12th Annual SECARB Stakeholders' Briefing - March 2017

# Citronelle Groundwater Services

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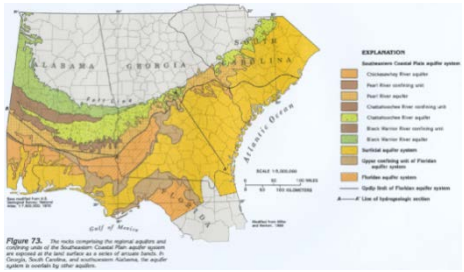
# Regulatory Context

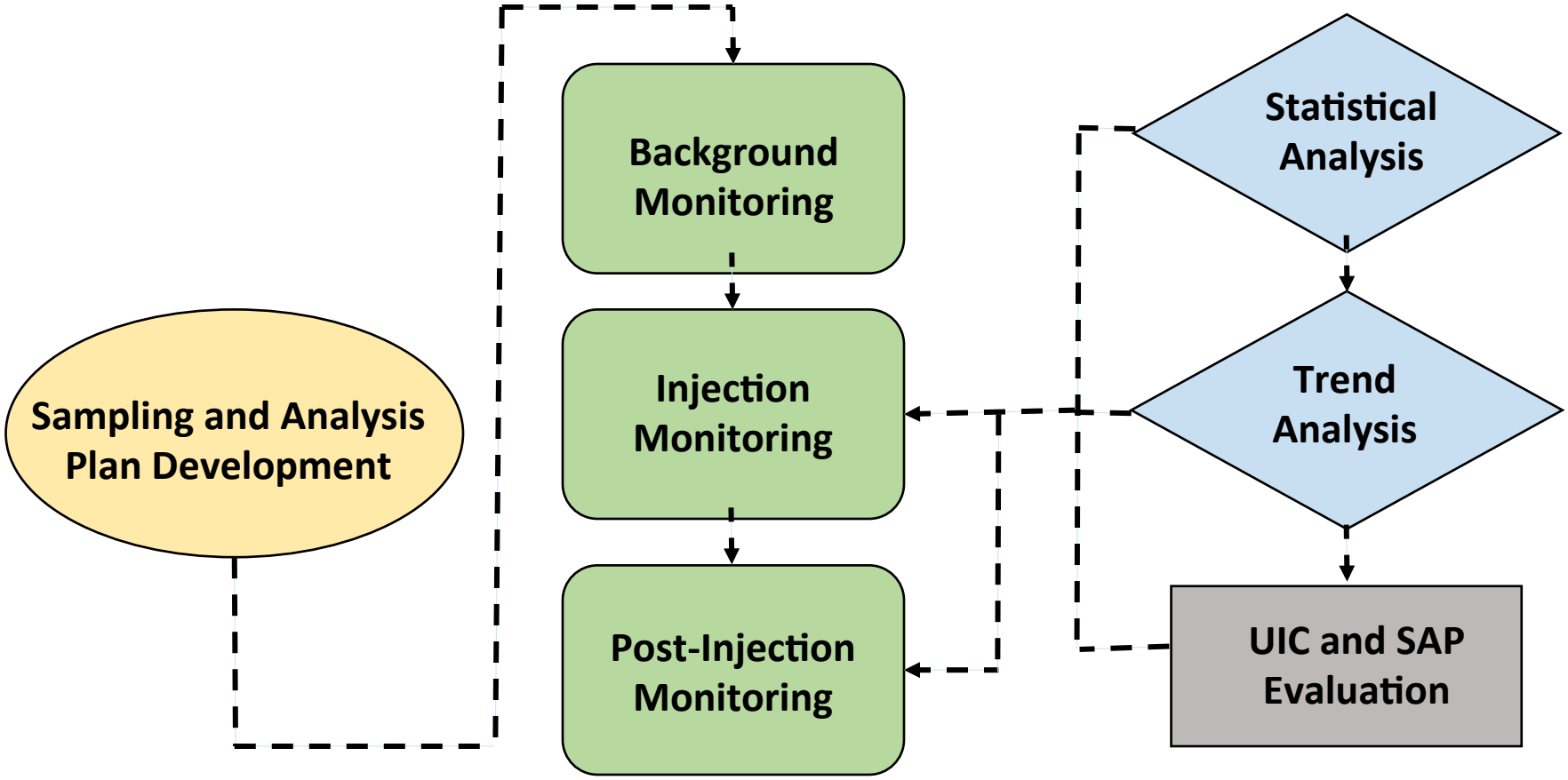
## MONITORING THE USDW AQUIFER

**Two Documents Guide the Monitoring Program:**

- **ADEM Underground Injection Control Permit**
  - Presents permit monitoring requirements
  - "Discharge Limits" based on Federal Drinking Water Standards
- **Sampling and Analysis Plan (SAP) to ADEM (State Agency)**
  - Additional data evaluations in SAP
  - Based on EPA's statistical "Unified Guidance" (March 2009)



