Application of Alkaline Activated Persulfate and Evaluation of Treatment Residuals

Remediation of Chlorinated and Recalcitrant Compounds
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"After ISCO, What Then?"

- Side-effects of In-Situ Chemical Oxidation (ISCO)
- Common questions:
  - Will biological treatment be possible after ISCO?
  - Will pH recover?
  - Will metals be mobilized?

Theory: Alkaline Activated Persulfate

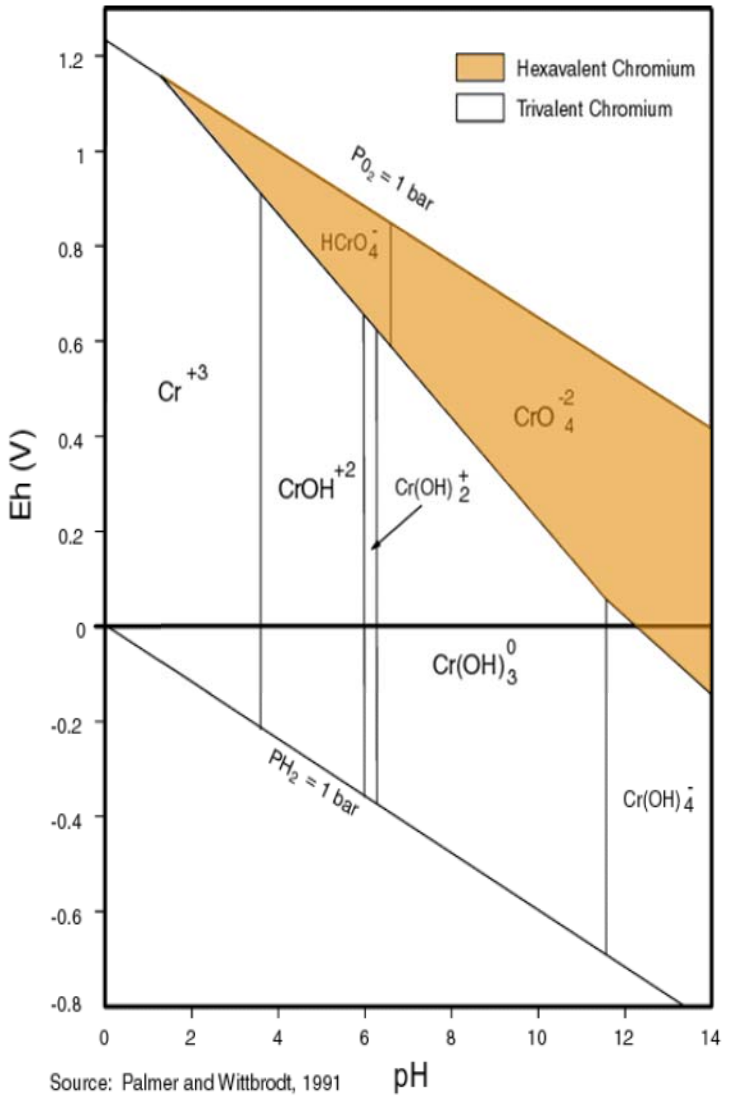
- Alkaline Activated Persulfate (AAP):
  - Typically activation occurs at pH > 10.5
  - Auto-decomposition reaction forms two sulfate radicals:

$$S_2O_8^{2-} \rightarrow 2\ SO_4^{-}\bullet$$

  - Add sodium hydroxide [NaOH] to raise pH
  - Overcome base soil buffering capacity and acid [H^+] production during oxidant reaction

Theory: Side-Effects of ISCO

- Change in pH
- Mobilization (or precipitation) of metals caused by:
  - pH effects
  - Change in redox conditions (oxidation/reduction of metals)
- Transformation
  - Example: Cr(III) to Cr (VI), etc



Source: Palmer and Wittbrodt, 1991

Theory: Attenuation Mechanisms

- Buffering capacity:
  - Redox (electron donors/acceptors)
  - pH buffering
- Solid-surface interactions and ion exchange:
  - Negative surface charges (influenced by pH)
  - Metal oxides [MnOx], [FeOx]
- Mineral dissolution-precipitation reactions:
  - Calcite [$CaCO_3$], gypsum [$CaSO_4$], etc.
- Dilution

The Problem: Solvent Contamination

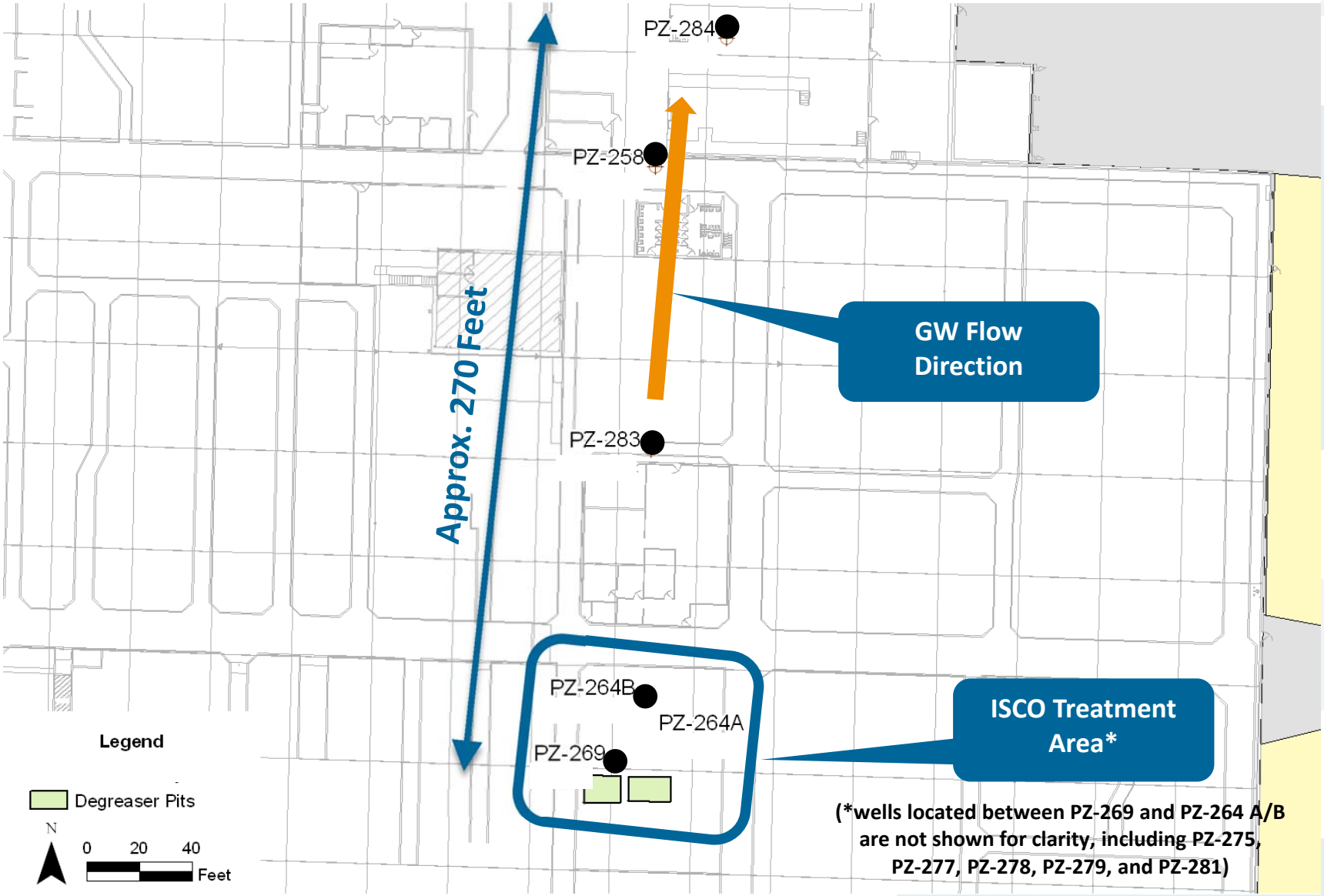
- Source Area:
  - 30 x 60 feet area
  - 15 feet thick
  - ~1,000 CY

Compound	Historical Max. Conc. (ug/L)
1,1,1-TCA	101,000
PCE	20,000
1,4-Dioxane	3,000

- Located beneath active manufacturing plant

- Treatment Goal:
  - Reduce groundwater to below 1 mg/L in source
  - Goal based on protection of downgradient receptor

Site Map



(*wells located between PZ-269 and PZ-264 A/B are not shown for clarity, including PZ-275, PZ-277, PZ-278, PZ-279, and PZ-281)

The Solution: ISCO Treatment

- Selected AAP for safety reasons
  - Greater in-situ stability
  - Reduced potential for gas evolution
- Evaluated AAP on bench scale
  - Soil buffering capacity
  - 2 to 4 g NaOH/Kg Soil

