Historic Oilfield Arsenic Sources: Implications for a Pit Groundwater Model, Lake St. John Field, LA, An Update

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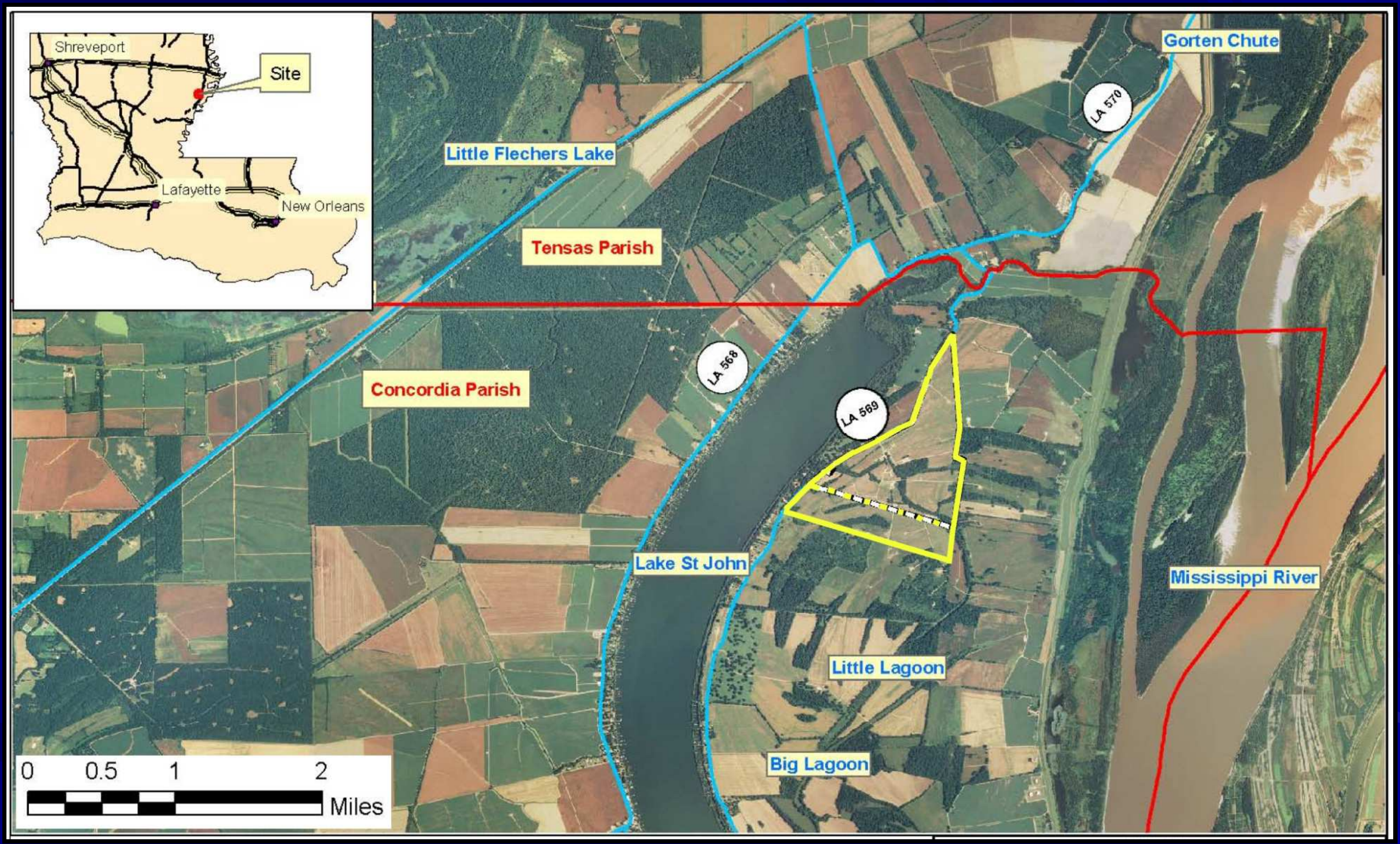
Presentation Objectives
Lake St. John Field, Concordia Parish, LA

- Update my IPEC 2014 talk to consider multiple hypotheses for origin of elevated shallow groundwater (GW) arsenic (As), iron (Fe) and chlorides (Cl) below old oilfield pits
- Historically arsenic (as corrosion inhibitor & possible herbicide) was used in the field; this arsenic origin in considered in evaluating origins(s) of shallow groundwater elevated arsenic in tank battery and emergency pit areas
- Consider if data (as of 4/15) reasonably support a 2008 reductive-dissolution GW pit model to partially or completely explain elevated arsenic patterns
- Point out several interesting questions arising from unique data set, including: if/how sediment-water equilibrium reflected; regional controls over ORP; importance of added iron/HFOs to arsenic (As) patterns; arsenic (As) geochemical associations above or at background levels and variations; significance of pit-area groundwater data taken within first year of pit closures

Public Record Usage for Interpretations

- The example from LSJ Field, LA, has a 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 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 analytical data: ICON; Pisani & Assoc., some Geosyntec)
- Work on the last case ended Feb. 2014; I have pursued this research since then, not retained concerning it, no discussions with past litigation experts (my opinions)

Study Area

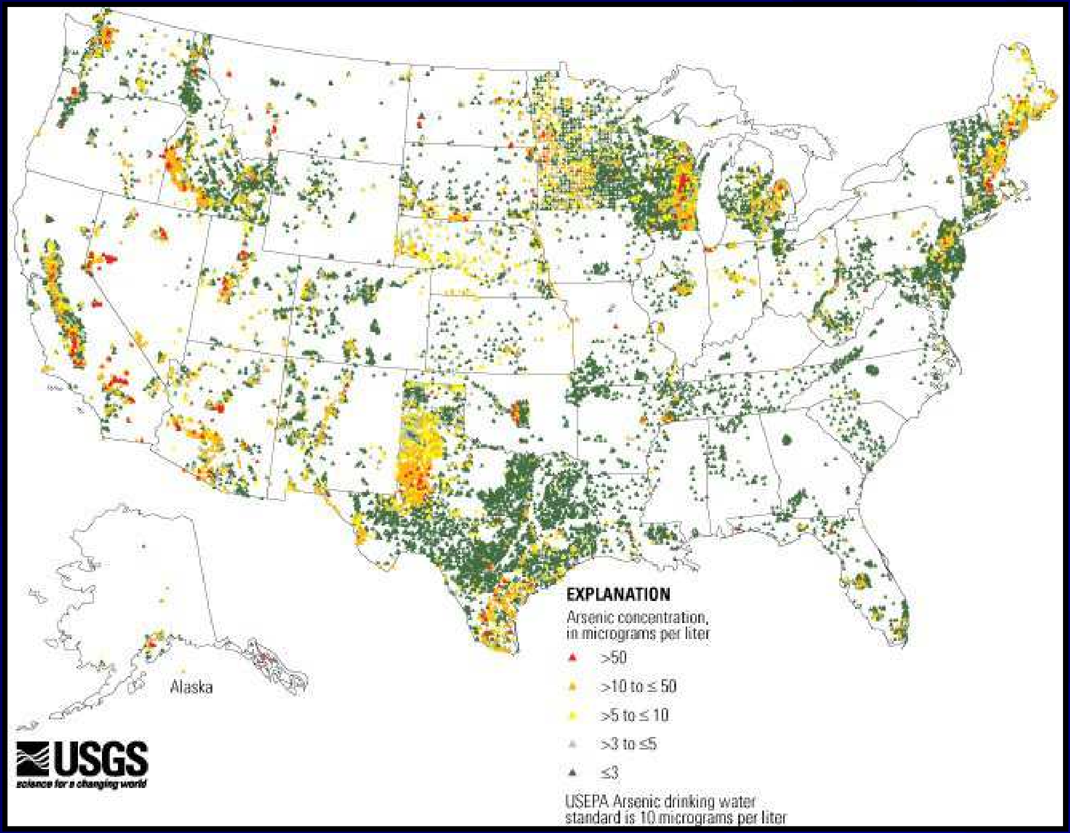


(Modified from Pisani & Associates report, 2008; LA OOC file # 006-007)

Lake St. John Field Example

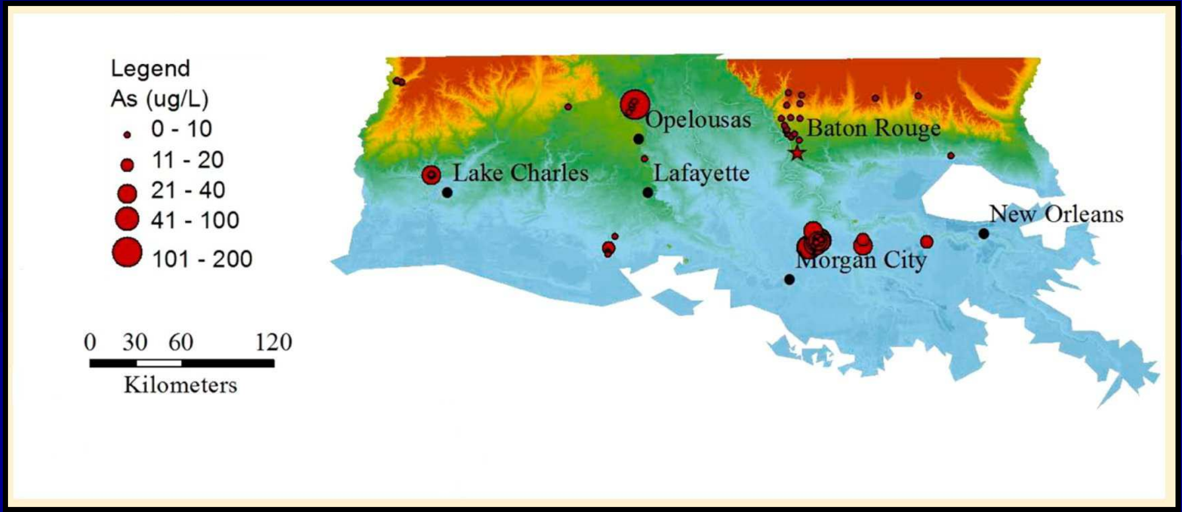
- Discovered in 1942, Tensas & Concordia Parishes, LA
- Major producing field for The California Company (Standard Oil of CA, later Chevron)
- Both unit (Cretaceous & some Tertiary age) & **lease production** (Wilcox Fm mainly)
- Outline of field study interpretations
  - Public records indicate 1950s arsenic corrosion inhibitor usage
  - Shallow groundwater geochemistry around old emergency pit areas documents its impact