# Groundwater Monitoring Program



# Potential Effects on Aqueous Geochemistry
## (Wilkin and Diguilio, 2010)

- Acidification
- Mobilization of Inorganics / Organics
  - Increased Alkalinity
  - Dissolved Inorganic Carbon Increase
  - Dissolved Metals Increase
- Intrusion of Saline Waters
- Controlling Factors for Potential Geochemical Changes:
  - Aquifer Mineralogy
  - Aquifer Buffering Capacity
  - Reaction Rates
  - Temperature, Pressure, Salinity

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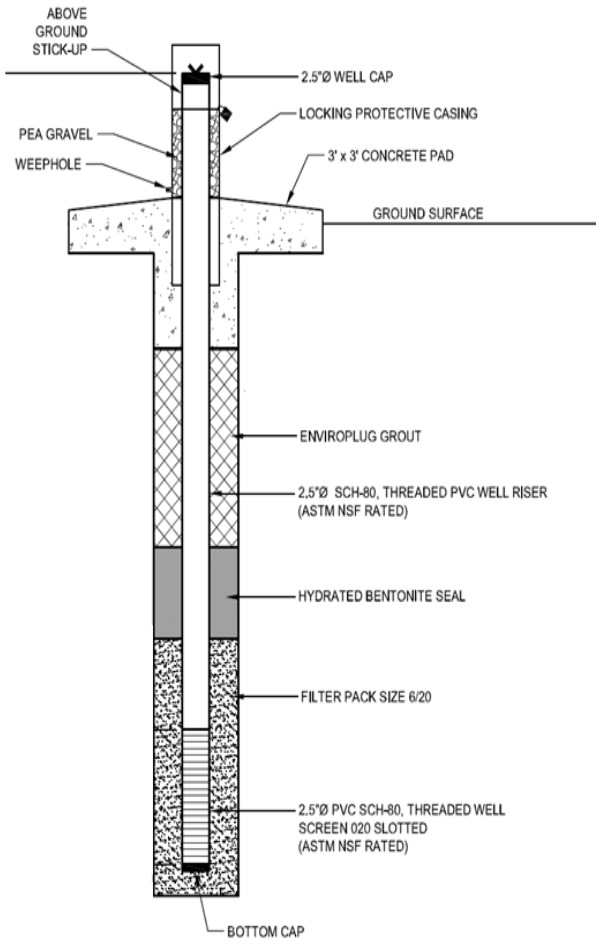
# USDW Monitoring Well Network

| Monitoring Well | Screened USDW | Well Depth (ft. BTOC) | Well TOC Elevation (ft. AMSL) |
|---|---|---|---|
| **D-9-7 MW-2S** | Miocene-Pliocene Aquifer | 170.8 | 165.56 |
| **D-9-7 MW-2D** | Miocene-Pliocene Aquifer | 501 | 165.4 |
| **D-9-9 MW-1** | Miocene-Pliocene Aquifer | 169.6 | 149.37 |
| **Water Supply Well Near D-9-8** | Miocene-Pliocene Aquifer/Watercourse Aquifer | ~143 | Not Surveyed |

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# Quarterly GW Monitoring to Date

- 3 pre-injection background events
  - January 11-12, 2012 (N=1)
  - March 13-15, 2012 (N=2)
  - July 18-19, 2012 (N=3)
- 8 injection monitoring events (N=4 to N=11) from November 2012 to August 2014
- 10 post-injection events. The latest N=21, was completed in February 2017
- 3 year post-injection site care monitoring period complete in September 2017


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# Comparison Values

| D-9-7 MW2D | | |
|---|---|---|
| **Analyte** | **UIC Permit Discharge Limits (µg/l)** | **Range of Valid Background Concentrations (µg/l)** |
| Aluminum | 200 | <100 - 4600 |
| Antimony | 6 | <5 |
| Arsenic | 10 | <5 |
| Barium | 2,000 | <10 - 29 |
| Beryllium | 4 | <3 |
| Cadmium | 5 | <5 |
| Chromium | 100 | <5 - 13 |
| Copper | 1,300 | <10 |
| Iron | 300 | <100 - 3200 |
| Lead | 15 | <5 - 5.5 |
| Manganese | 50 | <10 - 18 |
| Mercury | 2 | <0.2 |
| Nickel | 100 | <5 - 5.1 |
| Selenium | 50 | <10 |
| Silver | 100 | <5 |
| Thallium | 2 | <1 |
| Zinc | 5,000 | <20 - 69 |

Range of values because of the small background data set.

Selected naturally occurring background concentrations which exceed UIC Permit discharge.

