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Sulfate Delivery Using Permeable Filled Borings to Enhance Petroleum Hydrocarbon Biodegradation

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Sulfate Delivery Using Permeable Filled Borings to Enhance Petroleum Hydrocarbon Biodegradation Outline

- Remediation History and Objectives
- Site Background
- UC Davis Microcosm Study
- Treatment Strategy
- Permeable Filled Borings (PFBs)
- Performance Monitoring
- Conclusions

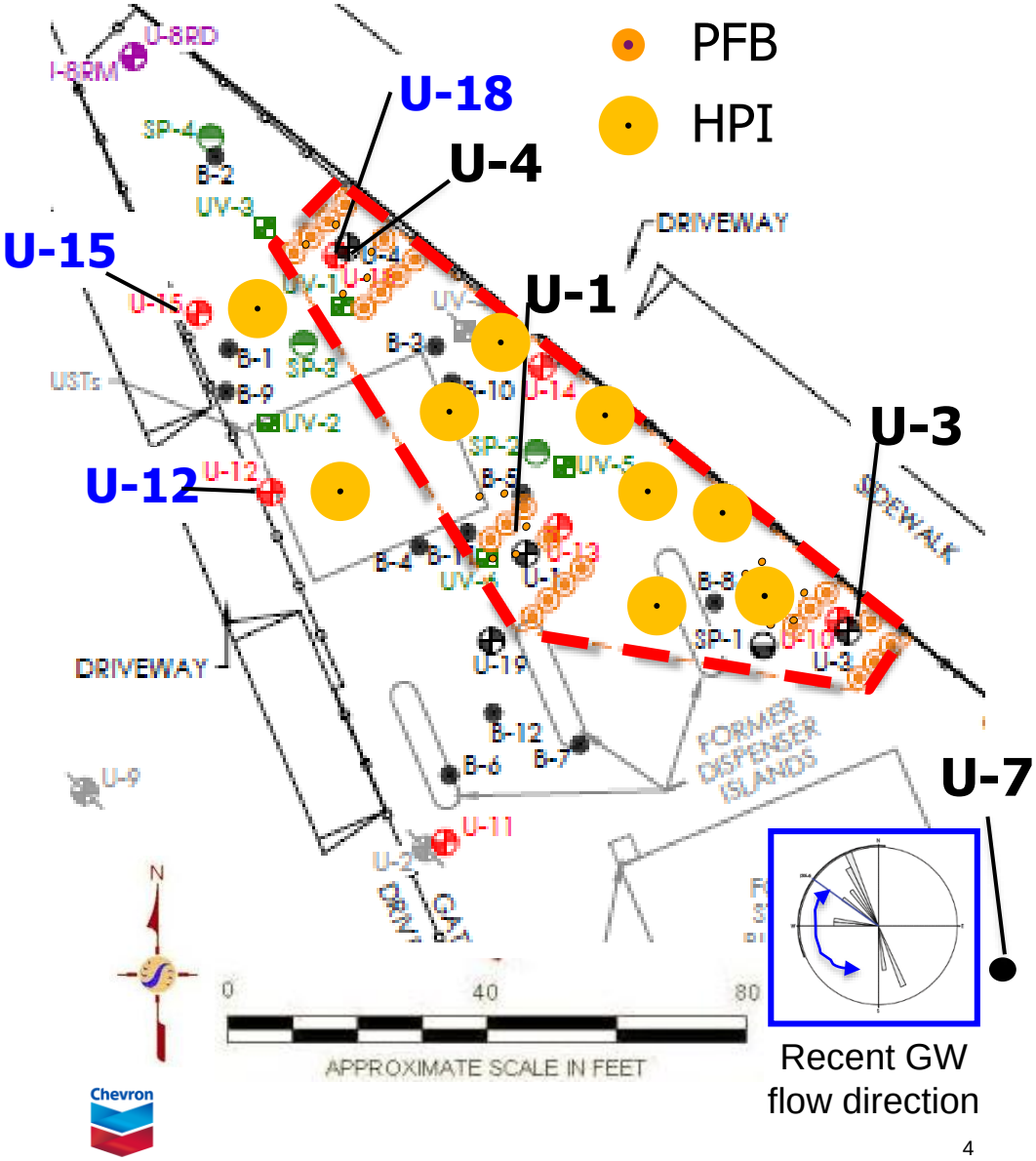
Former Service Station in Northern California Remediation History and Objectives

- In 1993 the service station ceased operations; all above and below ground facilities were removed.
- Remediation technologies applied 1992-2006:
  - Groundwater extraction, excavation, soil vapor extraction, Oxygen releasing compound, Biosparge, Ozone sparge
  - None of these technologies has been effective
- March 2015 regulatory meeting:
  - Regulators agreed to a sulfate release strategy
  - The remediation objective, based on the CA Low Threat Closure Policy, is benzene <1,000 ug/L in selected monitor wells

Remediation Objectives
Permeable Filled Borings (PFB) and High Pressure Injections (HPI) Locations

- Assumptions:
  - treatment monitored in selected wells (**blue for intermediate**, **black for deep**)
  - most important area within red dashed box
- Groundwater flow direction has varied significantly (~10 ft/yr)