❖ **NaOH Mass < Soil Buffering Capacity + acid generated by persulfate reaction**

- Two injection events

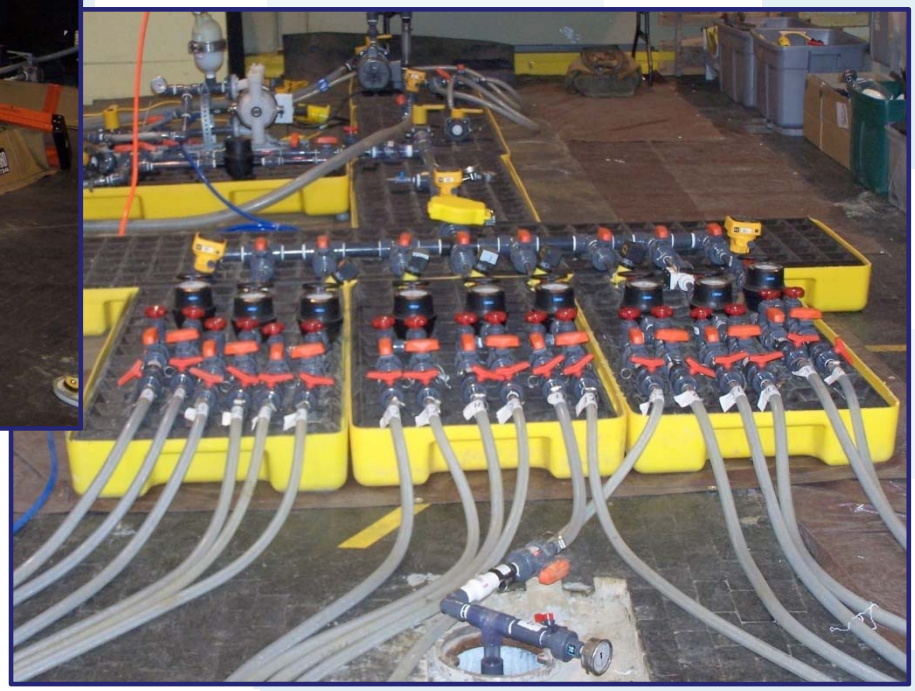
❖ **31,000 Kg Klozur (sodium persulfate)**