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# Detections

## MW-2D

| Date | Event | | Aluminum | Antimony | Arsenic | Barium | Beryllium | Cadmium | Chromium | Copper | Iron | Lead | Manganese | Mercury | Nickel | Selenium | Silver | Thalium | Zinc |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12-Jan-12 | | N=1 | • | | | • | | | • | | • | | • | | • | | | | • |
| 15-Mar-12 | B | N=2 | | | | | | | | | | | | | | | | | |
| 19-Jul-12 | | N=3 | • | | | • | | | • | | • | • | • | | | | | | |
| 8-Nov-12 | | N=4 | • | | | | | | | | • | | | | | | | | |
| 15-Feb-13 | | N=5 | • | | | | | | | | • | | | | | | | | |
| 30-Apr-13 | | N=6 | • | | | | | | | | • | | | | | | | | |
| 7-Aug-13 | I | N=7 | • | | | | | | | | • | | | | | | | | |
| 20-Nov-13 | | N=8 | | | | | | | | | | | | | | | | | |
| 18-Feb-14 | | N=9 | • | | | | | | | | • | | | | | | | | |
| 7-May-14 | | N=10 | • | | | | | | | | • | | | | | | | | |
| 7-Aug-14 | | N=11 | • | | | | | | | | • | | | | | | | | |
| 19-Nov-14 | | N=12 | • | | | | | | | | • | | | | | | | | |
| 5-Feb-15 | | N=13 | • | | | | | | | | • | | | | | | | | |
| 6-May-15 | | N=14 | • | | | • | | | | | • | | | | | | | | |
| 5-Aug-15 | | N=15 | | | | | | | | | | | | | | | | | |
| 20-Nov-15 | P | N=16 | | | | | | | | | | | | | | | | | |
| 26-Feb-16 | | N=17 | • | | | | | | | | • | | | | | | | | |
| 3-May-16 | | N=18 | | | | | | | | | | | | | | | | | |
| 10-Aug-16 | | N=19 | • | | | | | | | | | | | | | | | | |
| 16-Nov-16 | | N=20 | | | | | | | | | | | | | | | | | |

Consistent Detections of Aluminum and Iron

## MW-2S

| Date | Event | | Aluminum | Antimony | Arsenic | Barium | Beryllium | Cadmium | Chromium | Copper | Iron | Lead | Manganese | Mercury | Nickel | Selenium | Silver | Thallium | Zinc |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12-Jan-12 | | N=1 | | | | • | | | | | • | | • | | | | | | |
| 15-Mar-12 | B | N=2 | | | | • | | | | | • | | • | | | | | | |
| 19-Jul-12 | | N=3 | | | | • | | | | | • | | • | | | | | | |
| 8-Nov-12 | | N=4 | | | | • | | | | | • | | • | | | | | | |
| 14-Feb-13 | | N=5 | | | | • | | | | | • | | • | | | | | | |
| 30-Apr-13 | | N=6 | | | | • | | | | | • | | • | | | | | | |
| 7-Aug-13 | I | N=7 | | | | • | | | | | • | | • | | | | | | |
| 20-Nov-13 | | N=8 | | | | • | | | | | • | | • | | | | | | |
| 18-Feb-14 | | N=9 | | | | • | | | | | • | | • | | | | | | |
| 7-May-14 | | N=10 | | | | • | | | | | • | | • | | | | | | |
| 6-Aug-14 | | N=11 | | | | • | | | | | • | | • | | | | | | |
| 19-Nov-14 | | N=12 | | | | • | | | | | • | | • | | | | | | |
| 5-Feb-15 | | N=13 | | | | • | | | | | • | | • | | | | | | |
| 6-May-15 | | N=14 | | | | • | | | | | • | | • | | | | | | |
| 5-Aug-15 | | N=15 | | | | • | | | | | | | • | | | | | | |
| 19-Nov-15 | P | N=16 | | | | • | | | | | • | | • | | | | | | |
| 25-Feb-16 | | N=17 | | | | | | | | | | | • | | | | | | |
| 3-May-16 | | N=18 | | | | • | | | | | • | | • | | | | | | |
| 10-Aug-16 | | N=19 | | | | • | | | | | • | | • | | | | | | |
| 16-Nov-16 | | N=20 | | | | • | | | | | • | | • | | | | | | |

Consistent Detections of Barium, Iron, and Manganese

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# Detections

## MW-1

| Date | Event | | Aluminum | Antimony | Arsenic | Barium | Beryllium | Cadmium | Chromium | Copper | Iron | Lead | Manganese | Mercury | Nickel | Selenium | Silver | Thallium | Zinc |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12-Jan-12 | | N=1 | | | | • | | | | | • | | • | | | | | | |
| 14-Mar-12 | B | N=2 | • | | | • | | | | | • | | • | | | | | | • |
| 19-Jul-12 | | N=3 | | | | • | | | | | • | | • | | | | | | |
| 7-Nov-12 | | N=4 | | | | • | | | | | • | | • | | | | | | |
| 13-Feb-13 | | N=5 | • | | | • | | | | | • | | • | | | | | | |
| 29-Apr-13 | | N=6 | | | | • | | | | | • | | • | | | | | | |
| 6-Aug-13 | I | N=7 | | | | • | | | | | • | | • | | | | | | |
| 19-Nov-13 | | N=8 | • | | | • | | | | | • | | • | | | | | | |
| 17-Feb-14 | | N=9 | | | | • | | | | | • | | • | | | | | | |
| 6-May-14 | | N=10 | | | | • | | | | | • | | • | | | | | | |
| 5-Aug-14 | | N=11 | | | | • | | | | | • | | • | | | | | | |
| 18-Nov-14 | | N=12 | | | | • | | | | | • | | • | | | | | | |
| 4-Feb-15 | | N=13 | | | | • | | | | | • | | • | | | | | | |
| 6-May-15 | | N=14 | | | | • | | | | | • | • | • | | | | | | |
| 4-Aug-15 | | N=15 | | | | • | | | | | • | | • | | | | | | |
| 17-Nov-15 | P | N=16 | | | | • | | | | | • | | • | | | | | | |
| 25-Feb-16 | | N=17 | | | | • | | | | | • | | • | | | | | | |
| 2-May-16 | | N=18 | | | | • | | | | | • | | • | | | | | | |
| 9-Aug-16 | | N=19 | | | | • | | | | | • | | • | | | | | | |
| 15-Nov-16 | | N=20 | | | | • | | | | | • | | • | | | | | | |