NOTE: Size of PFBs and HPI radius of influence not to scale



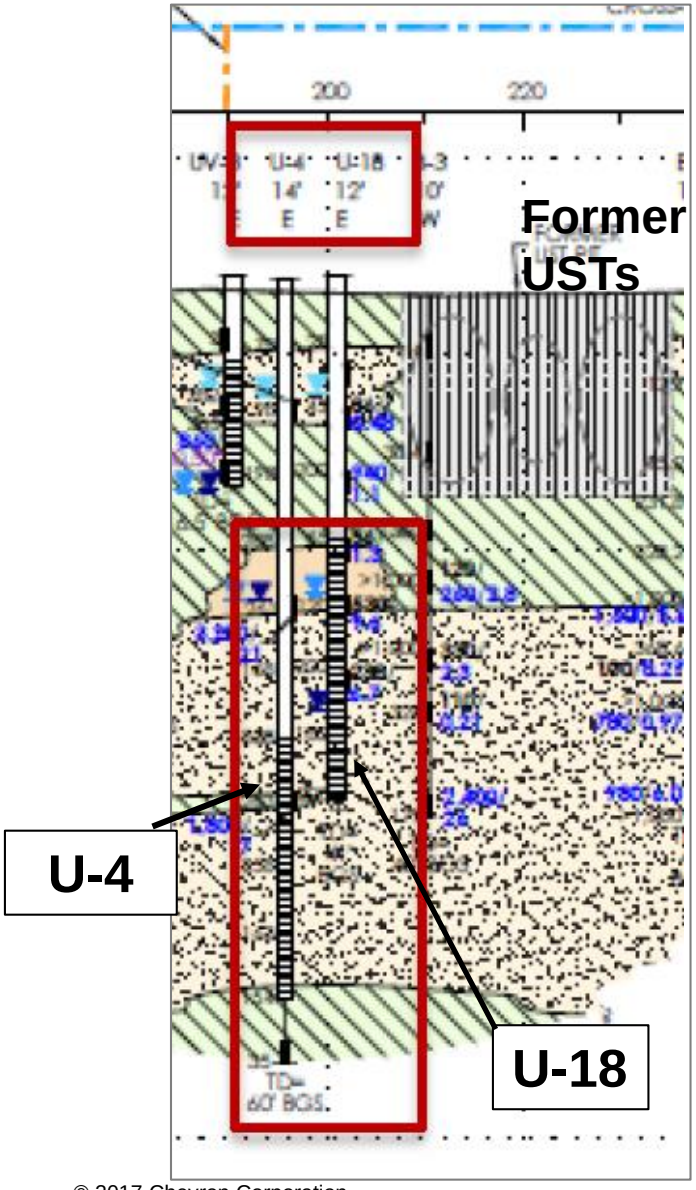
Remediation Objectives
BTEX* and Sulfate in PFB Monitor Wells
Pre-Remediation

*9/4/14

Well	Screen Interval (feet bgs)	Benzene (µg/L)	Toluene (µg/L)	Ethyl Benzene (µg/L)	Xylenes (µg/L)	Sulfate mg/L	Sulfate dates
U-1	36-56	13,000	260	440	180	<0.5 – 3.6	11/3/05 – 9/6/13
U-3	36-56	2,100	23	33	5	3.9	9/1/11
U-4	36-56	2,200	7	6	11	1.9	9/1/11
U-18	20-40	6,000	130	180	180	1.5 – 7.6	11/3/5 – 9/1/11
U-7 (upgradient)	25-40	ND	ND	ND	ND	737 – 1,420	9/1/11 – 9/6/13

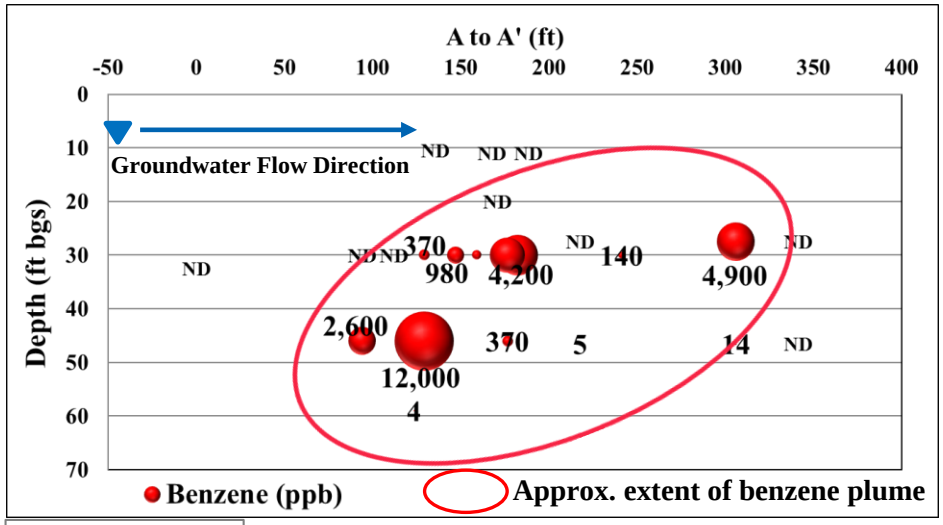
- TEX concentrations in target wells suggest NAPL is depleted in those compounds