❖ **15,300 Kg Sodium Hydroxide (NaOH)**

❖ **NaOH dose was equivalent to total NaOH demand**

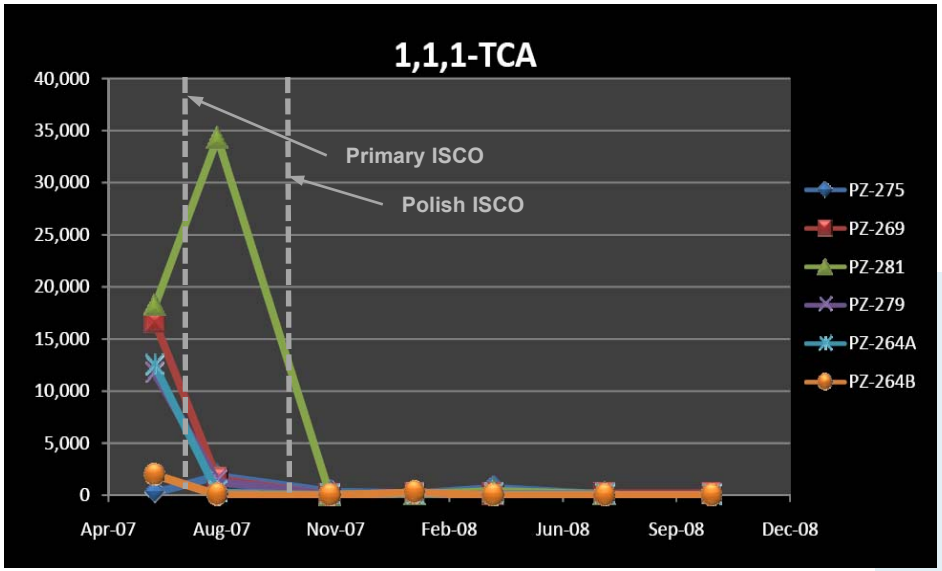
ISCO Equipment/Construction

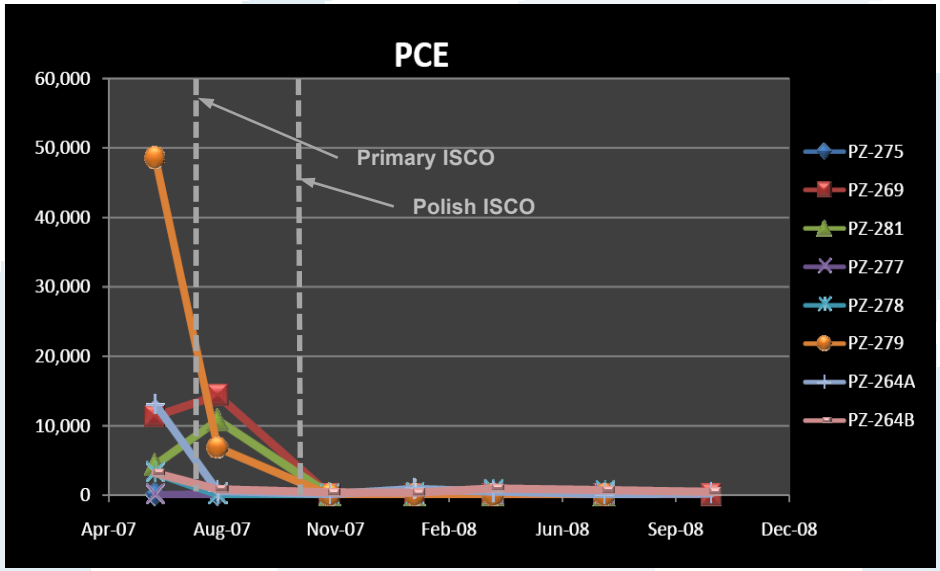
- Engineered small, mobile system

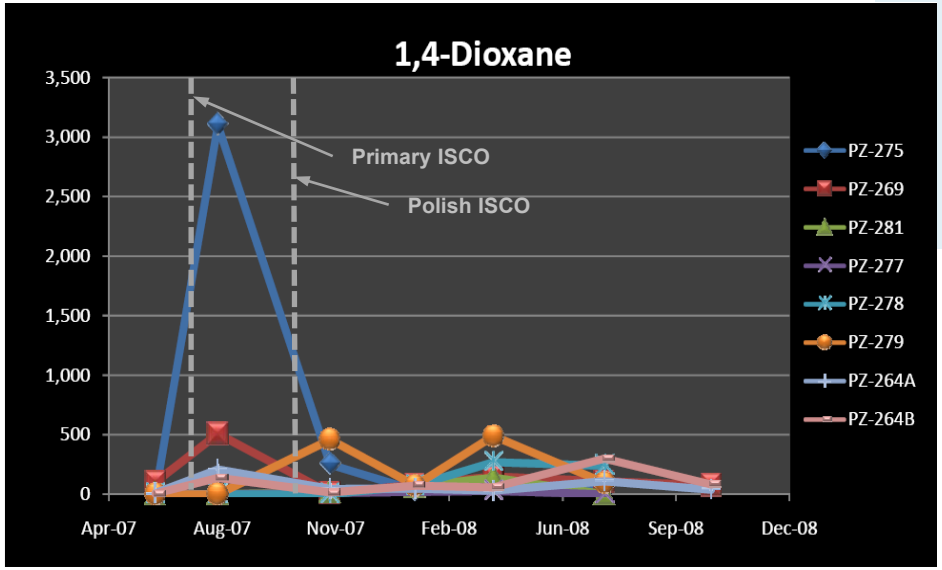


- Multiple wells injected into simultaneously

Long Term Monitoring Results-VOCs





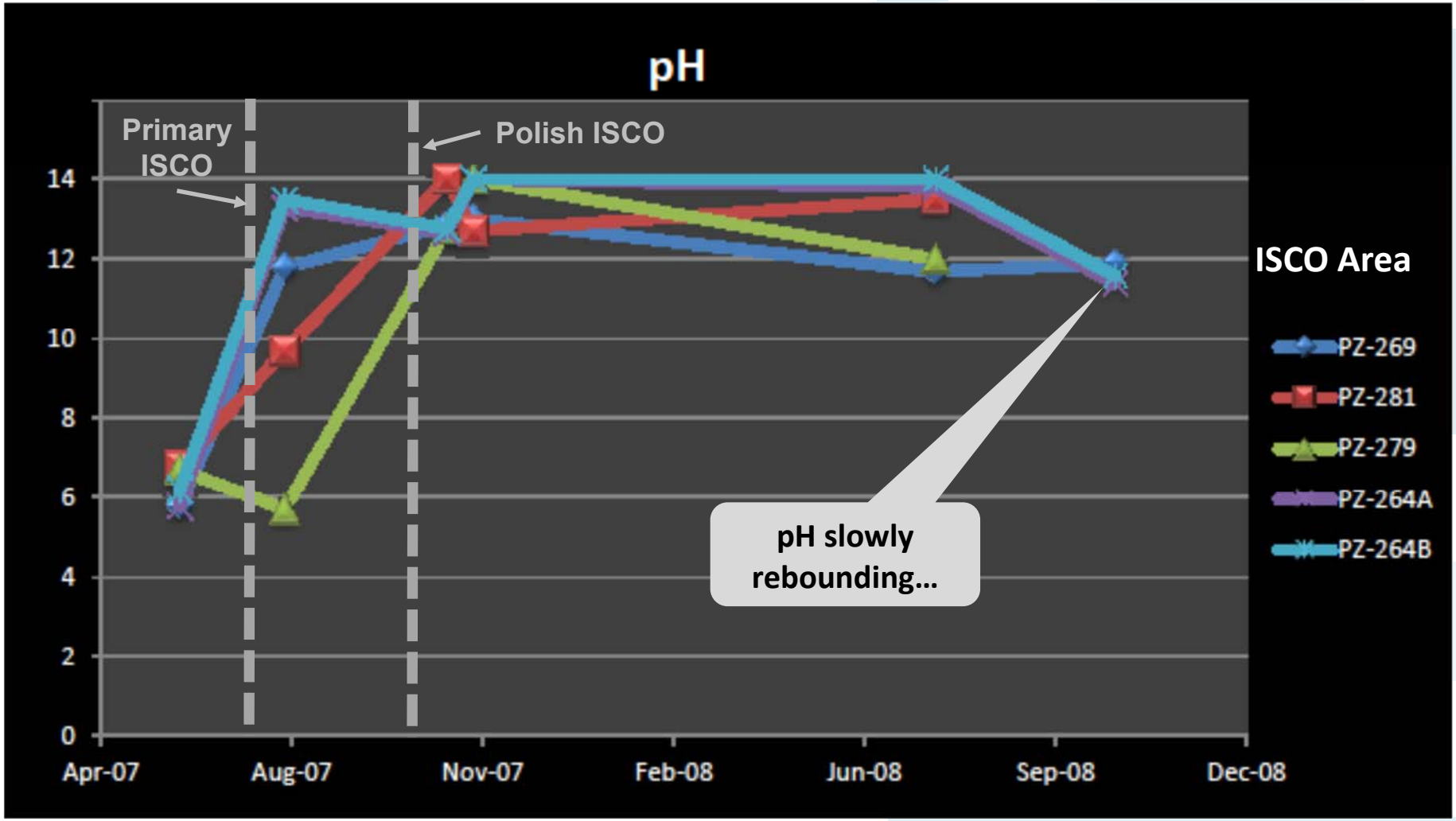


- 2-3 Orders Magnitude Reduction
- Target compounds remain below 1 mg/L
  (as of Oct 2010 sampling round)

What About the Treatment Residuals?

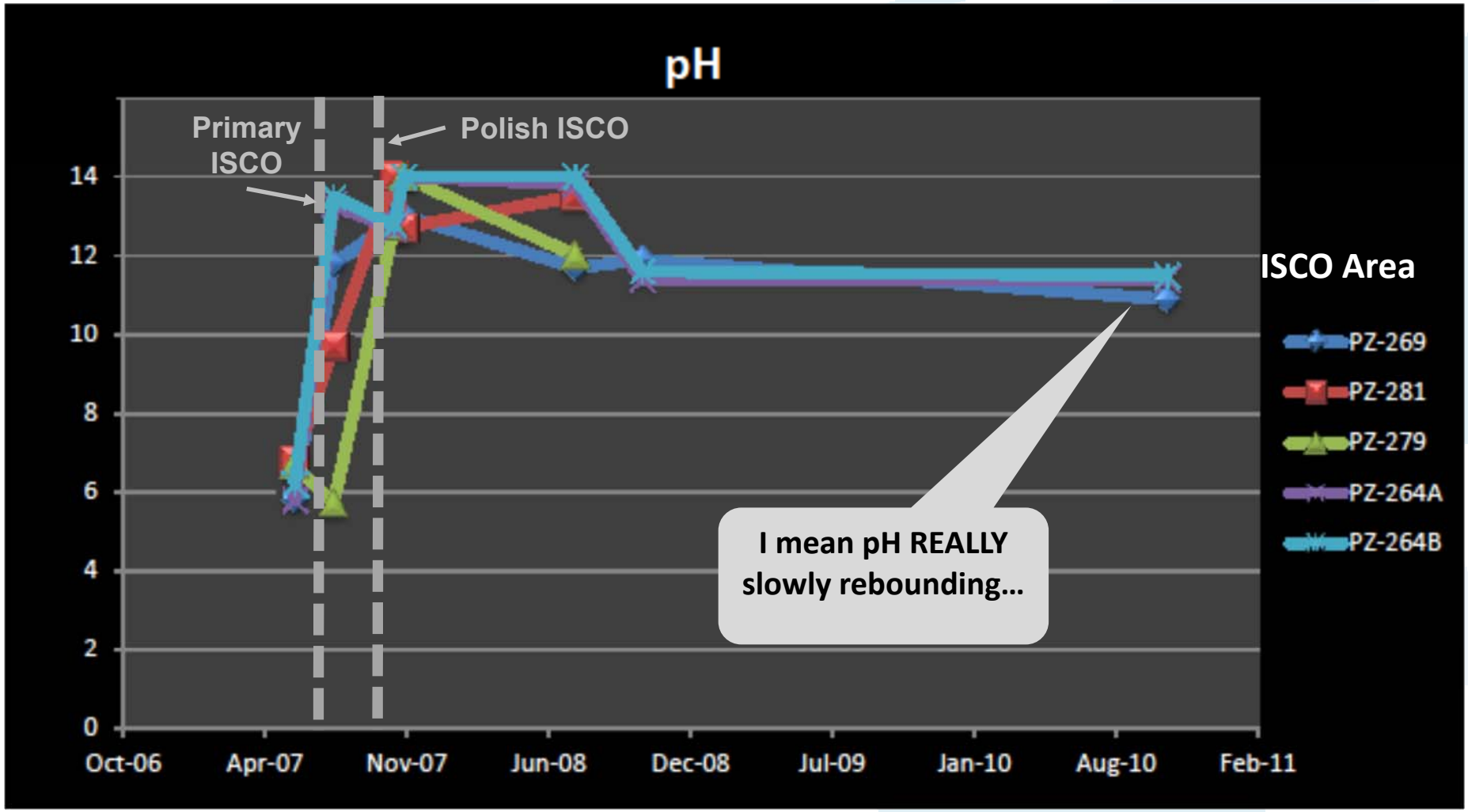
- Added significant amount of NaOH:
  - pH…will it recover?
- Persulfate → Sulfate:
  - Sulfate formed, will it attenuate?
- Metals:
  - Mobilization of As, Cr and other metals?

Aquifer pH: Treatment Area 2008



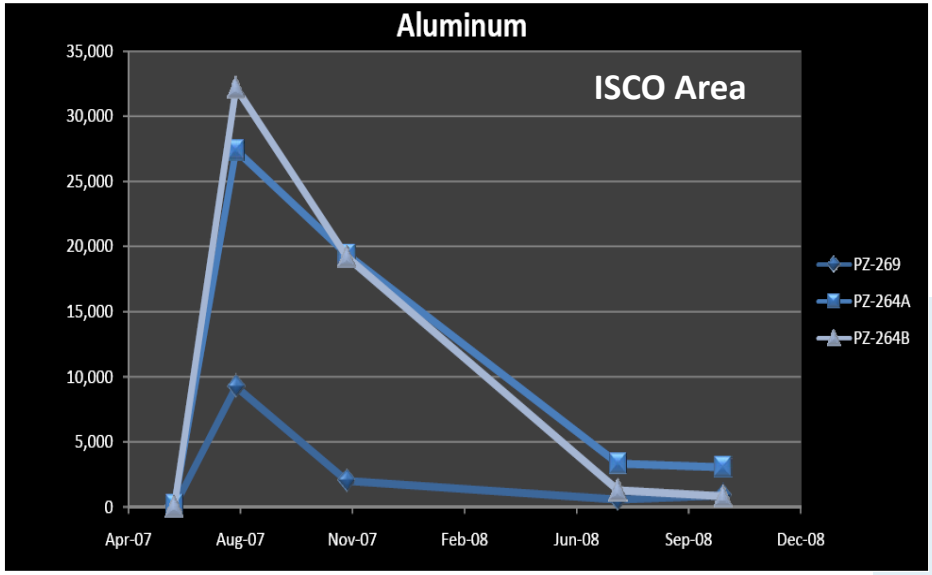
Average ORP: Pre-ISCO = -90 mV; During ISCO = -234 mV; Post ISCO: = -150 mV