Consistent Detections of Barium, Iron, and Manganese

## Water Well

| Date | Event | | Aluminum | Antimony | Arsenic | Barium | Beryllium | Cadmium | Chromium | Copper | Iron | Lead | Manganese | Mercury | Nickel | Selenium | Silver | Thallium | Zinc |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11-Jan-12 | | N=1 | | | | • | | | | | • | | • | | | | | | |
| 15-Mar-12 | B | N=2 | | | | • | | | | • | • | • | • | | | | | | • |
| 19-Jul-12 | | N=3 | • | | | • | | | | | • | | • | | | | | | |
| 8-Nov-12 | | N=4 | • | | | • | | | | | • | | • | | | | | | |
| 14-Feb-13 | | N=5 | • | | | • | | | | | • | | • | | | | | | • |
| 30-Apr-13 | | N=6 | • | | | • | | | | | • | | • | | | | | | |
| 7-Aug-13 | I | N=7 | • | | | • | | | | | • | | | | | | | | |
| 20-Nov-13 | | N=8 | | | | • | | | | | • | | • | | | | | | |
| 18-Feb-14 | | N=9 | • | | | • | | | | | • | | • | | | | | | |
| 7-May-14 | | N=10 | | | | • | | | | | • | | • | | | | | | |
| 7-Aug-14 | | N=11 | | | | • | | | | | • | | • | | | | | | |
| 19-Nov-14 | | N=12 | | | | • | | | | | • | | • | | | | | | |
| 5-Feb-15 | | N=13 | | | | • | | | | | • | | • | | | | | | |
| 6-May-15 | | N=14 | | | | • | | | | | • | | • | | | | | | |
| 5-Aug-15 | | N=15 | | | | • | | | | | • | | • | | | | | | |
| 19-Nov-15 | P | N=16 | | | | • | | | | | • | | • | | | | | | |
| 25-Feb-16 | | N=17 | | | | • | | | | | • | | • | | | | | | |
| 3-May-16 | | N=18 | | | | • | | | | | • | | • | | | | | | |
| 10-Aug-16 | | N=19 | | | | • | | | | | • | | • | | | | | | |
| 16-Nov-16 | | N=20 | | | | • | | | | | • | | • | | | | | | • |

