GOLDER

July 4th Fireworks as an Unconventional Source of Groundwater Contamination

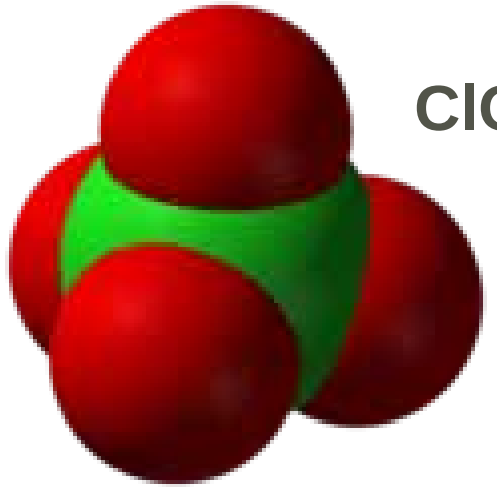
Unreacted Perchlorate survives the show to impact groundwater

Joel Henry & Alyssa Olson

October 17, 2019

GOALS

Perchlorate is an excess reagent in fireworks.



Perchlorate Ion ClO_4^-

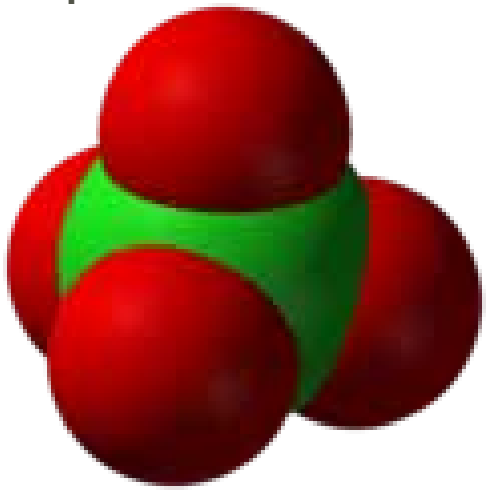
1) How much perchlorate survives?

2) What is the fate of unreacted perchlorate?

3) Fireworks, and other “one-time” events, need to be considered in Wellhead Protection Planning

AGENDA

ClO_4^-



Perchlorate Ion

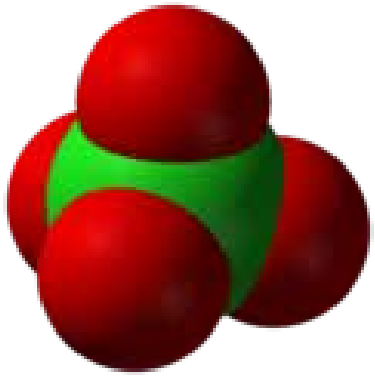
Perchlorate Refresher

Literature – Perchlorate & Fireworks

Evart Case Study

Conclusions

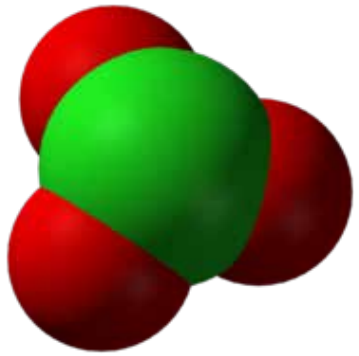
Chloro-Oxyanions



ClO_4^-

Perchlorate

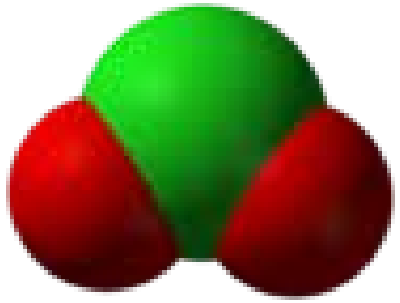
Cl^{+7}



ClO_3^-

Chlorate

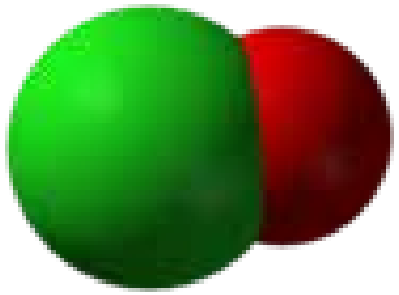
Cl^{+5}



ClO_2^-

Chlorite

Cl^{+3}



ClO^-

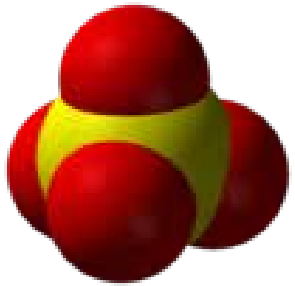
Hypochlorite

Cl^{+1}

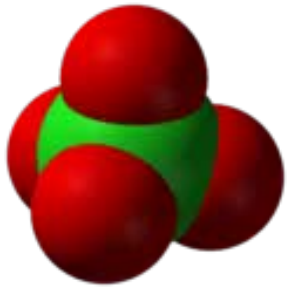
Decreasing oxidation state of chloride ion

Tetrahedral Oxyanions

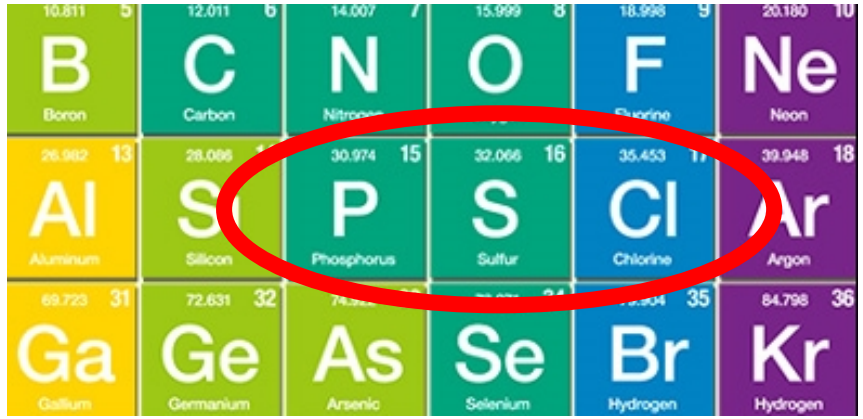
Phosphate – PO_4^{-3}



Sulfate – SO_4^{-2}



Perchlorate – ClO_4^-



- **HIGHLY SOLUBLE**
- Naturally-occurring
- Perchlorate is not nearly as abundant or biologically-active

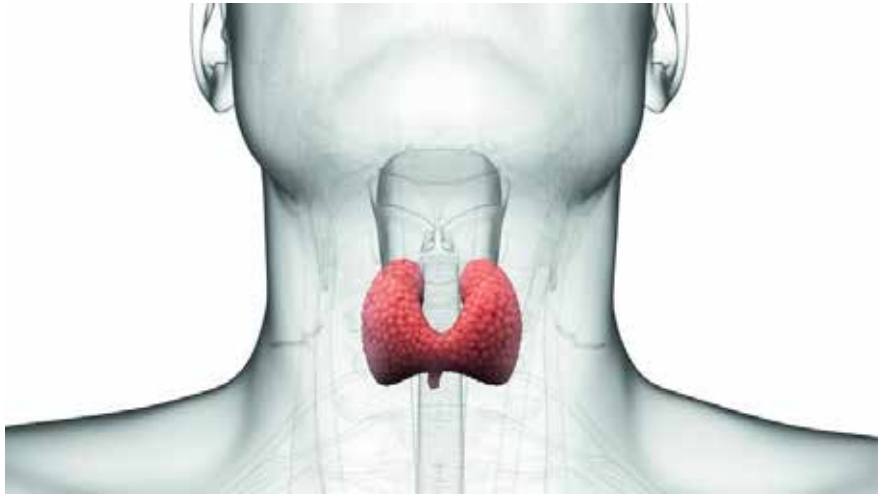
Regulatory – Drinking Water

- 56 µg/L - US EPA Drinking Water Criteria (proposed)
- 15 µg/L - US EPA Drinking Water Health Advisory Benchmark (non-enforceable)
- 6 µg/L - California
- 2 µg/L – Massachusetts
- 1 µg/L – California (Public Health Goal)
- Unregulated in Michigan

Health Effects

THYROID GLAND

- Iodide Uptake Inhibitor
- Substitutes for iodine in thyroid
  - Slows thyroid function
  - Disrupt hormones needed for normal growth
- Women and children most at risk



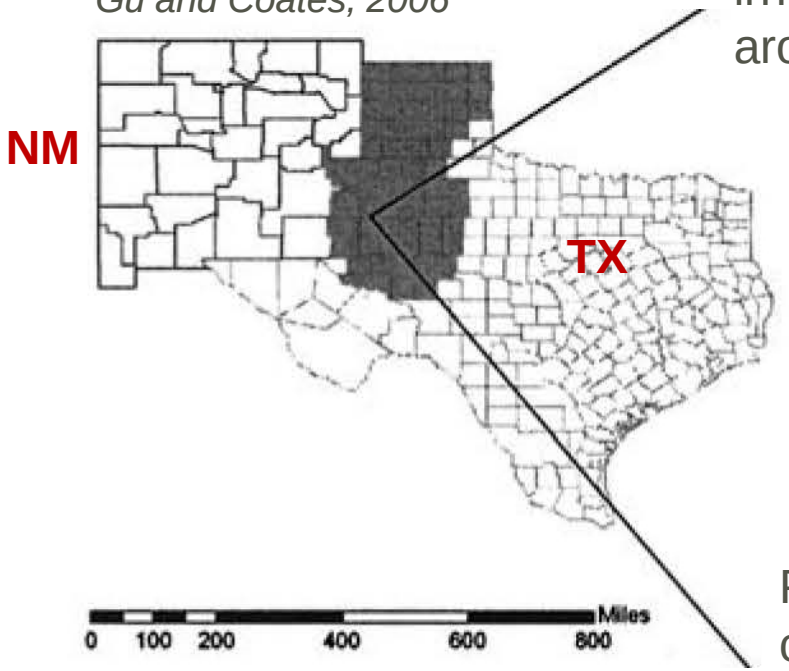
Natural Sources

- Lightning – O_3 + Cl^- à perchlorate

Michigan precipitation:
0.1 µg/L

- Accumulates in desert soils:
  - Chile – Atacama desert
  - Death Valley
  - West Texas / Eastern New Mexico

Gu and Coates, 2006



~60-county highly-irrigated area around Lubbock, TX

Perchlorate concentrations 1-20 ug/L or higher in groundwater

“Unnatural” Sources

- Aerospace / Military (90%)
- Sodium Hypochlorite Solution (~10 ppm)
- Imported Chilean fertilizer
- **Fireworks**
  - **0 to 70% perchlorate**

Solid rocket boosters
about 70% NH_3ClO_4

Literature: Fireworks and Rain

Long Island, NY

- Baseline concentration **~0.1** µg/L
- Peak concentration of **2.5** µg/L
- Peaks immediately after July 4, multiple locations

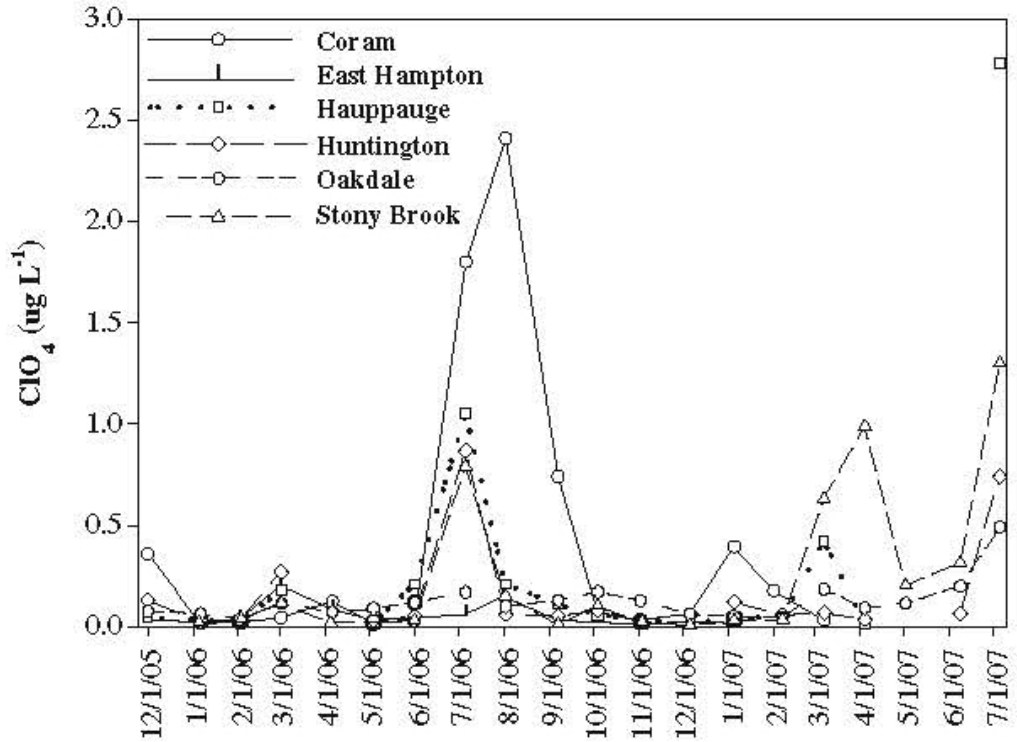


Fig. 2 Monthly perchlorate concentrations for total deposition samples. Collection at Coram was discontinued after March 2007 and discontinued at East Hampton after January 2007