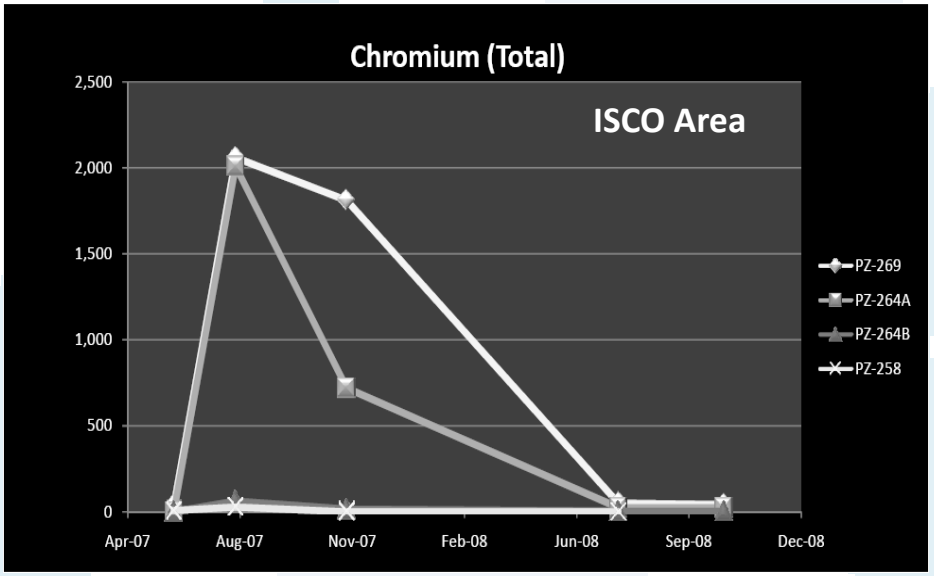
Aquifer pH: Treatment Area 2010



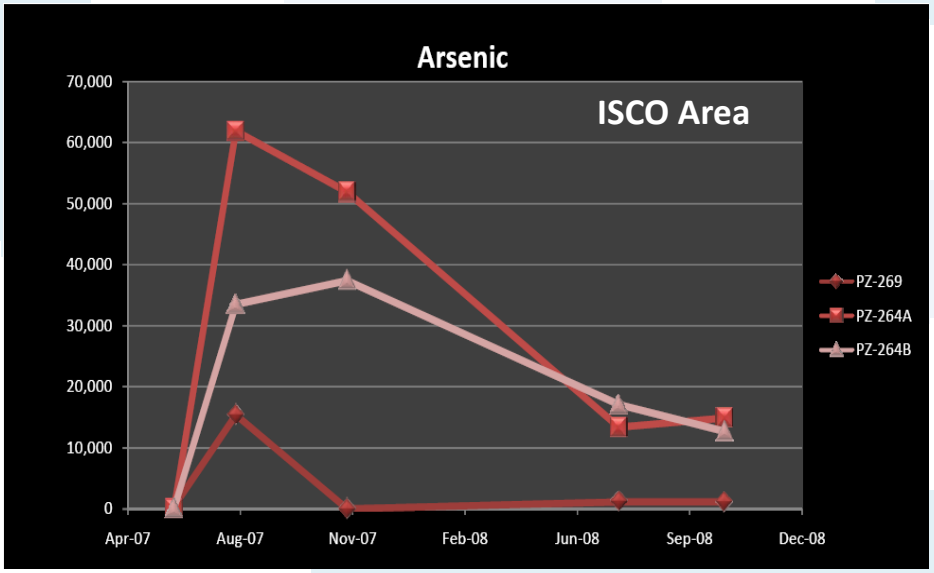
Post ISCO ORP (2010) = -117 mV

Residual Effects: Metals (2008)



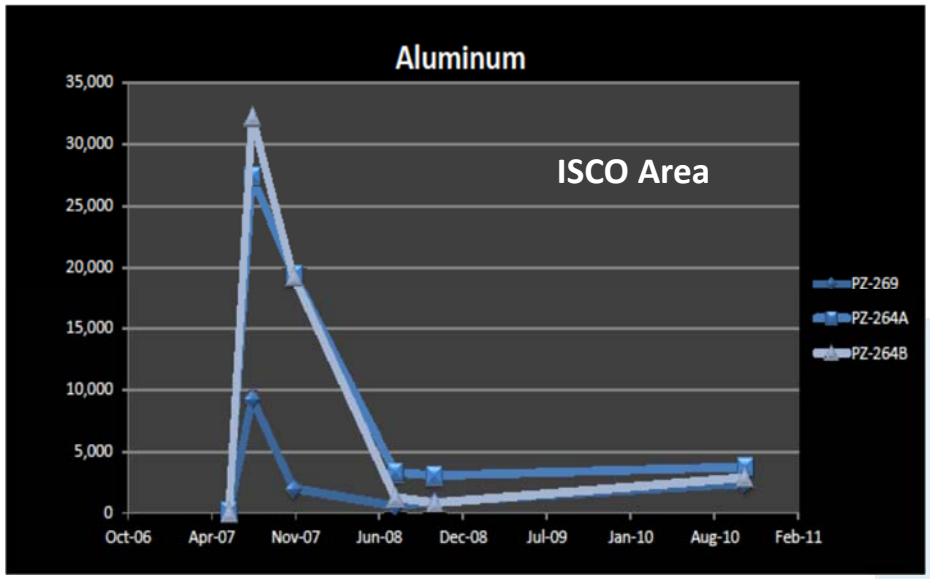


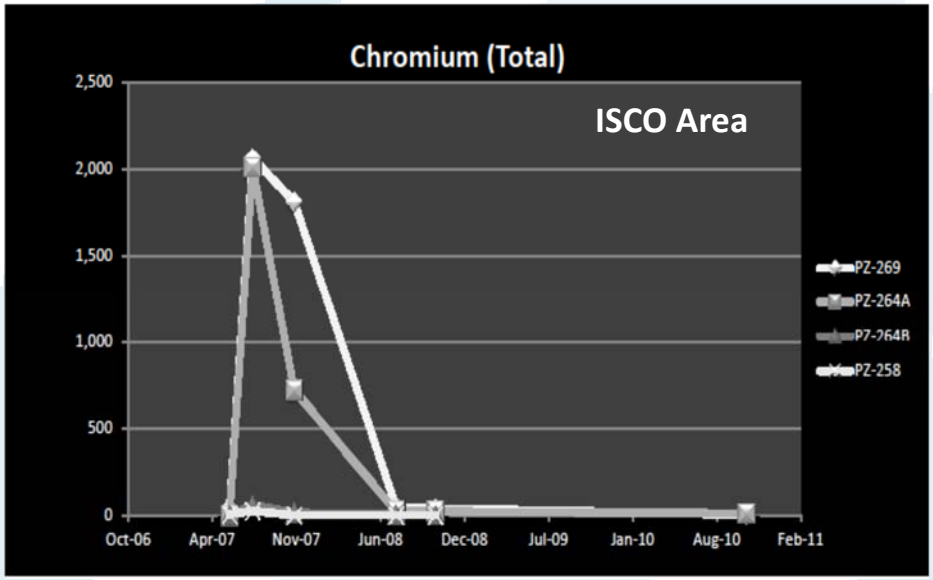
- Significant but temporary increases in Al, Cr, and As
- Levels trending downwards within target area
- Consistent with pH-Eh diagrams

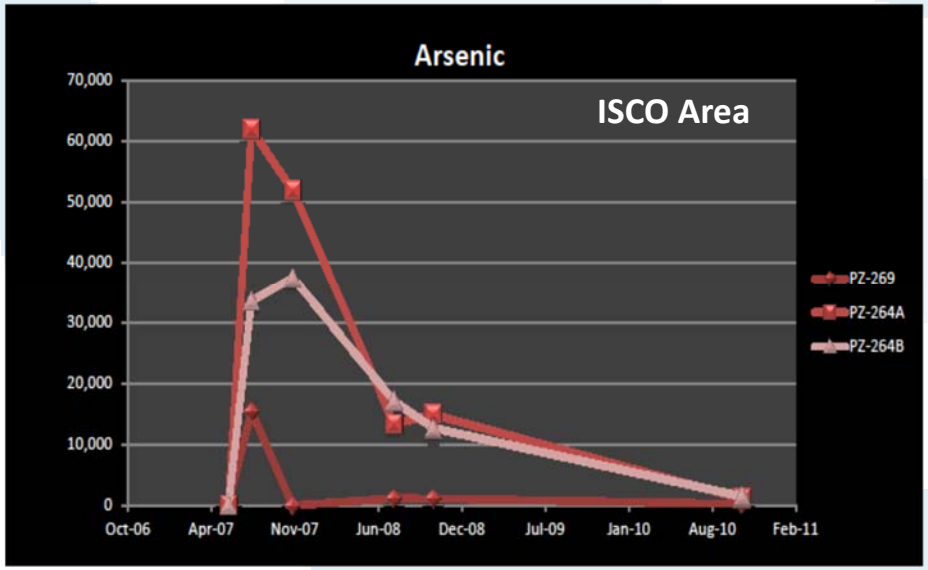


All Concentrations in ug/L

Residual Effects: Metals (2010)





