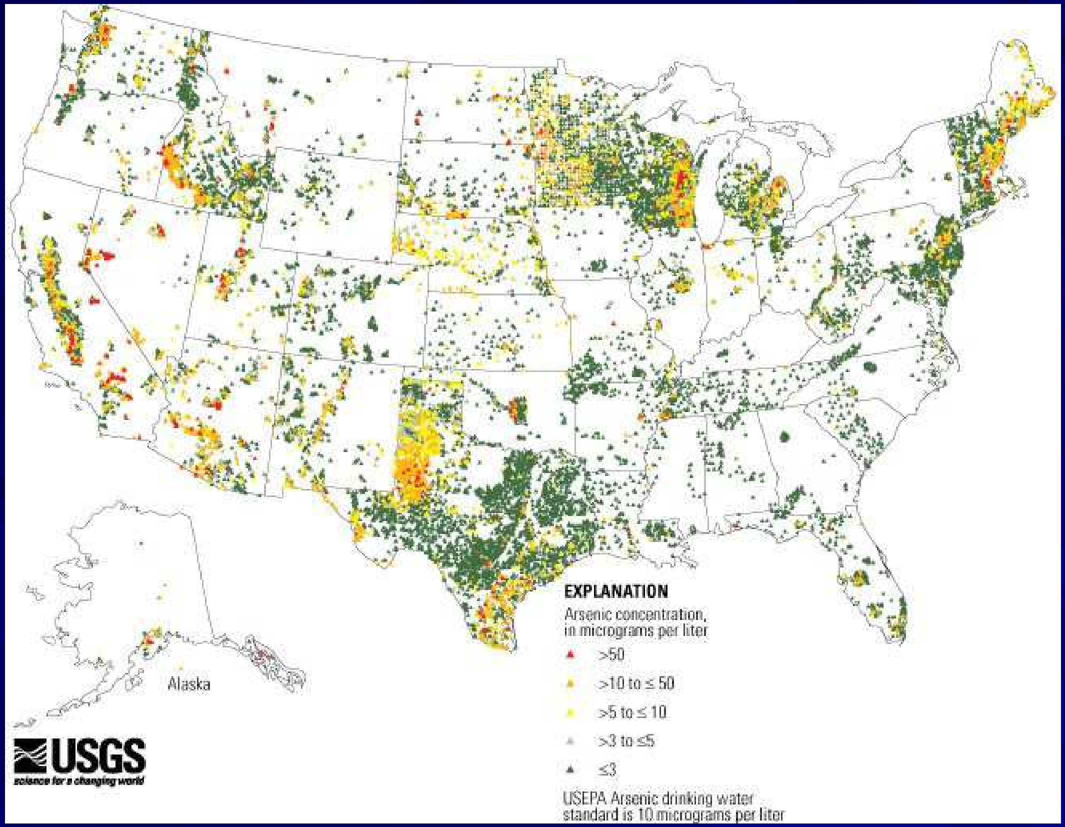
- The example from LSJ Field, LA, has large public record available due to litigation (court records in one case) and especially due to LA Act 312 (2006+) & LA Office of Conservation (OOC) oversight of oilfield cleanup of all oilfield litigation “legacy” sites (reports, raw data; hearing records…)
- I was a defense expert retained in the two cases that generated public records above; geologist, oilfield historian (environmental companies responsible for cleanup plans: Pisani & Assoc., ICON; some Geosyntec)
- My work on last case ended Feb. 2014; I have pursued this research since then, not retained by anyone, no discussions with other past experts (MY OPINIONS)

Arsenic in an Oilfield Area GW-Origins?

- Groundwater arsenic (As) above 0.01 mg/l occurs in Louisiana (natural variability + ?)
- Groundwater arsenic above 0.01 mg/l occurs in old “legacy” oilfield areas
- Groundwater arsenic models & assumptions in the U.S. are affected by larger studies from the northern and northeastern U.S. and international

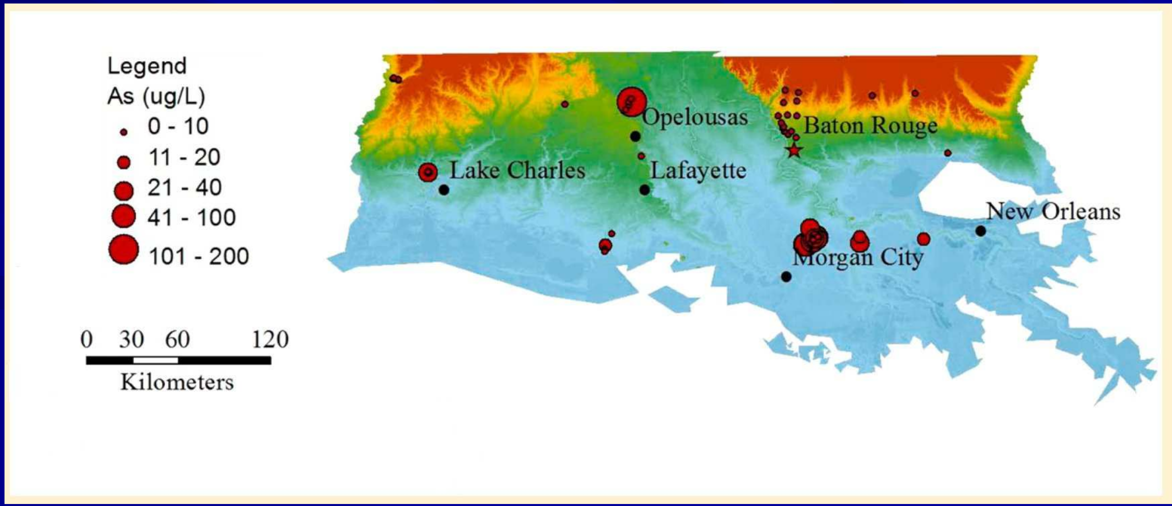
Issues

- Arsenic models are useful, but extrapolated to Gulf Coast oilfield regions of different geology & hydrogeology, and may not consider impacts from “oilfield chemistry”
- “Oilfield chemistry” & its potential component impacts (esp. iron) have a history, & pits often record it
- The detailed history of oilfield pits--how used, its shallow fluid movement patterns, how “disturbed” over time—is important



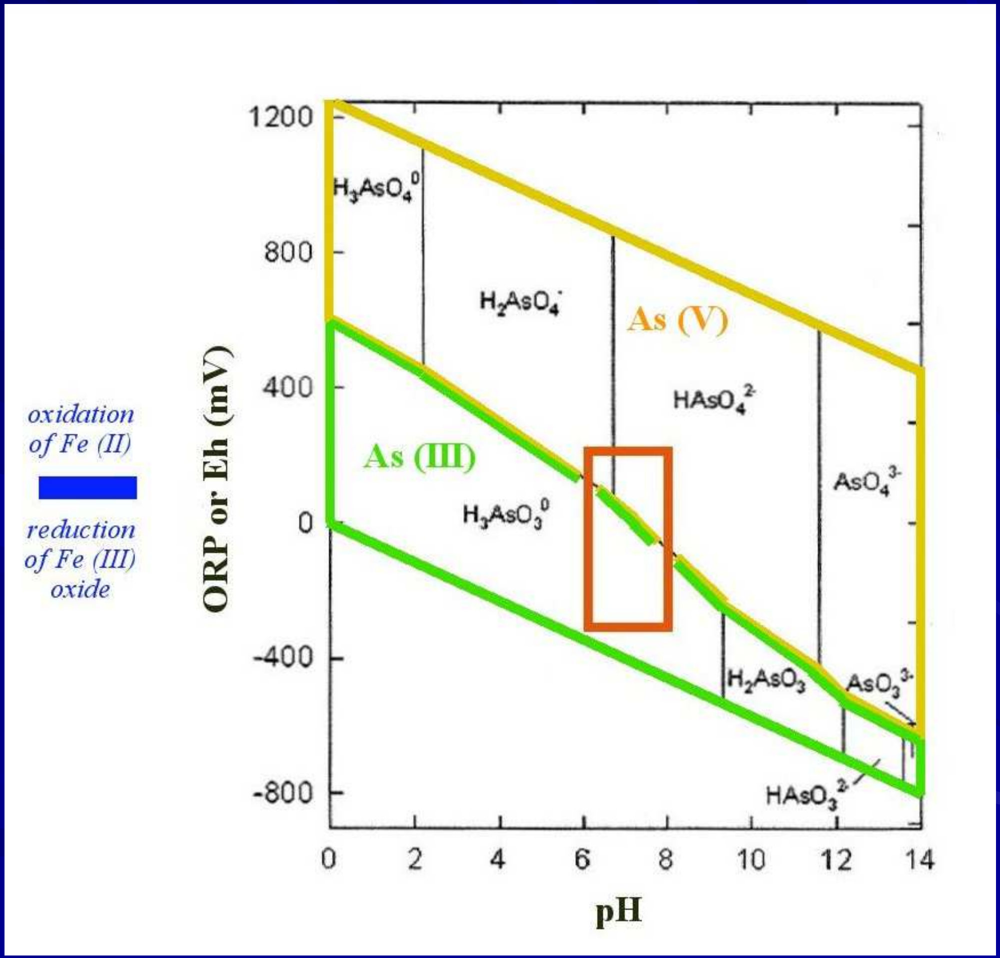
LA groundwater published arsenic record limited, but Miss. R. alluvium waters can be elevated (USGS 2000)

Modern work, shallow groundwater As values from S. LA, 78 wells, up to 0.200 mg/l (Yang et al, 2014)