Consistent Detections of Barium, Iron, and Manganese

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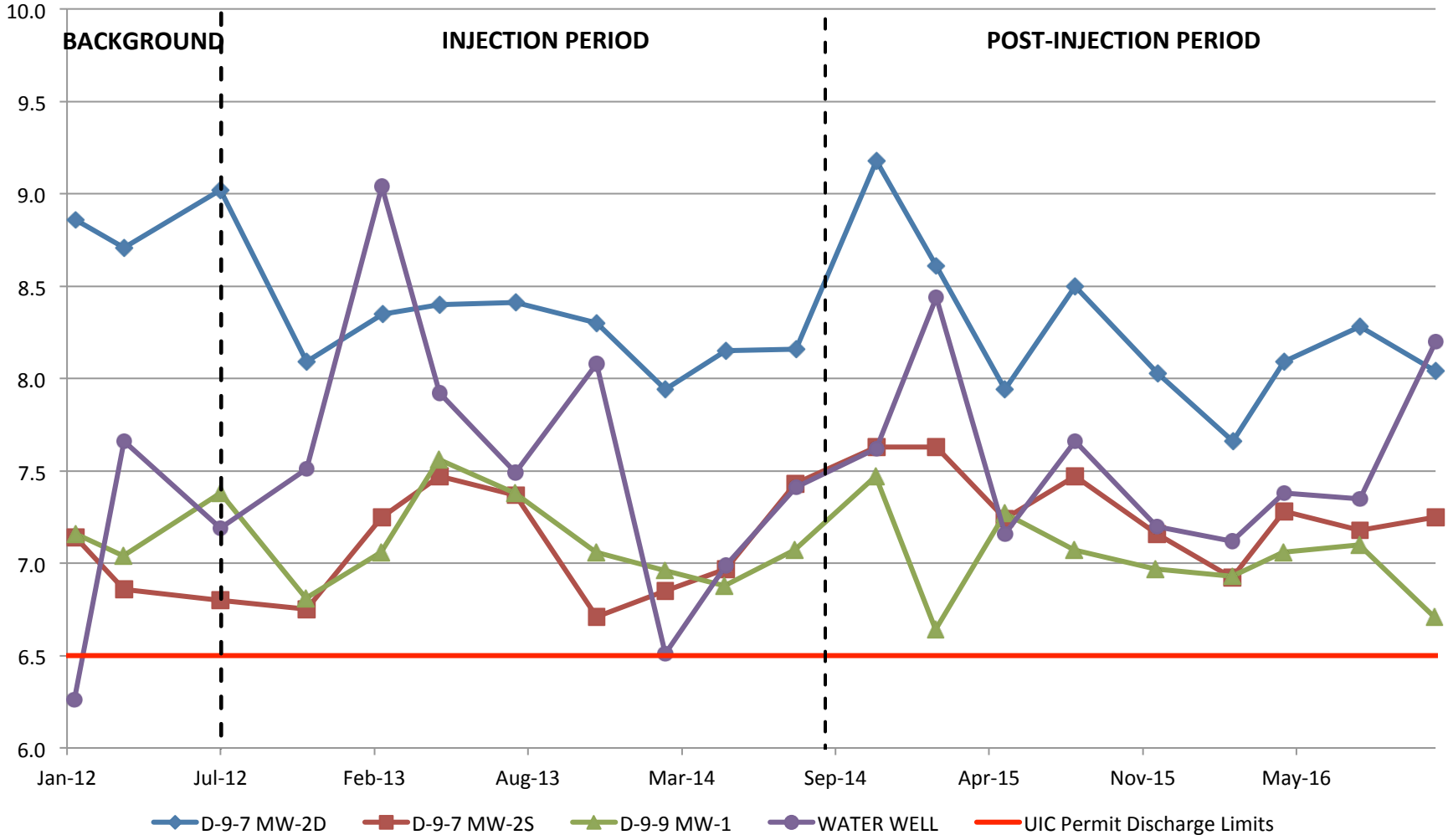
# pH

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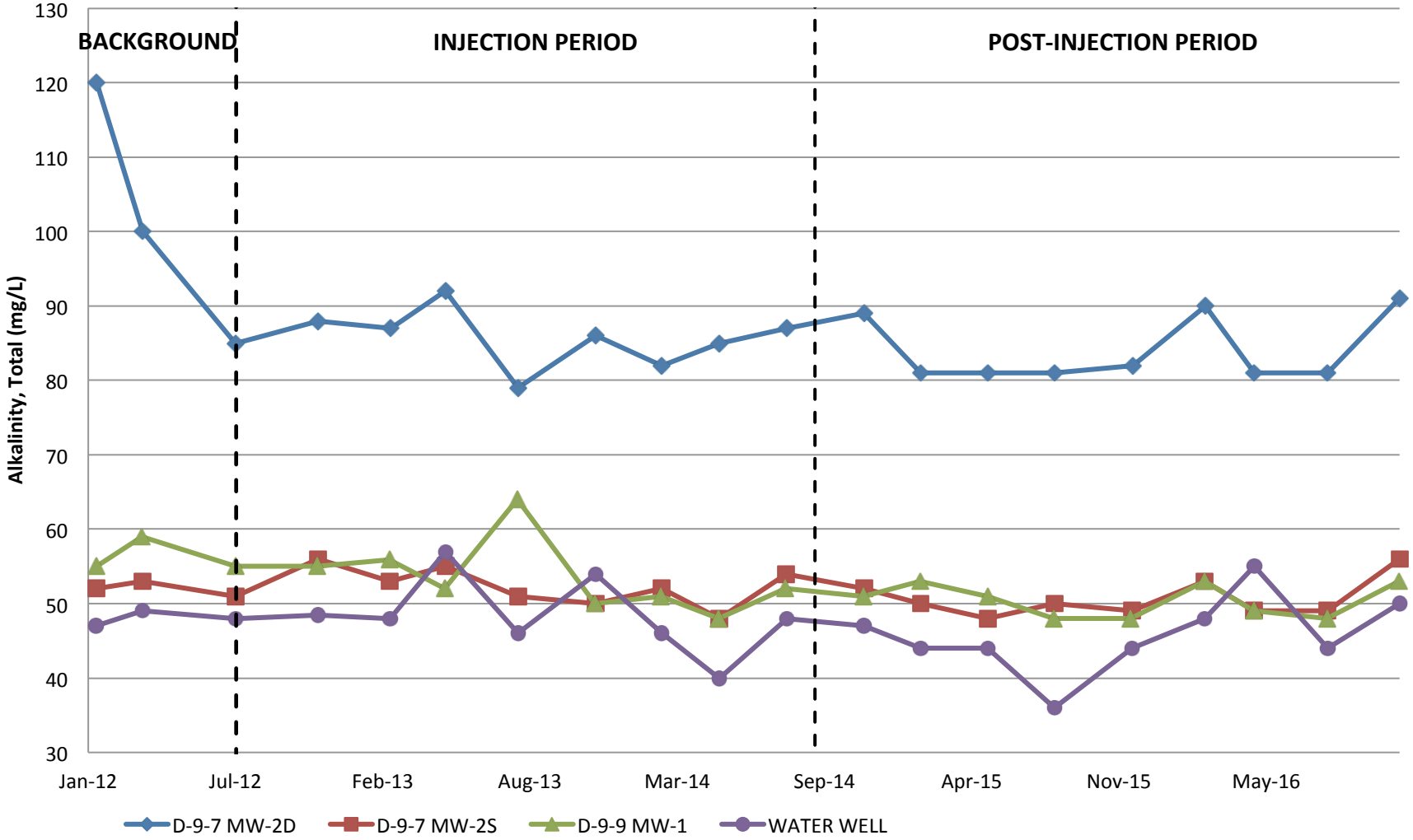
# ALKALINITY