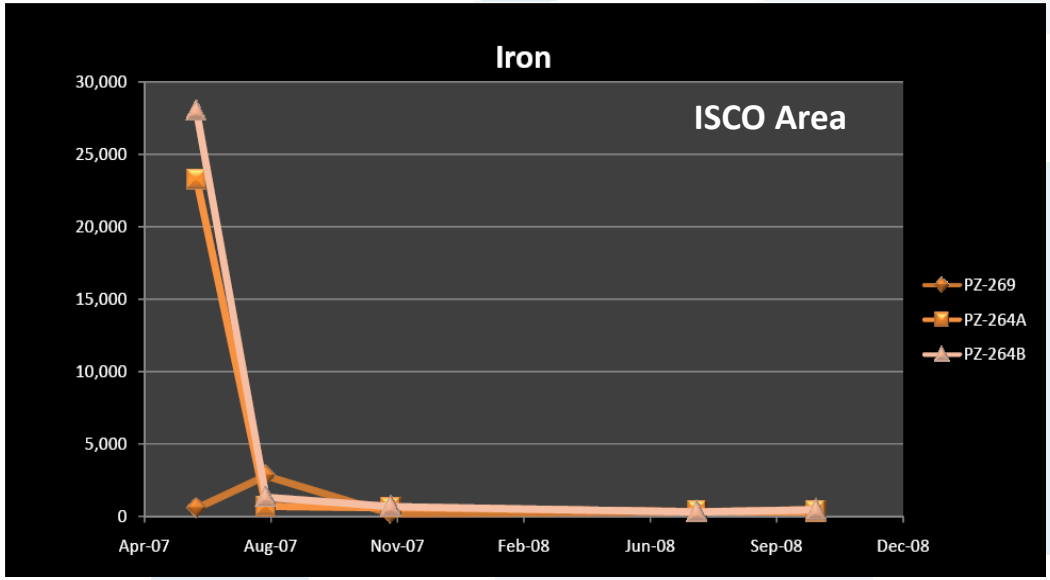


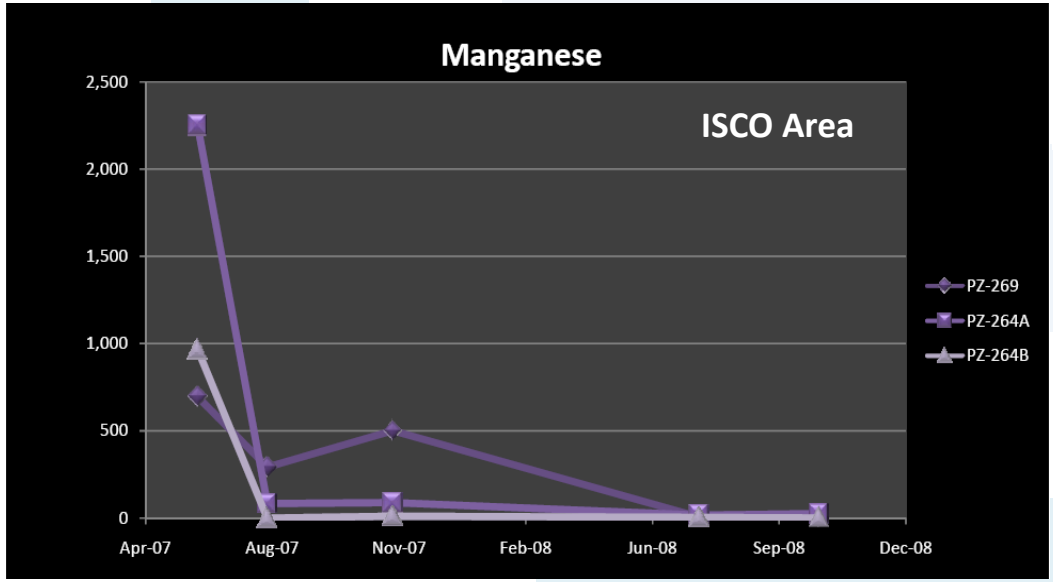
- Cr and As attenuated
- Al appears to be slightly increasing as of 2010, but still low

All Concentrations in ug/L

Residual Effects: Metals (2008)

- Precipitation of Fe and Mn occurred
- No significant rebound through 2008
- <u>Behavior is consistent with pH-Eh diagrams</u>

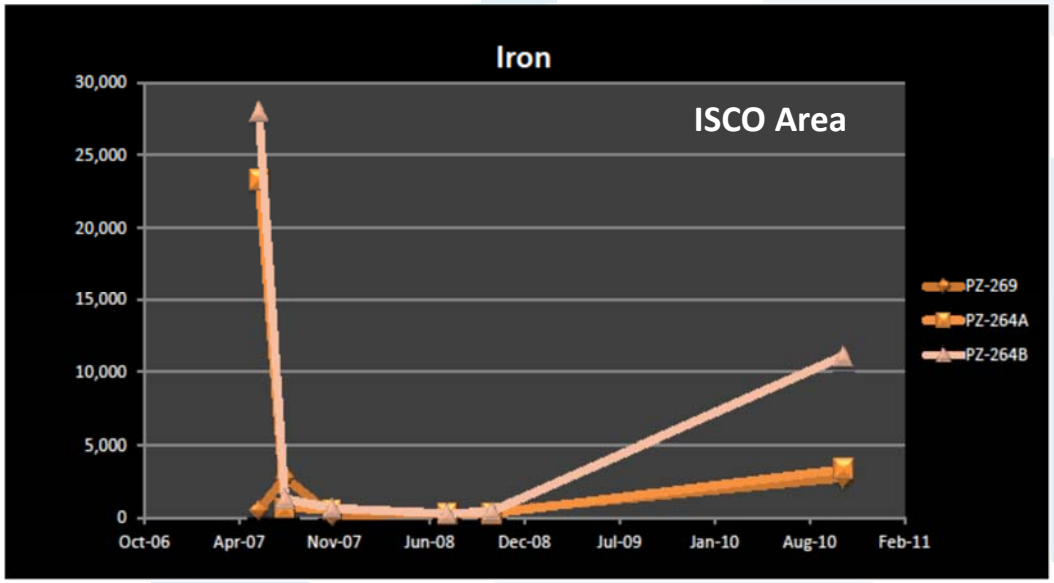


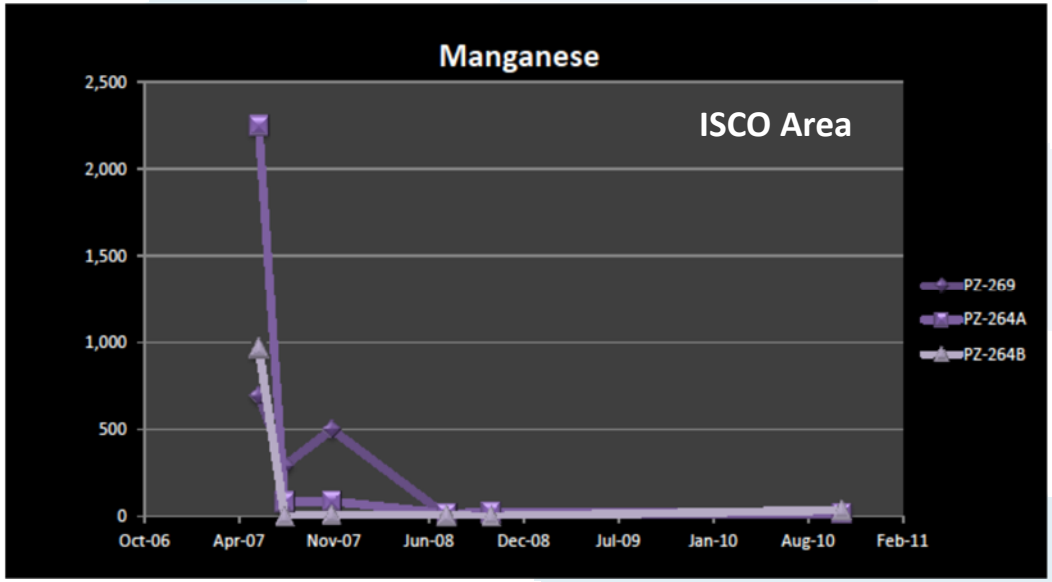


All Concentrations in ug/L

Residual Effects: Metals (2010)