Munster et al. 2008 (Water Air Soil Pollut v.198, 1, 149)

Literature: Fireworks and Groundwater

UMass-Dartmouth, 2007

- **10 years** of fireworks from same location
- **30-60 µg/L** in groundwater at shallow wells adjacent to launch area

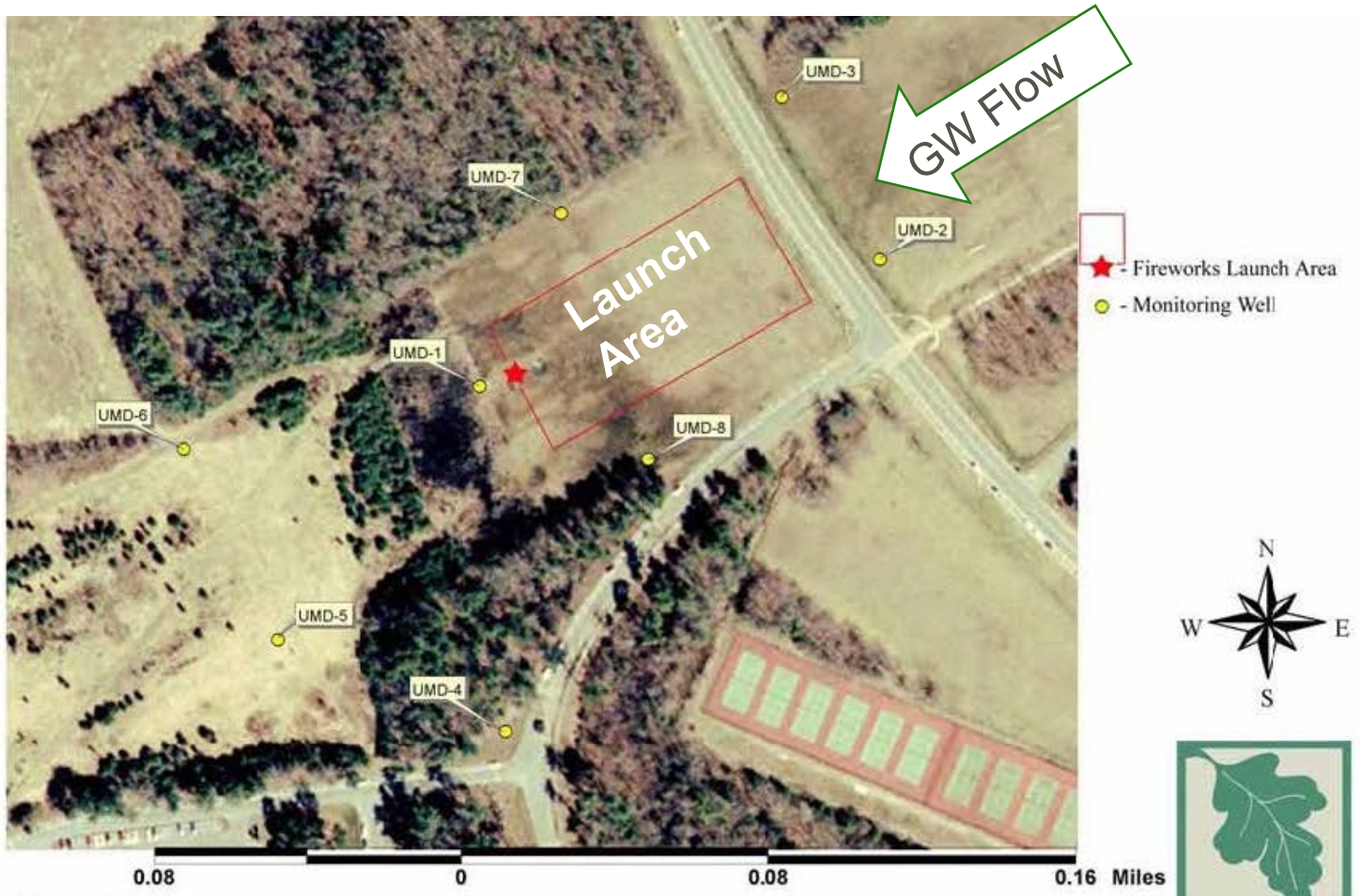
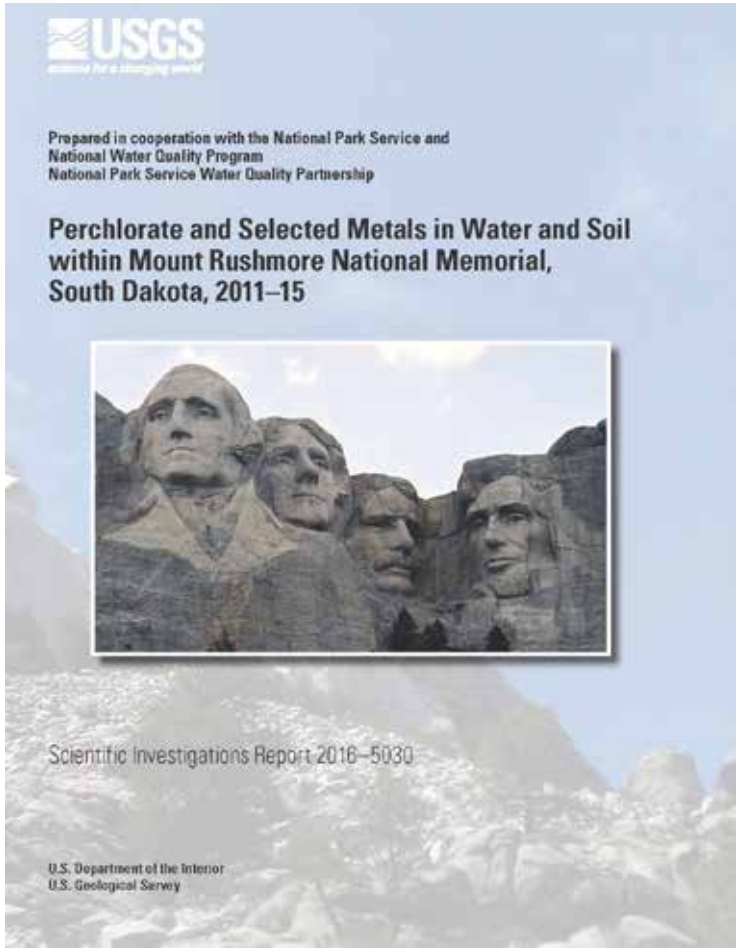


Figure 2
University of Massachusetts Dartmouth Campus
Perchlorate Study Area
Monitoring Well Locations

Literature: Fireworks and Water Supply

Mount Rushmore

- Up to **38 µg/L** in GW samples (200-500 ft wells)
- Up to **54 µg/L** in SW samples (intermittent streams)
- Attributed to fireworks launched annually from above/behind monument



USGS Scientific Investigations Report 2016-5030

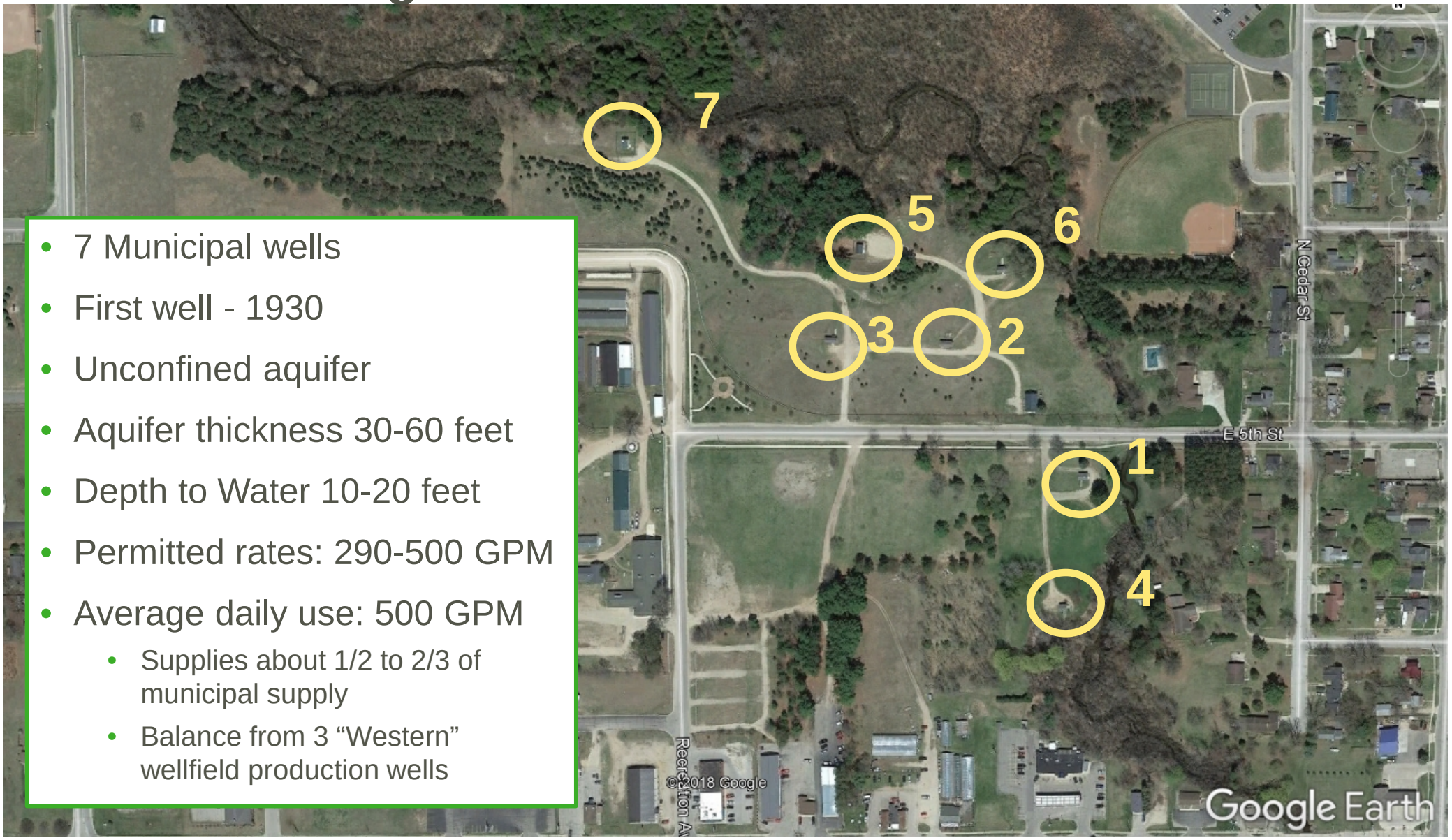
Unanswered Questions

Mass released varies by:

- Type of fireworks (0-70% perchlorate)
- Mass/number of fireworks in a show
- Environmental variables
  - Temperature, humidity, wind speed and direction
- Transport mechanisms
  - Paper wrappers; dust; vapors

Setting – Evart, Michigan

Setting - *Twin Creek Wellfield* – Evart MI



- 7 Municipal wells
- First well - 1930
- Unconfined aquifer
- Aquifer thickness 30-60 feet
- Depth to Water 10-20 feet
- Permitted rates: 290-500 GPM
- Average daily use: 500 GPM
  - Supplies about 1/2 to 2/3 of municipal supply
  - Balance from 3 “Western” wellfield production wells

Setting – *Groundwater Flow Directions*

Winter 2014 – Spring 2015

Remedial Actions

Purge perchlorate out through existing production wells

- ✓ Three wells offline - highest concentrations – greatest mass flux
- ✓ One well to sanitary sewer
- ✓ NPDES permit, WET testing
- ✓ Two wells to surface water
- ✓ Move as much production as possible to Western wellfield (2 wells)
- ✓ Start constructing new 3rd well in Western wellfield
- ✓ **MOVE NEXT YEAR'S FIREWORKS!!!**