Site Background
Cross Section for U-4 and U-18

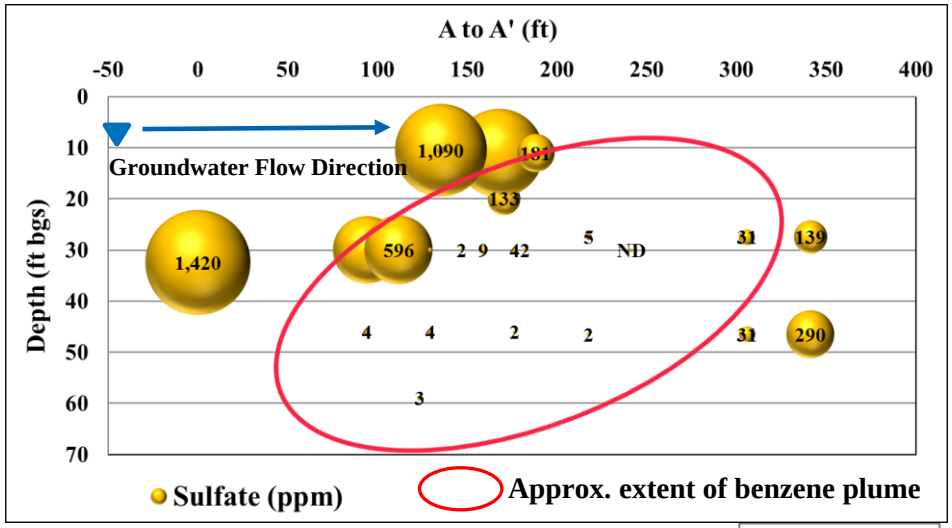


PFB monitor wells completed in the intermediate and deep water-bearing zones

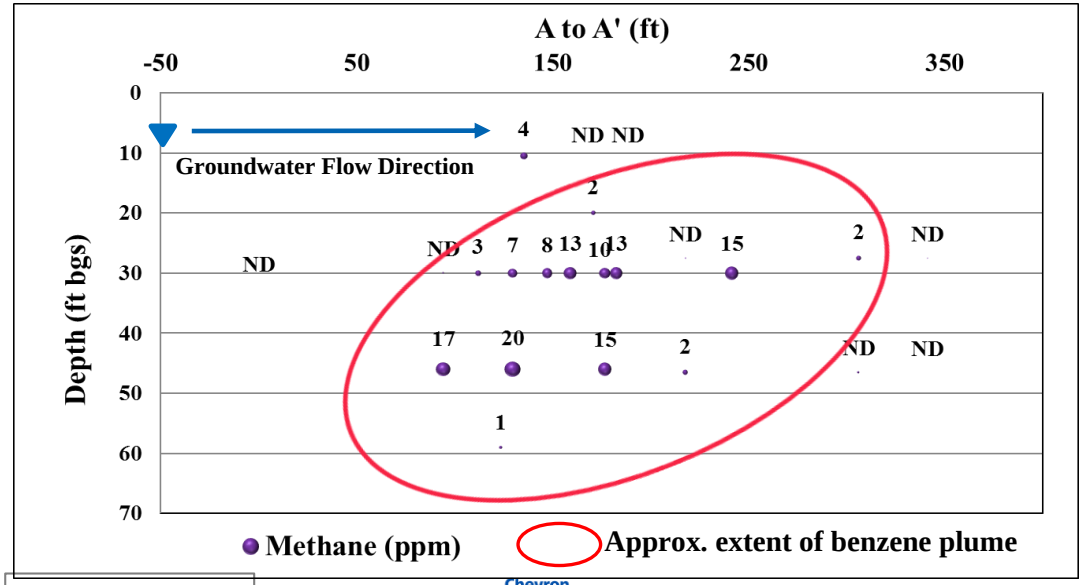
Site Background
Longsect Plots for Benzene, Sulfate and Methane – April 2012



Benzene



Sulfate



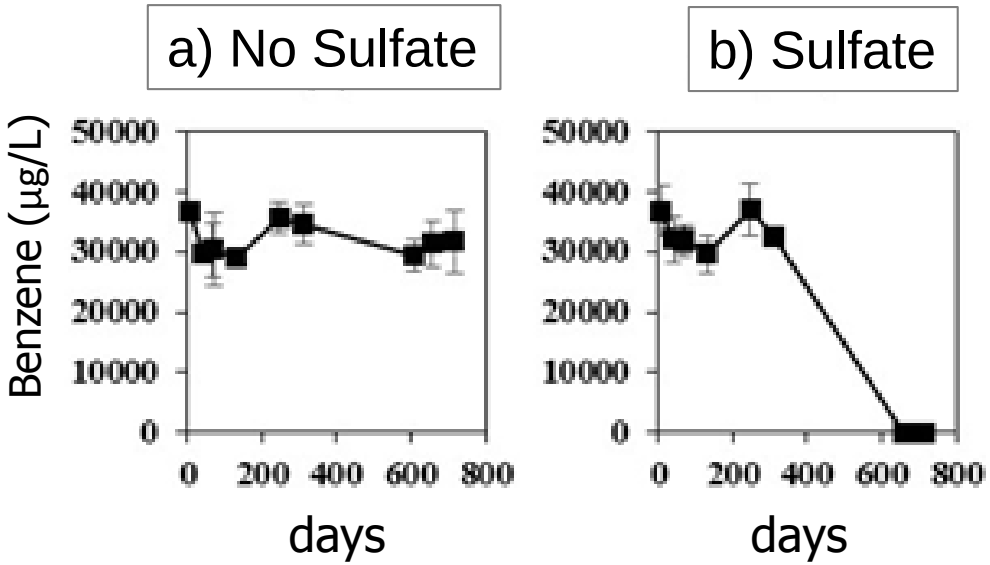
Methane

Microcosm Results

UC Davis Laboratory Microcosm Results

Mixed background levels of sulfate (1,500 mg/L) with benzene (40 mg/L) in lab study with site sediments and groundwater

Added Benzene +Sulfate at start



- No benzene degradation without sulfate (a), though methane was generated
- Benzene degradation with sulfate (b)
- Suspect long lag time in microcosms may have been due, in part, to long storage and artifacts of handling of core materials, not initially intended for microcosms

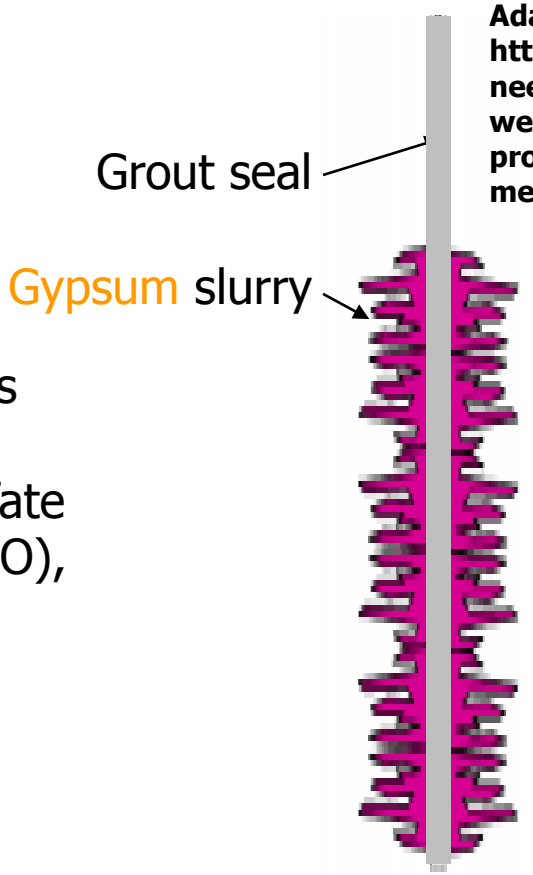
Treatment Strategy
Permeable Filled Borings (PFBs) and High Pressure Injections (HPIs)

Schematics of the idealized installations

PFB cluster

Gypsum is hydrated calcium sulfate ($CaSO_4 \cdot 2H_2O$), a widely available mineral

HPI



Adapted from http://www.geoengineer.org/education/web-based-class-projects/geoenvironmental-engineering/