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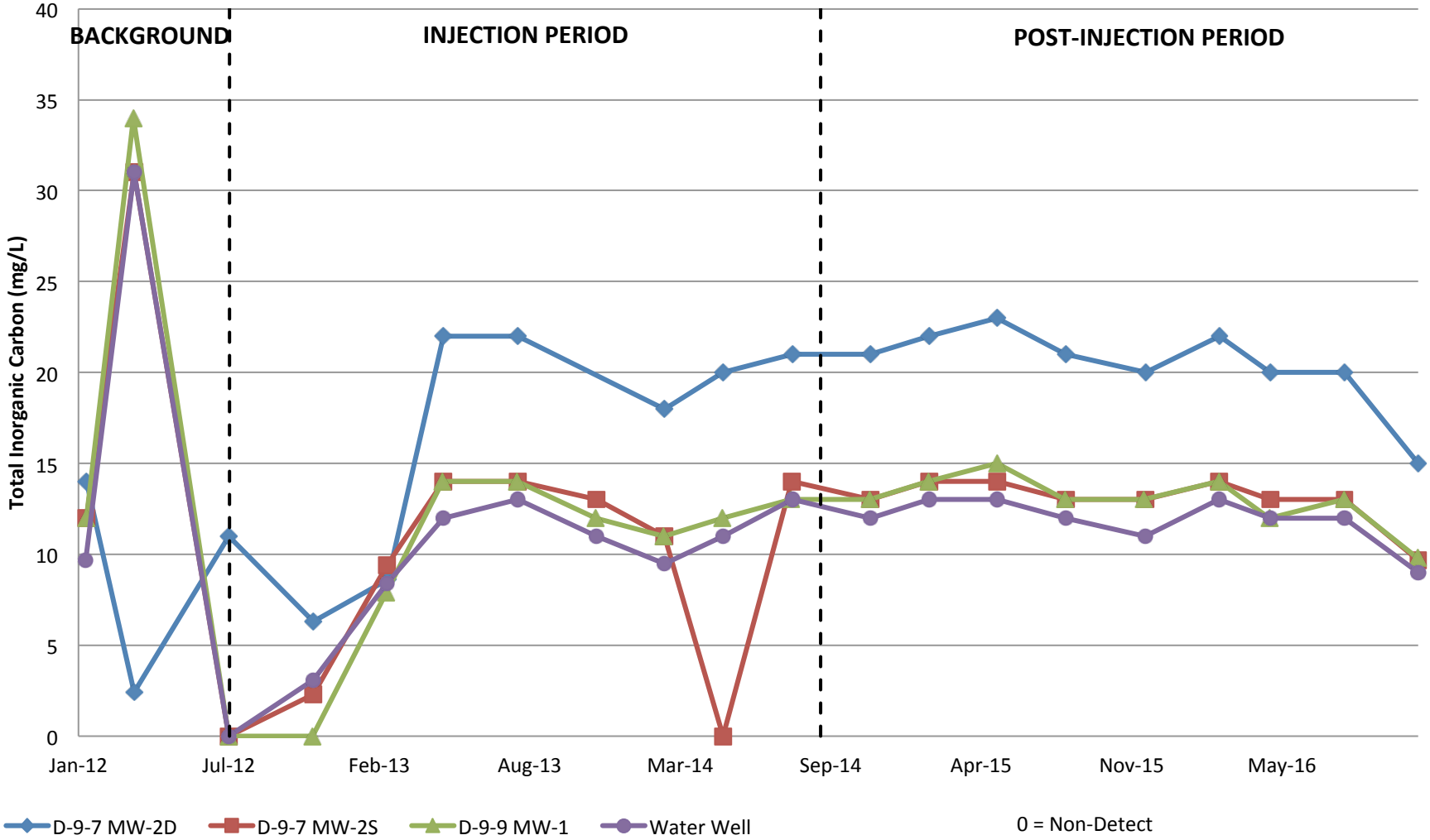
# TOTAL INORGANIC CARBON