Groundwater Arsenic



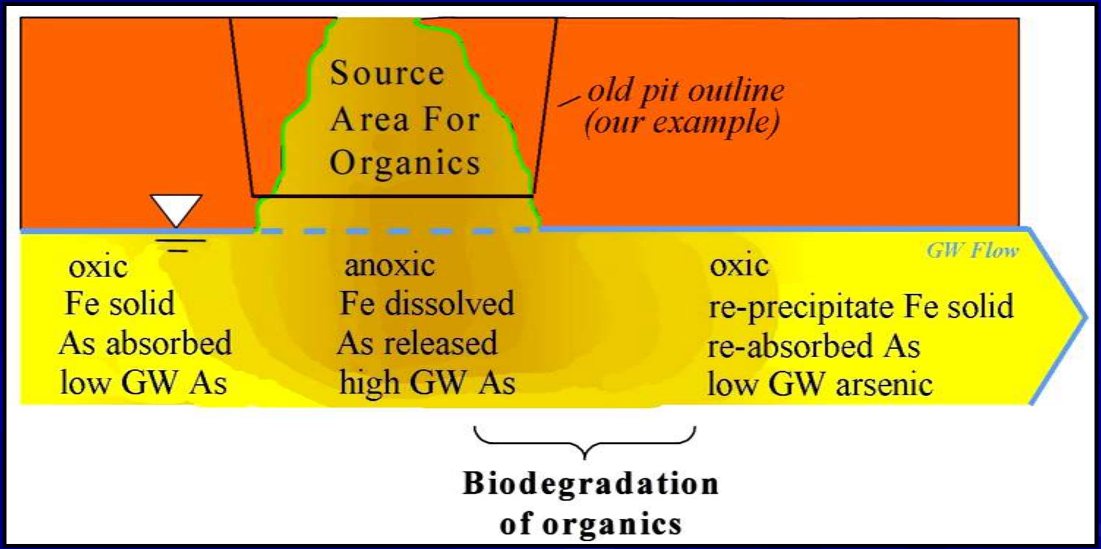
LA groundwater published arsenic record limited, but Miss. R. alluvium waters can be elevated (USGS 2000)

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



Basic Model: Reductive Dissolution of Iron Oxides

- Fe oxides common in our LA sediment, possible As absorbed
- As released into GW with "reductive dissolution" when some cause for a reducing environment (organics, oil, clay…)
- Fe oxides re-precipitate as GW move into oxidizing zone, re-absorb As
- Model looks for relations between ORP, Fe, As
- Does not address anthopogenic As, Fe
- Does not address As desorption (phosphates)

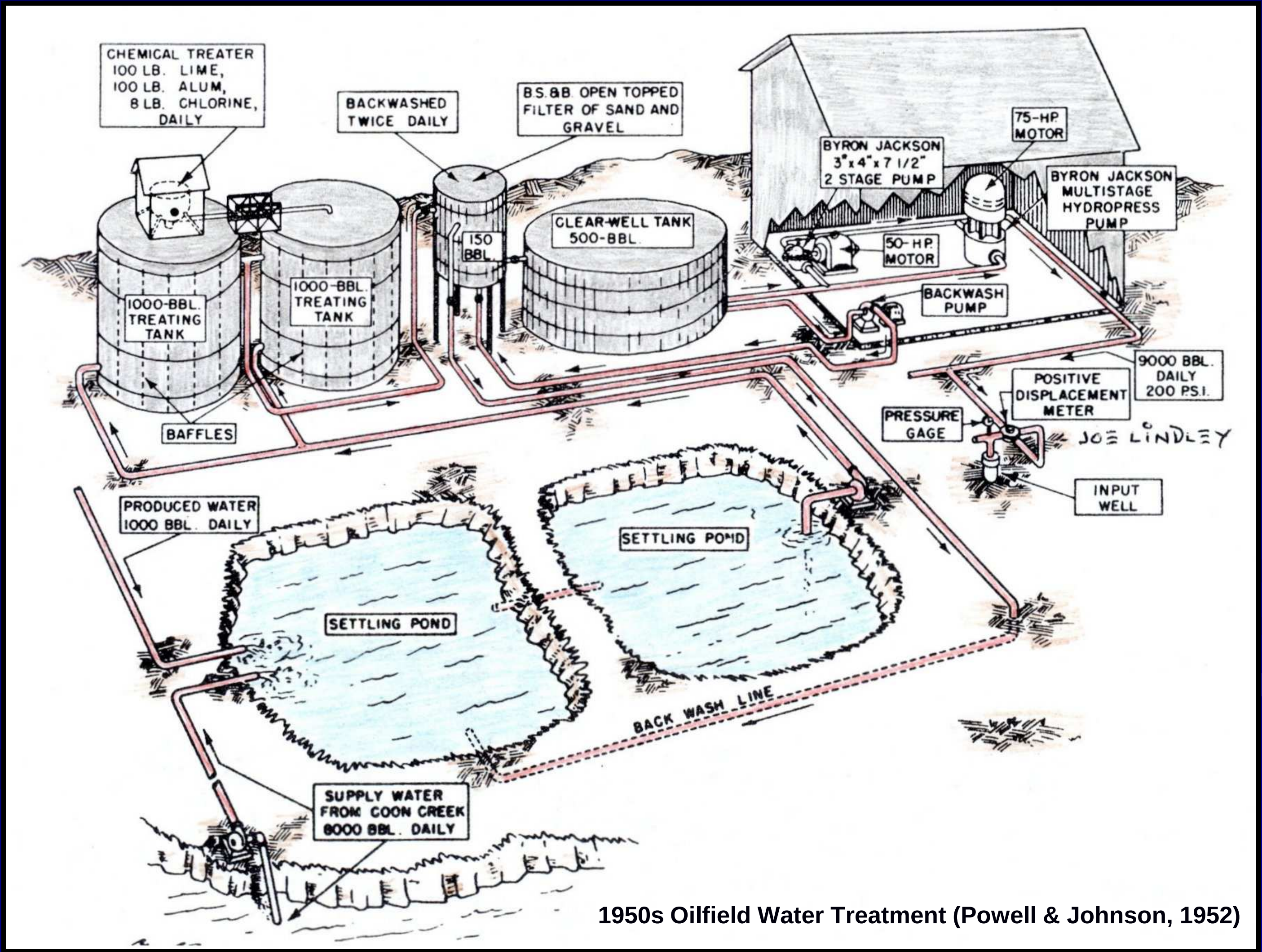


(Diagram modified from petroleum refinery & oil spill example, Ghosh et al., 2003)

Groundwater Arsenic Geochemical Models & Oil Field Sites

- Arsenic models are useful, but
  - model study areas extrapolated to Gulf Coast oilfield regions of different geology & hydrogeology, and
  - a model may not consider impacts from “oilfield chemistry” and anthropogenic activities
- Waste “oilfield chemistry” has a history, & pits often record this history
- Models need to consider anthropogenic possibilities in these old oil fields and other industrial sites

Amorphous Iron Precipitates: Long History of Study in Oilfield Chemistry (Hydrous ferric oxides—HFOs)



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

Iron Analyses, LSJ Field Produced Water

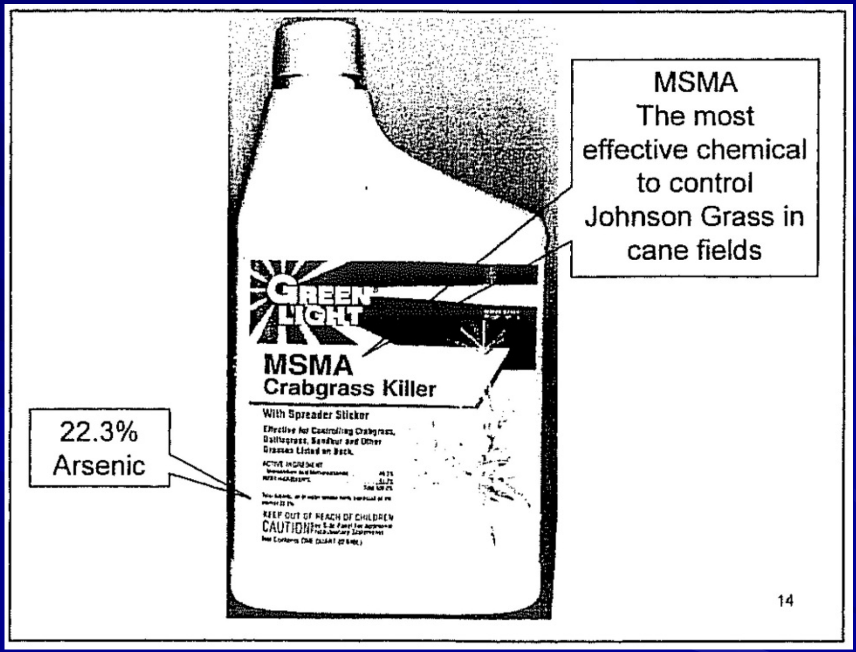
- 1945 analysis, 14 ppm (Cl 13,820 ppm)
- 1959 analysis, 90 ppm (Cl 80,908 ppm)
- 1970 analysis, 215 ppm (Cl 101,135 ppm)
- 1995 analysis, 21 mg/l (Cl 59,449 ppm)

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

GENERAL OBSERVATION: Many oil fields had decades (into 1970s, esp.) of elevated dissolved iron in produced water, and thus potentially into pits

Historic Arsenic Uses/Contaminants w/ Potential Environmental Signatures

- Pesticides
  - Concordia Parish cotton, 1910+
  - Vegetable gardens, trees
  - Cattle dipping vats
- Herbicides
  - Inorganic & organic
  - Land & aquatic weed killer
    - Oilfield usage documented
- Industrial
  - Corrosion inhibitor
  - Oilfield waste (produced water, barite mud sulfide impurities, oil,…)
  - Detergents, fertilizers (phosphorous)
  - Other



Griffin presentation on oilfield legacy litigation (2006)