Treatment Strategy
Sulfate Delivered through PFBs and HPIs

At time of installation, depth to water ~ 25 ft bgs

- **PFBs** created by hollow stem auger in 24, 9-inch diameter borings, Sept-Oct 2015
  - Backfilled with gypsum/gravel mix (gypsum = $CaSO_4 \cdot 2H_2O$)
  - **8400 pounds of sulfate** contained within 15,000 pounds of gypsum
  - Estimated PFB lifetime is 7-9 years for steady groundwater flow
- **HPIs** used gypsum powder mixed with hydrant water to create slurry
  - Nine injections, August and October 2015
  - **180 pounds of sulfate** contained within 312 pounds of gypsum
  - Average 1600 mg/L gypsum injected, or 890 mg/L as sulfate

Permeable Filled Borings
Options for gypsum/gravel mix

Crushed gypsum

1/4" (6.3 mm) screen retention 9.40%, passing = 90.60%
40 mesh (0.425 mm) retention 37.00%, passing = 63%"

Physical properties

	Gypsum	3/8" Granite	3/8" Rhyolite	3/8" Lava
Porosity (-)	*0.49**	0.46	0.48	0.52
Bulk Density (g/cc)	*1.17*	1.52	1.12	0.93
Solid Density (g/cc)	*2.31***	2.81*	2.13*	1.95*

* calculated
** from literature

Crushed Granite

Crushed Lava

Crushed Rhyolite

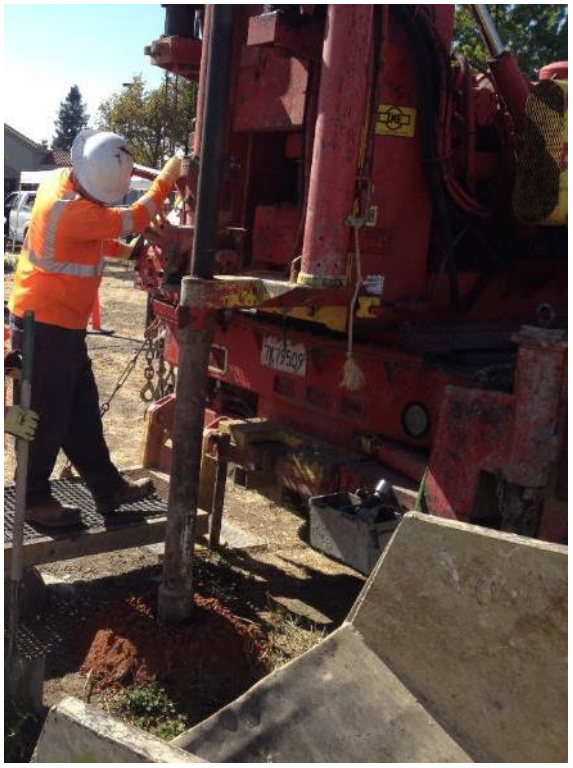
Wikipedia: Rhyolite "..the extrusive equivalent to granite rock"

Permeable Filled Borings
Delivery and Emplacement of PFBs

Bags of pre-mixed gravel/gypsum

Pre-mixed gravel/gypsum

Augering to depth



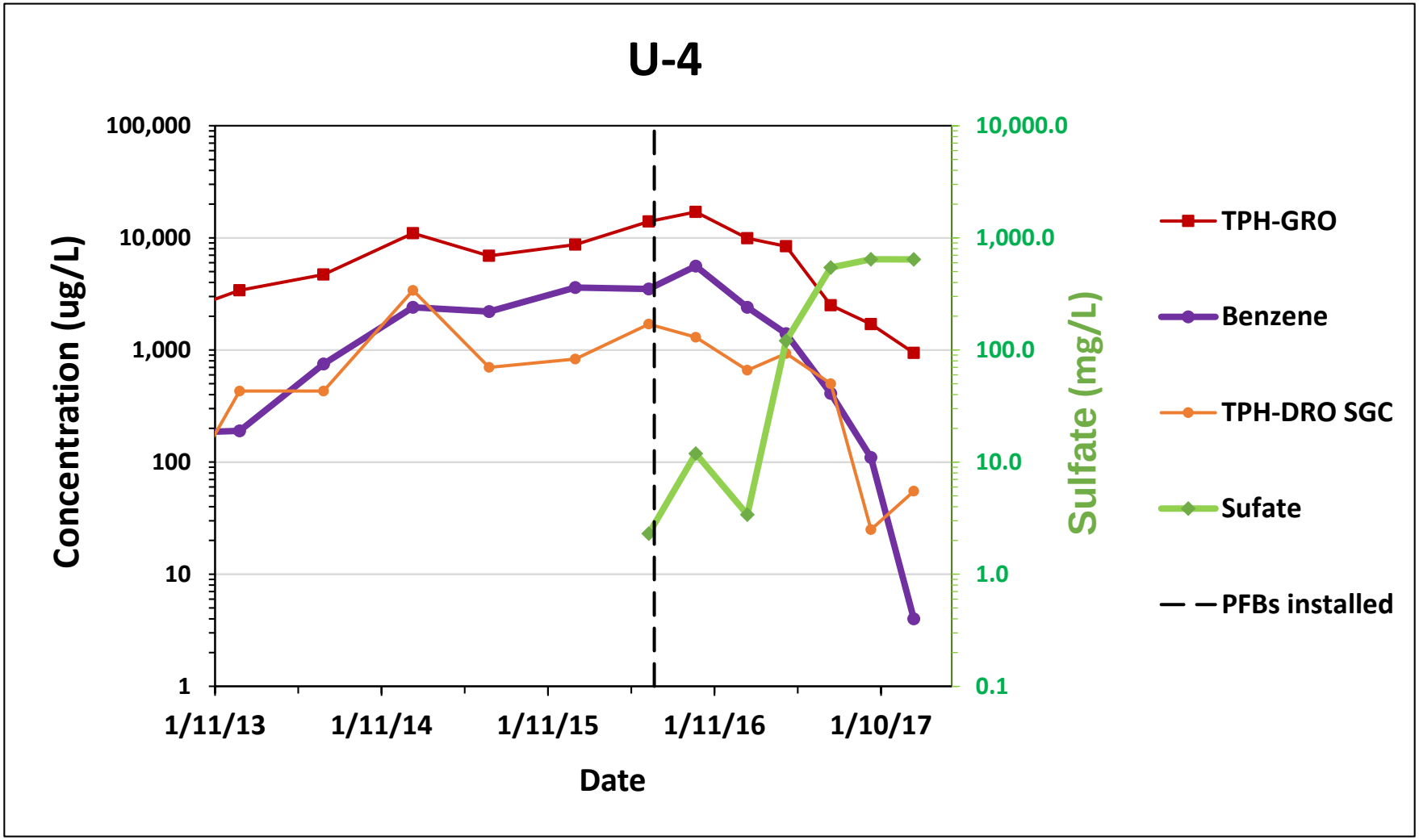
Most efficient way to get pre-mix into auger