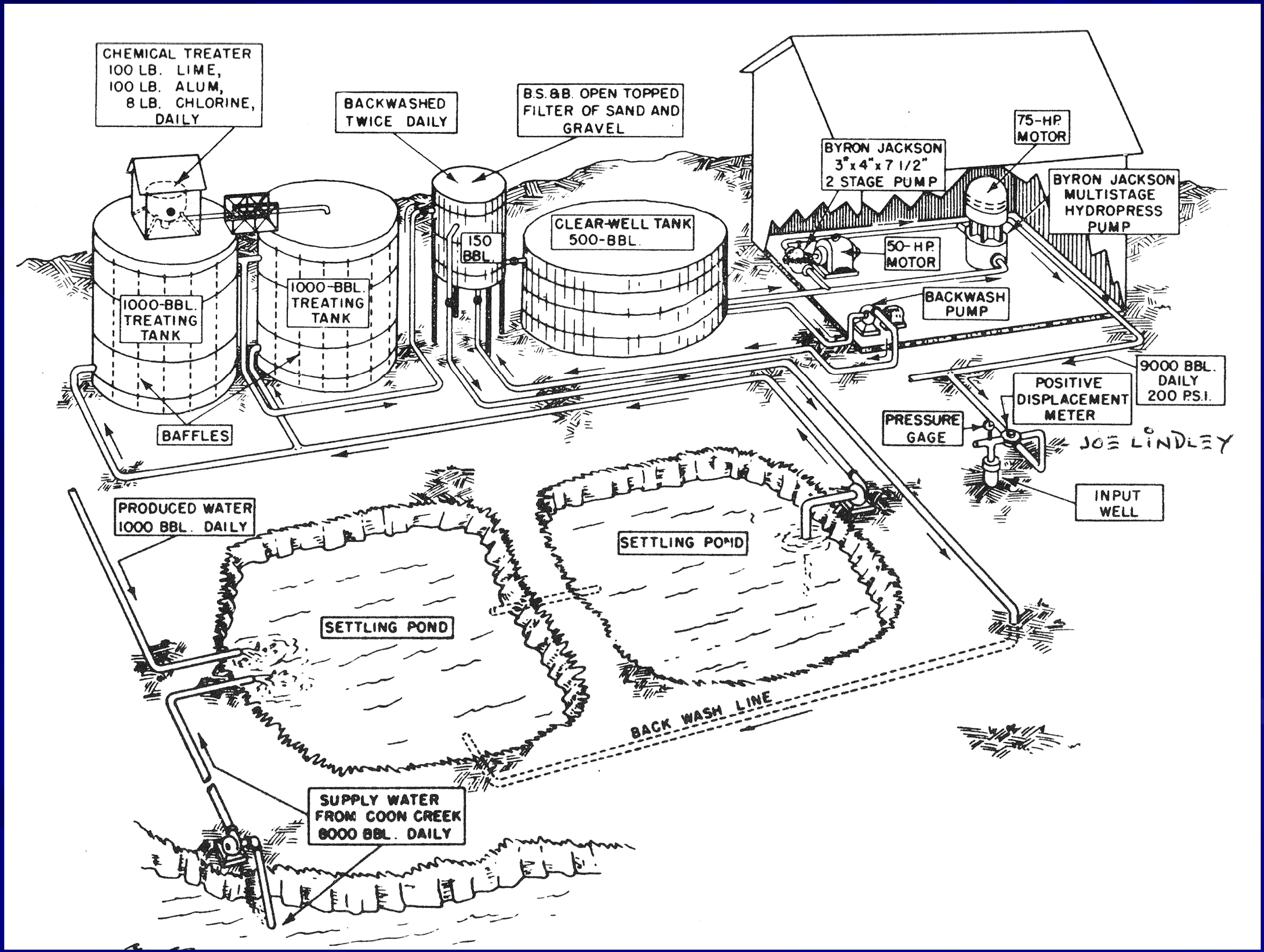


Reductive Dissolution of Iron Oxides: The Basic Model

- An equilibrium diagram for system As-O_2-H_2O
- Iron oxides common in our LA sediment
- As bound to iron oxides, released into GW with "reductive dissolution" when some cause for a reducing environment (organics, oil, clay…)
- Iron oxides re-precipitate as GW move into oxidizing zone, also locks up As
- Does not address As desorption (phosphates)
- Model looks for relations between ORP, Fe, As



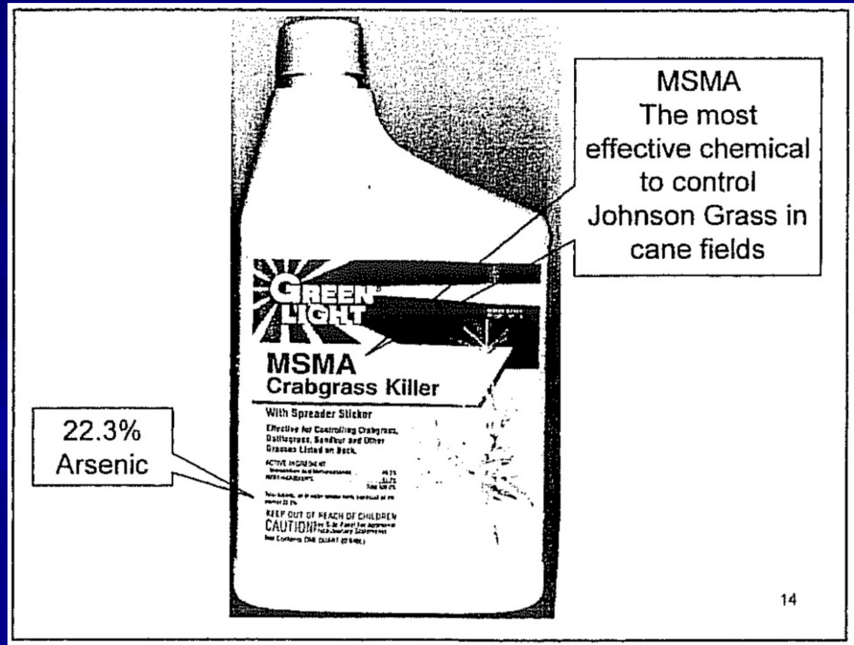
Amorphous Iron Precipitates in the Oilfield—long history in oilfield chemistry (Hydrous ferric oxides—HFOs)



1950s Oklahoma Oilfield Water Treatment (Powell & Johnson, 1952)

Historic Arsenic Usage

- Pesticides
  - Concordia Parish cotton, 1910+
  - Vegetable gardens, trees
  - Cattle dipping vats
- Herbicides
  - Inorganic & organic
  - Land & aquatic weed killer
    - Oilfield usage
- Industrial
  - Corrosion inhibitor
  - others



Griffin presentation on
oilfield legacy litigation (2006)

Arsenic in Produced Water

- U. S. Oilfields
  - Studies elsewhere from late 1950s (White) through 2005
  - As values range from ND to 1.6 mg/l
  - LA data from 1989 and onward range from ND to 0.5 mg/l
  - 7 studies!
- No produced water analysis (As) for my example

Number of Analyses/values	Range of Detected Arsenic
2	120 – 500 ug/l [a]
6	70 – 119 ug/l
7	11 – 69 ug/l
27	nd – 10 ug/l

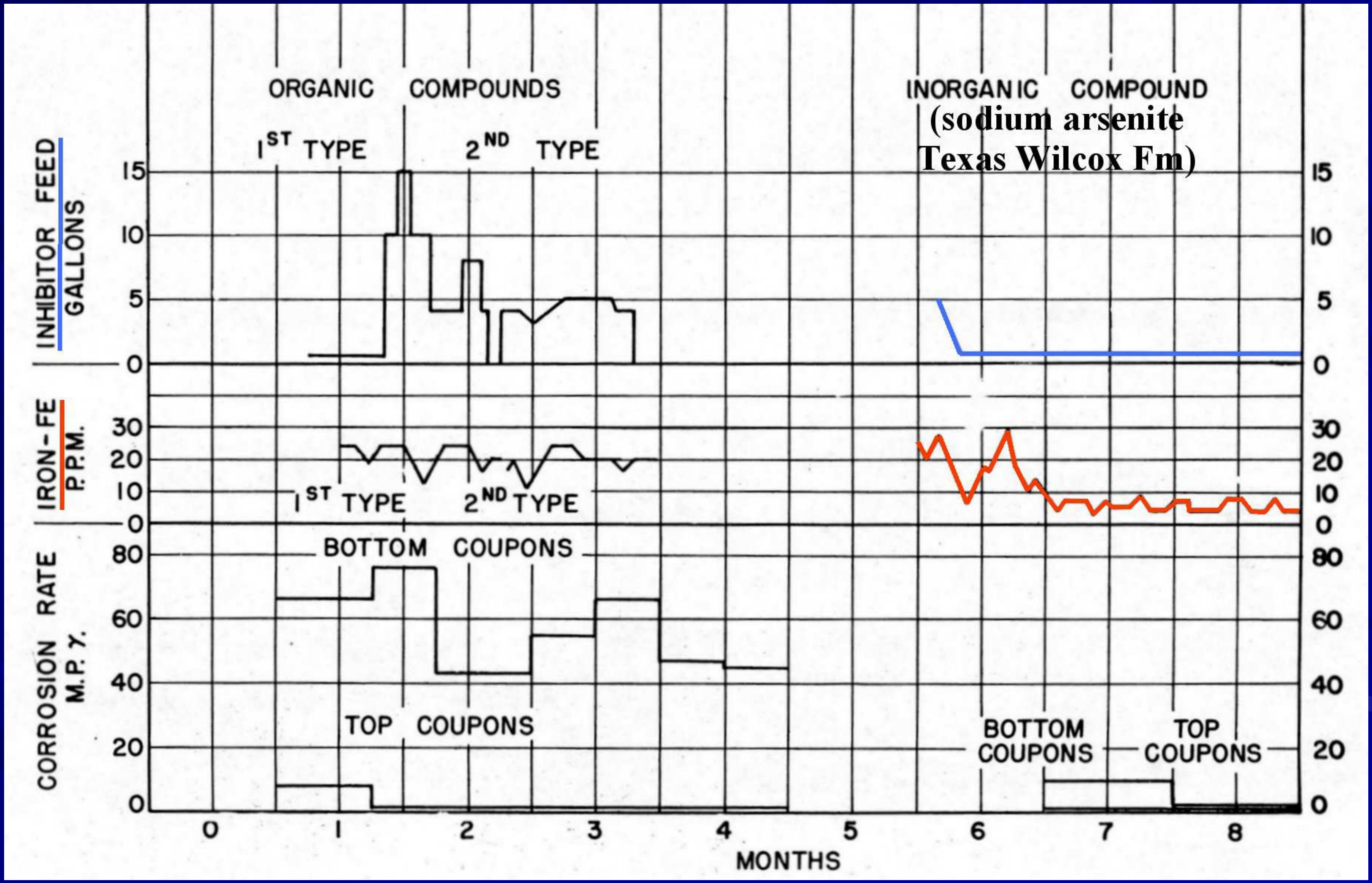
S. Louisiana & GOM

1989 and later publications

OilField Arsenic Corrosion Inhibitors Historic U. S. Summary

- Acid Corrosion Inhibitor
  - 1932, Michigan oilfield acid job, limestone
  - 1934, arsenic is important acid job inhibitor, but organics now available
  - Early 1960s, decrease As usage, but good for high-T wells
  - In 1970s, arsenic inhibitor phase-out in acid jobs
- Production Corrosion Inhibitor
  - 1949, Reported first usage in Texas Wilcox trend (Jones, 1955)
  - 1954, CA survey, 17 fields;
    65 % pumping wells used inorganic inhibitors (arsenical compounds and chromates) (Hill & Davie, API, 1955)
  - 1957, LA Stream Control Commission minutes report phase-out of oilfield arsenic corrosion pellets, stripper fields
  - 1960, general end of U. S. oilfield arsenic corrosion inhibitors (Gardner, 1960); move to organics