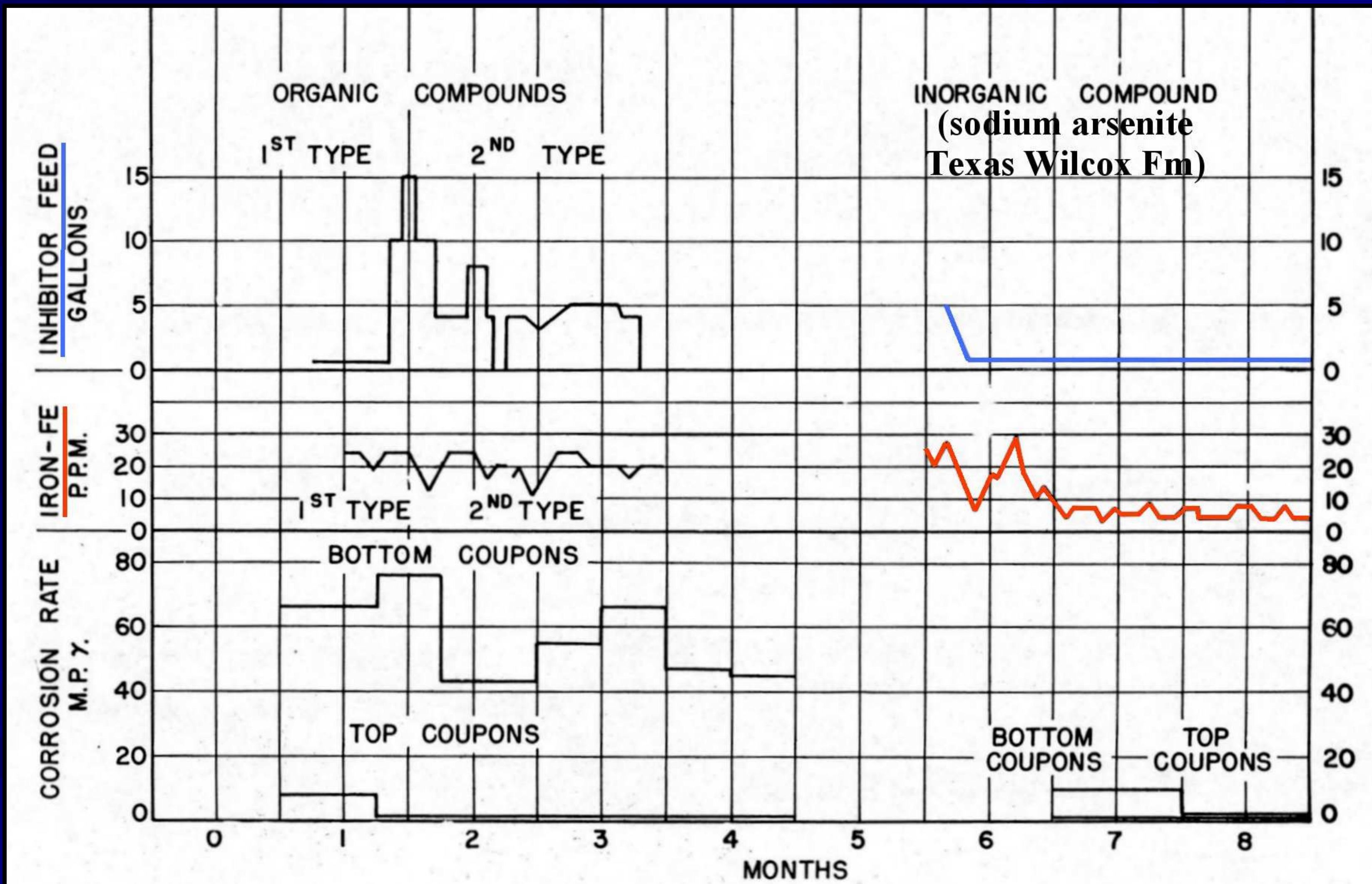
Anthropogenic Arsenic in Oilfields Continued (cow studies)

- Veterinary journals document the presence of anthropogenic arsenic used around oilfield facilities
- Recognized around pits, tanks and flowlines
- Past usages in oil fields
  - as “rust inhibitor and herbicide” (Coppock & others, 1996)
  - as “soil sterilant” (“N-sol-40” w/ 400,000 ppm arsenic; Morgan & others, 1984)
  - As “corrosion inhibitor” (Edwards & others, 1979)

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, 1963); move to organics

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



Jones (1955)

(Jones, 1955)

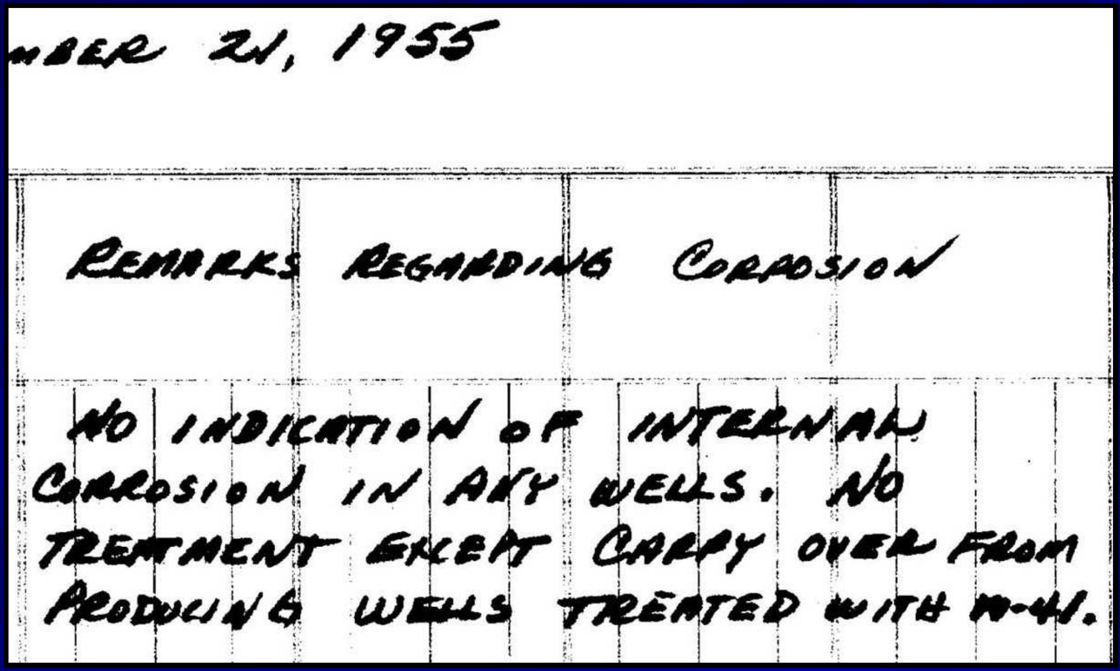
LSJ Field Public Documents, Arsenic Corrosion Inhibitors

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 19(?)74 – 1892	COCKFIELD	8111	500	9000	600	
3. SWD WELL #3 Wilcox	PERF	2764/2938 – 2934/2968	SPARTA	2792	325	5000	600	
4. SWD WELL #4 Ba#6 Unit Wilcox	PERF	2916 – 2946	SPARTA	1500	300	2800	600	
5. L.R. ALLWOOD #6 Ba# #1+2	PERF	1967 – 2000	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	000	
				22,738		38,850		
8. Marks #16	Perf.							

(LA OOC Tensas Poppadoc hearing, 2009; Miller/ICON reliance documents, 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 patented by Standard Oil of CA, is one example of arsenic corrosion inhibitors used in some 1950s oilfields of the U.S.

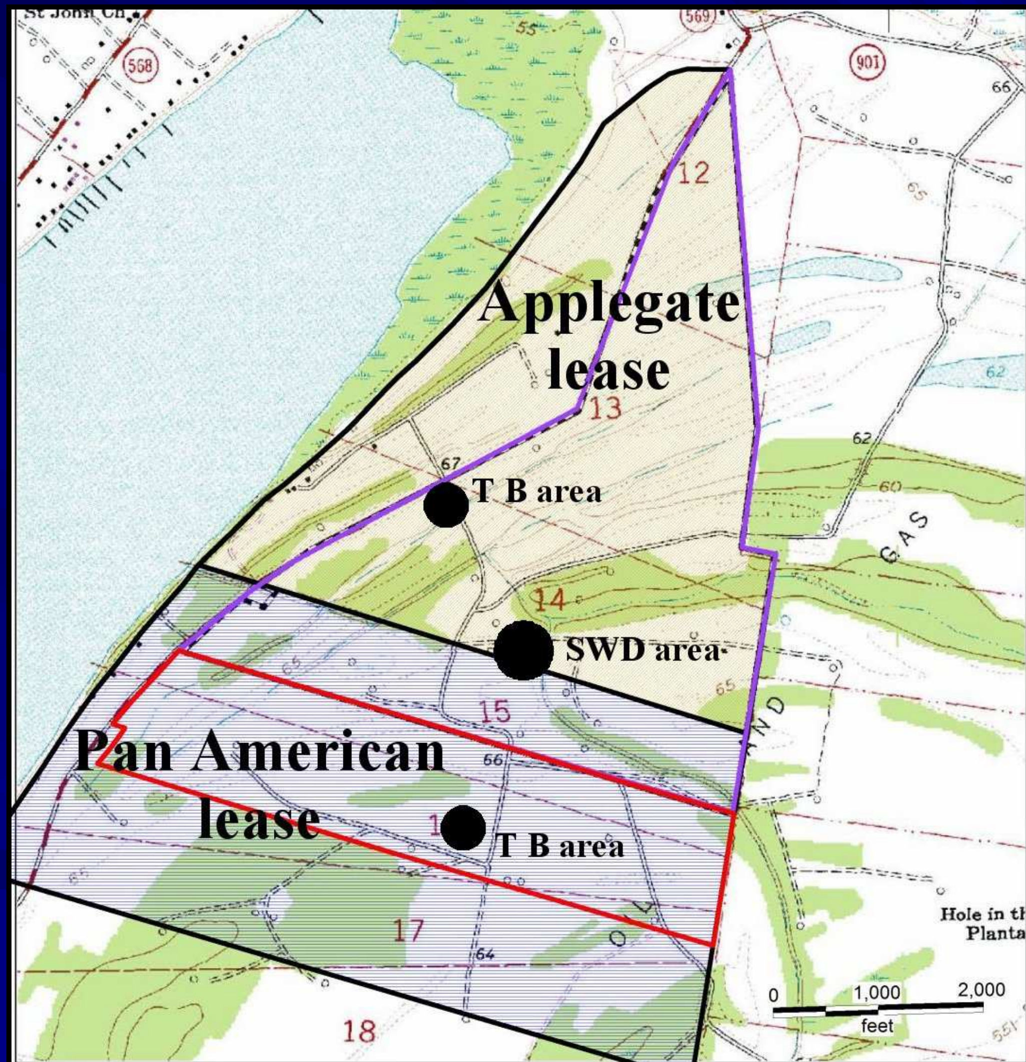
Its history is available in public documents.