Monitor, monitor, monitor

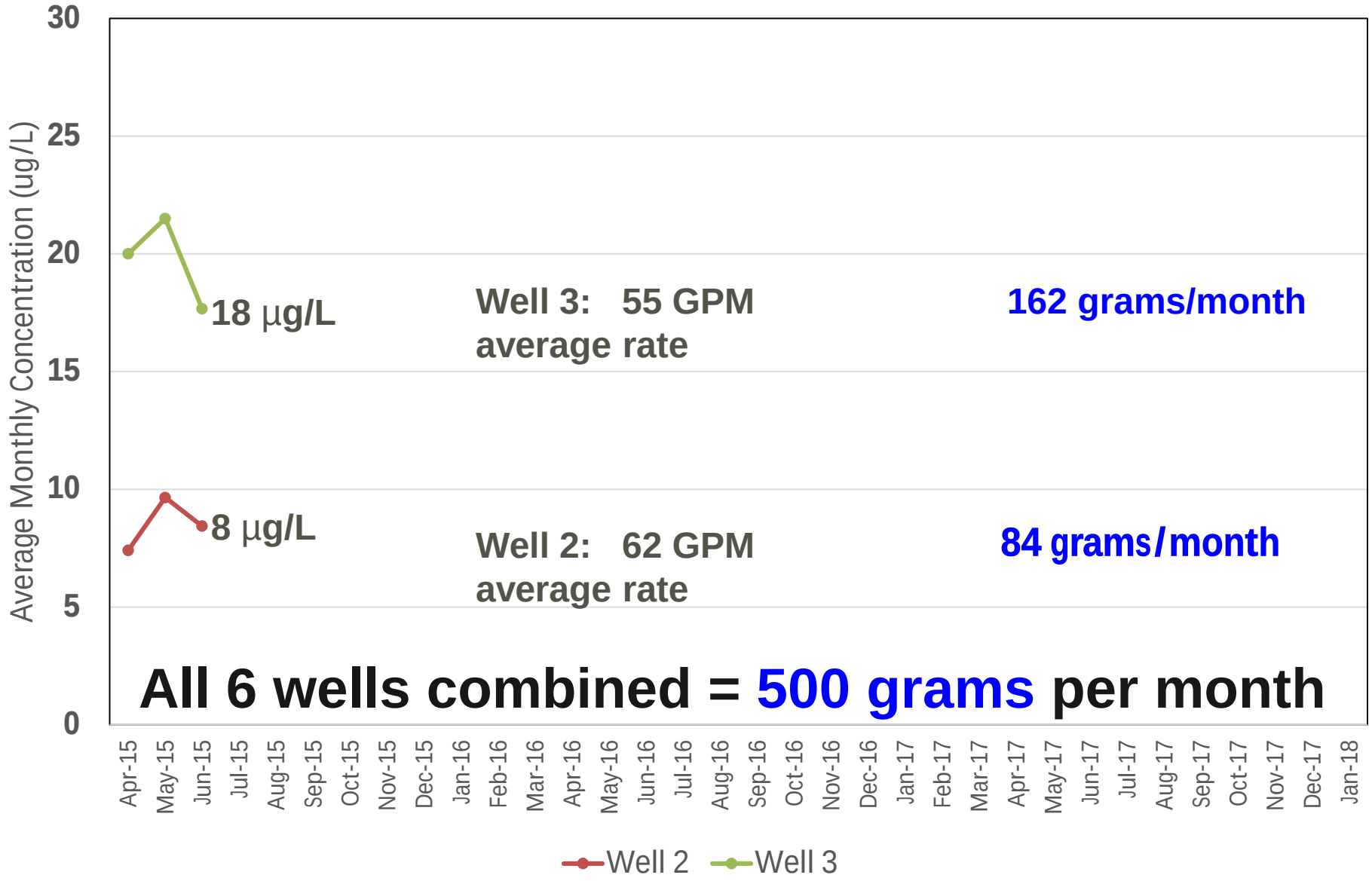
- ✓ Bi-weekly sampling of all production wells
- ✓ Monthly average ClO_4 x monthly pumping volume = mass flux

Monitoring

- Every 2 weeks – Sample municipal wells and water towers
- Obtain monthly pumping records from City
- Calculate monthly **mass flux**

Concentration of perchlorate (m/v) X Withdrawal rate of production wells (v/t) = Flux of perchlorate (m/t)

3 Months (June 2015)



Possible Sources

What accounts for a pound of perchlorate each month?

Hypochlorite Solution

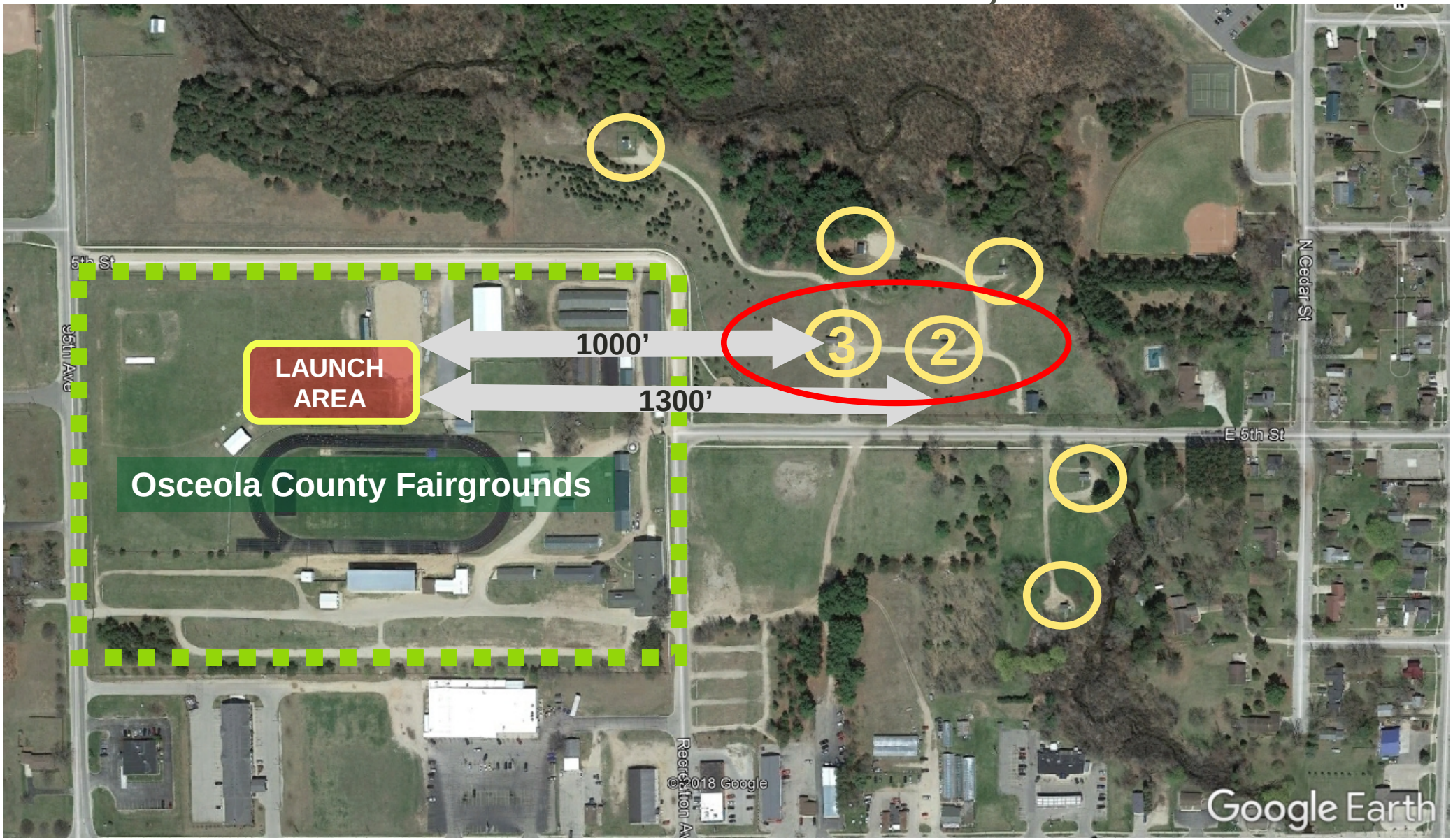
- By-product of manufacturing, age
- 14 mg/L (14,000 µg/L)

1 pound/month of perchlorate would require 155 drums

Roads; dust control brines, flares

Bleach / Cleaning Products at Fairgrounds

Twin Creek Wellfield – Evart, MI



June 2015 – What we didn’t know

- Were perchlorate concentrations rising or falling in groundwater?
- How high would concentrations go, and for how long?
- How much perchlorate was in the aquifer, or in the unsaturated soils?
- How much per show?
- Where and how was the perchlorate deposited – wind dispersal, unreacted powder, used wrappers, launch area?

June 2015 – What we did know

- Sandy glacial outwash
- High recharge rates (12-16 in/yr)
- Groundwater velocity ~3 ft/day
- Removing ~1 pound per month
- Assuming that fireworks are the primary source of perchlorate
- Another fireworks show coming up on **July 4, 2015**

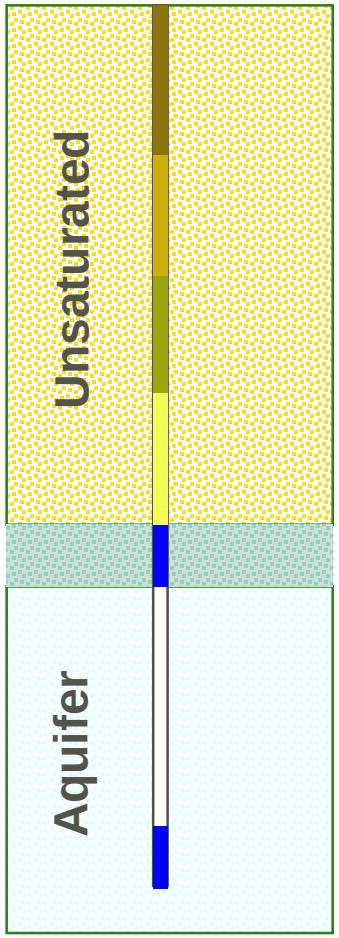
July 4, 2015

- Warm, humid, light breeze
- Half-hour of fireworks
- July 5, 2015 – picked up wrappers & litter

Rain Events

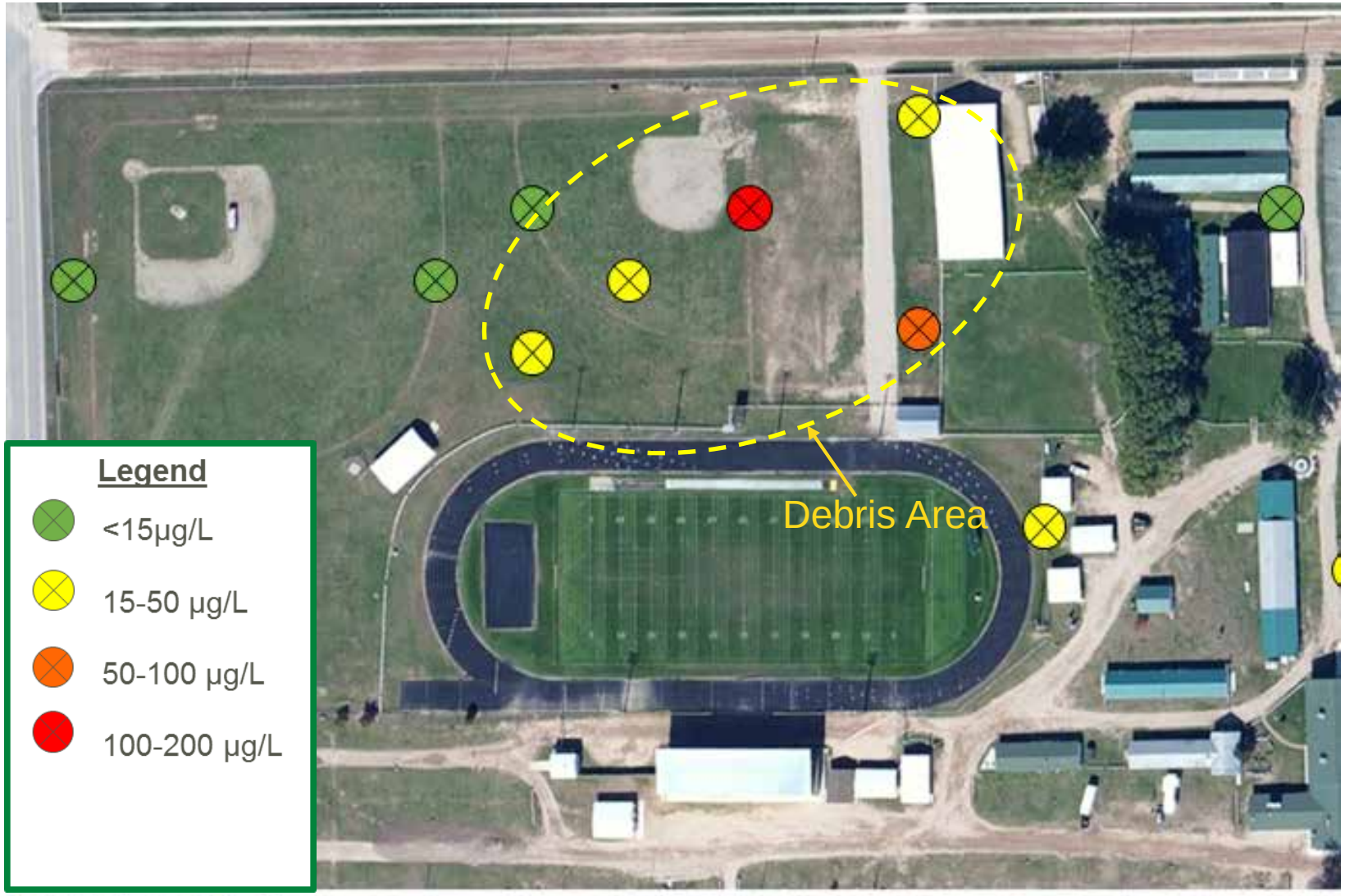
- July 7 – 0.5 inch of rain
- July 14 – 0.5 inch of rain
- Aug 3 - 1.5 inches of rain