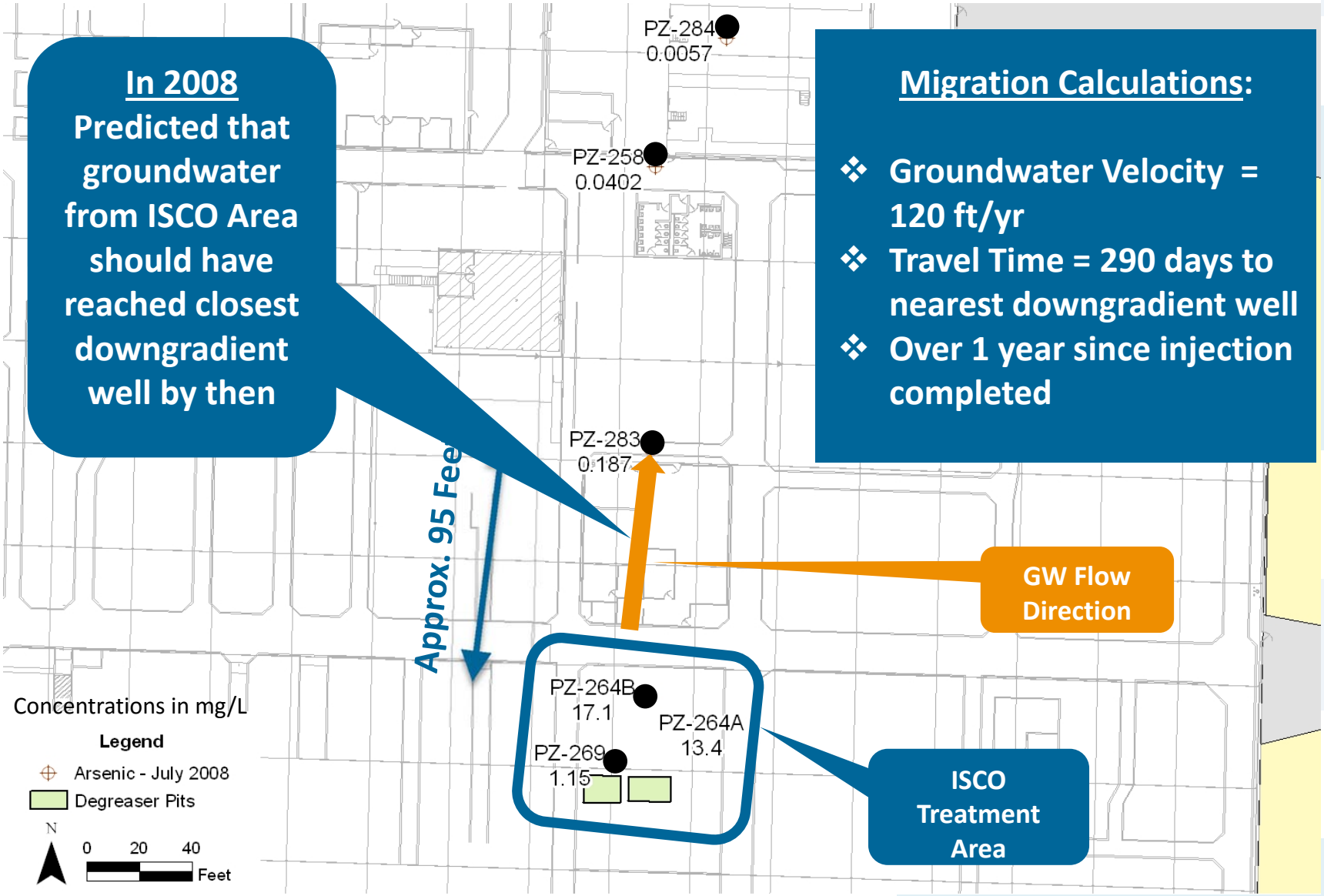
- Iron is rebounding
  - this is also happening downgradient…
  - More on that later..
- Manganese still low





All Concentrations in ug/L

Have Impacts Migrated Downgradient?



In 2008
Predicted that groundwater from ISCO Area should have reached closest downgradient well by then

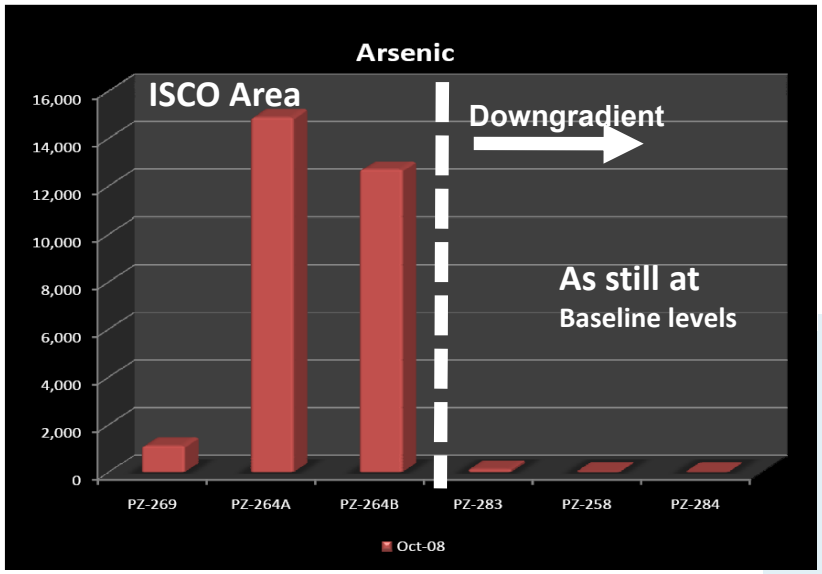
Migration Calculations:

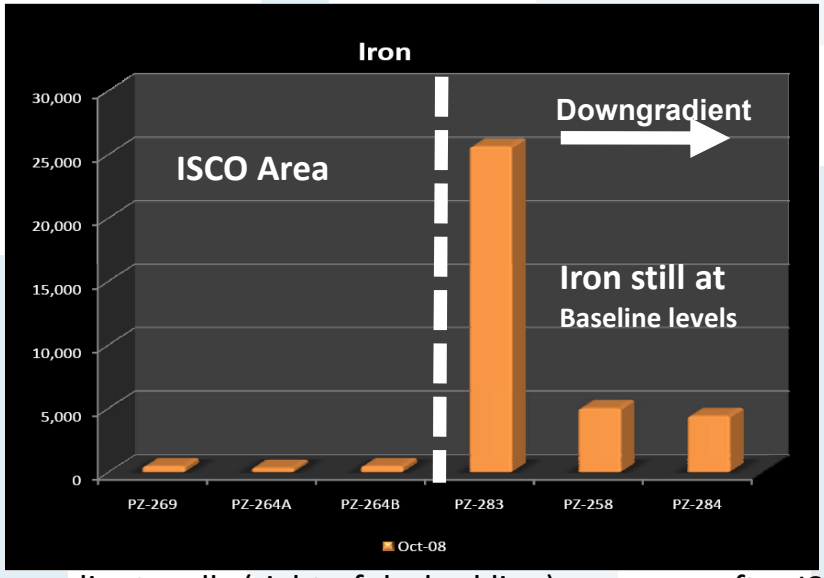
- Groundwater Velocity = 120 ft/yr
- Travel Time = 290 days to nearest downgradient well
- Over 1 year since injection completed

GW Flow Direction

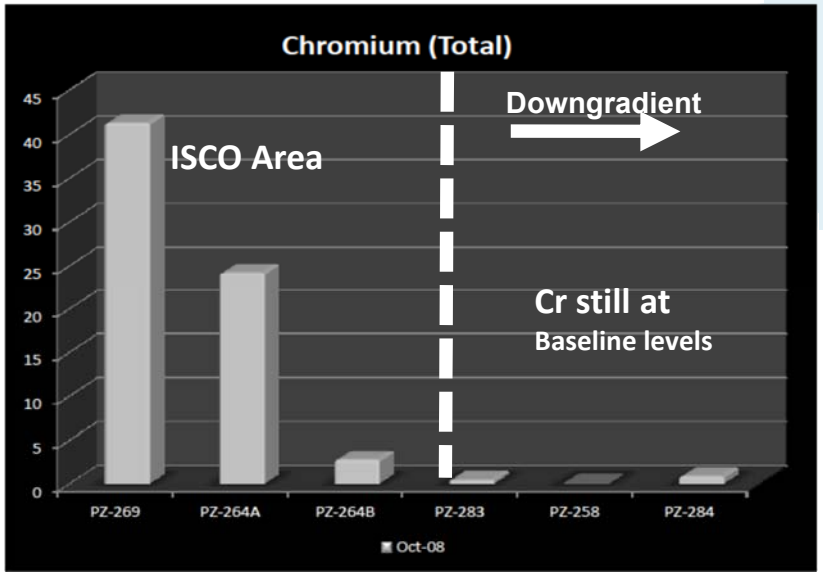
ISCO Treatment Area

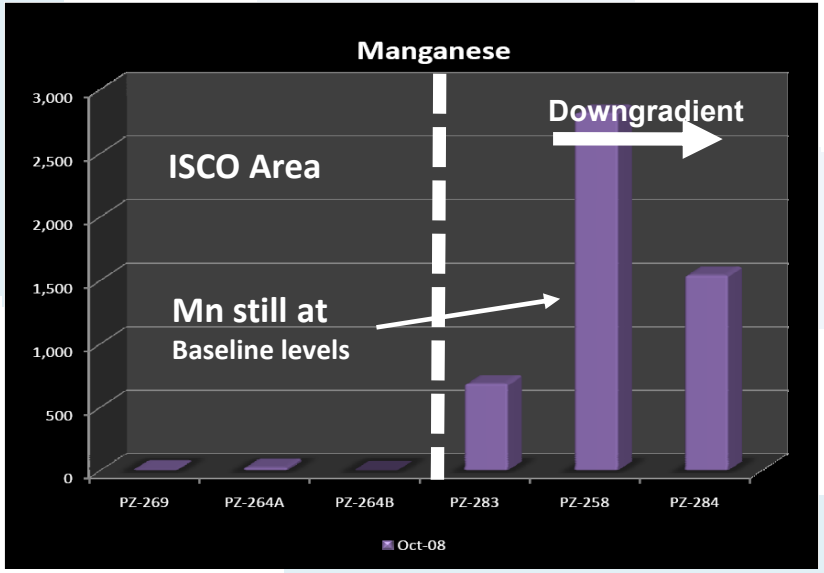
Downgradient Water Parameters (2008, One Year After Treatment)