W-41 History

- 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, trademark application granted for “Ortho W-41,” also used is “W-41,” for arsenic corrosion inhibitor (42 % sodium arsenite) (EPA, 1973)

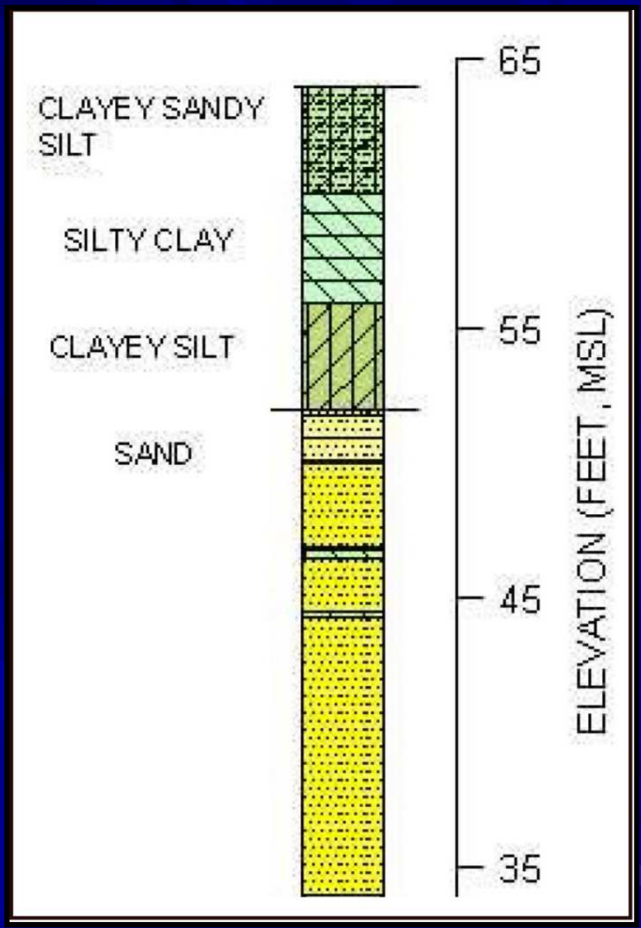
(My Opinion from the public record: W-41 was used in the LSJ Field in the 1950s; organic inhibitors were used after that)

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



Mississippi River Alluvium & Aquifer at LSJ Field

- Braided stream gravels at base; cuts into underlying Catahoula Fm sands
- Mostly point-bar sands
- Fining-up into levee, overbank, floodplai n deposits (clay/silt)
- This near-surface unit is aquifer's confining layer



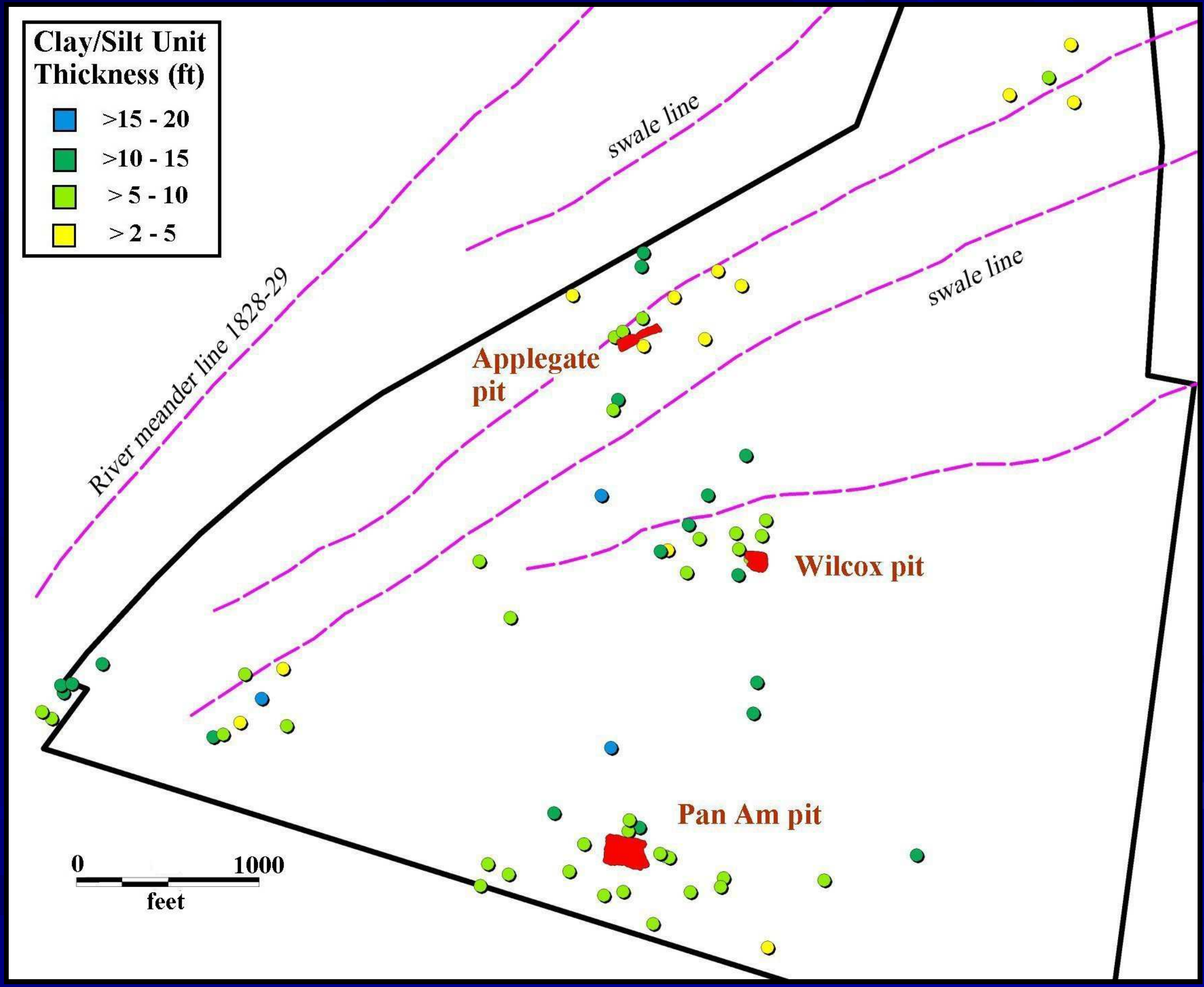
(Typical near-surface section from Pisani & Assoc., 2008; LA OOC file # 006-007)

1968 Pit Descriptions, Study Area

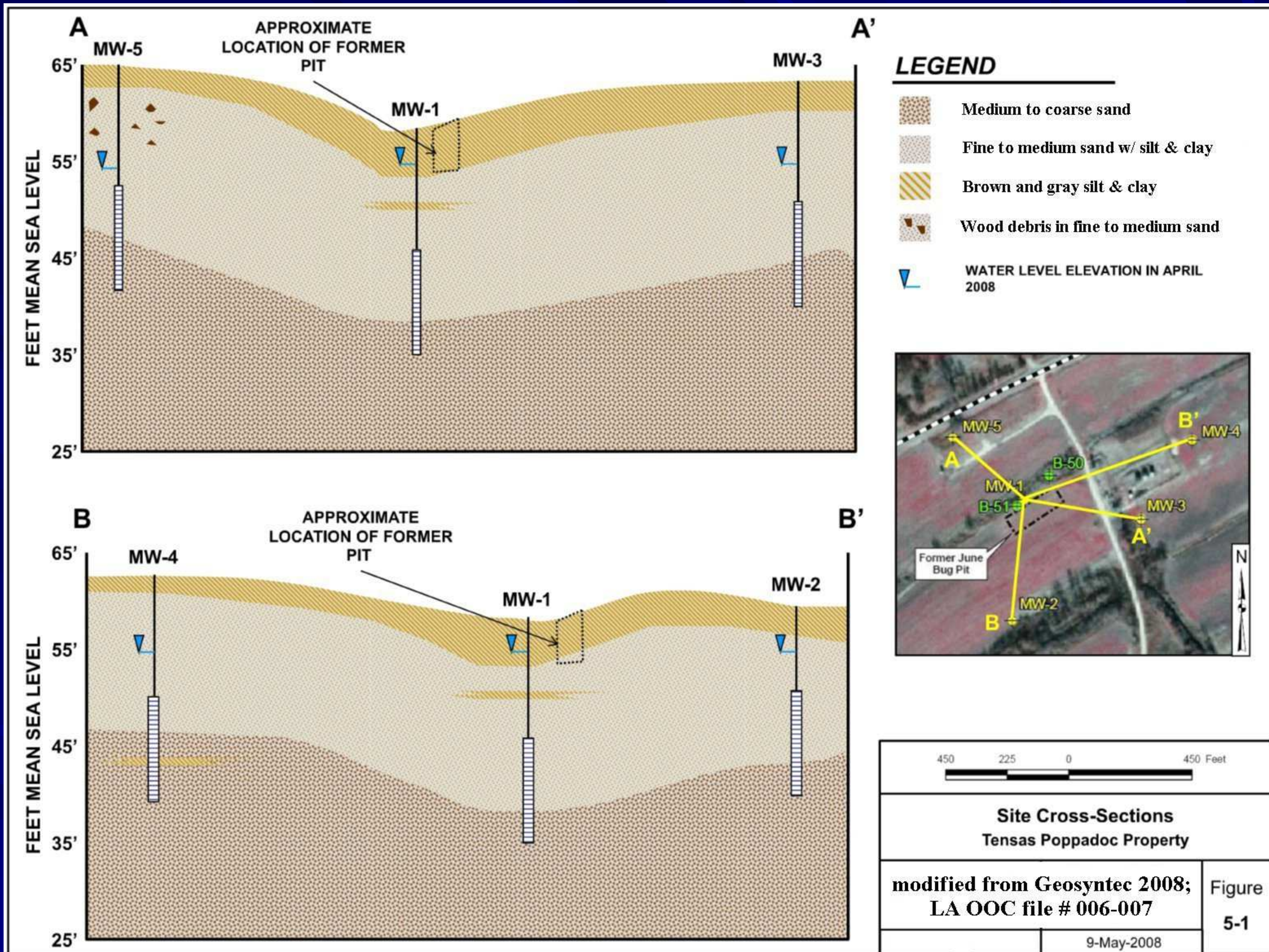
- Applegate Pit (closed ~ 1984; re-closed 2007)
  - 70’ x 150’ x 8’ (include 2’ levee)
  - Usage “only in emergency”
- Wilcox Pit (closed 1990)
  - 100’ x 100’ x 8’ (include 2’ levee)
  - Usage “well backwashing” (and emergency)
- Pan American Pit (closed ~ 1984; re-closed 2010)
  - 150’ x 200’ x 8’ (include 2’ levee)
  - Usage “only in emergency”

(LA OOC Tensas-Poppadoc hearing; exhibit Tensas/Miller 2455-56)

Fine-grained Unit Thickness



(data from all soil boring descriptions of ICON, Pisani & Assoc., and Geosyntec; meander & swale lines after Saucier, 1967)


A
A'
MW-5
APPROXIMATE LOCATION OF FORMER PIT
MW-1
MW-3
65'
55'
45'
35'
25'
FEET MEAN SEA LEVEL
B
B'
MW-4
MW-2
LEGEND
Medium to coarse sand
Fine to medium sand w/ silt & clay
Brown and gray silt & clay
Wood debris in fine to medium sand
WATER LEVEL ELEVATION IN APRIL 2008
B-50
B-51
Former June Bug Pit
N
450
225
0
450 Feet
Site Cross-Sections
Tensas Poppadoc Property
modified from Geosyntec 2008;
LA OOC file # 006-007
Figure
5-1
9-May-2008

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

- The analyses from Pisani & Associates, ICON (G. Miller), are numerous and of high-quality (Geosyntec data are limited but of high-quality)
- Shallow groundwater data are most reflective of potential old oilfield 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