Source Area Investigation



3-4 soil samples per boring

1-2 water samples per boring



Source Area Results- November 2015

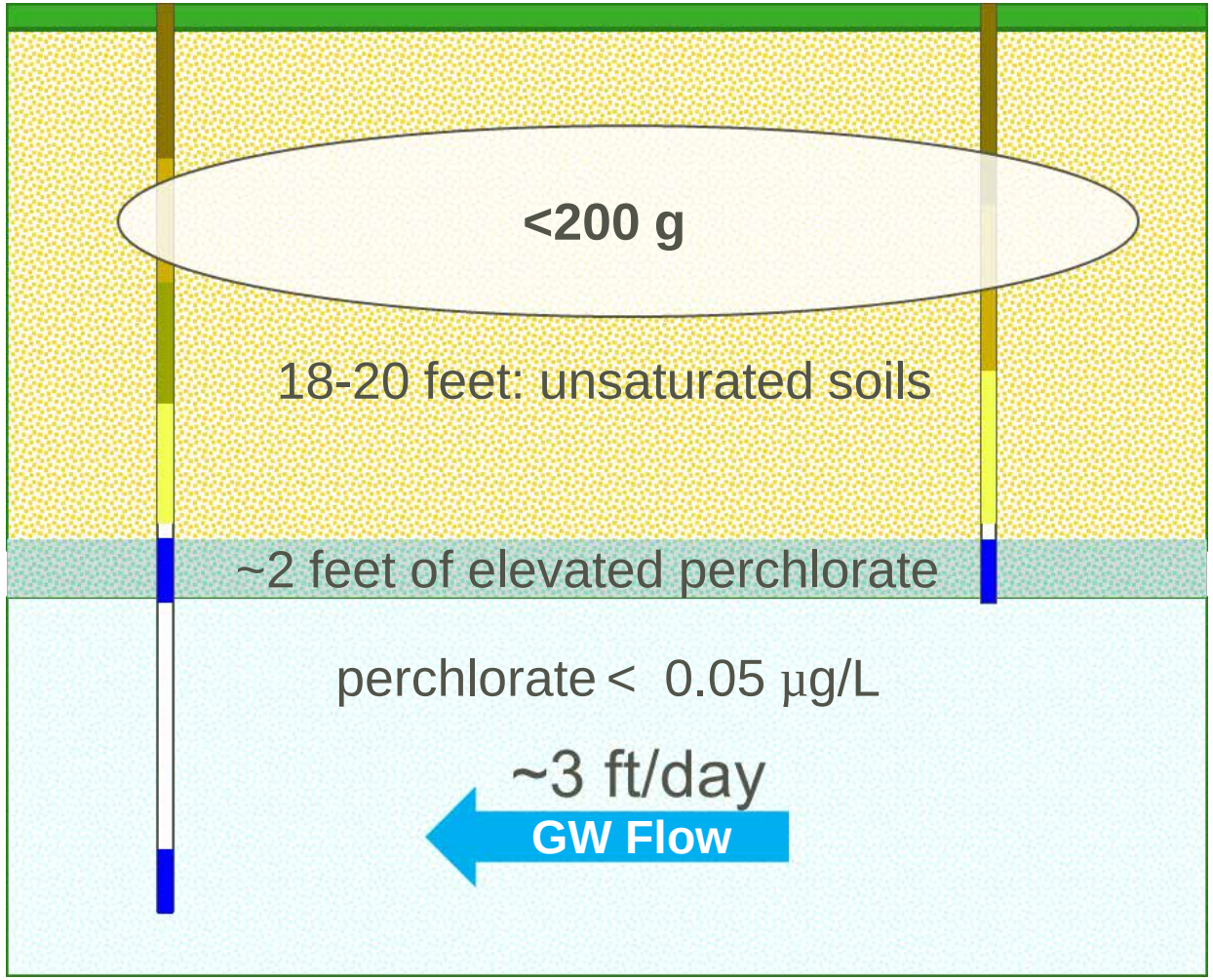
SOILS

- Less than ½ pound perchlorate

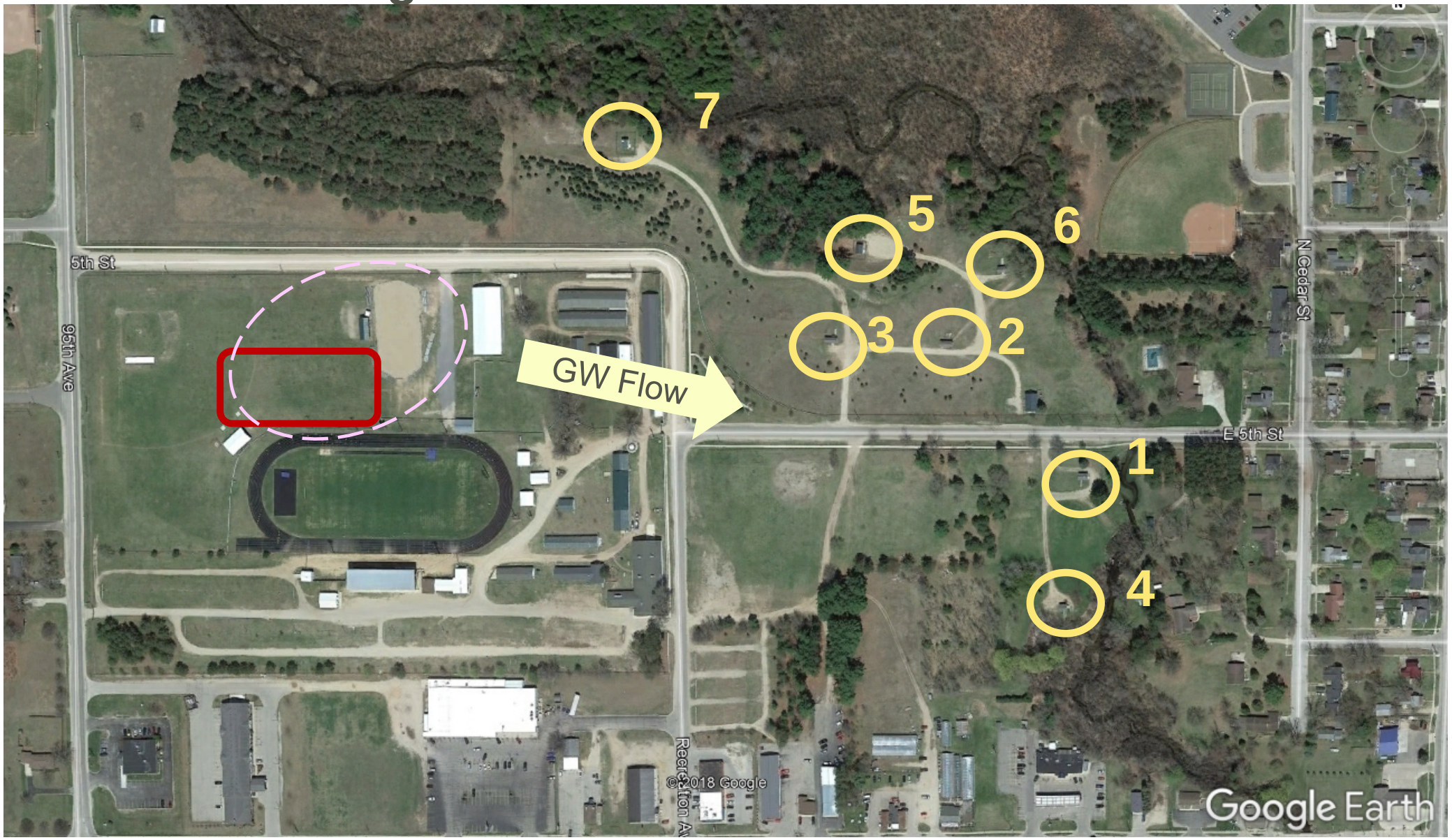
WATER

Highest concentrations were at water table

- Maximum: 240 µg/L