Borings above PFB fill were backfilled with ~2 feet of hydrated bentonite followed by cement grout to surface

Benzene, TPH-GRO, TPH-DRO and Sulfate vs. Time

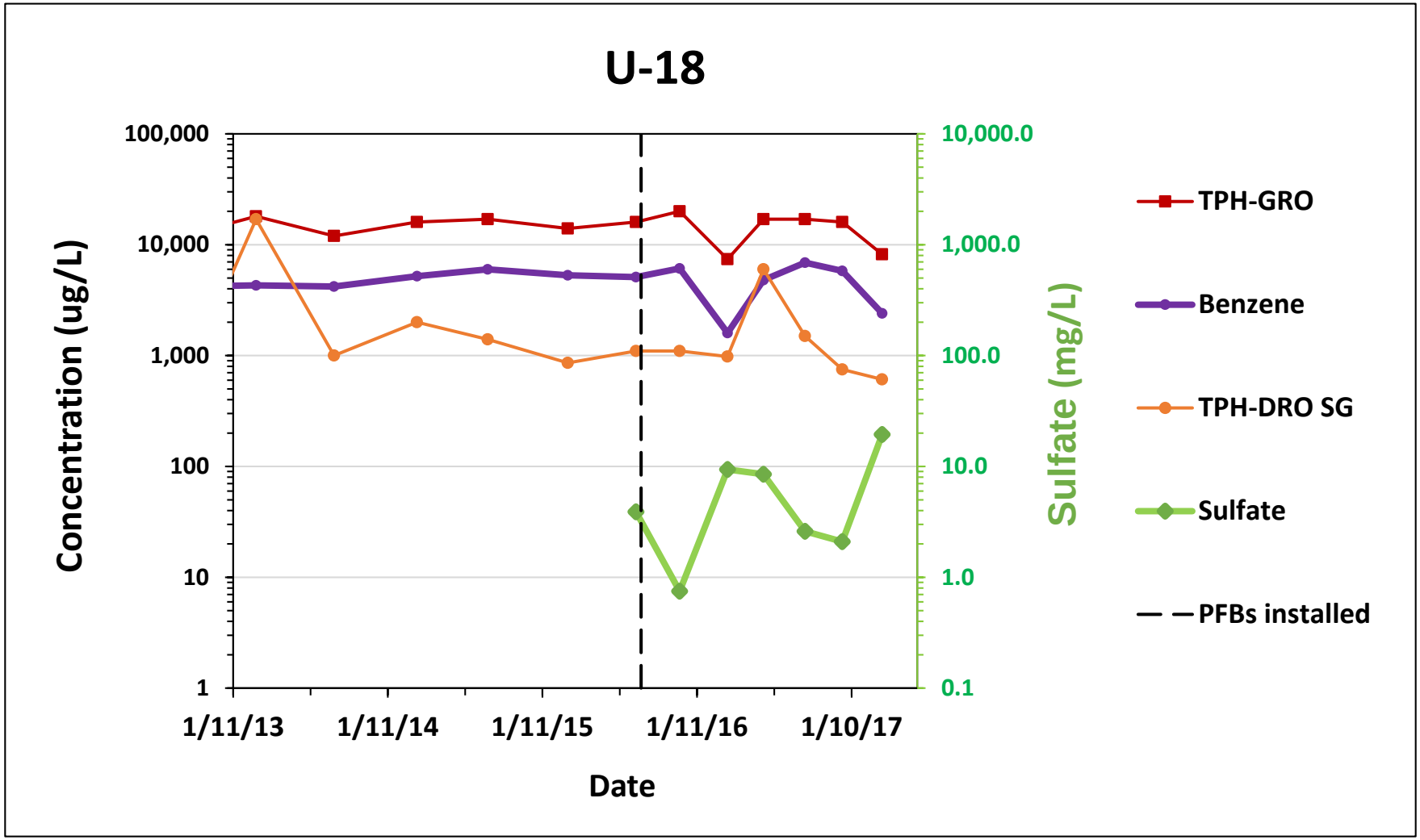
PFBs provide adequate sulfate to meet demand