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

- Pisani & Associates (2012 report; LA OOC file # 007-007) 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 data from Tensas Parish landfill, ND up to 0.16 mg/l (~ 25 mi away, 1994 to 2014 data, LDEQ EDMS # AI 43506)
- The LSJ field study area has localized shallow groundwater measurements above these values
- Limited arsenic species measurements at LSJ field; both arsenic species were present (As III and As V) in similar amounts

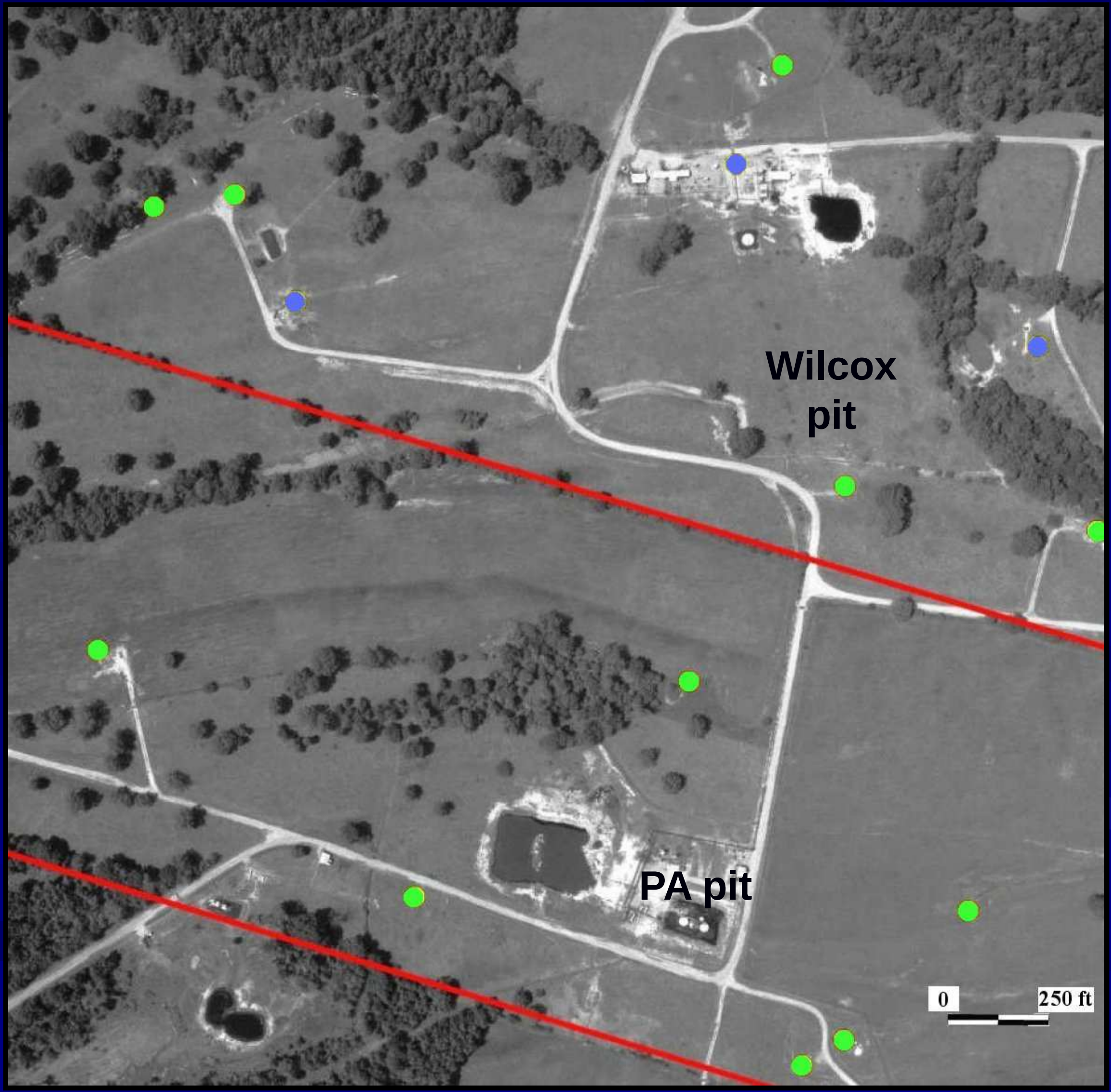
Arsenic in Pit Soils, Sediment, & Waters

- 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 analyzed in soils/sediment range from 1 to 10 mg/kg; one (Deuel,1987) Wilcox pit sample at 16.9 mg/kg

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

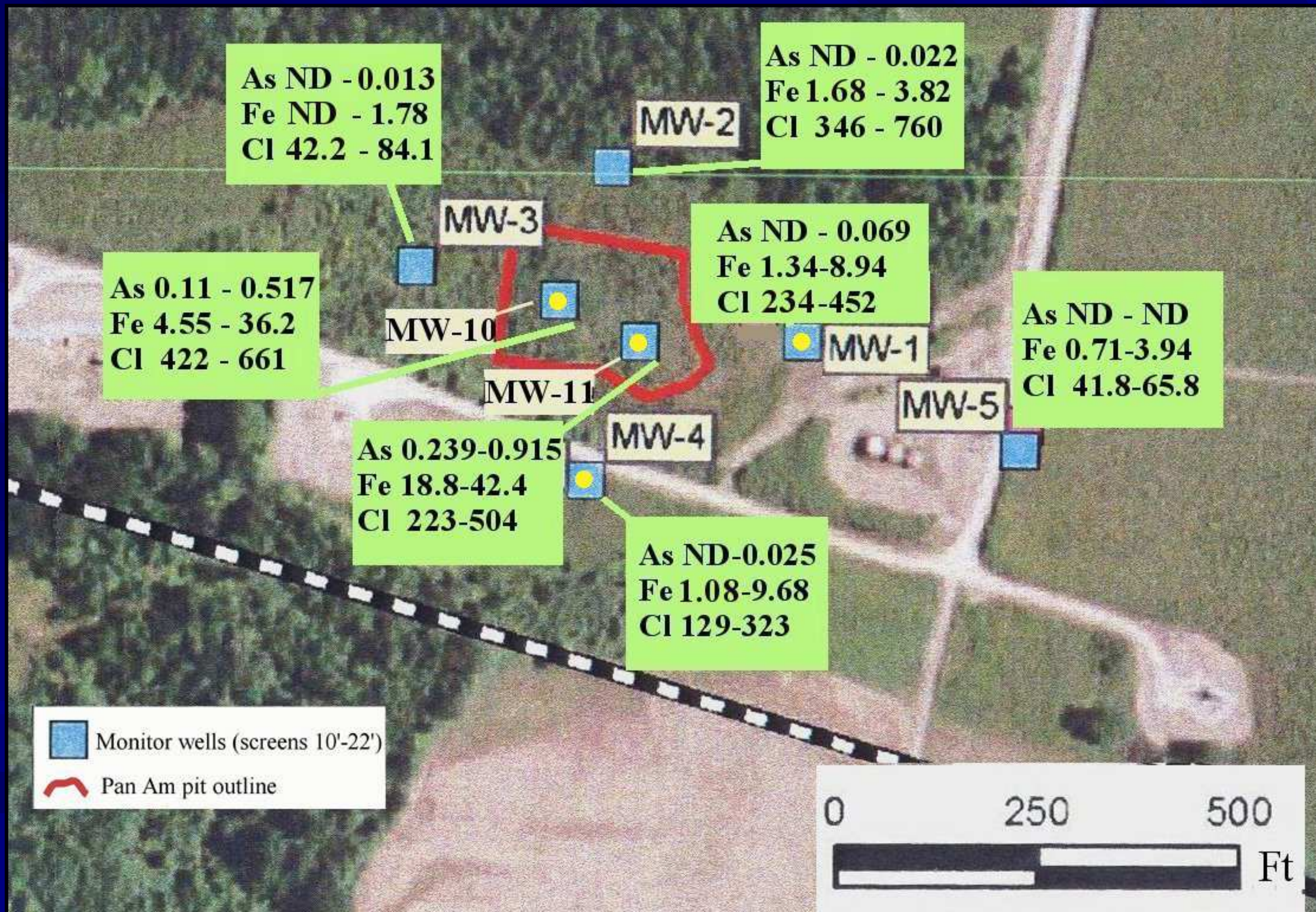
(LA OOC Tensas Poppadoc hearing, exhibits Tensas/Miller 00152-00510;
LA OOC file # 006-007, reports of ICON 2008, Pisani & Assoc., 2008 & 2012;
LA OOC file # 007-007, reports of Pisani & Assoc., 2010 & 2015)

Wilcox & Pan Am Pit Areas, 1974



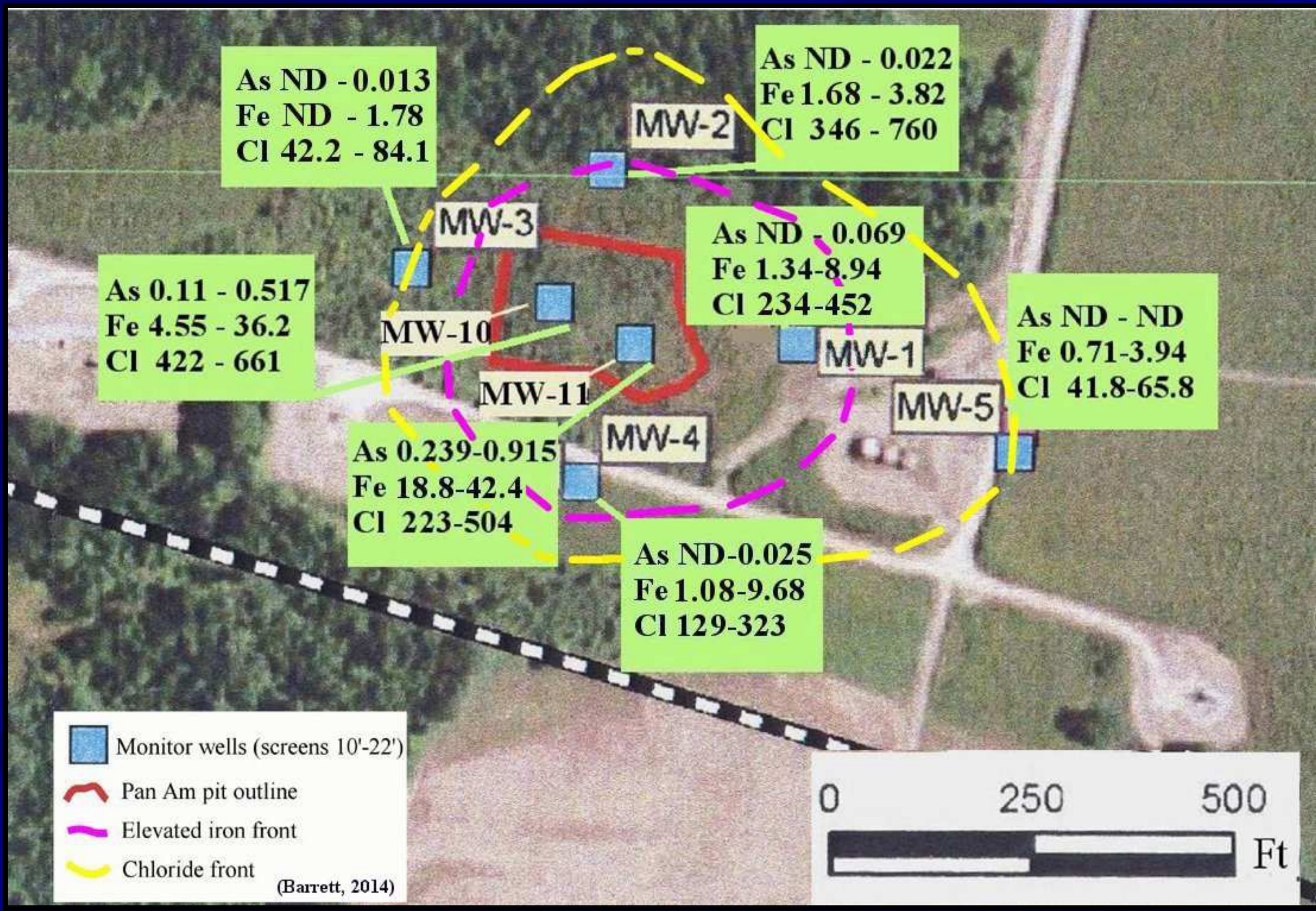
(oil wells in green, SWD wells in blue)