Iron & 1950s Arsenic Inhibitor in Produced Water (Wilcox Trend, Texas)



Jones (1955)

(Jones, 1955)

LSJ Field Produced Water + Iron

- 1945 analysis, 14 ppm (Cl 13,820 ppm)
- 1959 analysis, 90 ppm (Cl 80,908 ppm)
- 1970 analysis, 215 ppm (Cl 101,135 ppm)
- 1995 analysis, 21 mg/l (Cl 59,449 ppm)

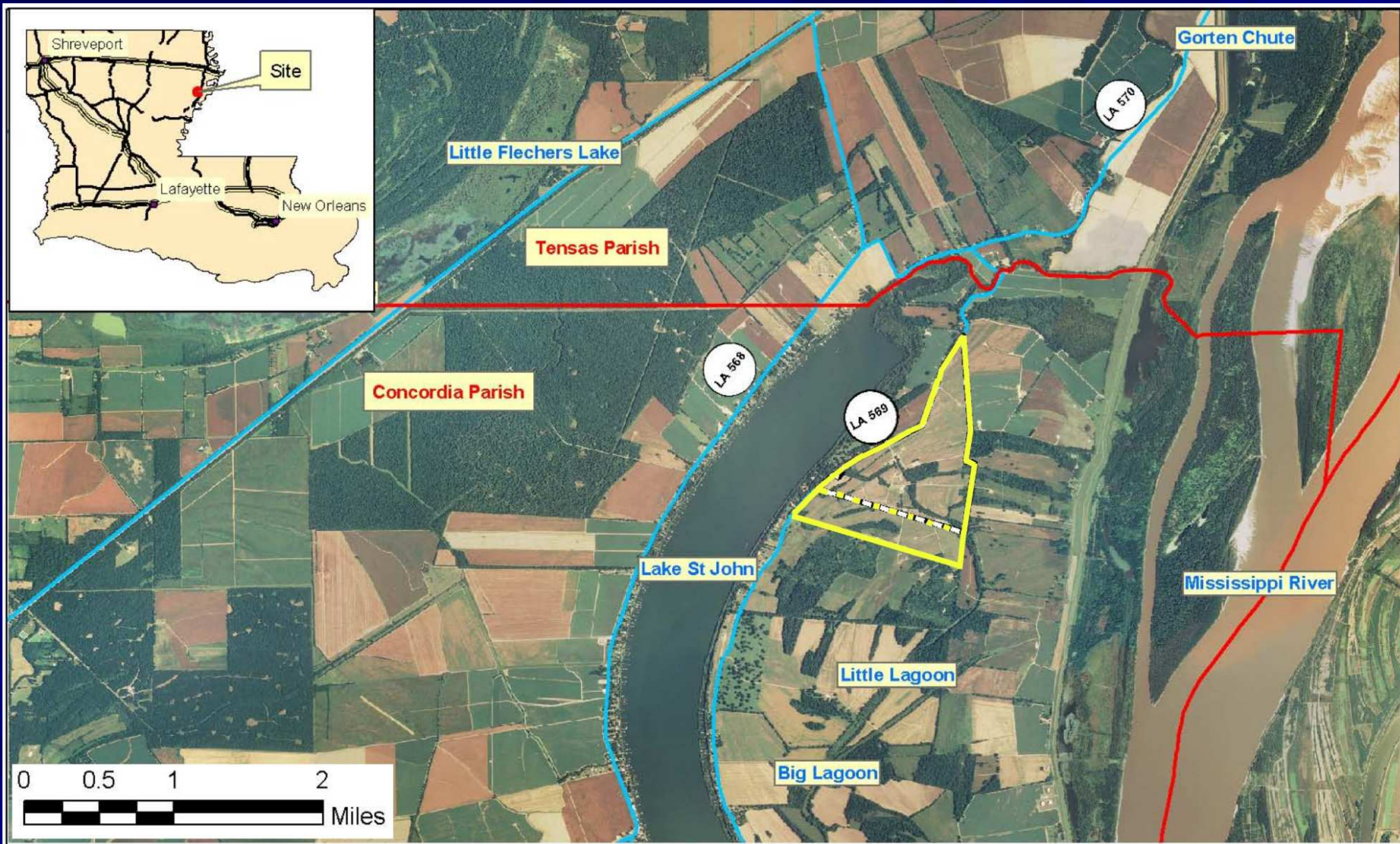
(OOC, Poppadoc hearing files, 2009;
Norman reliance documents, v. 52-53)

GENERAL OBSERVATION: While an old oilfield may have used arsenic inhibitors within the 1950s, more likely is that many oil fields had many possible decades (into 1970s, esp.) of elevated dissolved iron in produced water, and thus into pits

Lake St. John Field Example

- Discovered in 1942, Tensas & Concordia Parishes, LA
- Major producing field for The California Company (Standard Oil of CA)
- Both unit (Cretaceous & some Tertiary age) & **lease production** (Wilcox Fm mainly)
- Outline of remaining presentation
  - Public records supporting 1950s arsenic inhibitor use
  - Modern shallow groundwater geochemistry around lease emergency pit usage areas

Study Area



(Modified from Pisani report, 2008; OOC Poppadoc file # 006-007)

LSJ Field Public Documents, Arsenic Corrosion Inhibitors

- Letters, Oct-Nov 1950, north side of field, test program for chemical inhibitors, liquid injectors and solid pellets
  - *Oct 23:* "A most promising type of inhibitor is sodium arsenite, which we intend to make use of in the very near future."
  - *Oct 27*: "have been advised of the promising results of sodium arsenite in corrosion mitigation work"
  - *Nov 13*: "In view of the fact that it is intended to try out sodium-arsenite pellets in the very near future, it is felt desirable to postpone any trial of the down-hole injector until results from that method of corrosion inhibition can be obtained."

(OOC Poppadoc hearing, 2009; Miller/ICON reliance docs, v. 25, Exhibit P-1066)

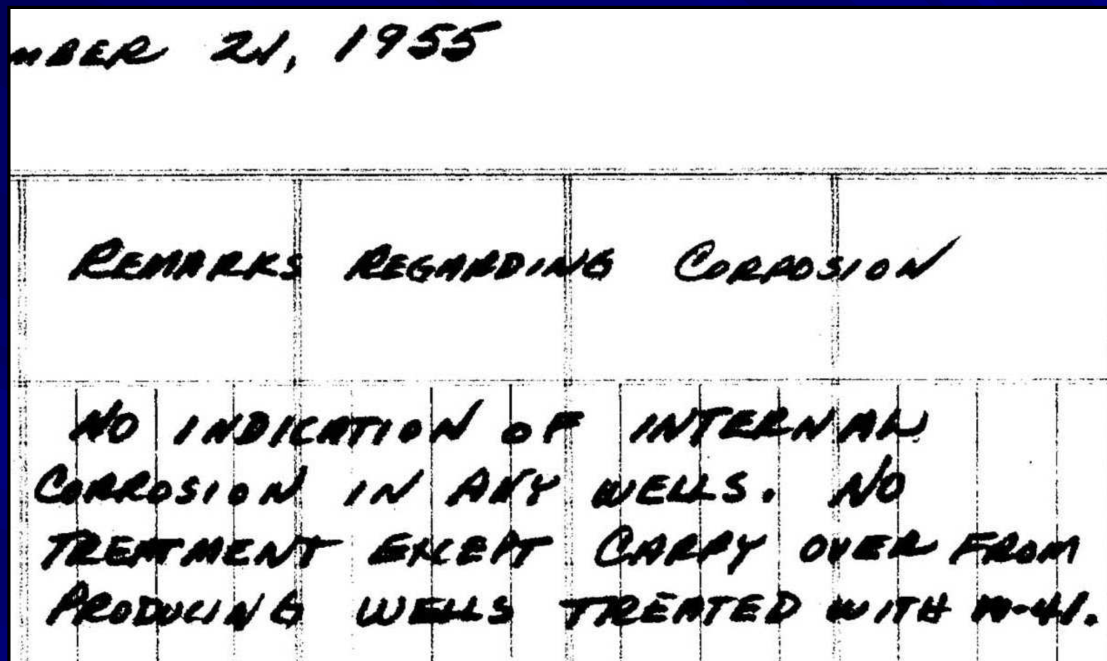
LSJ Field Public Documents, Arsenic Corrosion Inhibitors

SALT WATER ~~[illegible]~~ WELLS – LAKE ST. JOHN FIELD. NOVEMBER 21, 1955

Well Name	Type Completion	Completion Interval	Sand	Present Rate BWPD	Status Press PSI	Estimated Cap. Rate BWPD	Estimated Cap. Press PSI	Remarks Regarding Corrosion
1. SWD. Well #1 Wilcox	Perf.	1768 – 1787 1796 – 1804 1819 – 1823	Cockfield	1664	300	3050	600	No indication of internal corrosion in any wells. No treatment except carry over from producing wells treated with M-41.
2. SWD Well #2 Ba# #1+2	Perf	1850 – 1880 1974 – 1992	Cockfield	8111	500	9000	600	
3. SWD Well #3 Wilcox	Perf	2764 2938 – 2954 2968	Sparta	2792	325	5000	600	
4. SWD Well #4 Ba#6 Unit Wilcox	Perf	2916 – 2946	Sparta	1500	300	2800	600	
5. L.R. Alwood #6 Ba# #1+2	Perf	1967 – 2000 ~~[illegible]~~ –	Cockfield	Shut-in	Will not take fluid			
6. Lancaster #1 Plant	Perf	1715 – 1745 1630 – 1646	Cockfield	Shut-in	Will not take fluid			
7. Pasternack #2 Plant	Perf.	(1597 1725 | 1607 1750)	Cockfield	2034	350	5000	600	
8 E. Scott #6 Ba# #4	Perf.	2350 2400	Sparta	5137	300	9000	600	
9. Unit # 26 Plant	Perf	1760 1790	Cockfield	1500	300	5000	600	
				22,738		38,850		
8. Marks #16	Perf.							