- <0.05 µg/L within a few feet of the water table



Setting - *Twin Creek Wellfield* – Evart MI



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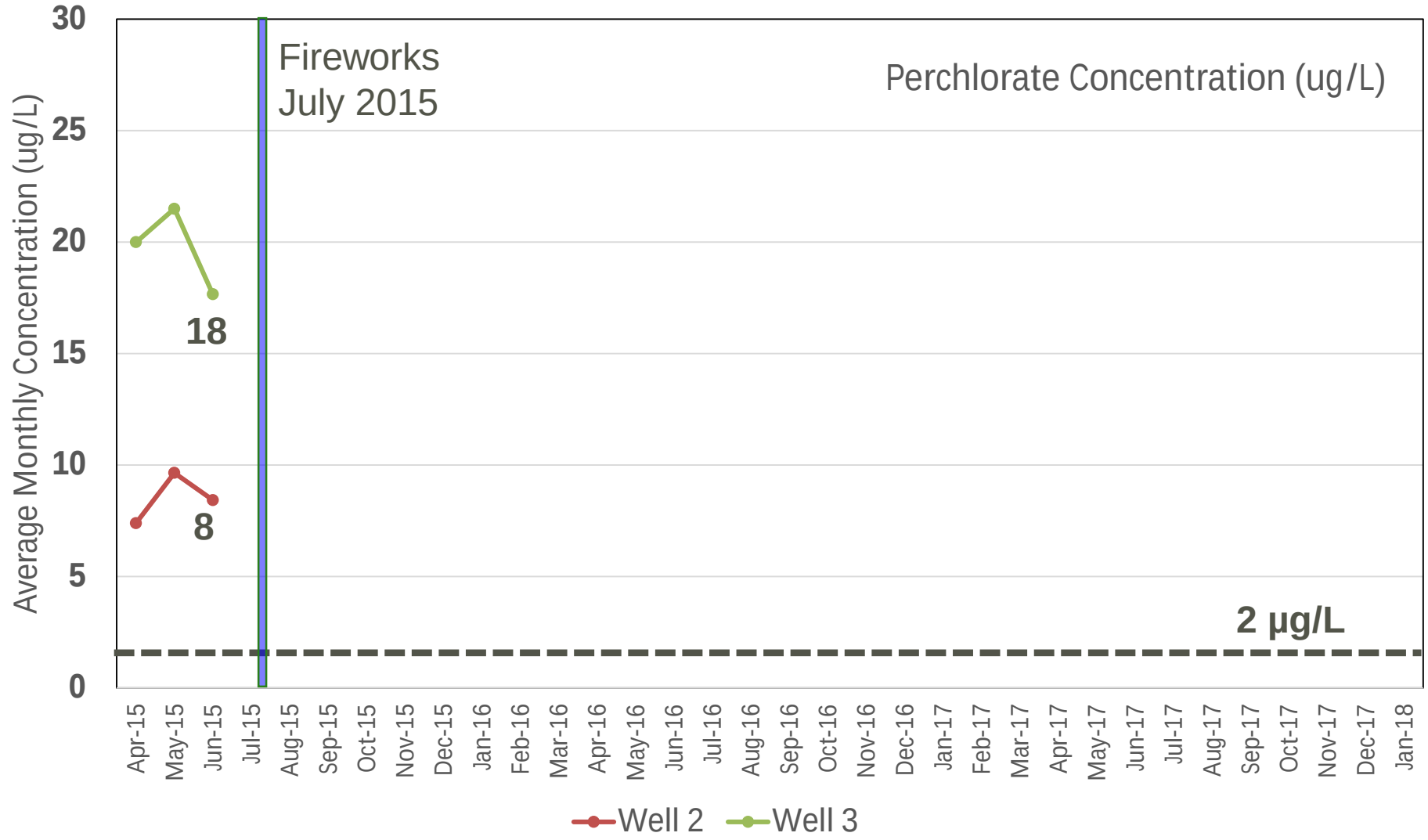
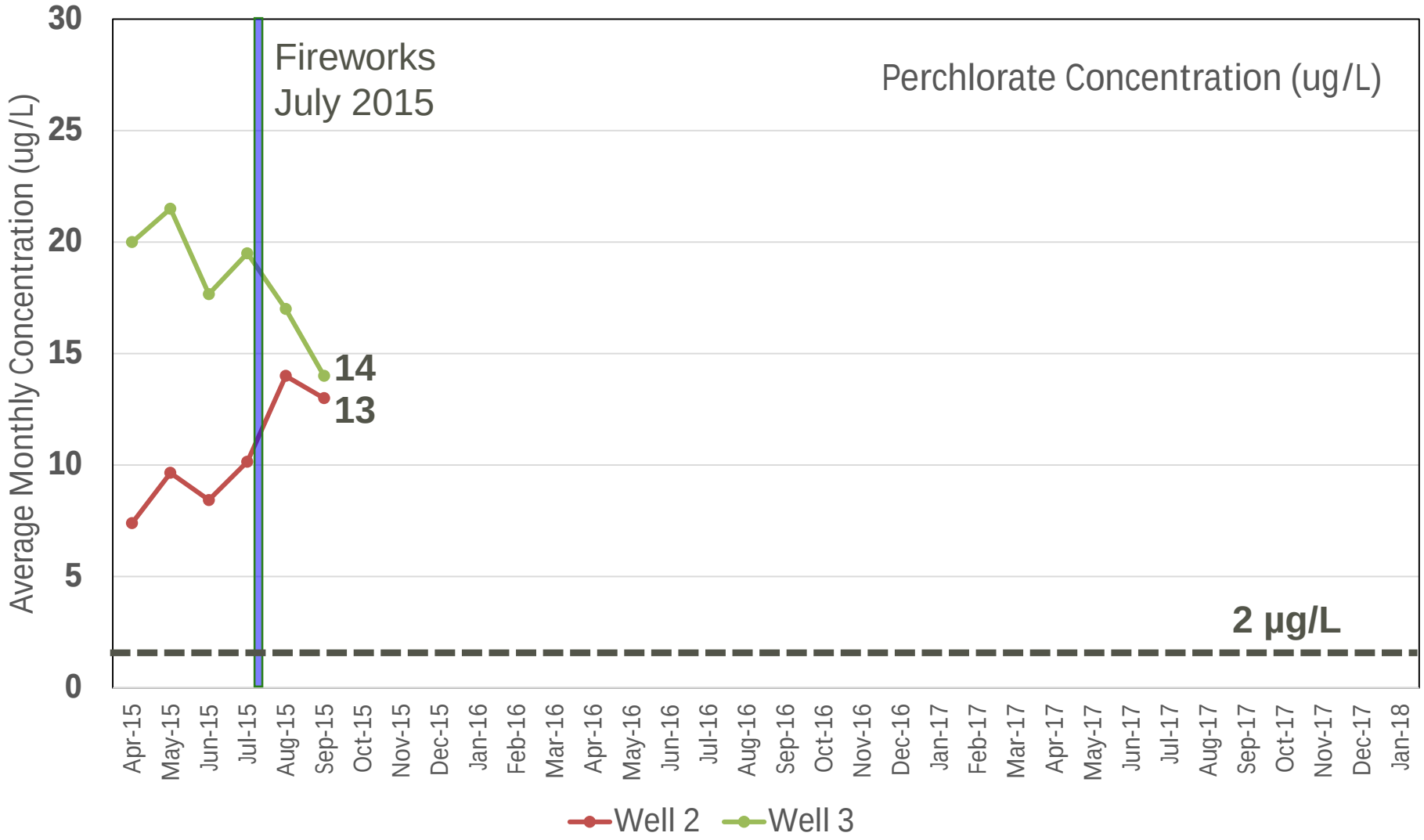
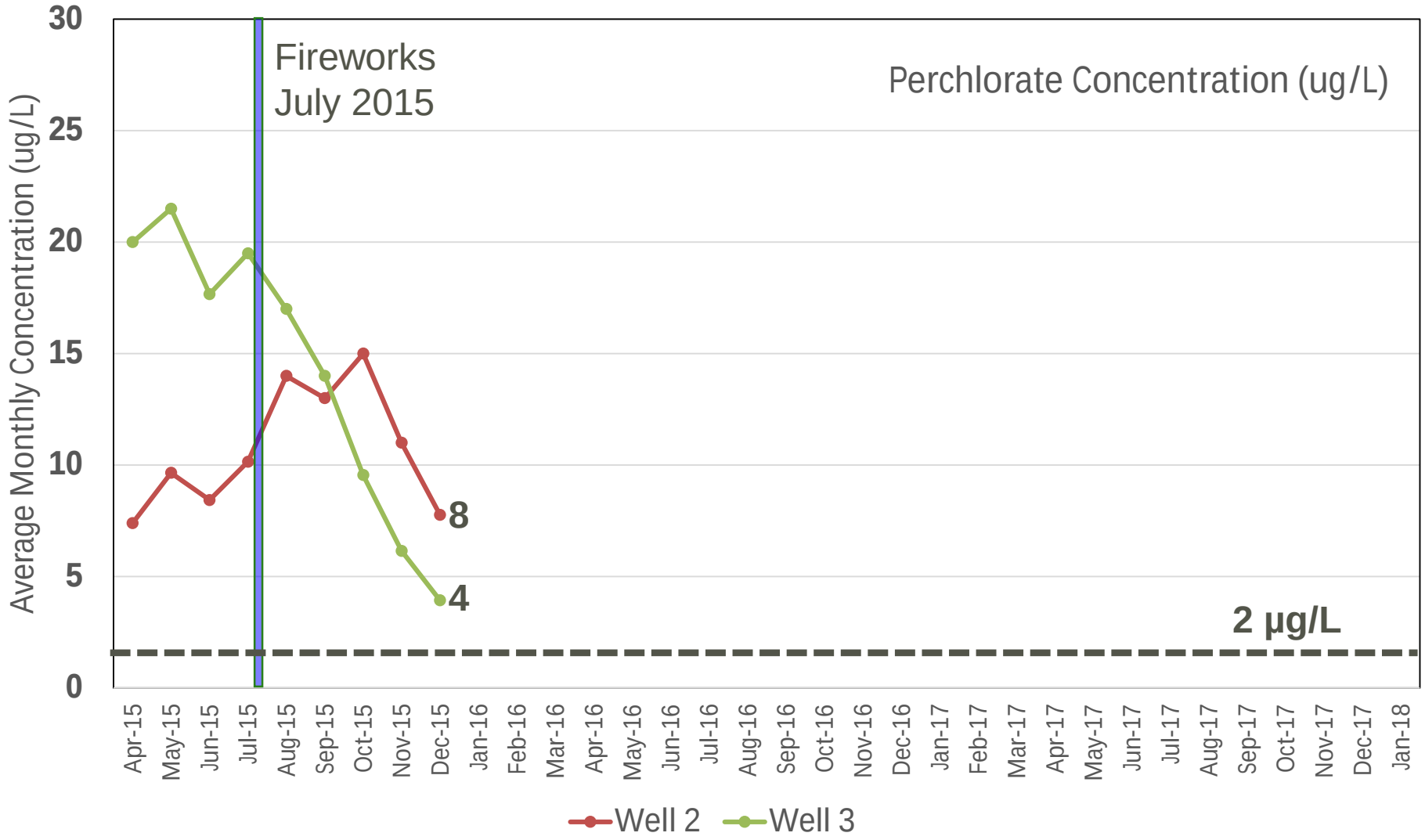


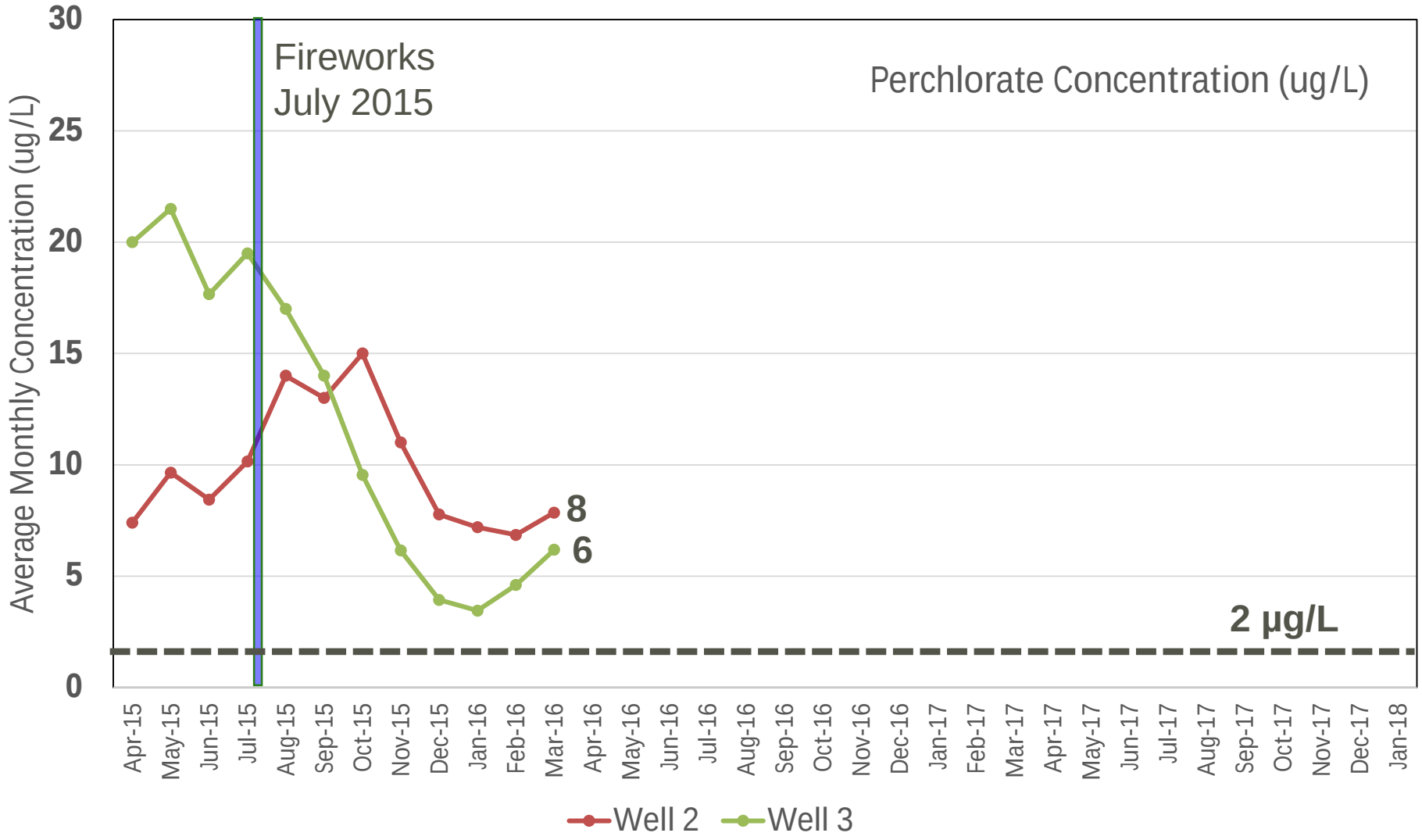
6 Months (September 2015)