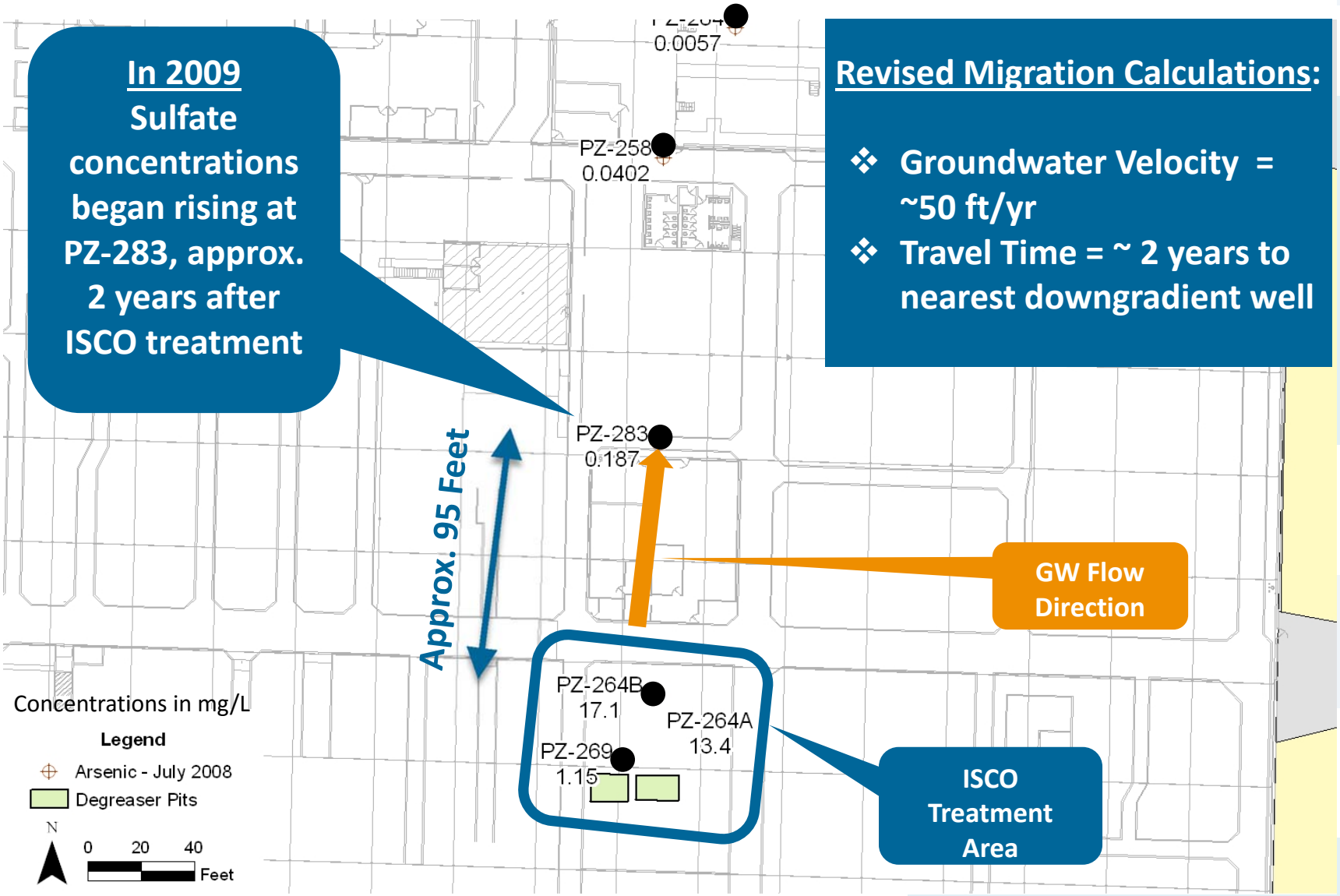
*Comparison of upgradient wells (left of dashed line) to downgradient wells (right of dashed line), one year after ISCO





All Concentrations in ug/L

Have Impacts Migrated? (2-3 Years Later)



In 2009
Sulfate concentrations began rising at PZ-283, approx. 2 years after ISCO treatment

Revised Migration Calculations:

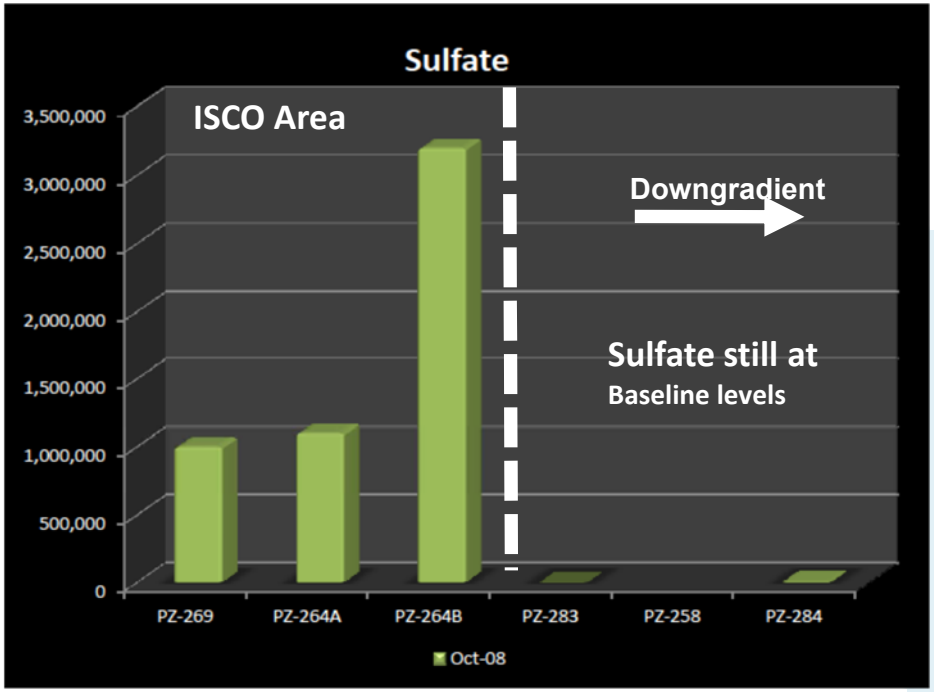
- **Groundwater Velocity = ~50 ft/yr**
- **Travel Time = ~ 2 years to nearest downgradient well**