(Poppadoc hearing, 2009; Miller/ICON reliance docs, v. 28; Tensas/Miller 02469-02470)

W-41 History


MBER 21, 1955

REMARKS REGARDING CORROSION

NO INDICATION OF INTERNAL CORROSION IN ANY WELLS. NO TREATMENT EXCEPT CARRY OVER FROM PRODUCING WELLS TREATED WITH W-41.

W-41, an arsenic corrosion inhibitor, is one example of arsenic corrosion inhibitors used in some 1950s oilfields of the U.S.

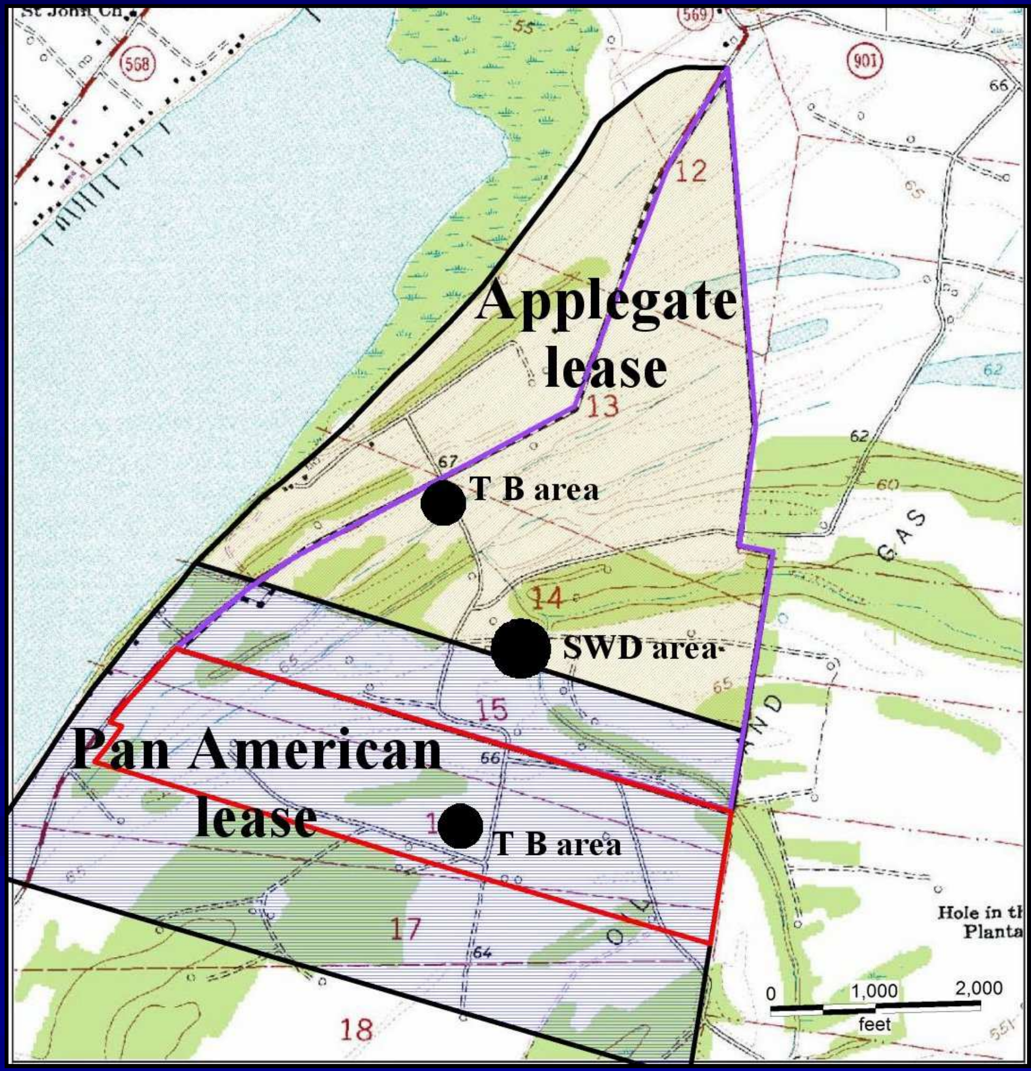
Its history is available in public documents.

W-41 History—Standard Oil of California

- California Research Corp (As & oilfield corrosion)
  - Dec 1950, 2 patents, Rohrback et al (1954)
  - Mar 1951, 2 patents, Rohrback et al (1953)
  - Dec 1951, patent, Rohrback et al (1953)
  - Oct 1954, patent, Frisius (1959)
- California Spray-Chemical Corp
  - 1952, Patent application granted in 1953 for “Ortho W-41,” also used is “W-41,” for arsenic corrosion inhibitor (42 % sodium arsenite) (EPA, 1973)

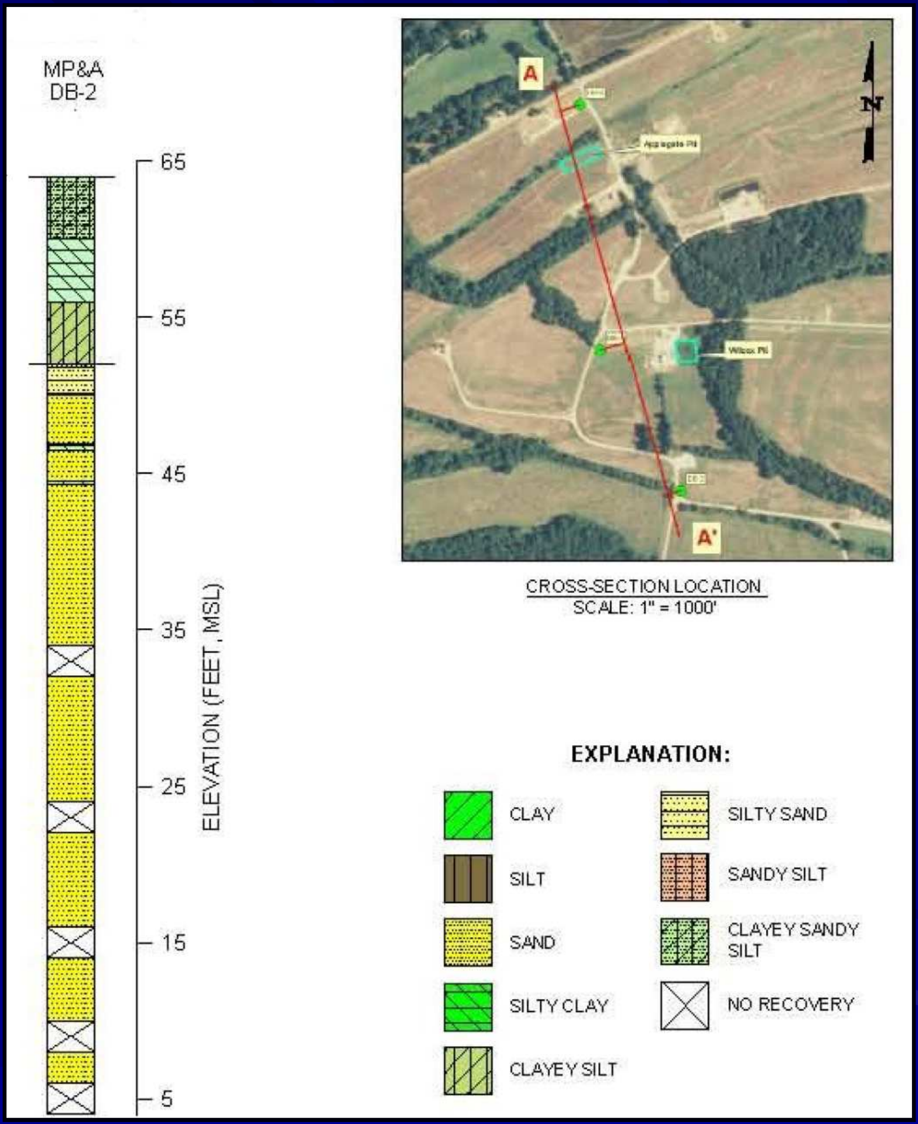
(My Opinion from the public record: W-41 was used in the LSJ Field in the 1950s; organic inhibitors were used after that)

LSJ Field: Study Area of Lease Tank Battery and SWD Emergency Pits



Mississippi River Alluvium & Aquifer

- Braided stream gravels at base
- Mostly point-bar sands
- Fining-up into levee, overbank, floodplain sections (8-12 feet here)
- This near-surface unit is aquifer confining layer



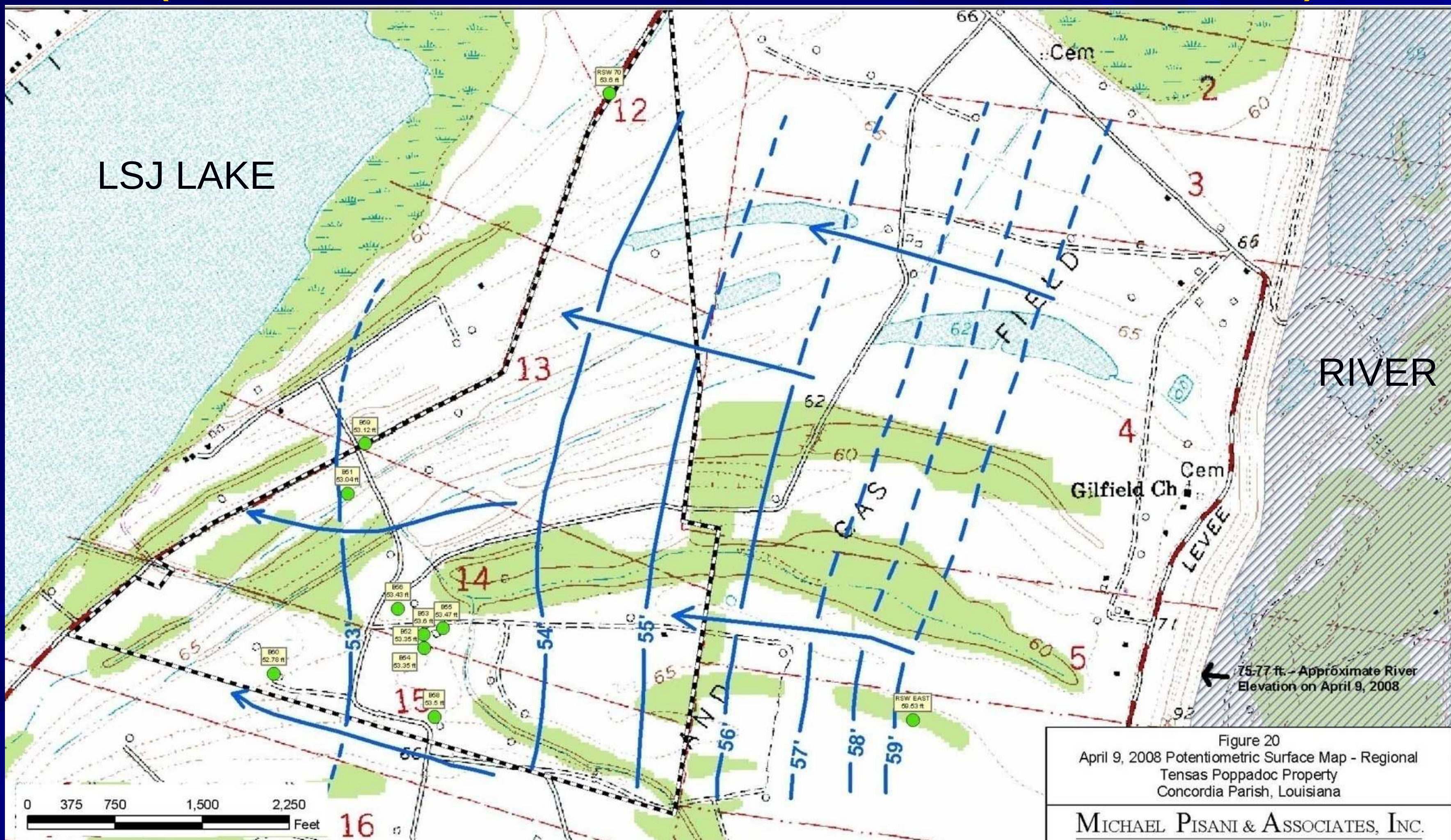
(Modified from Pisani report, 2008; OOC Poppadoc file # 006-007)