Pan Am Pit Area, GW Data Ranges (in mg/l) from 2010-2015

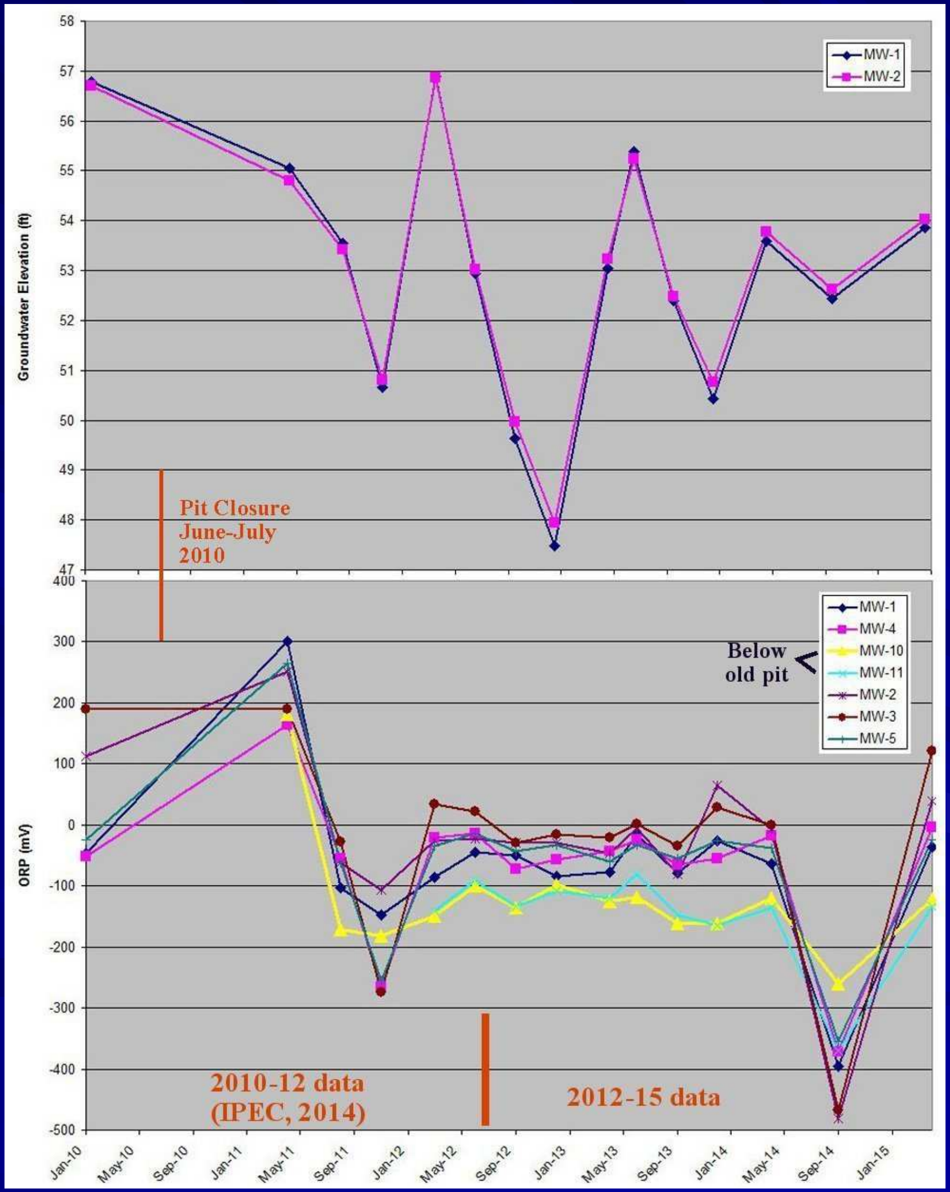


(data from LA OOC, Tillman file #007-007, Pisani & Assoc. reports 2012-2015)