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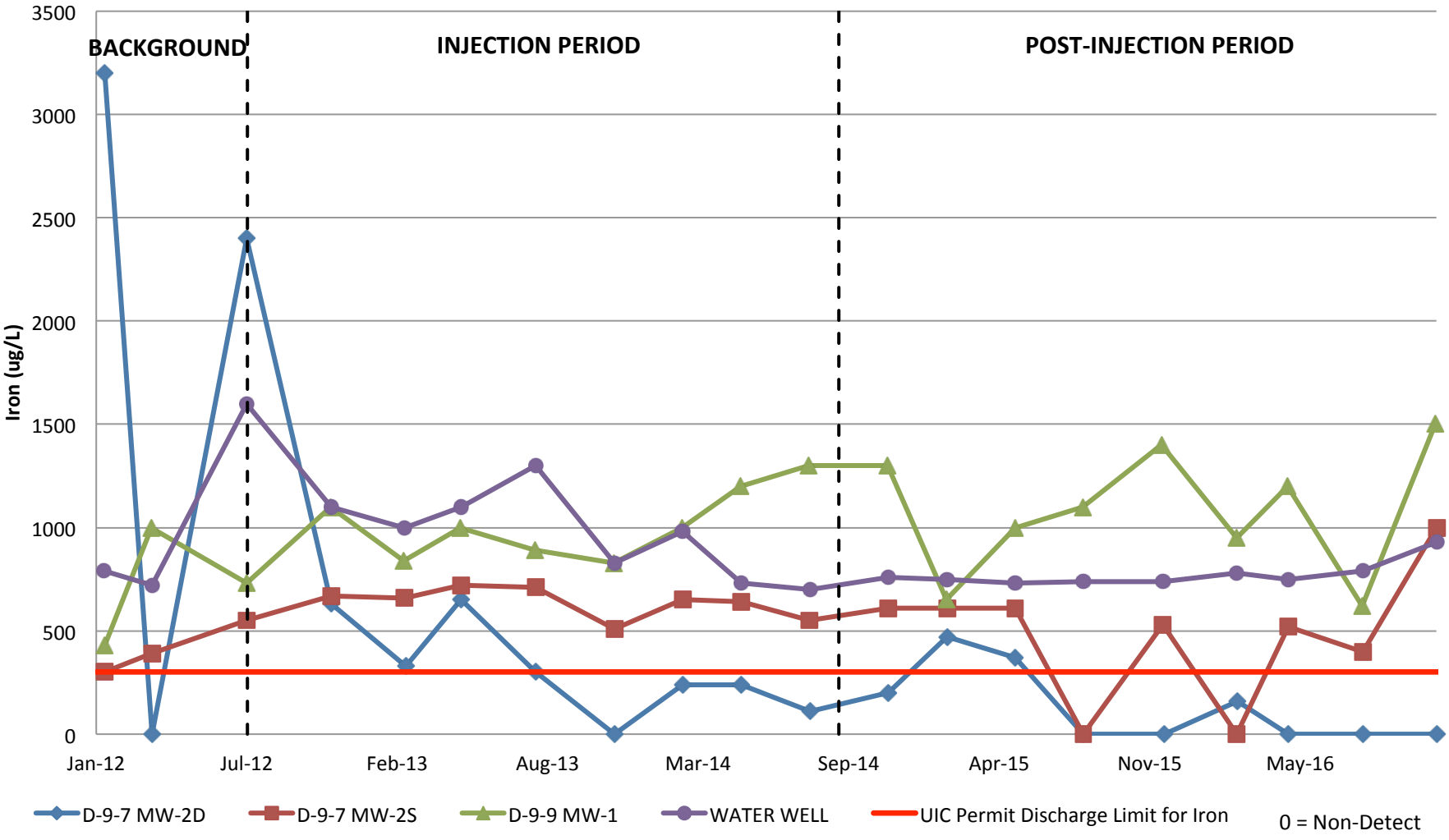
# Iron