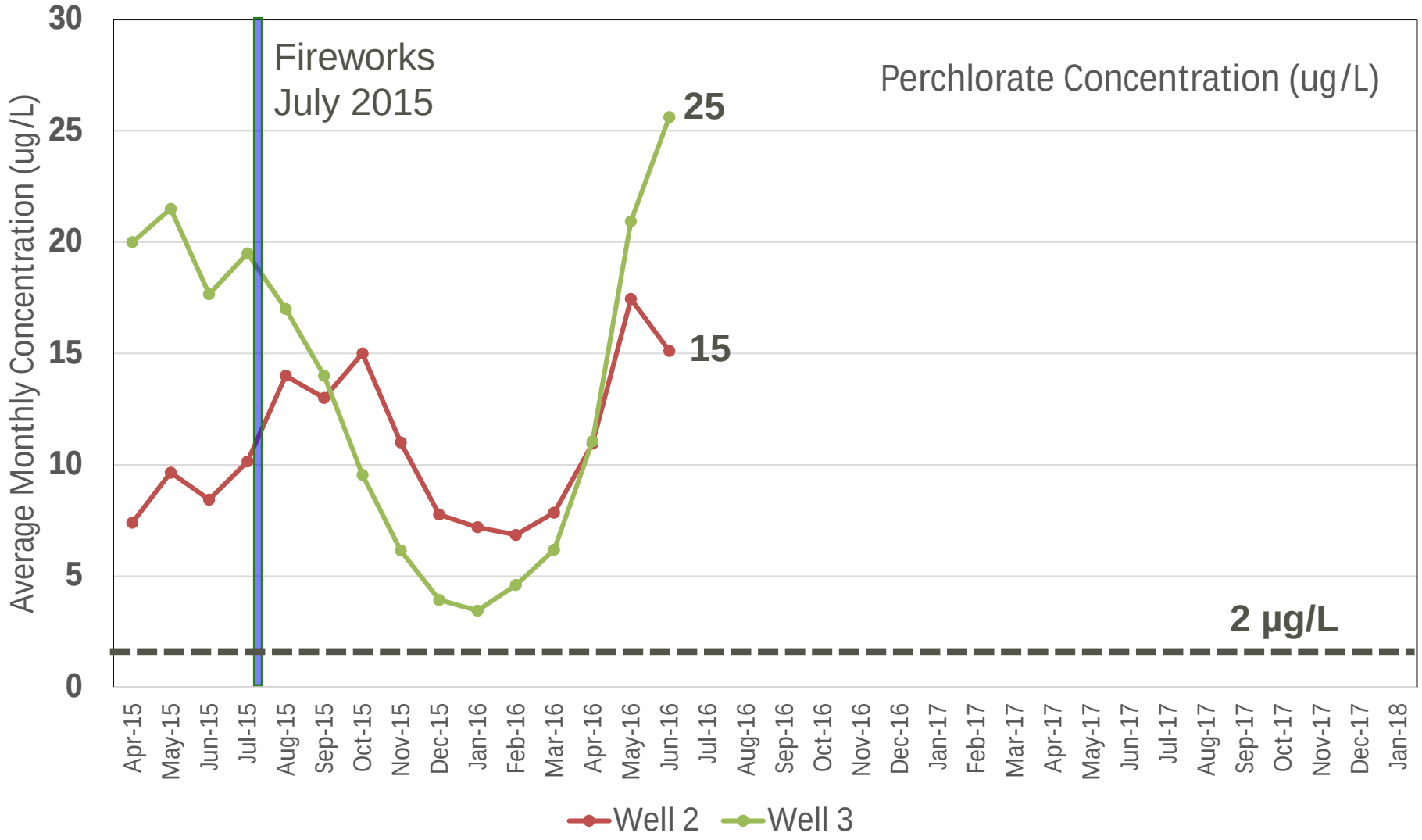
9 Months (December 2015)



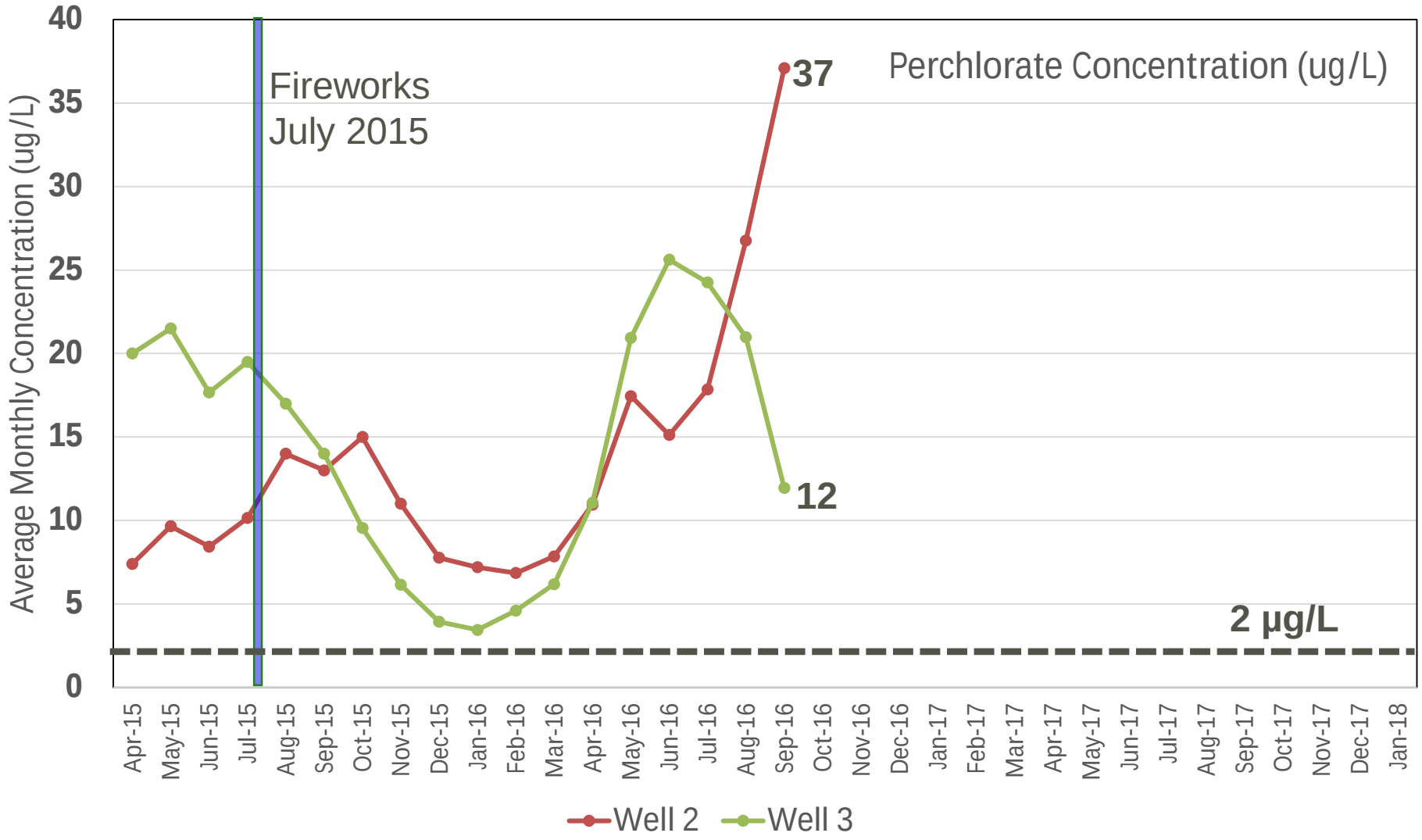
12 Months (March 2016)



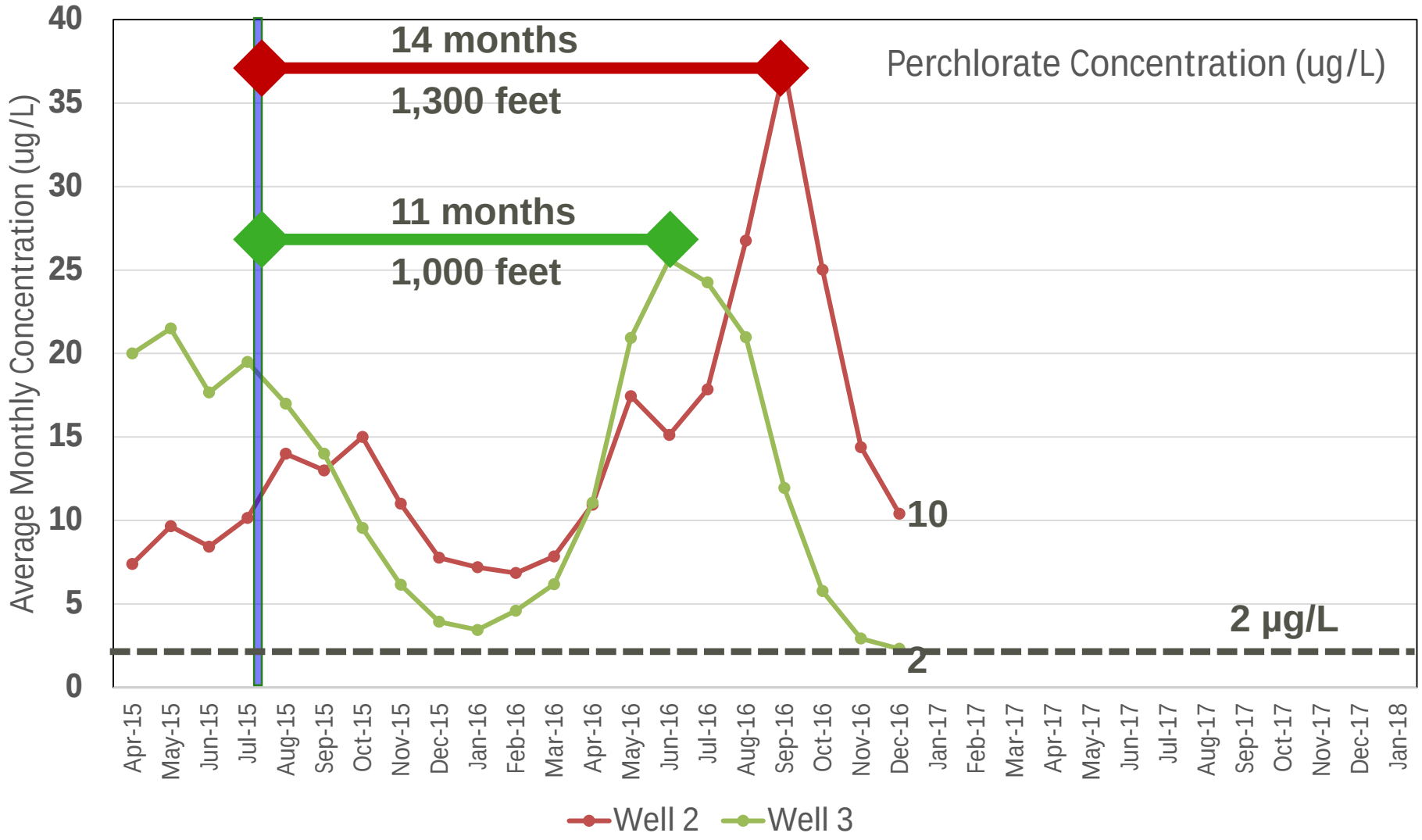
15 Months (June 2016)



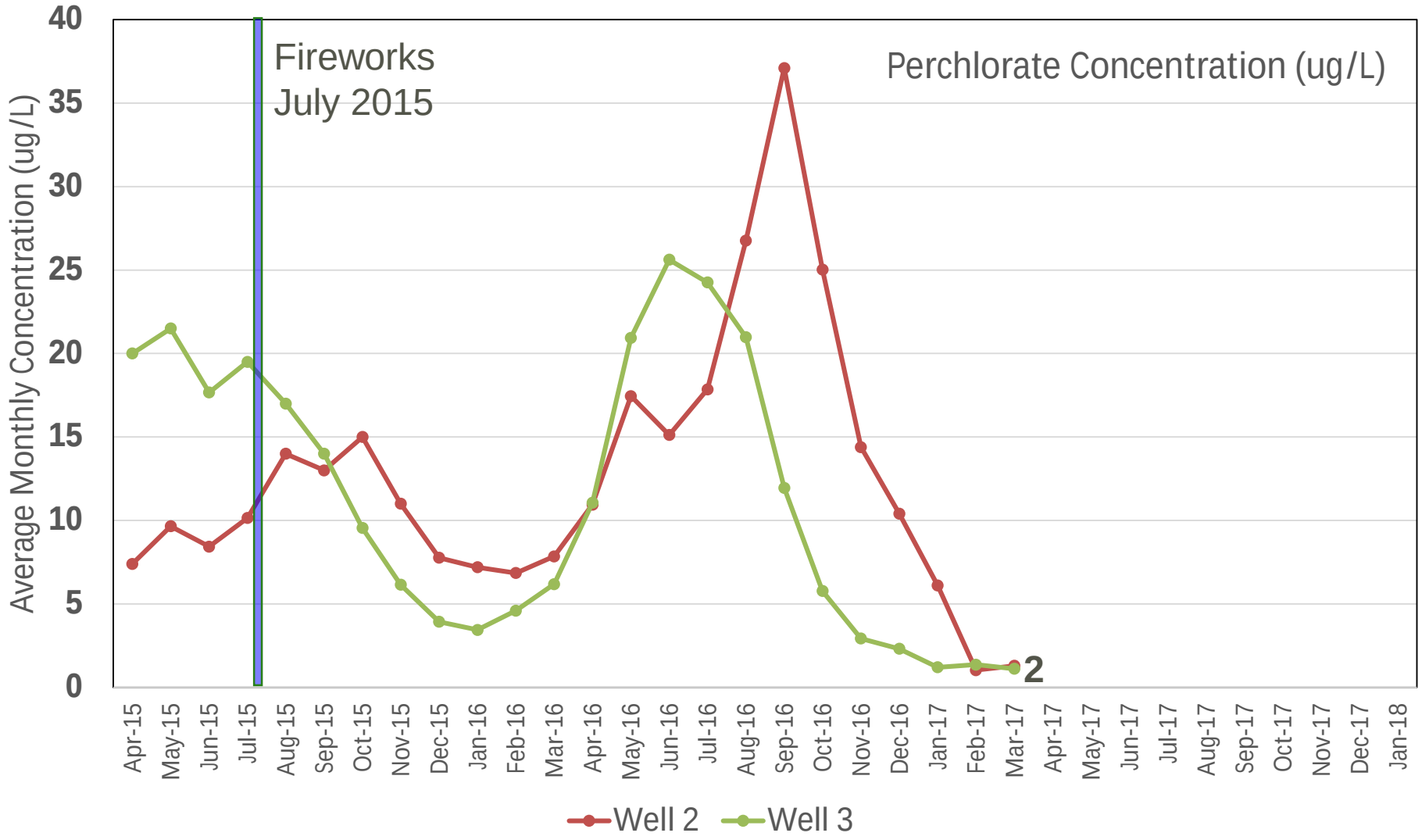
18 Months (September 2016)