Toluene, Ethylbenzene and Xylenes each <20 ug/L since September 2014

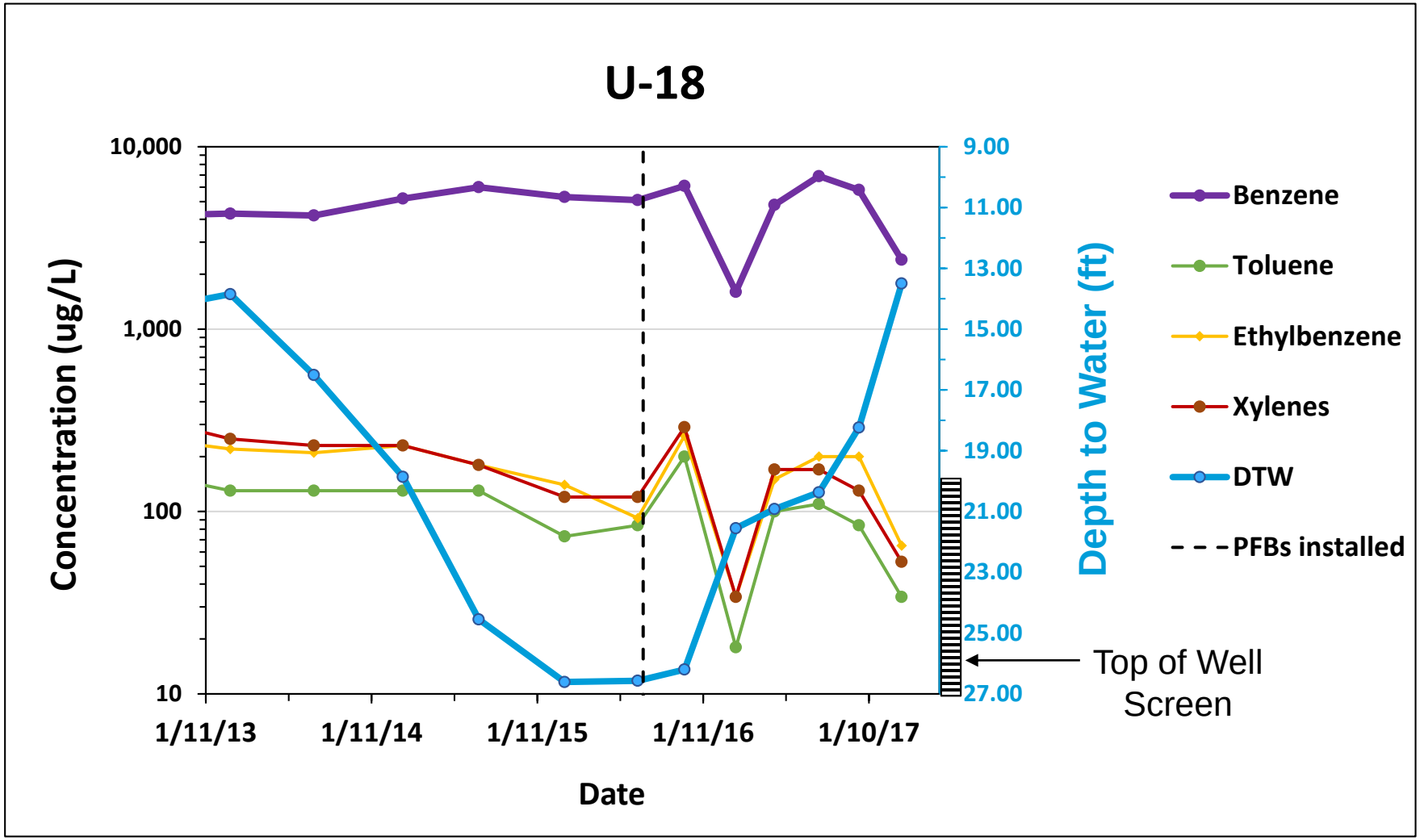


Benzene, TPH-GRO, TPH-DRO and Sulfate vs. Time

Non-benzene demands for sulfate

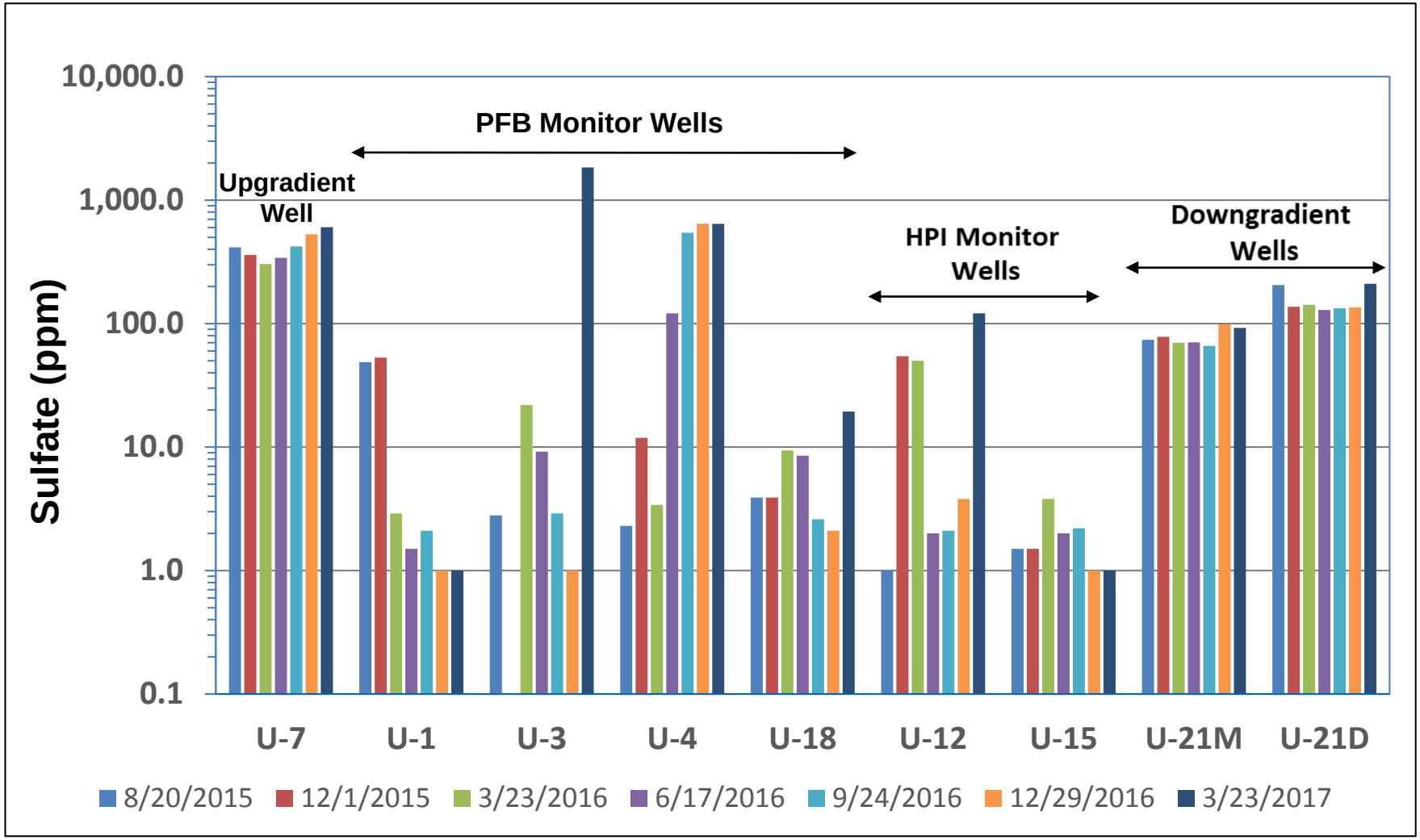