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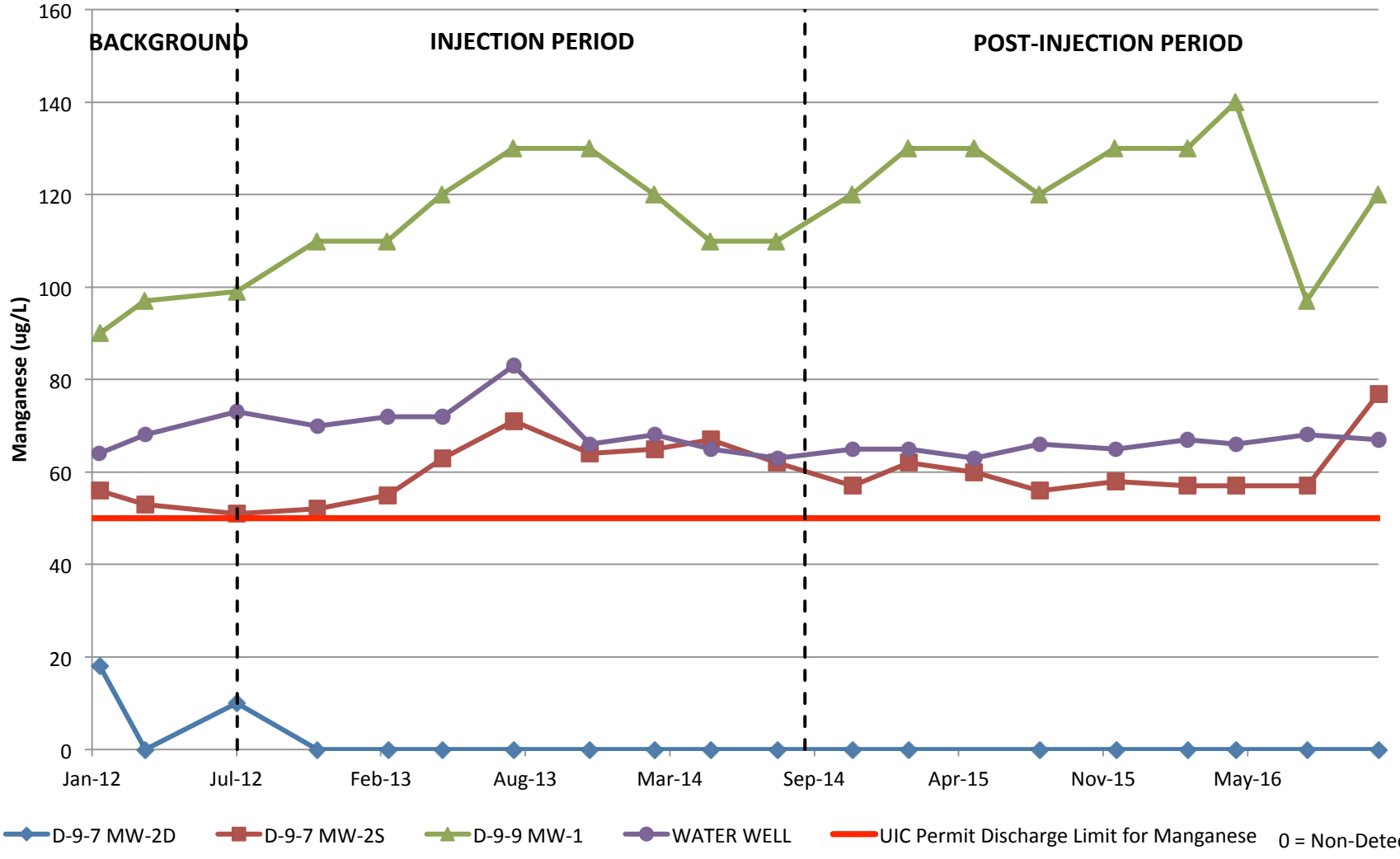
# Manganese

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# Statistical Approach

- Three analytical approaches to the data set:
  - Confidence Limits to Compare to UIC Discharge Limits: determines if a detection exceeding the UIC permit discharge limit and the range of background concertation is statistically significant
  - Evaluate Statistically Significant increases or decreases for concentrations above laboratory reporting limits, per SAP
  - Mann-Kendall Trend Determination: determines if a statistically significant upward or downward trend exist.
- EPA's *Unified Guidance* for statistics referenced / utilized

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# Summary of Statistical Evaluation Results

- The latest data is evaluated to determine which analytes required statistical analysis.
- "Value to value" comparisons show some exceedances of the UIC Permit values.
- The SAP statistical analyses show statistically significant changes for some the parameters (eg. metals, pH and TIC).
- Mann-Kendall trend analysis show a statistically trend for some parameters
- Similar results for the statistical evaluations for injection and post-injection

# Summary

- Research suggests the most likely indicators for $CO_2$ influence are (Wilkin and Diguilio, 2010) :
  - Decrease in pH
  - Increased Alkalinity
  - Dissolved Inorganic Carbon Increase
  - Dissolved Metals (i.e., Fe/Mn) Increase
- Multiple lines of evidence are warranted for conclusions;  Aqueous geochemistry is a complex system
- Individual potential indicators for $CO_2$ influence are noted in quarterly reports
- Currently, monitoring and reporting of results continues
- Stakeholder input is encouraged for this important project
- ADEM evaluation and discussion is encouraged

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# Summary of Statistical Evaluation Results

- Results from N=20 event show statistically significant trends for pH and iron (purple shading), however recent events have been within background range.
- Several lines of evidence for the influence of carbon dioxide at the monitoring wells were absent during the N=20 sampling event (blue shading).



**Statistically Determined Potential Lines of Evidence for Carbon Dioxide Influence**

| Monitoring Well | Decrease in pH | Increase in TIC | Increase in Alkalinity | Increase in Metals Concentrations |
|---|---|---|---|---|
| D-9-7 MW-2D | Yes | No | No | No |
| D-9-7 MW-2S | No | No | No | No |
| D-9-9 MW-1 | No | No | No | Fe |
| Water Supply Well | No | No | No | No |

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# Closing

Questions and Comments?

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THANK YOU

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