Shallow Groundwater Data (8’ to 22’ below surface) Used in This Talk

- The data from Pisani & Associates, ICON (G. Miller), is large and of high-quality (Geosyntec data is less but of high-quality)
- Shallow groundwater data are most reflective of old impacts & possible controlling influences in pit areas
- Groundwater wells at deeper depths (60’-80’, + below surface) do not have arsenic values above natural variability range; deeper alluvium waters are a variation within the larger sediment/water geochemical system

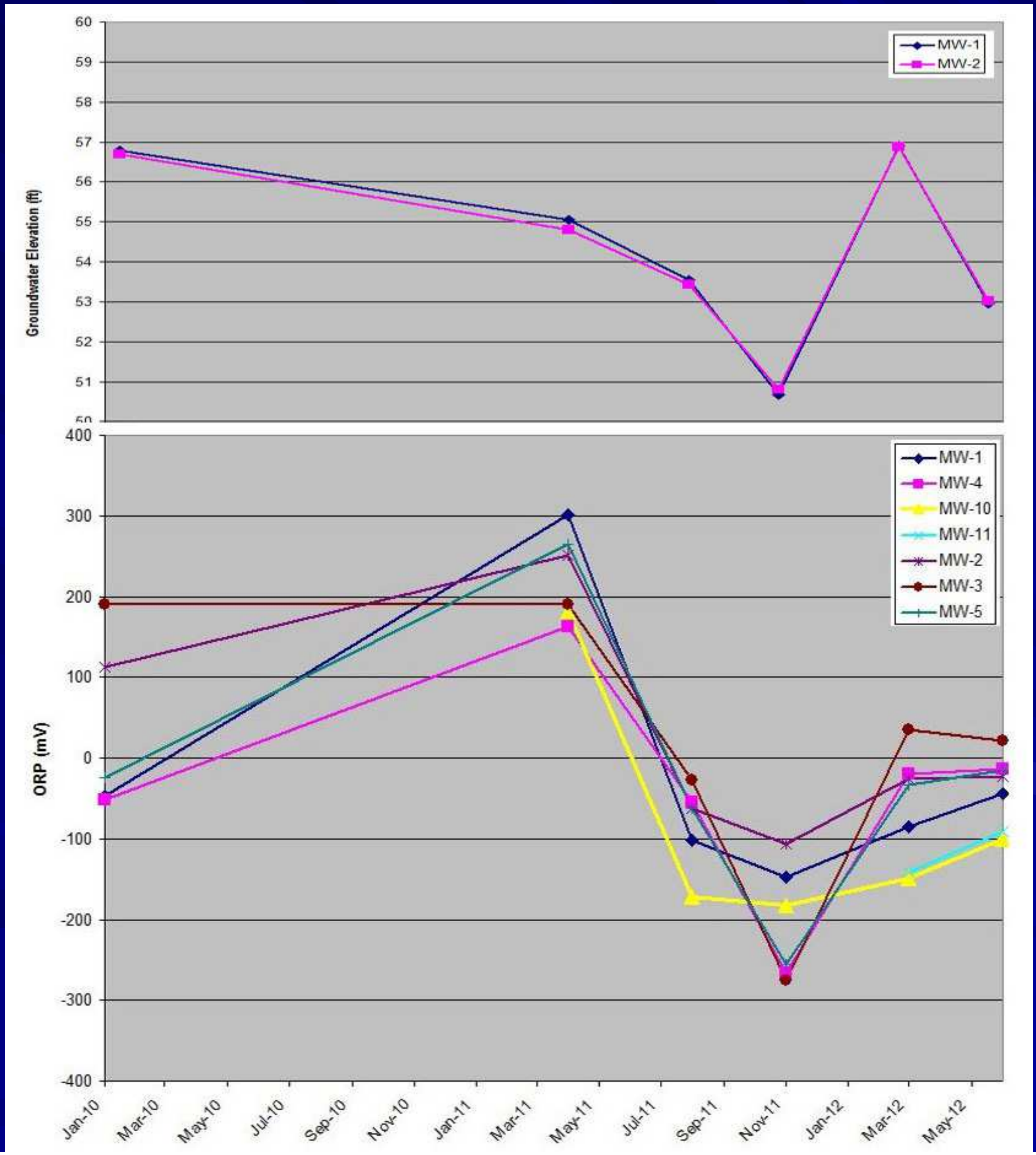
Regional Shallow Groundwater Movement, near the Mississippi River

(back & forth, net movement towards river--Pisani)



(Pisani Report, 2008; OOC Poppadoc records, file # 006-007)

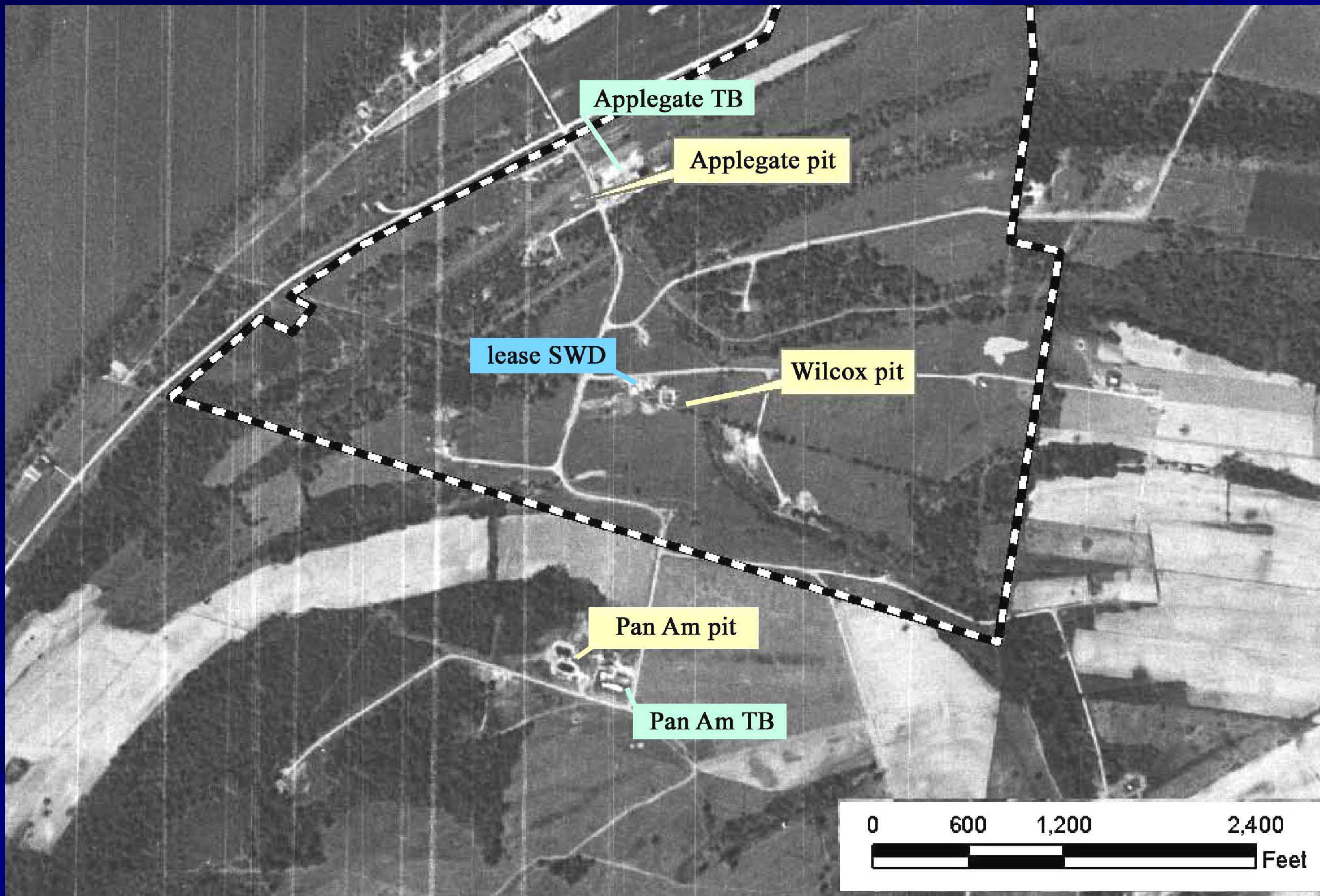
Pan Am Pit Area, ORP & GW Elevation



What is the LSJ Field Area's Dissolved Arsenic Natural Variability?