Pan Am Pit Area, Iron & Chloride Boundaries if Related to Pit



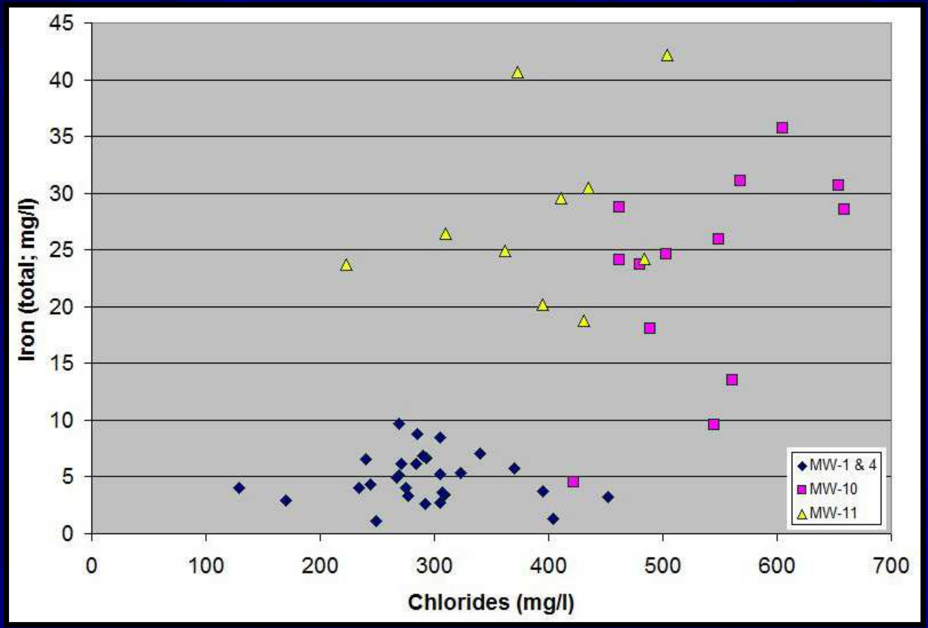
Pan Am Pit Area, ORP & GW Elevation

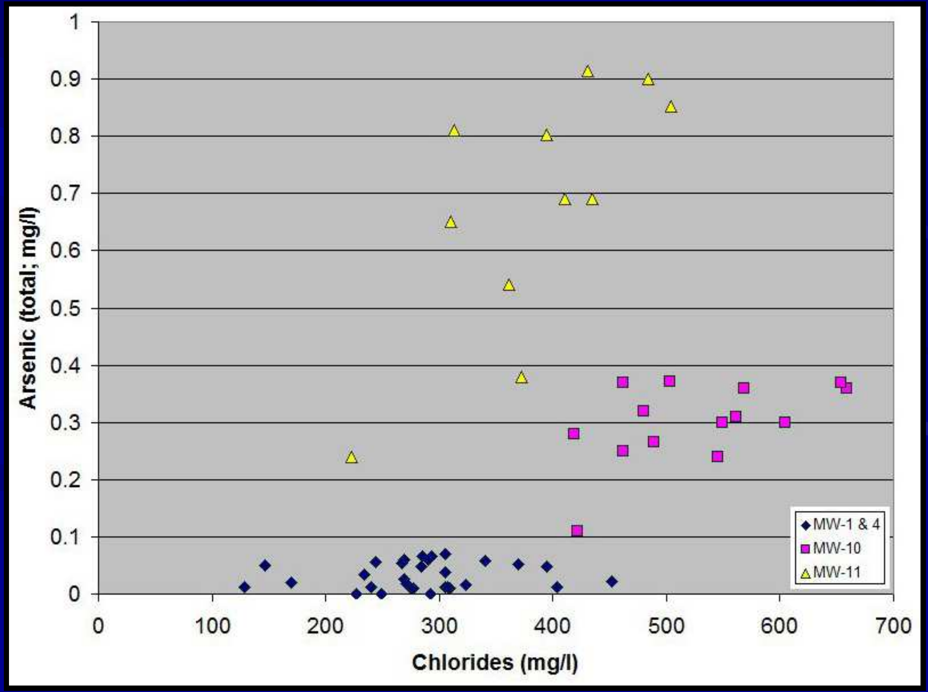


Pan Am Pit GW 2010-2014

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

– Higher arsenic w/ chlorides under pit, probable oilfield water source impact

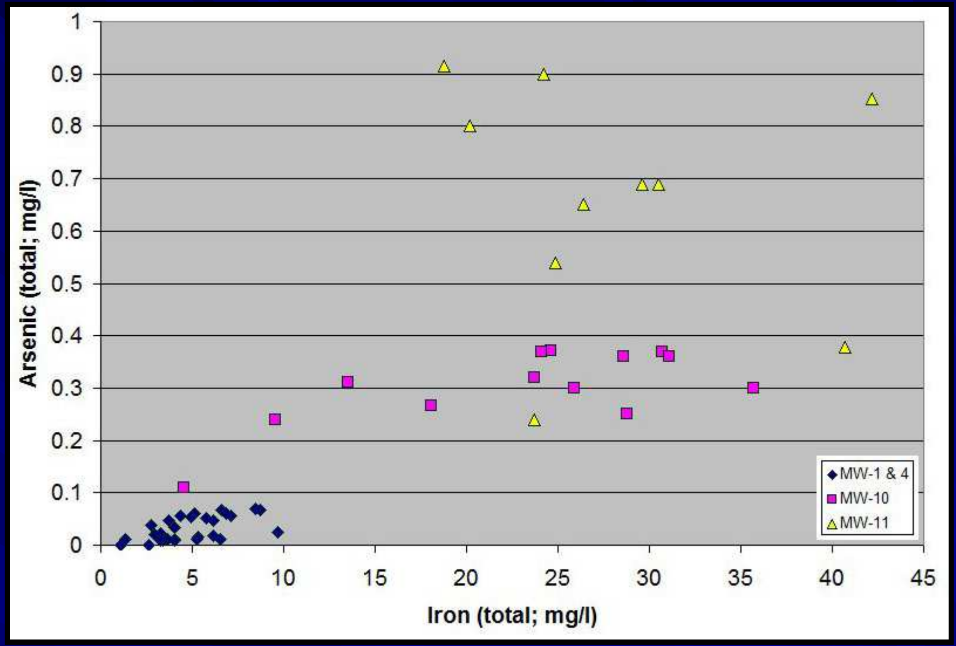


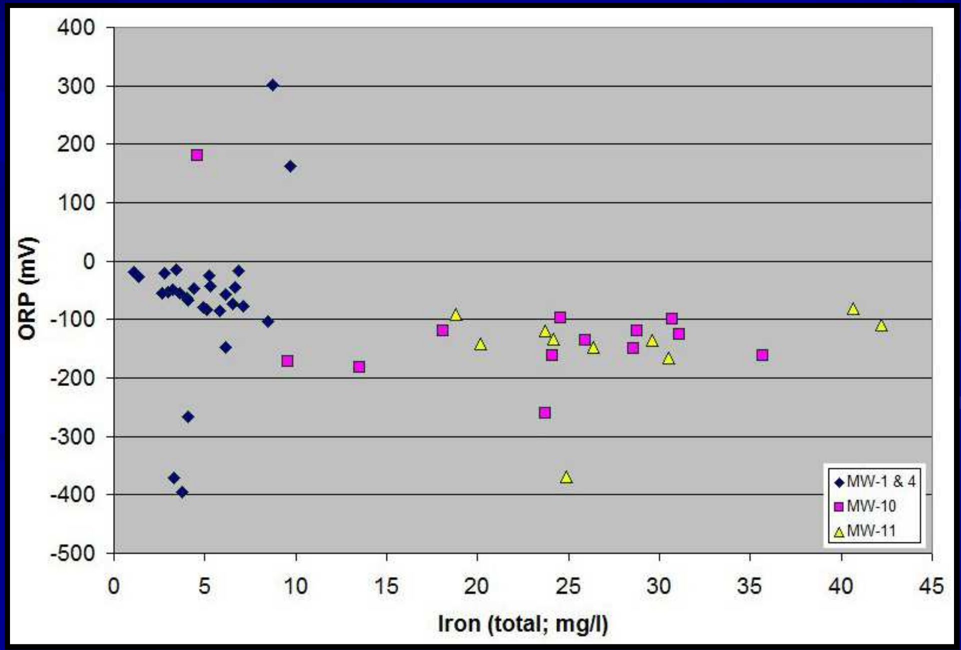


Pan Am Pit GW 2010-2014

– As vs. Fe
  - varies in relation to pit proximity

– ORP v. Fe
  - There is not an obvious relationship between ORP variability and Fe



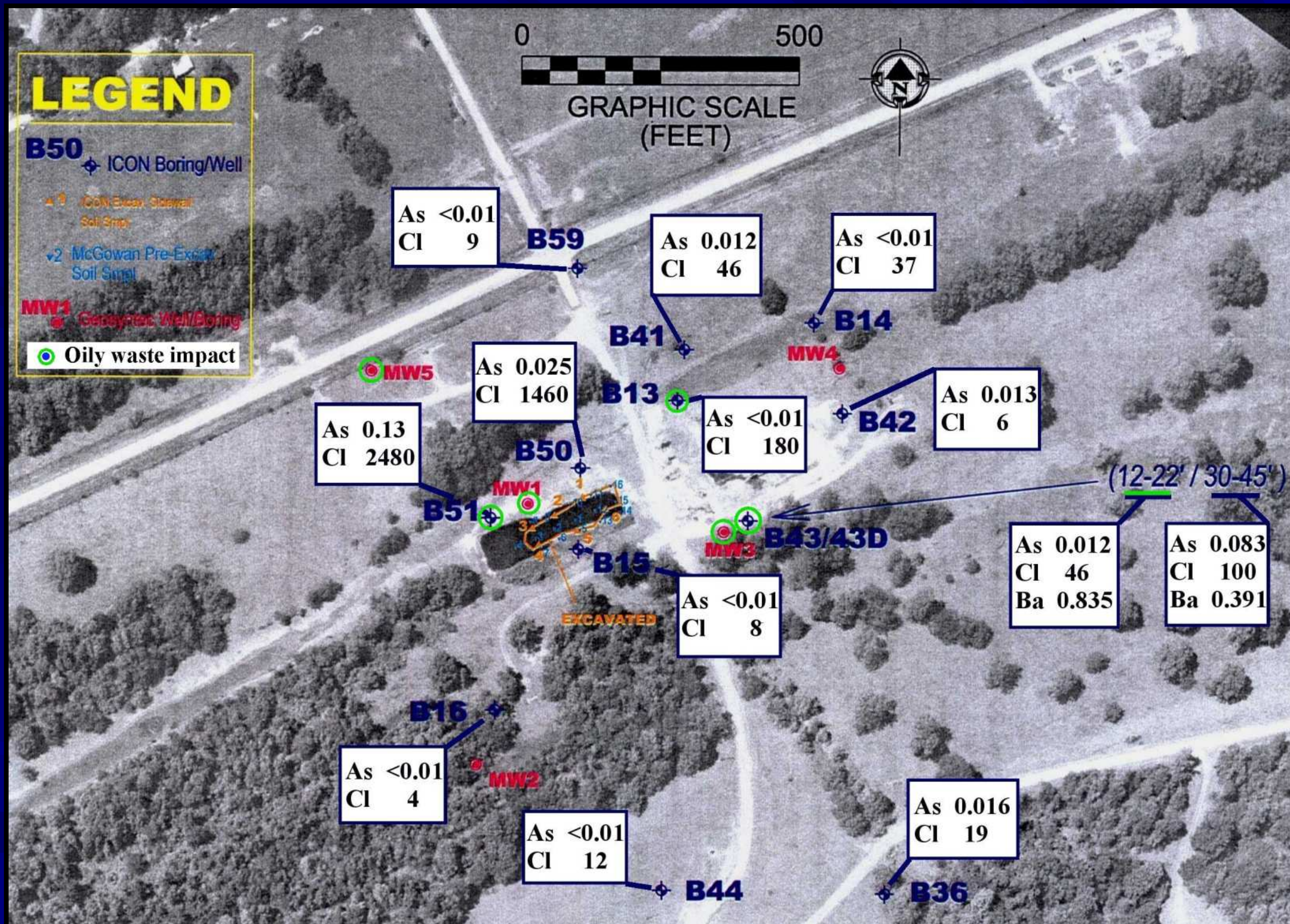


Applegate Lease

- Pisani (2008, 2015) contours 250 mg/l chloride (yellow line)
- I labeled highest dissolved arsenic hits over 0.10 mg/l (2006-2015 data)
- Occurs In SWD & tank battery pit areas

(Pisani 2008, 2015 chloride contour maps
From reports in LA OOC file #006-007)

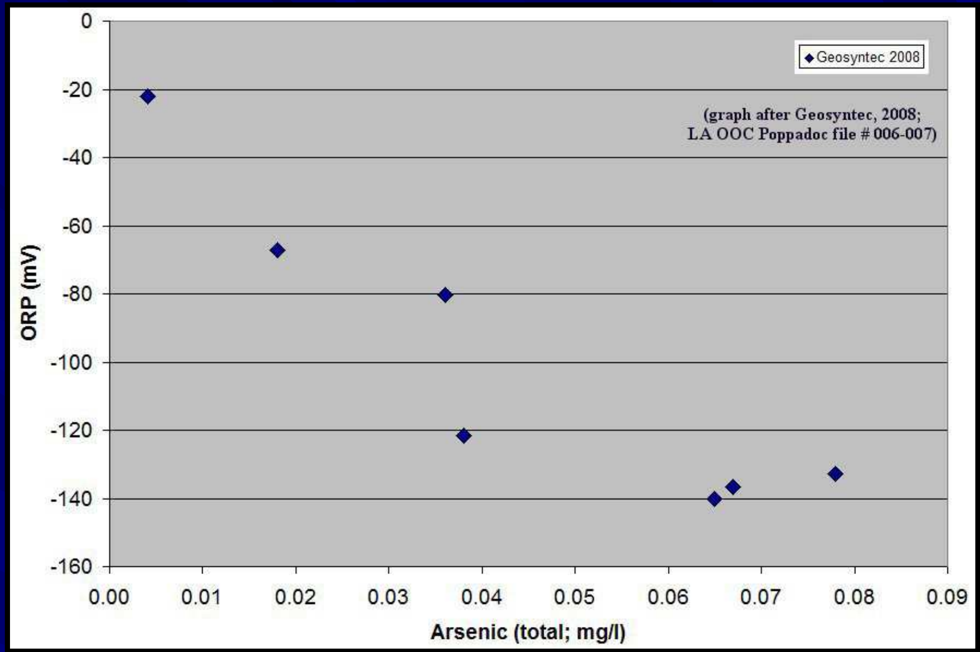
Applegate Pit Area, GW Analyses (in mg/l) from 2006-07

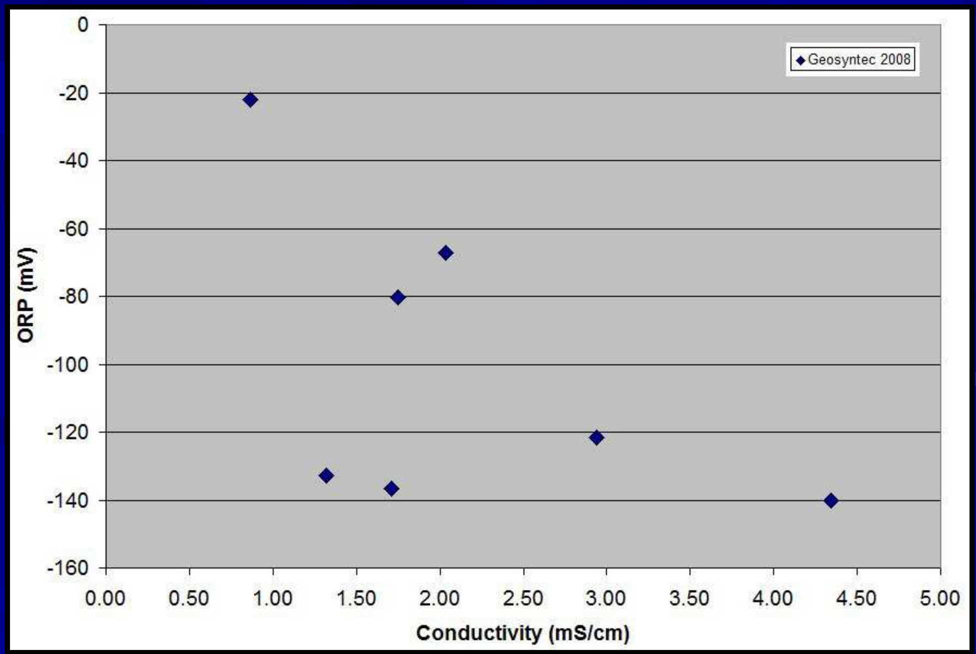


(ICON analyses plotted on ICON base map, 1974 aerial; LA OOC Tensas-Poppadoc hearing, ICON 2008 report)