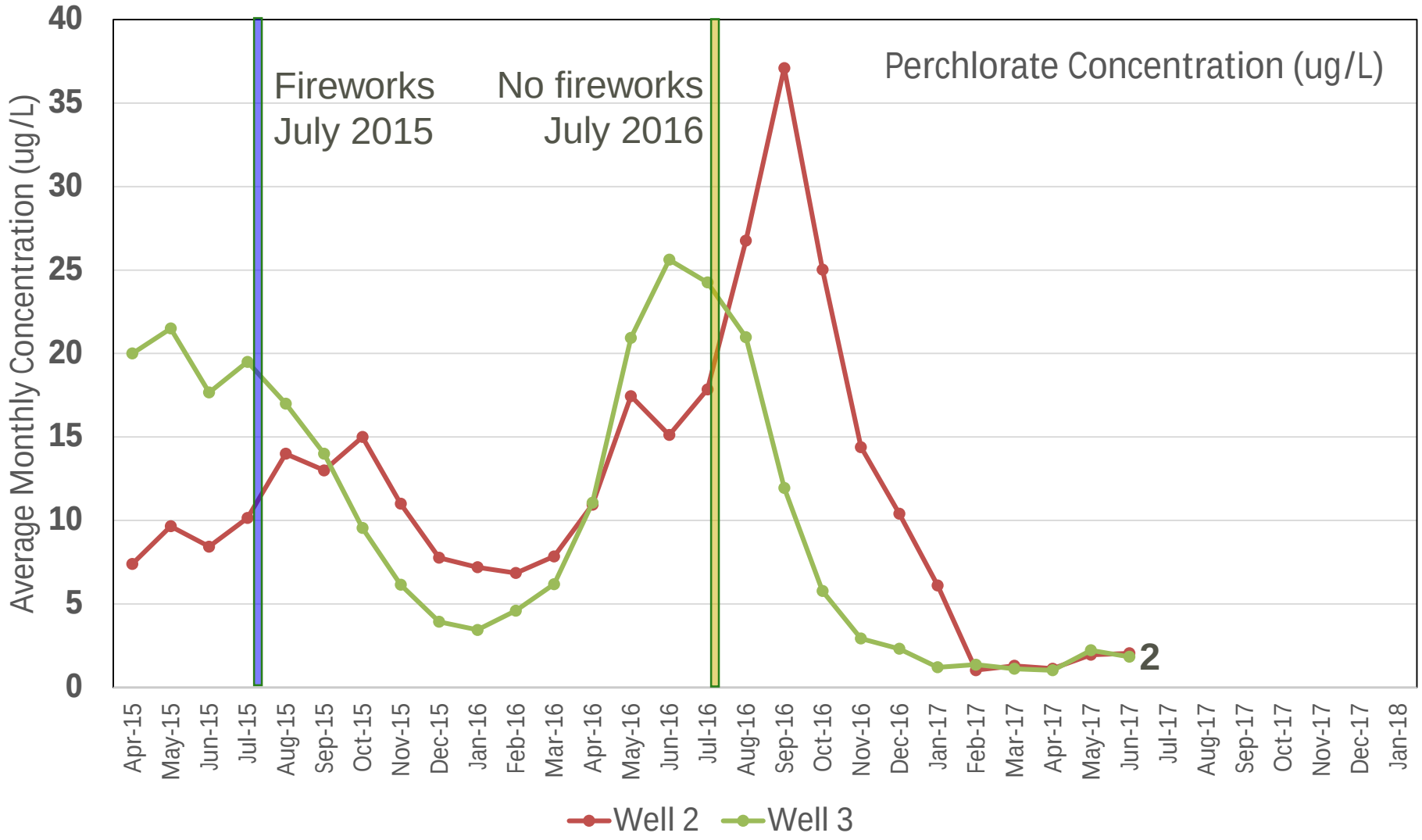
21 Months (December 2016)



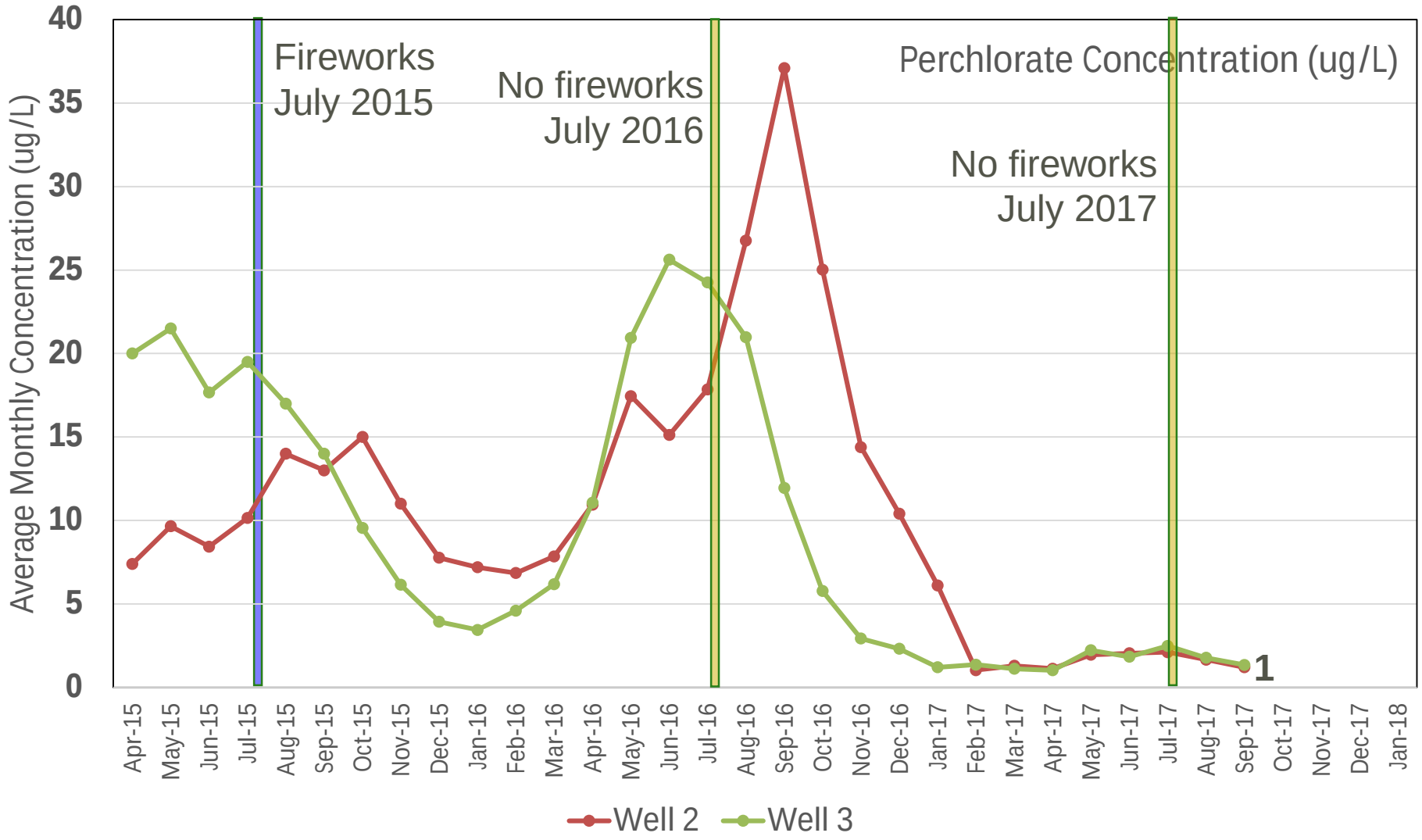
24 Months (March 2017)



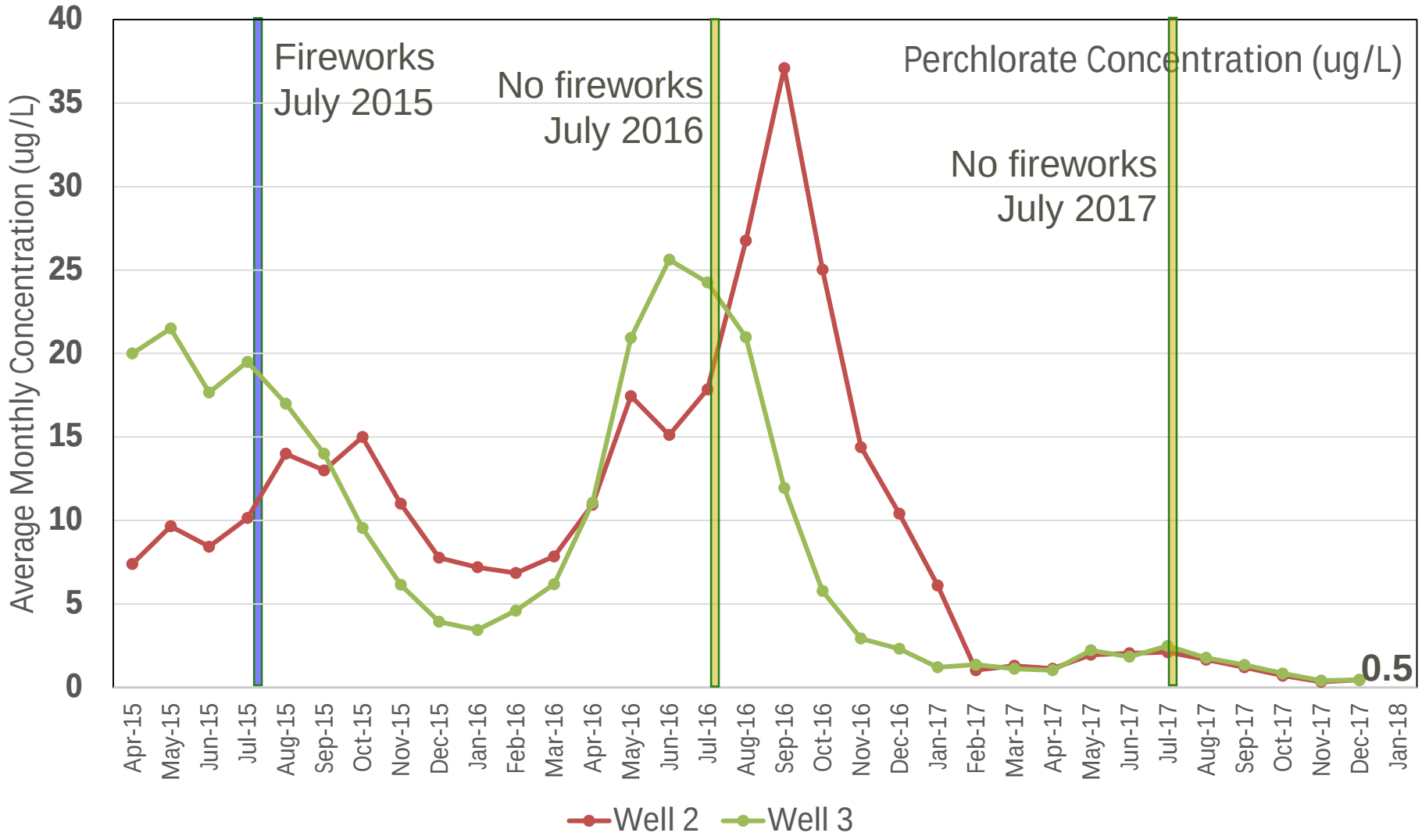
27 Months (June 2017)