Benzene, Toluene, Ethylbenzene, Xylenes and Depth to Water (DTW) vs. Time



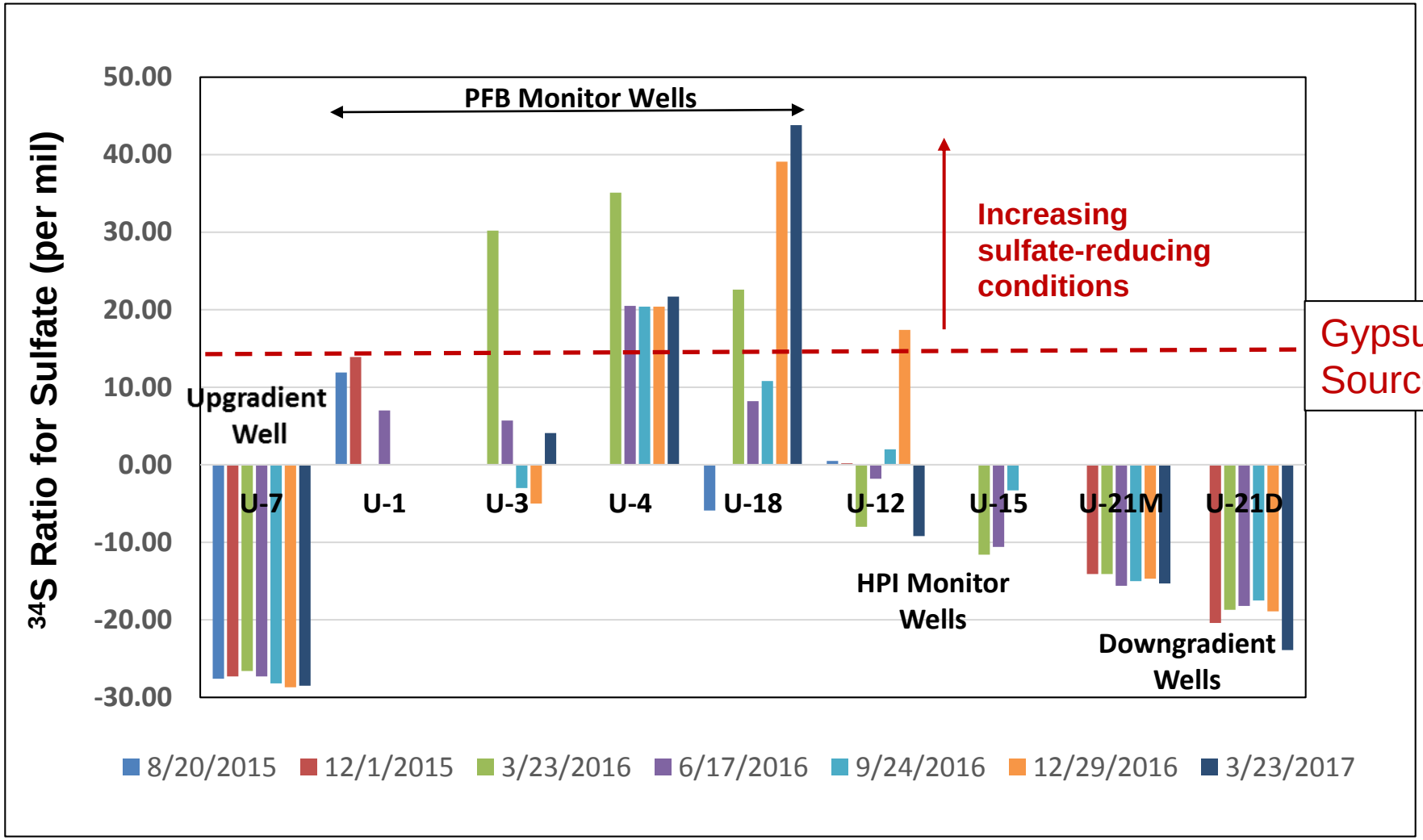
Sulfate vs. Time for Monitor Wells

8/20/15 is Pre-Remediation



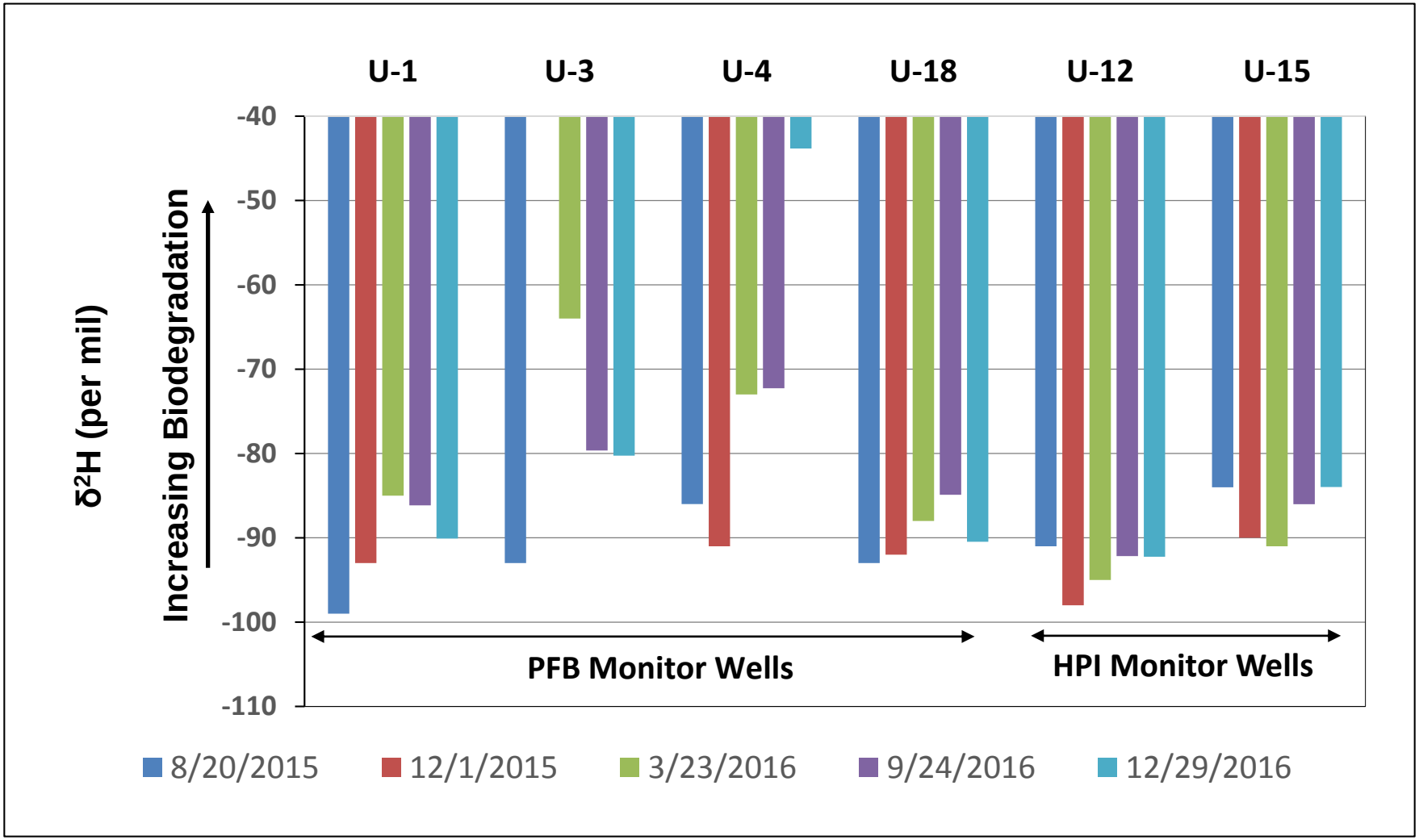
Sulfur Isotope Ratio ($^{34}S/^{32}S$) for Sulfate