GW Flow Direction

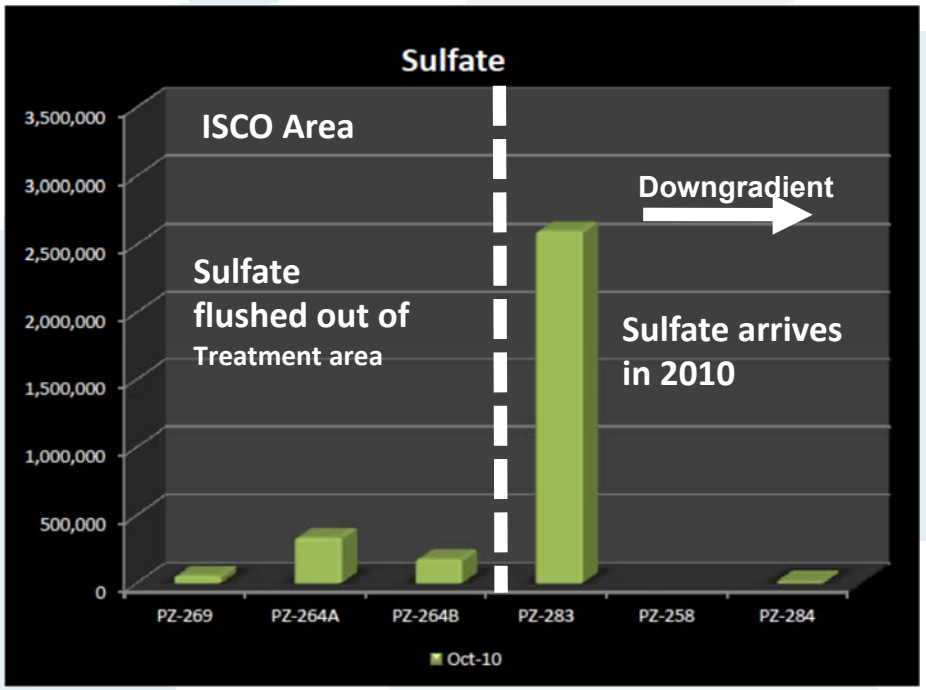
ISCO Treatment Area

Sulfate Concentrations After Treatment

2008 – One Year After*



2010 – Three Years After*

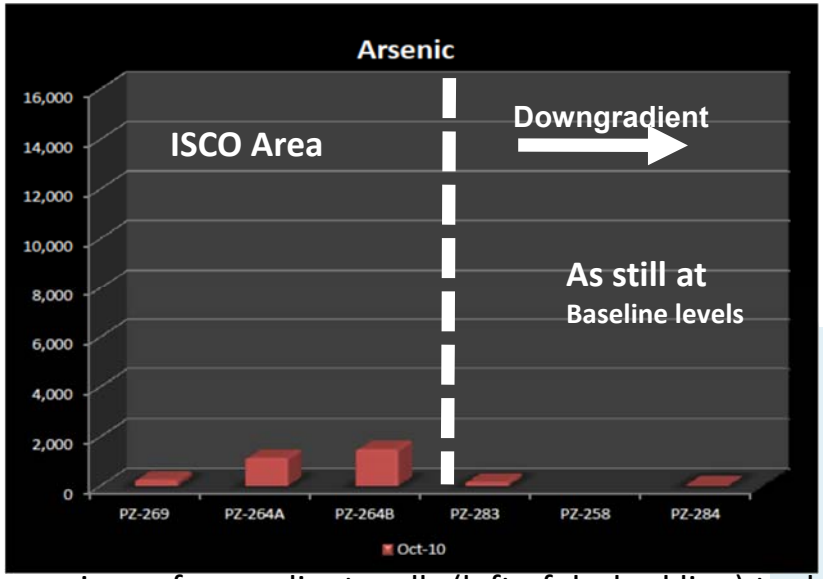


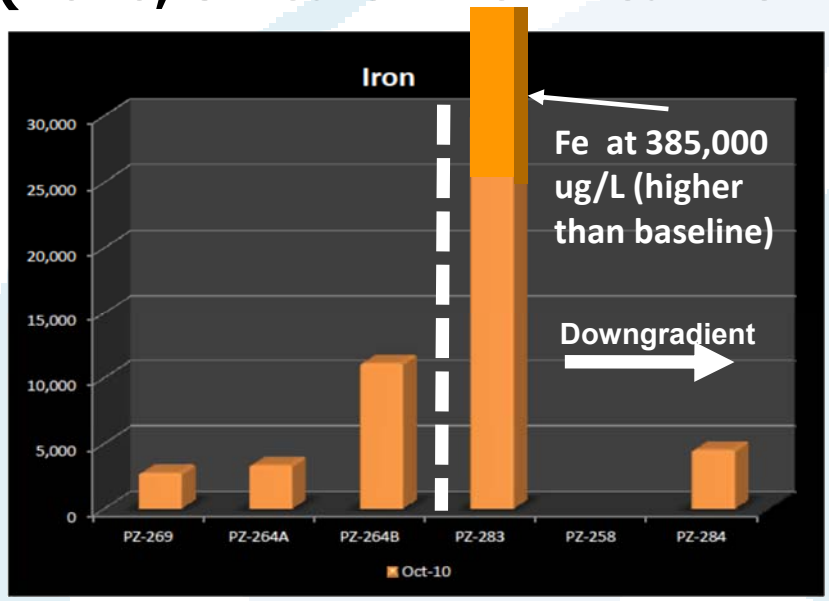
All Concentrations in ug/L

- Sulfate flushed out of target area
- Sulfate arrives at PZ-283 in 2010
- If Sulfate migrated…did Arsenic and Chromium too?

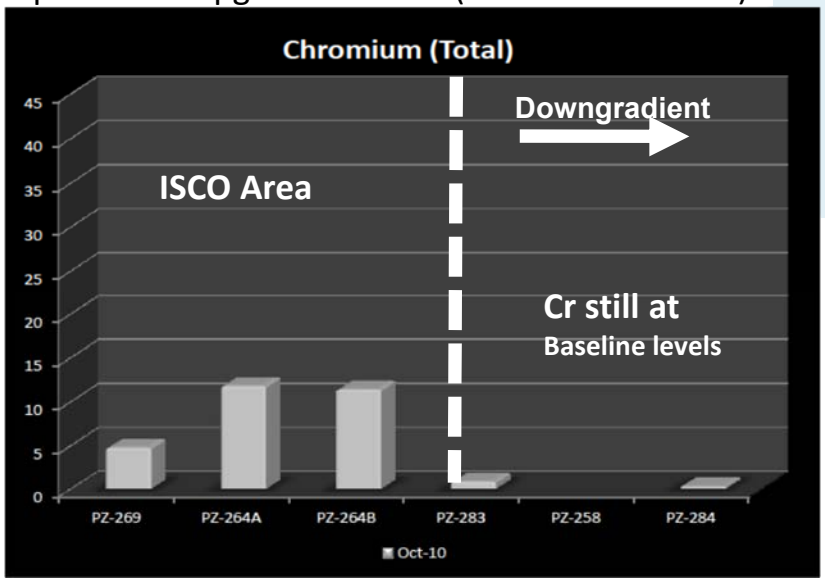
*Comparison of upgradient wells (left of dashed line) to downgradient wells (right of dashed line), 1 and 3 years after ISCO treatment

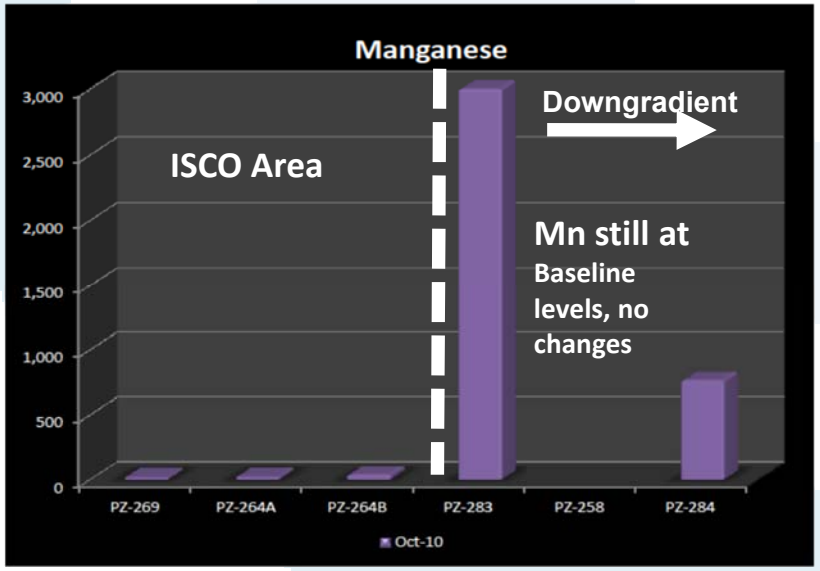
Downgradient Water Parameters (2010, 3 Years After Treatment)





*Comparison of upgradient wells (left of dashed line) to downgradient wells (right of dashed line), one year after ISCO





All Concentrations in ug/L

Downgradient Effects?

- pH:
  - pH remains elevated in source area, but no impact downgradient
  - Mass balance on NaOH buffer vs. soil buffering capacity
    - Buffering capacity approximately equal to dosage applied
    - No downgradient effect, but pH in treatment area will take long time to recover
- Metals:
  - As, Cr, etc. were elevated in source after treatment, but attenuated
  - No evidence of migration of As, Cr out of source area
  - Naturally occurring dissolved Fe, Mn precipitated in source area
- Sulfate Migration:
  - Interesting spike in iron concentrations, coinciding with sulfate arrival downgradient
  - May enhance anaerobic biodegradation (not evaluated yet)

Conclusions

- Treatment successful for solvent contamination
- Metals Migration:
  - No evidence of metals migration beyond treated areas
  - NaOH dosage balanced with buffering capacity, pH not impacted downgradient
- Sulfate Migration:
  - May enhance anaerobic biodegradation
  - Secondary MCLs
- Site-specific, attenuation reactions
  - In this case, metals behaved as expected (Eh-pH)
  - ISCO bench testing can help

Thank You!

For More Information
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