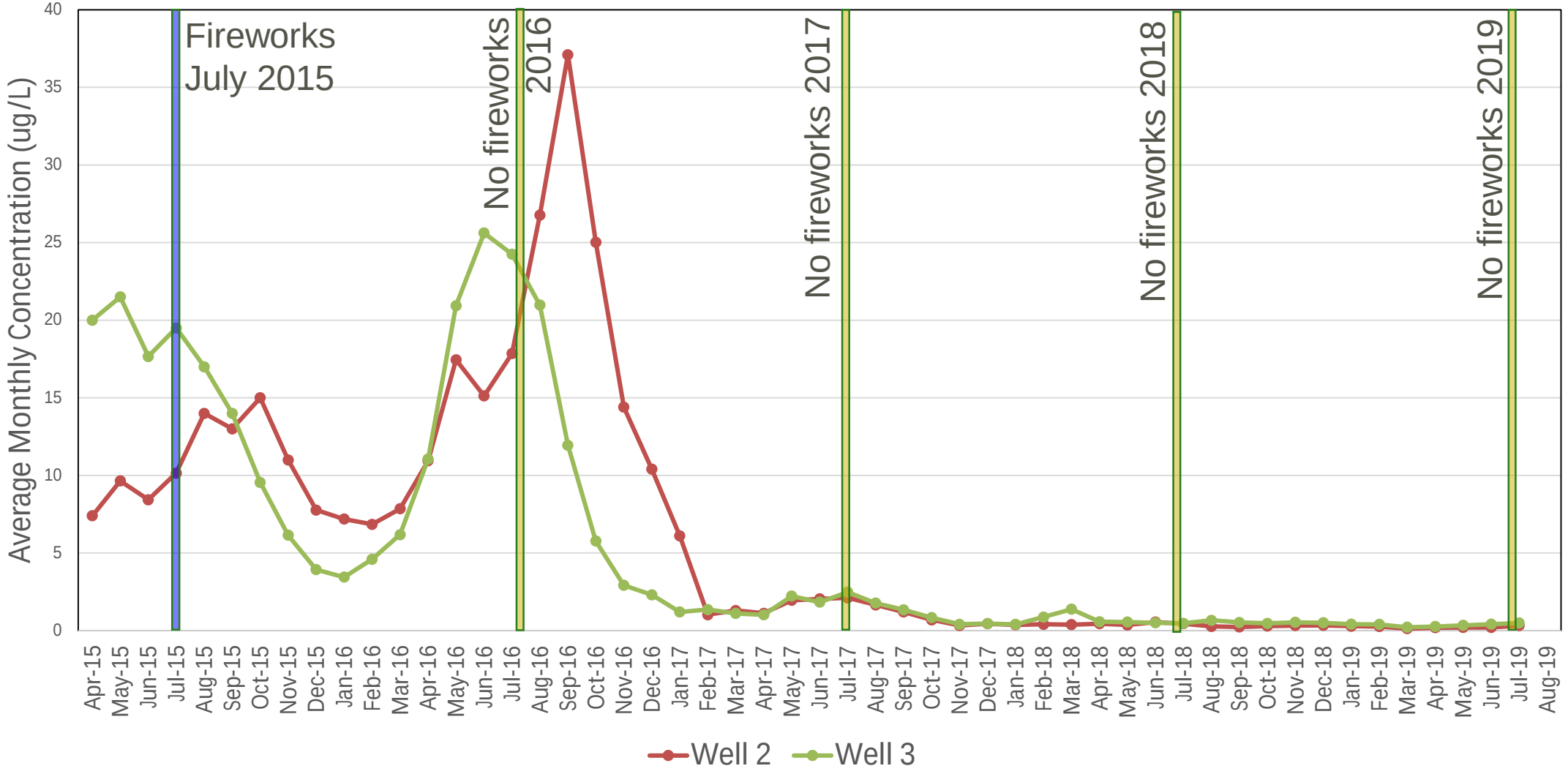
30 Months (September 2017)



33 Months (December 2017)

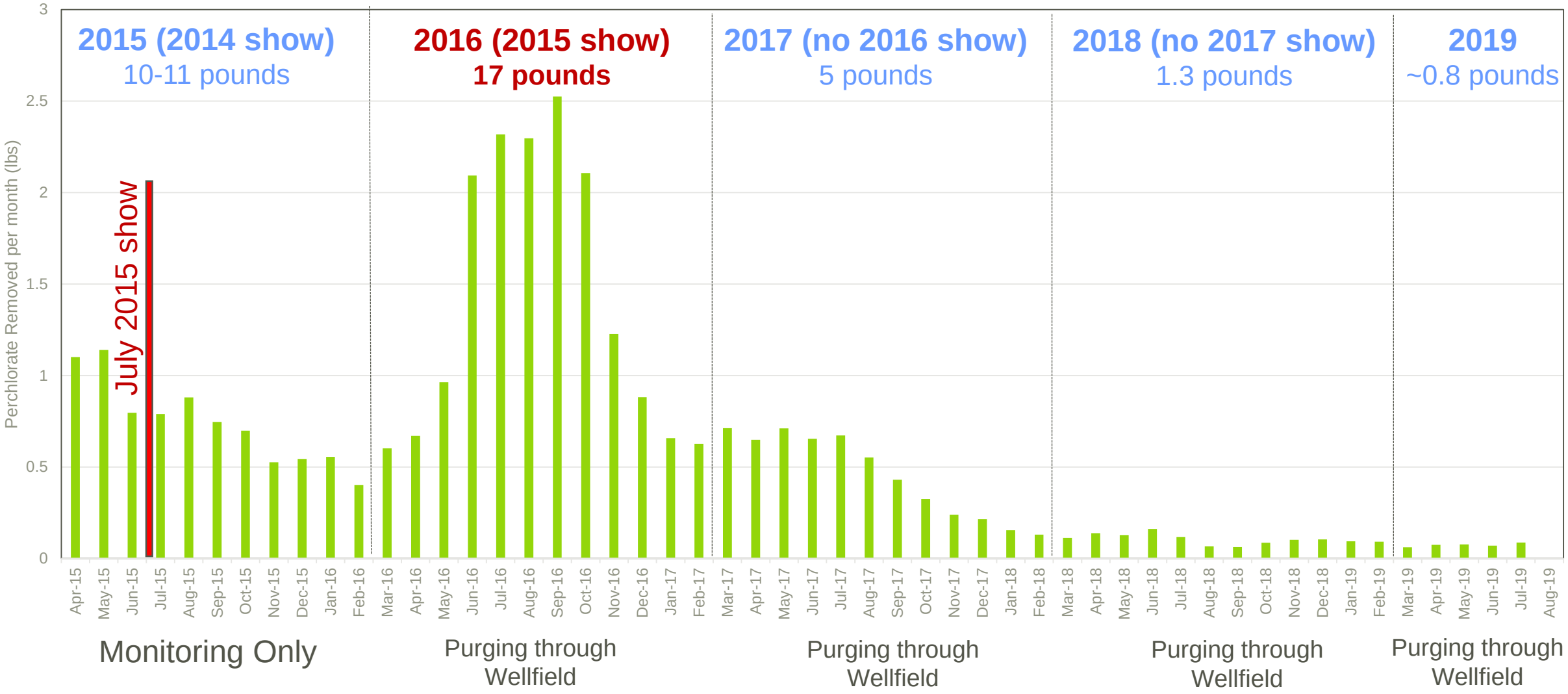


52 Months (July 2019)



Mass Flux

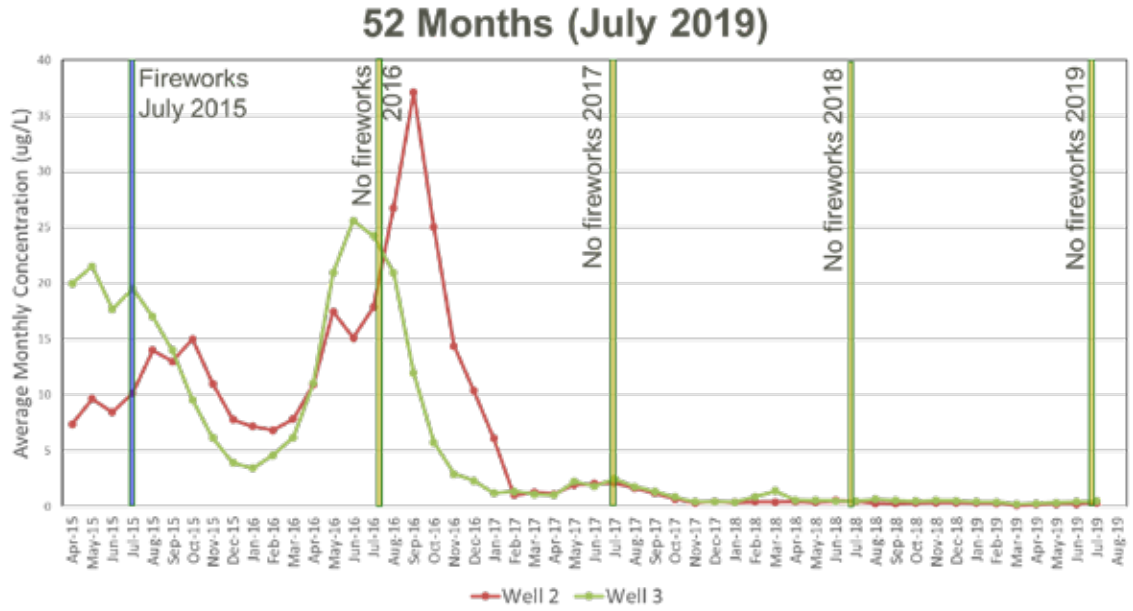
POUNDS OF PERCHLORATE BEING REMOVED EACH MONTH



Case Study Conclusions

Small-Town Show – 30-40 minutes

- 400-500 shells, 4-5 kg each = 2,000 kg
- 2,000 kg fireworks, 40% perchlorate = ~800 kg perchlorate
- Recovered in wellfield = ~5-10 kg (10-20 lbs.)
- ~1% to groundwater
- Very little retained in soils (<1/2 lb.)

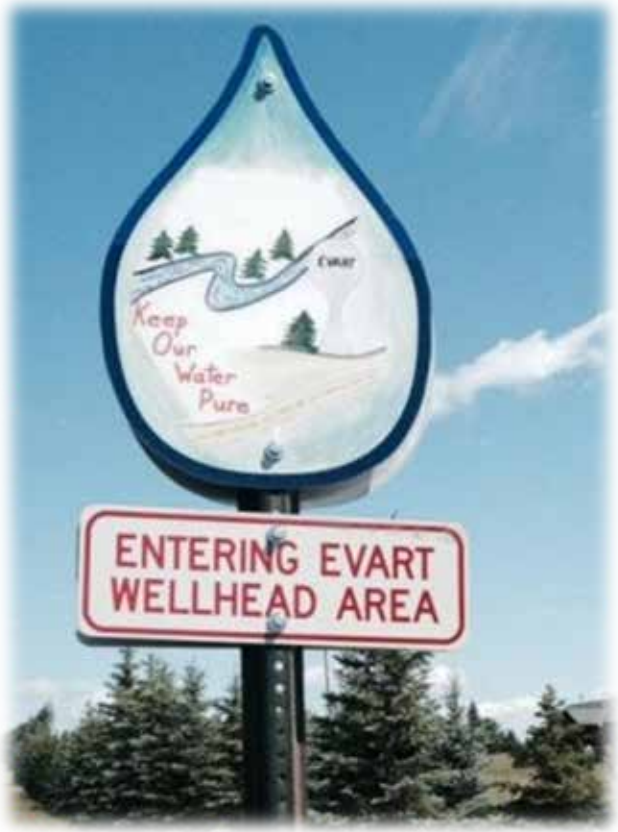


Backyard Scenario

- 100 lbs fireworks
- If 40% perchlorate, and 1% is unreacted = ~200 grams
- Heavy rain – 1 inch over 1 acre = 100,000 Liters
- 200g/100,000 L = 2 mg/L (2,000 ug/L)

Future Considerations

- Overall consumption is increasing, ~300 million pounds (US)
- 3,500 public shows per year in Michigan
- 10x more “consumer” fireworks than “display”
- Perchlorate regulations are coming
- Consider one-time events (such as fireworks) in wellhead protection



Acknowledgements

The Healthy Hydration Company™

S.S. Papadopulos & Associates, Inc.

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Thank you.