Baseline data are not available if sulfate was not detected

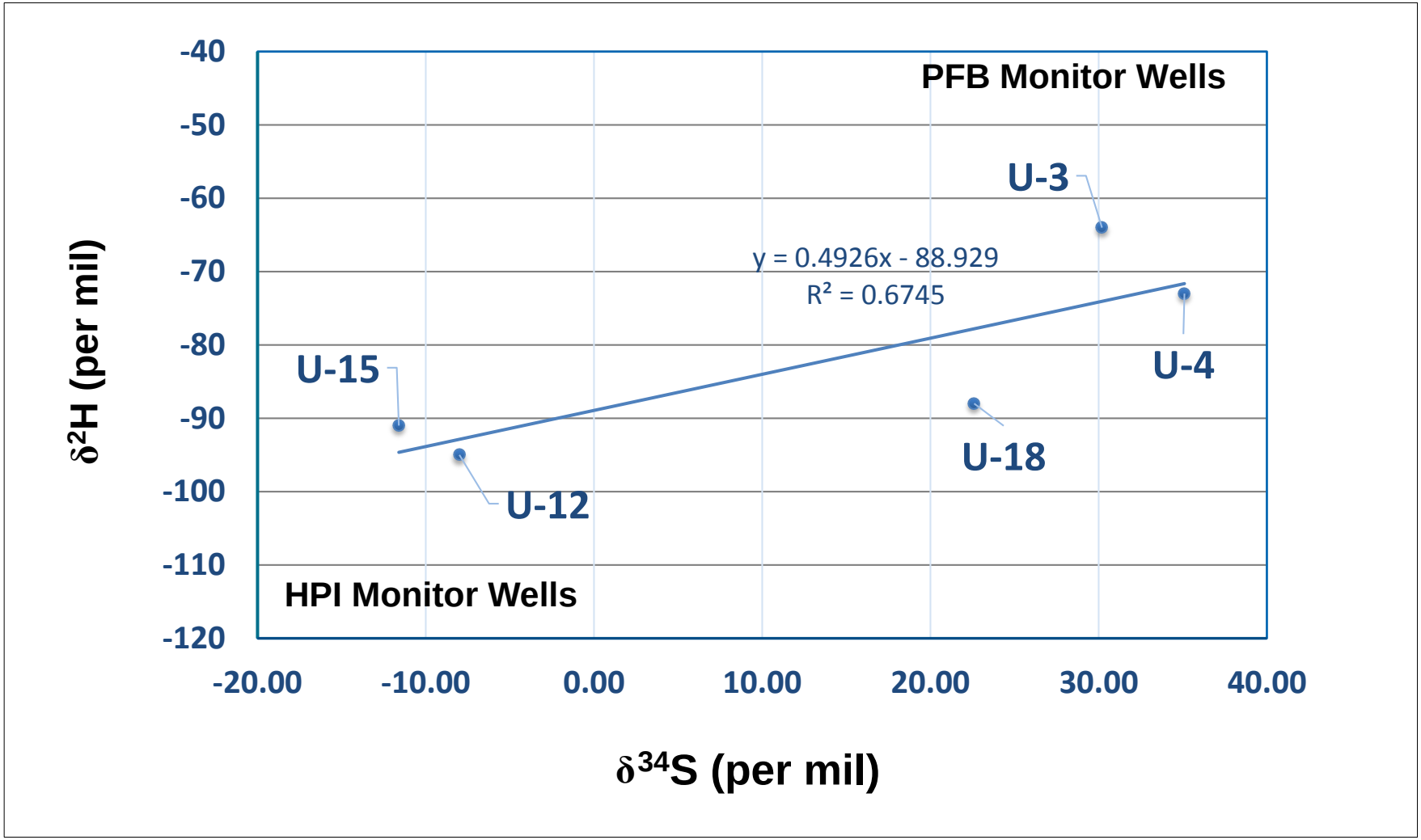


Hydrogen Isotope Ratio (δ^2H) for Benzene

PFB Monitor Wells show strongest evidence for biodegradation



$\delta^{34}S$ in Sulfate versus $\delta^{2}H$ in Benzene
March 2016



Sulfate Delivery Using Permeable Filled Borings Conclusions

- Isotopic evidence ($\delta^{34}S\text{-}SO_4$) for sulfate participating in hydrocarbon biodegradation
- Hydrogen isotopic enrichment for benzene suggests enhanced biodegradation, particularly in the vicinity of the PFBs
- Sulfate reducing conditions are enhanced, resulting in decreasing hydrocarbon concentrations
- Results to date are promising; gypsum-filled borings may provide effective delivery of sulfate as an electron acceptor

Funding provided by Chevron Environmental Management Company