- Pisani & Associates (2012 report; OOC Tillman records) interpret the natural range from non-detect (ND) up to 0.12 mg/l
- A study in shallow allluvium across the River in Mississippi has an As range of ND to 0.10 mg/l (Welsh et al, 2010; also phosphorous)
- ICON monitor data from below Tensas Parish landfill (~25 mi away), up to 0.16 mg/l (LDEQ EDMS AI # 43506)
- Given this & LA data to date, note shallow groundwater measurements above 0.16 mg/l in study area to consider possible anthropogenic impacts

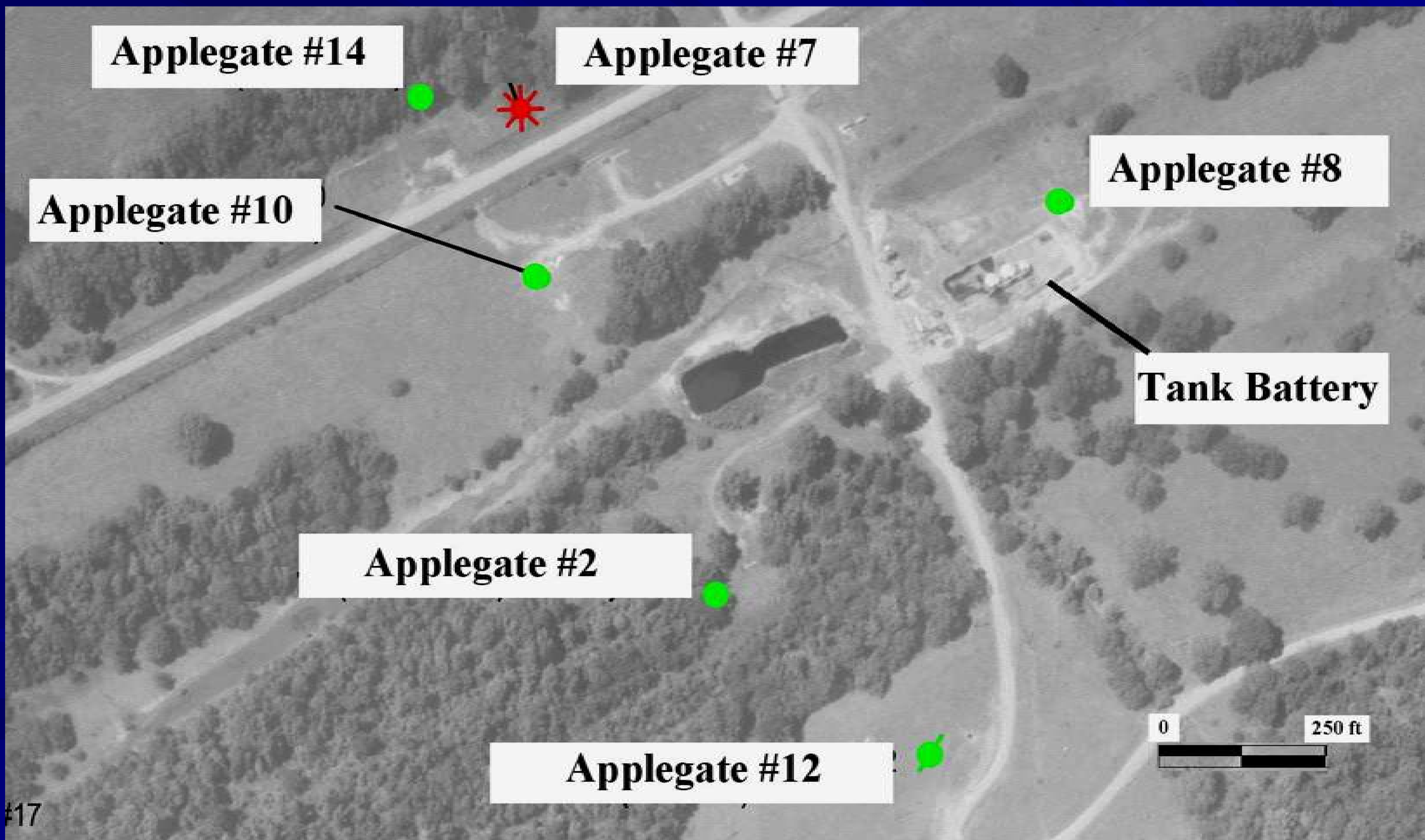
Three “Emergency” Pits (1952 aerial)



Pit Descriptions, Study Area, OOC 1968

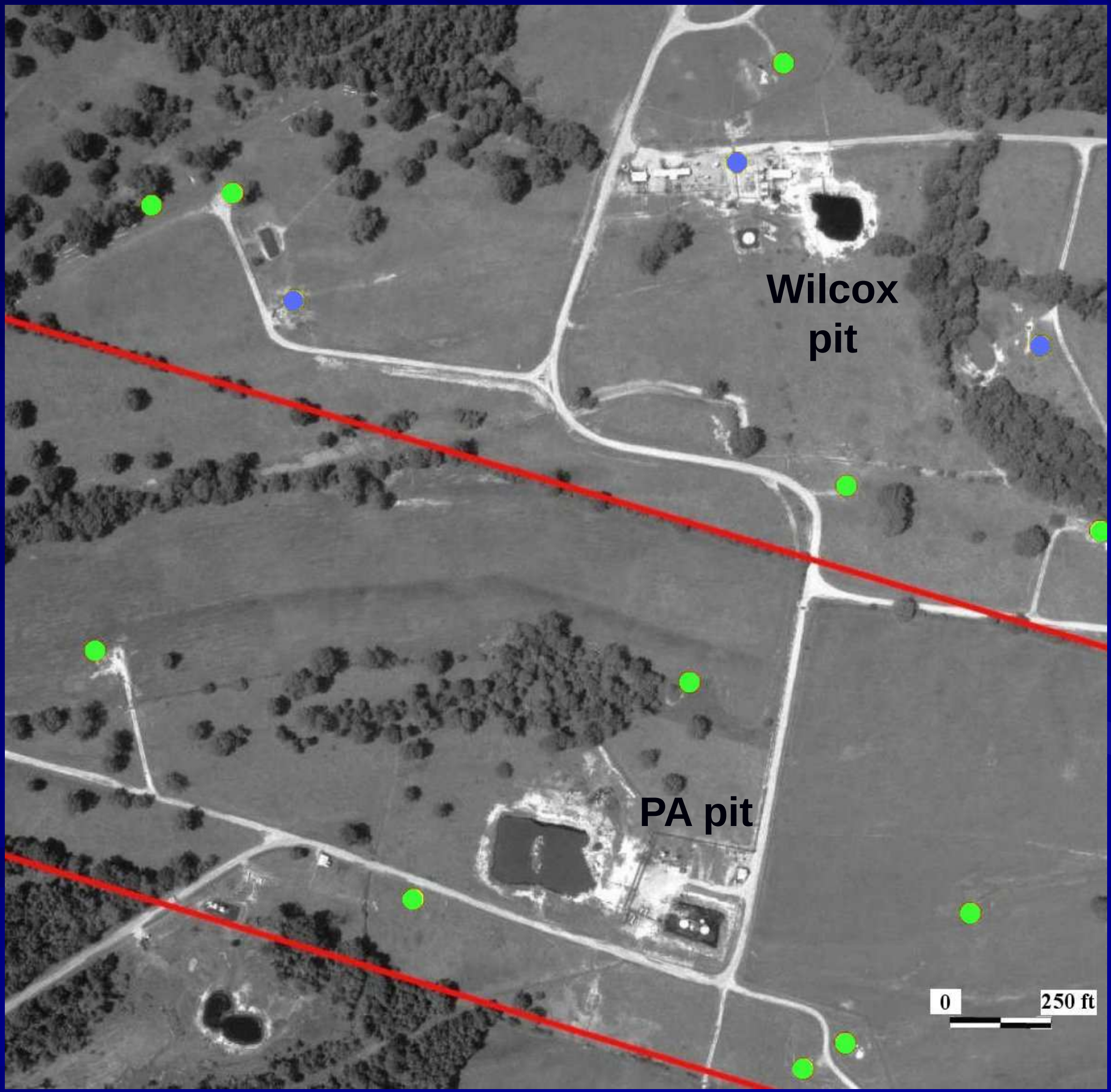
- Applegate Pit (closed ~ 1984)
  - 70’ x 150’ x 8’ (include 2’ levee)
  - Usage “only in emergency”
- Wilcox Pit (closed 1990)
  - 100’ x 100’ x 8’ (include 2’ levee)
  - Usage “well backwashing” (and emergency)
- Pan American Pit (closed ~ 1984)
  - 150’ x 200’ x 8’ (include 2’ levee)
  - Usage “only in emergency”

Applegate Pit Area, 1974



Wilcox & Pan Am Pit Areas, 1974

(oil wells in green, SWD wells in blue)



Arsenic in Pit Soils, Sediment, & Waters

- 55 years after alleged As usage, the pit solids of today have arsenic ranges within Parish soil ranges
  - Pits modified, rebuilt 2-3 times during usage
  - Pan Am & Applegate pit closure ~1984; both re-closed (Applegate 2007; Pan Am 2010); Wilcox pit closed in 1990
  - As analysed in “soils” range from 1 to 10 mg/kg

- A 1984 G & E study found elevated arsenic in Applegate (0.04 mg/l) and Pan Am (0.05 mg/l) pit surface waters. The 2 ft of bottom sludge ranged from 3 to 4.5 mg/kg As

  (OOC Poppadoc hearing, ICON/Miller & Norman exhibits)