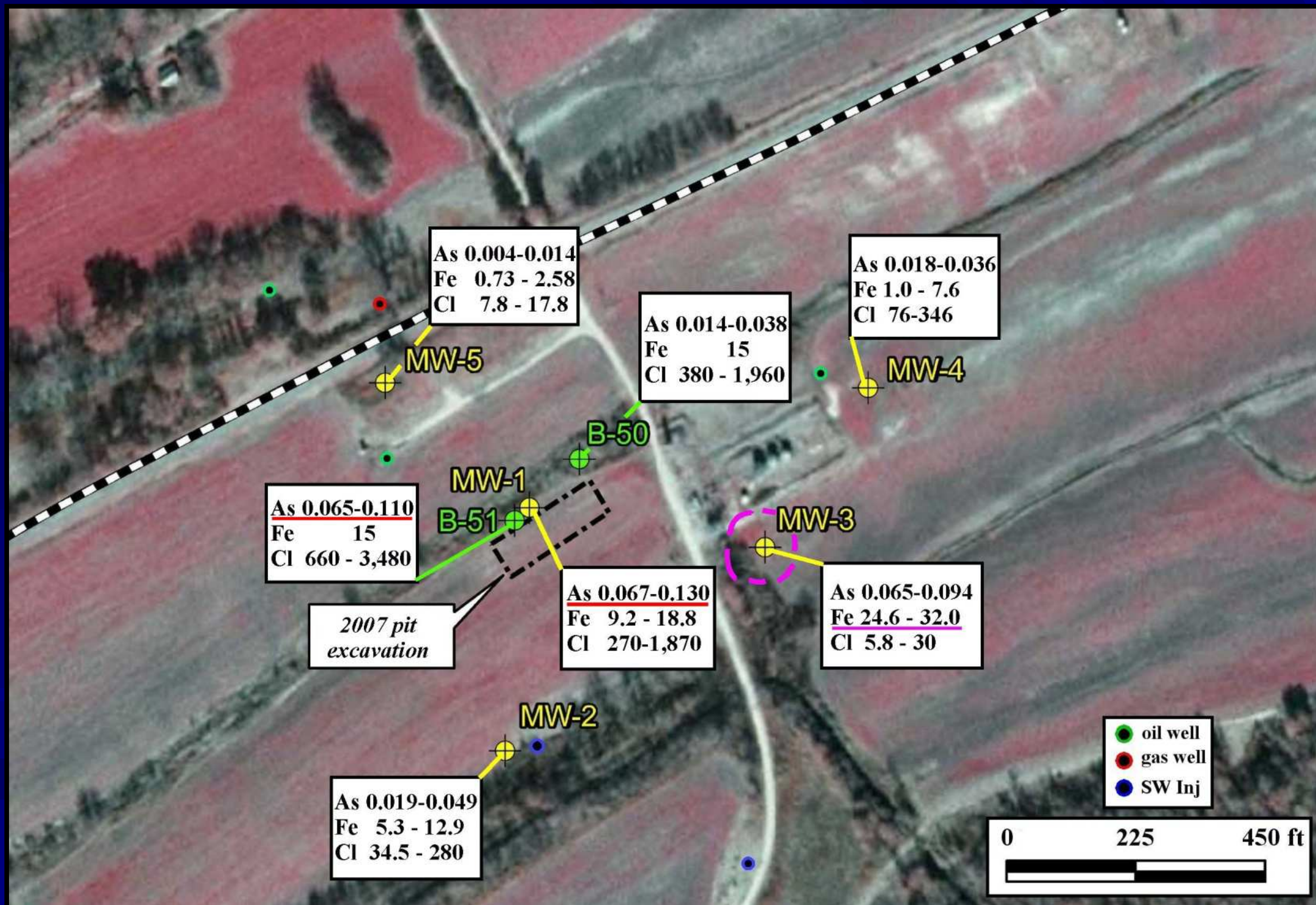
Applegate Pit

- Geosyntec GW data, April of 2008 (only ORP data acquired)
- Sampled six months after partial pit digout/new fill, and during high GW elevation, reverse GW movement towards the lake
- If apparent As relationships with ORP and Fe…
- Then apparent relationship of ORP and conductivity (salinity) ?





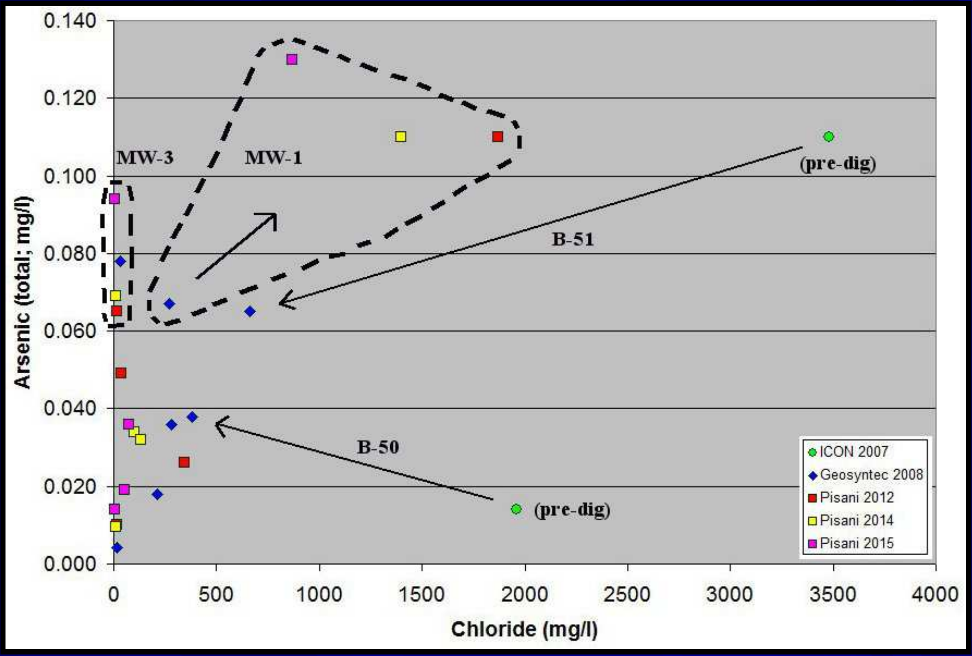
Applegate Pit Area, GW Data Ranges (in mg/l) from 2008-2015

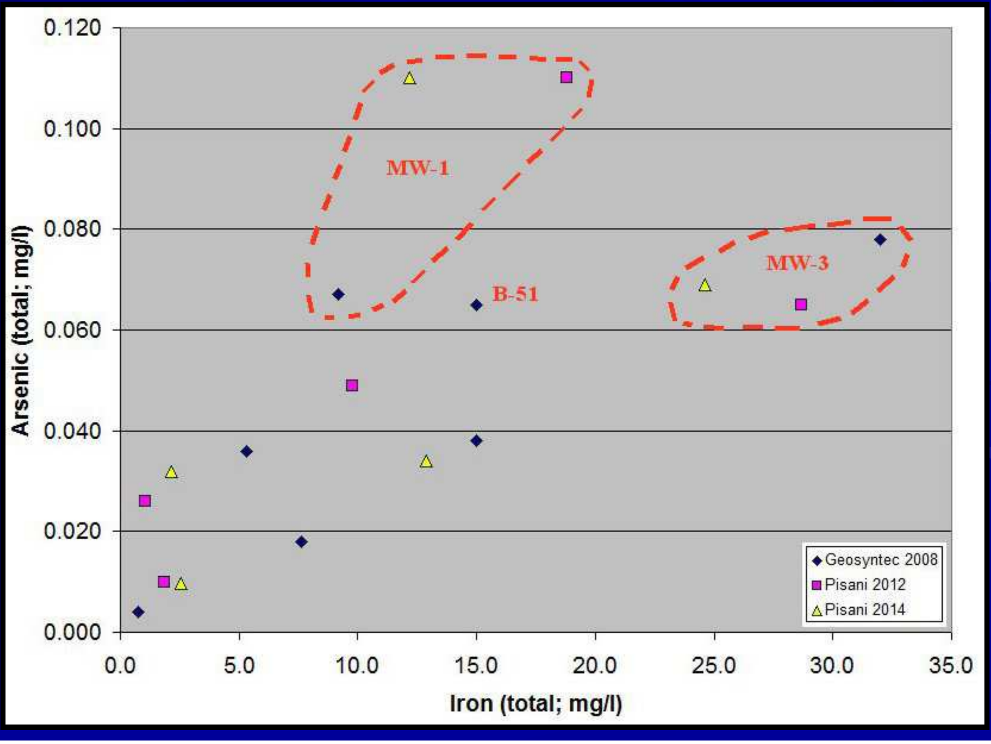


Data from OOC Poppadoc file # 006-007; Geosyntec Report, 2008, Pisani 2012-2015

Applegate Pit

- All data, 2007-15 (no ORP except 2008)
- The 2008 data are generally lower values compared to 2007 and 2012-15
- The April 2008 sampling was 6 months after pit re-closure & during high GW and river elevations (GW flow away from river)
- MW-3 has elevated Fe, why?





Patterns & Interpretations: Conclusions

- GW under the Pan Am pit moderately reduced, but no clear relation of ORP with As and Fe
- Areas of oily waste impacts do not always have elevated As
- High Fe values (interpreted as added) with elevated arsenic and associated Cl indicate oilfield impacts
- Other Fe sources besides soil available (produced water, rusty old flowlines, etc)
- Arsenic corrosion inhibitor usage in the 1950s likely source of elevated dissolved arsenic in studied pits at LSJ field
- In addition, arsenic-based herbicides & rust inhibitors possibly used in the past around oilfield facilities—this usage and its modern impacts usually not considered
- The Geosyntec 2008 reductive-dissolution model for elevated GW arsenic & iron below pits is not supported by additional data; plus, based on one-time sampling of ORP, As & Fe (six months after pit closure)

A Possible Model

- Observed ion mobility in GW from PA pit: Cl > Fe > As
- HFOs added to emergency pits from produced water over decades; As usage in 1950s, 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 or source origins
- One monitor well (MW-3) in Applegate area has elevated Fe (and possibly As) that is not related to the pit; the Fe is a clue that another source is responsible

Selected References

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