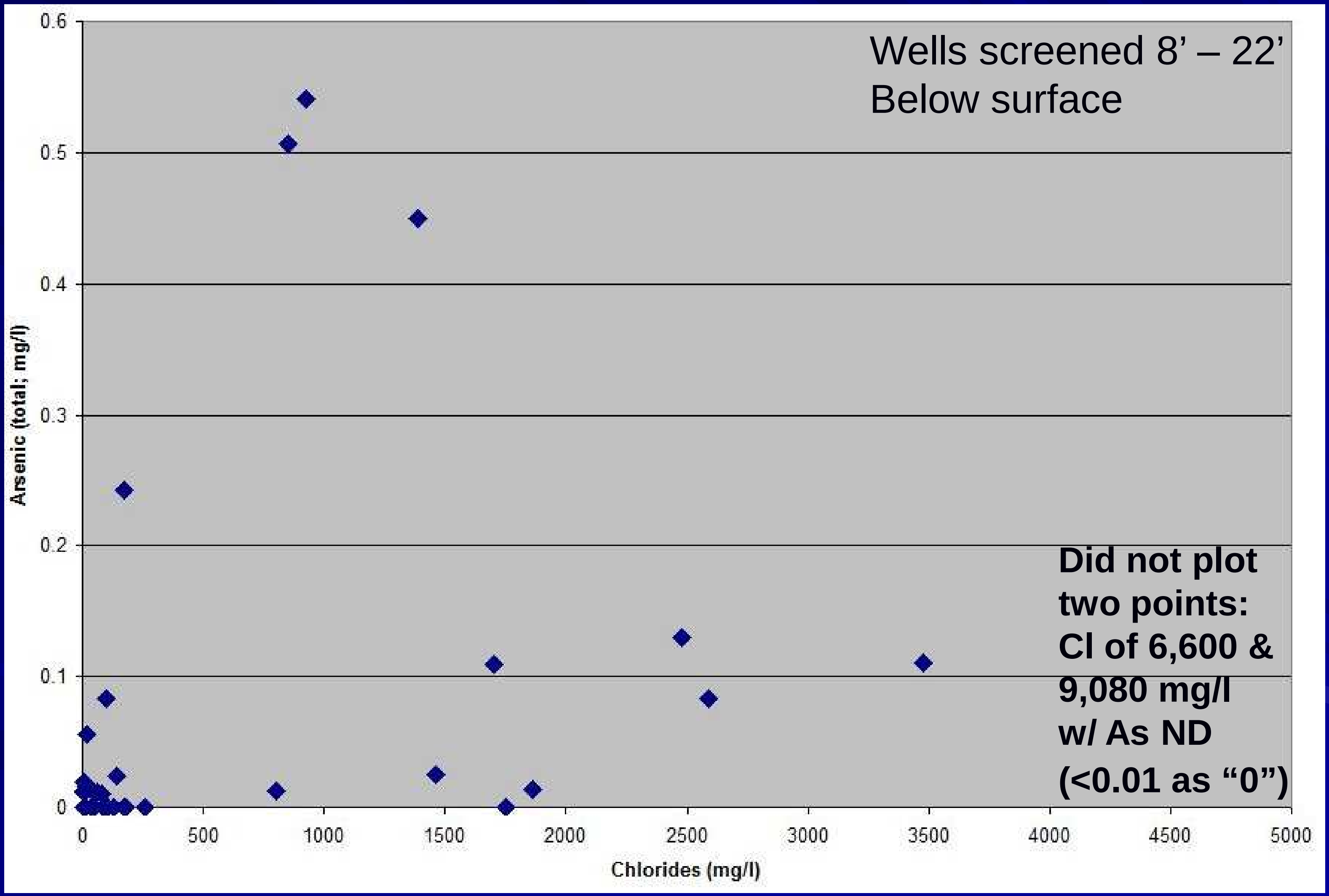
- GENERAL STATEMENT: Pit surface characteristics may not be in “equilibrium” with older shallow surface leakage characteristics

Applegate Lease

- Pisani 2008 report
- (OOC file #006-007) contours 250 mg/l chloride (yellow line)
- I labeled dissolved arsenic over 0.160 mg/l
- Occurs In Wilcox SWD & pit area

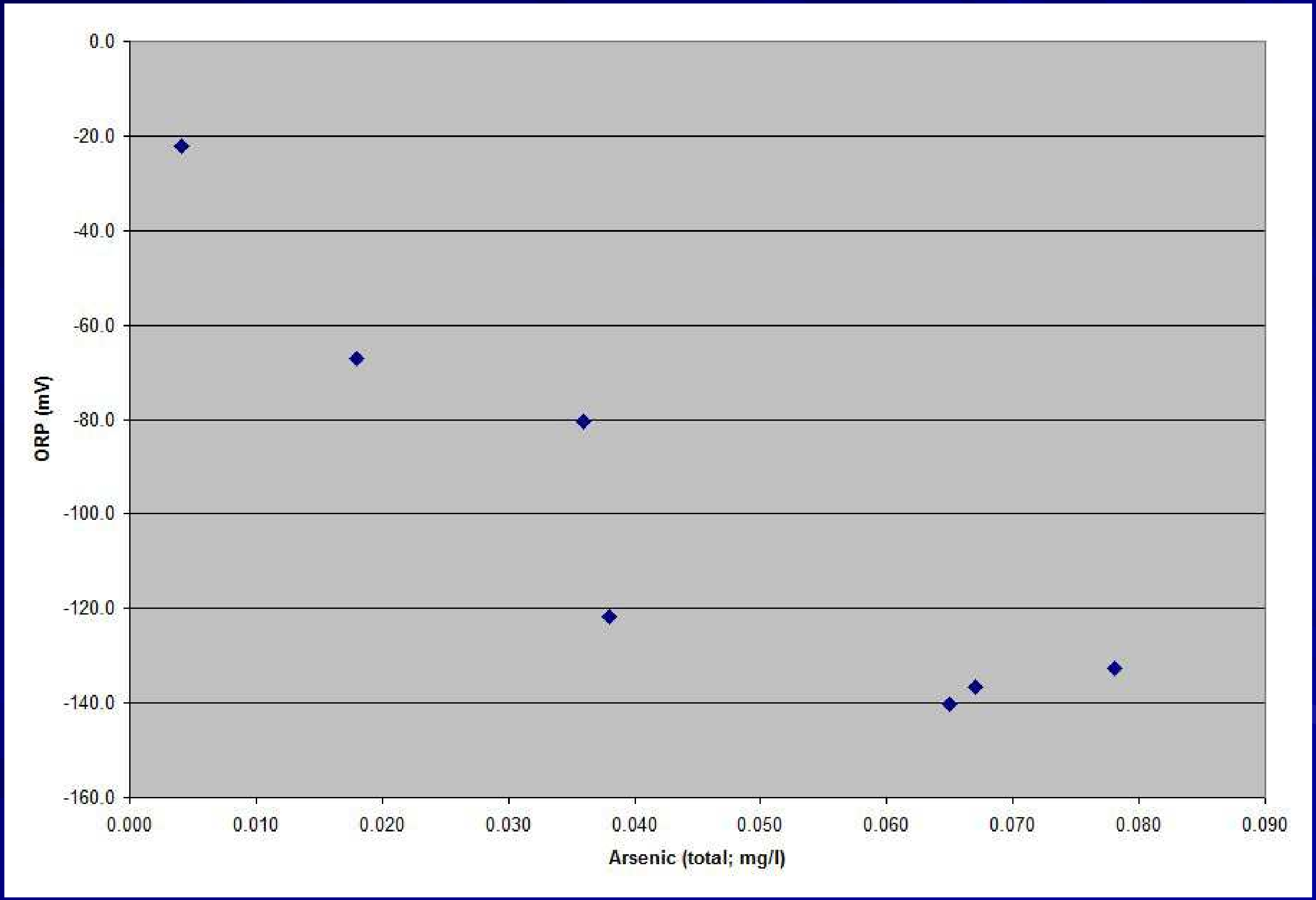
Applegate Lease Area, Shallow GW

(Fe not measured; ORP not flow-thru cell)



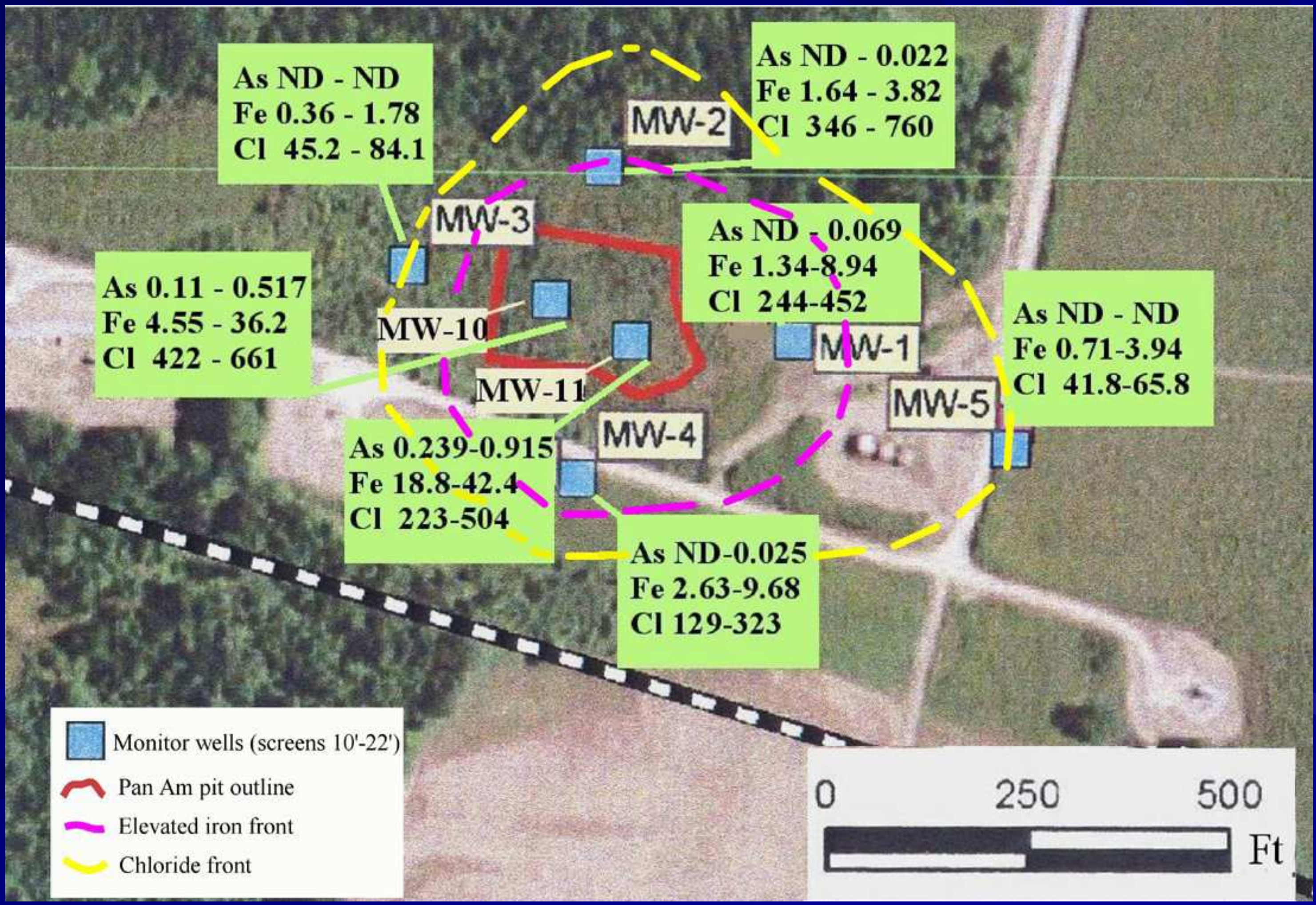
(OOC Poppadoc file #006-007, ICON 2006-07 data)

Applegate Pit



(Geosyntec data, 2008 rpt; OOC Poppadoc file #006-007)

Pan Am Pit Shallow GW 2010-12: Contour Shapes, Chloride & Iron (if relation to pit)

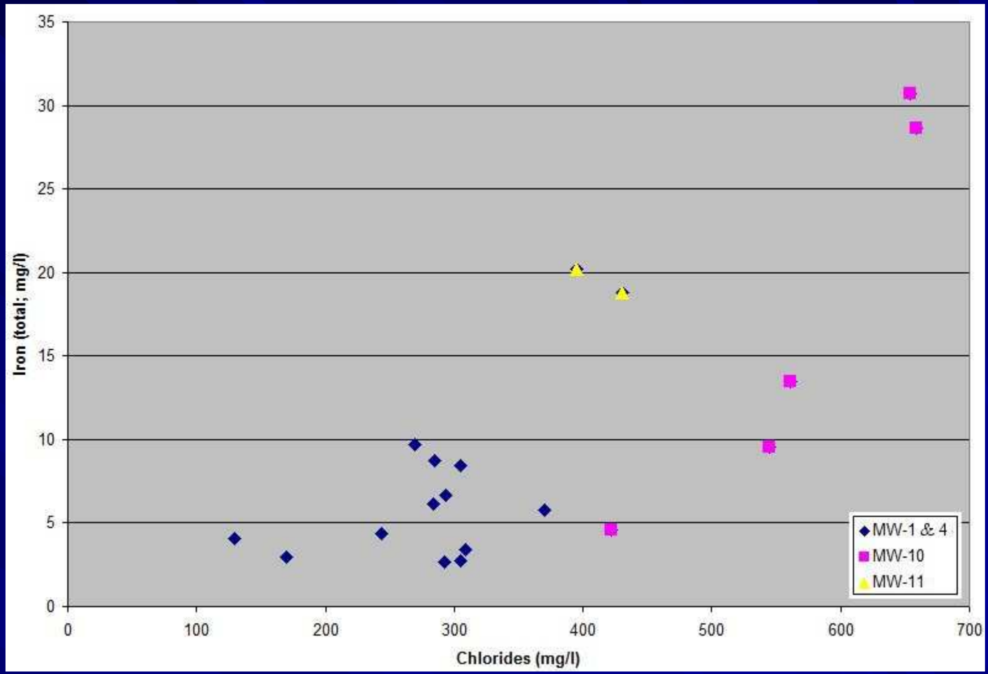


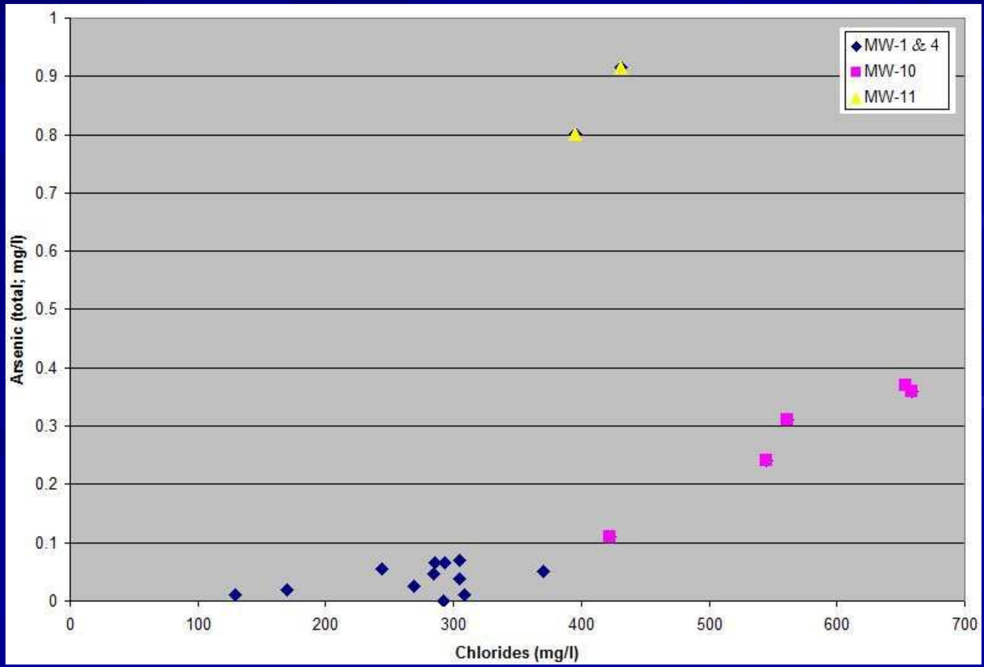
(OOC Tillman file #007-007; Pisani monitor rpt data)

Pan Am Pit GW Chlorides

– Higher iron w/ chlorides under pit; probable oilfield water source impact

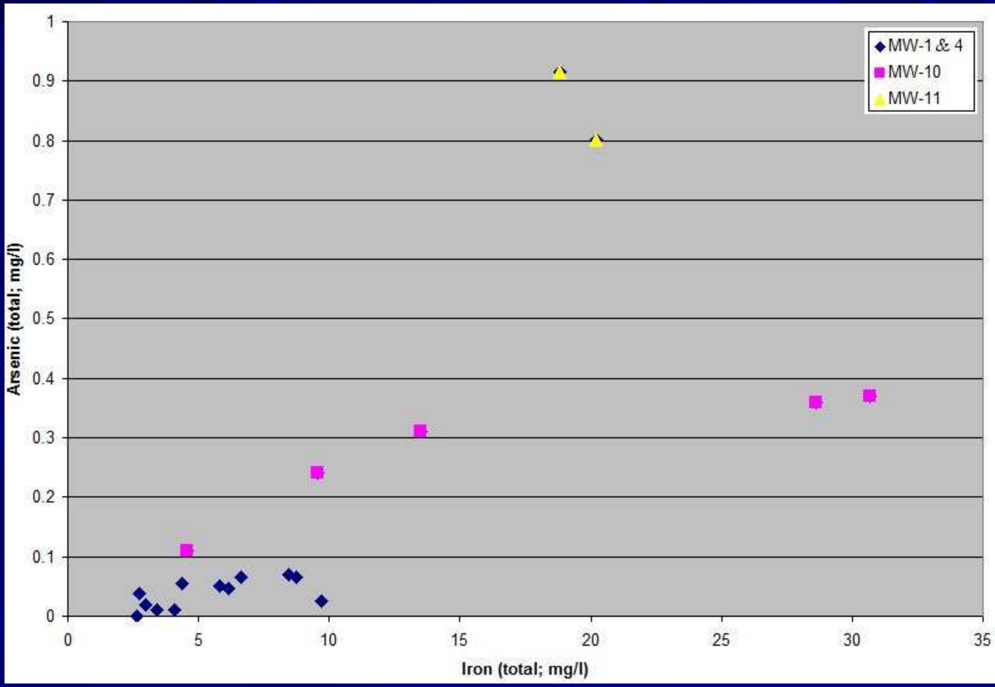
– Higher arsenic (over 0.160 mg/l) w/ chlorides under pit, probable oilfield water source impact



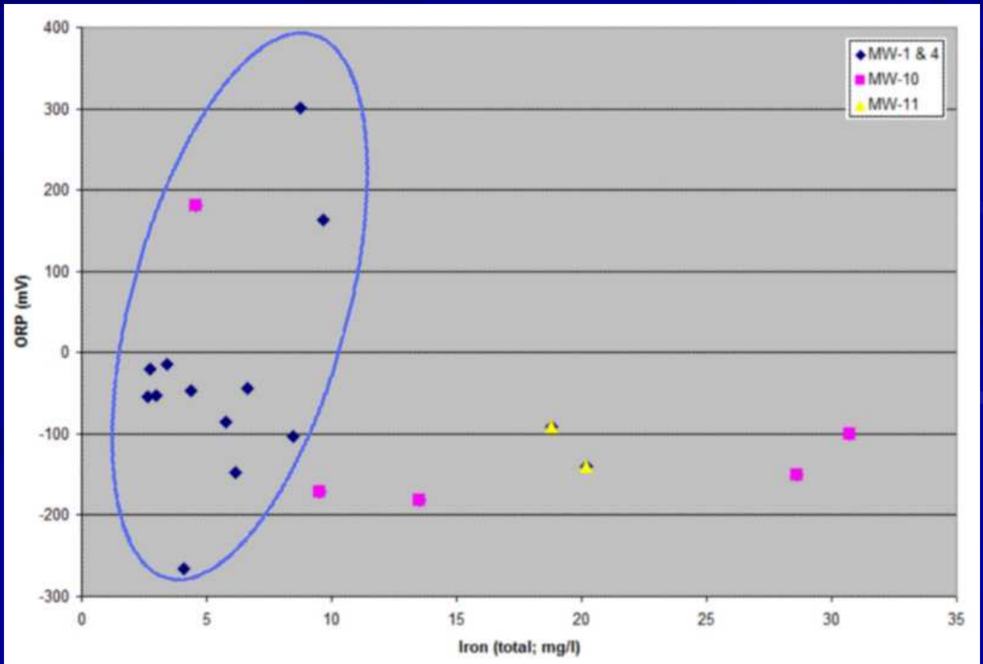


Pan Am Pit GW Iron

– As v. Fe relationship varies in relation to pit proximity



– ORP v. Fe
  - Patterns different from under the pit to outside the pit



A Possible Model

- Observed ion mobility in GW from pit: Cl > Fe > As
- HFOs added to emergency pits from produced water over decades; As limited, but strongly absorbed by HFOs when present
- In pit bottom, oily sludge and sometimes stagnant saltwater above this, reducing; GW below reducing
- Movement of reducing water with Cl, Fe ($\pm$ As) where pit seepage, into sediment with Fe grain coatings
- GW away from pit more oxidizing, see Fe front
- Added As stays within or close to pit boundaries; the movement of <u>added</u> iron further away from pit may be affecting natural arsenic patterns previously only related to iron oxide grain coatings

Conclusions

- The geochemistry of pit impacts and signatures is greatly enhanced by historic knowledge
- Arsenic GW models for oilfield pits are useful, but oilfield chemistry & past pit functions will strongly modify generic models
- IRON and possibly phosphorous are important to further research (i.e., data, monitoring over time) for pit GW models
- Past supplied produced waters' dissolved iron to an oilfield pit may be impacting localized natural dissolved arsenic variability
- Chlorides important marker for recognizing oilfield impact boundaries