IN SITU VADOSE ZONE PERCHLORATE REMEDIATION USING EMULSIFIED VEGETABLE OIL

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Richard Royer, PhD

Collaborators

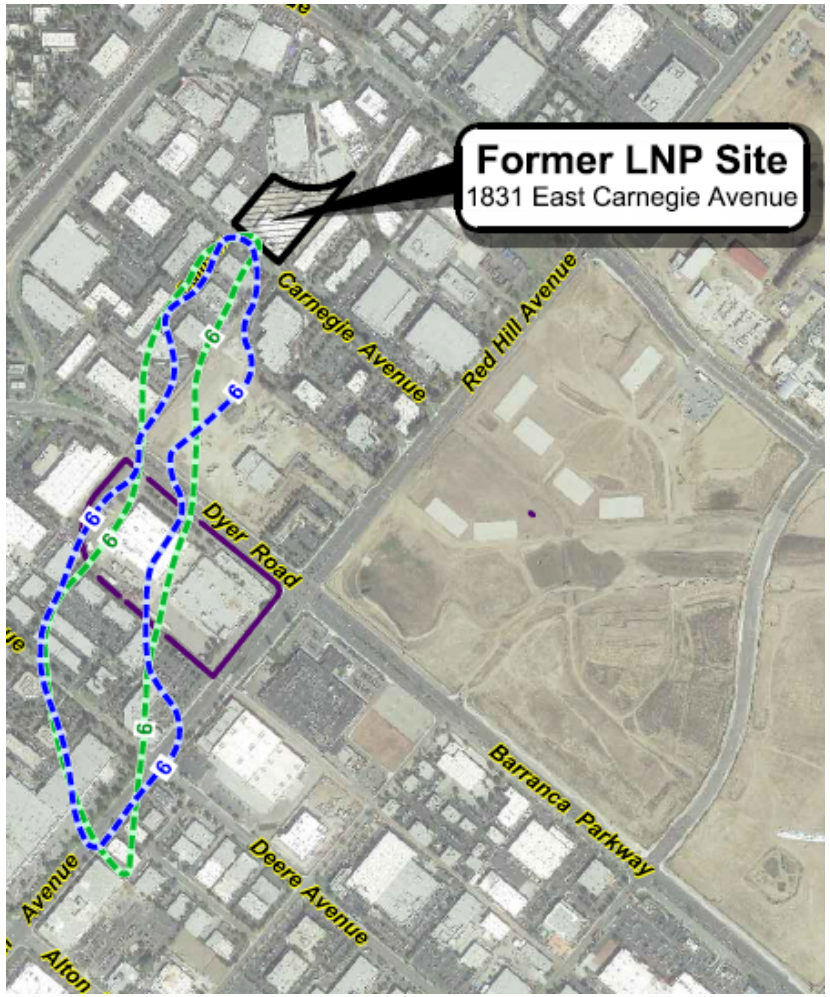
John Wood - Split Rock Diversified

Bettina Longino, PhD - Arcadis

Greg Hamer - WSP

Nick Amini, PhD and Mona Behrooz, PhD - Santa Ana RWQCB

Setting and Background



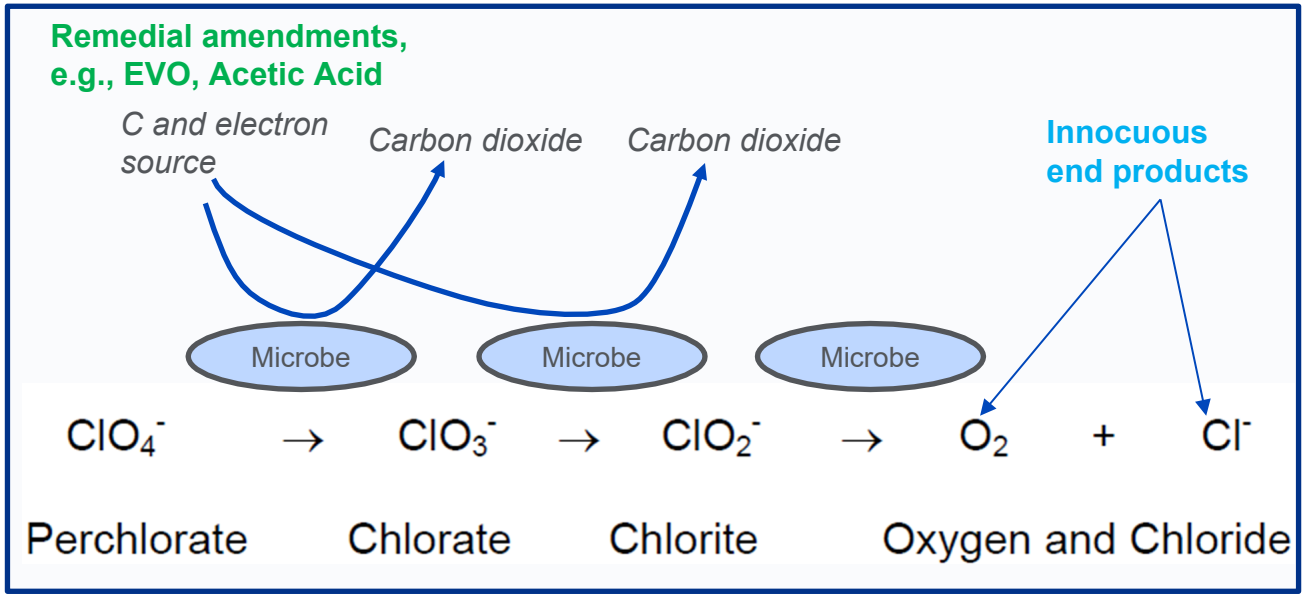
Regulatory review by Santa Ana Regional Water Quality Control Board (RWQCB)

On Site:

- Perchloric acid used 1973-1992
- Perchlorate in soil and groundwater (GW)
- GW hydraulically controlled since 2003
- GW extraction and treatment ongoing
- Geology: primarily fine-grained material with irregularly occurring, laterally discontinuous silt and sand interbeds
- Depth to groundwater ~15-16’ bgs

Offsite plume being controlled and treated by EVO biobarrier

Perchlorate and Bioremediation



Key Characteristics:

- Extremely water soluble
- Non-volatile, stable in water
- Little to no retardation
- Organisms responsible for perchlorate reduction are widespread
- Readily used as a terminal electron acceptor under moderately reducing condition (after nitrate)
- Very rapid degradation kinetics – hours to days for complete destruction

Vadose Zone Perchlorate Remediation

Vadose zone remedial options informed by the characteristics of perchlorate and site soils

- High water solubility and low to no adsorption to soil
- Readily biodegradable under anaerobic conditions
- Fine grained (low K) soils result in vadose zone moisture content similar to saturated zone

Options for *in-situ* remediation of perchlorate in vadose zone soil include:

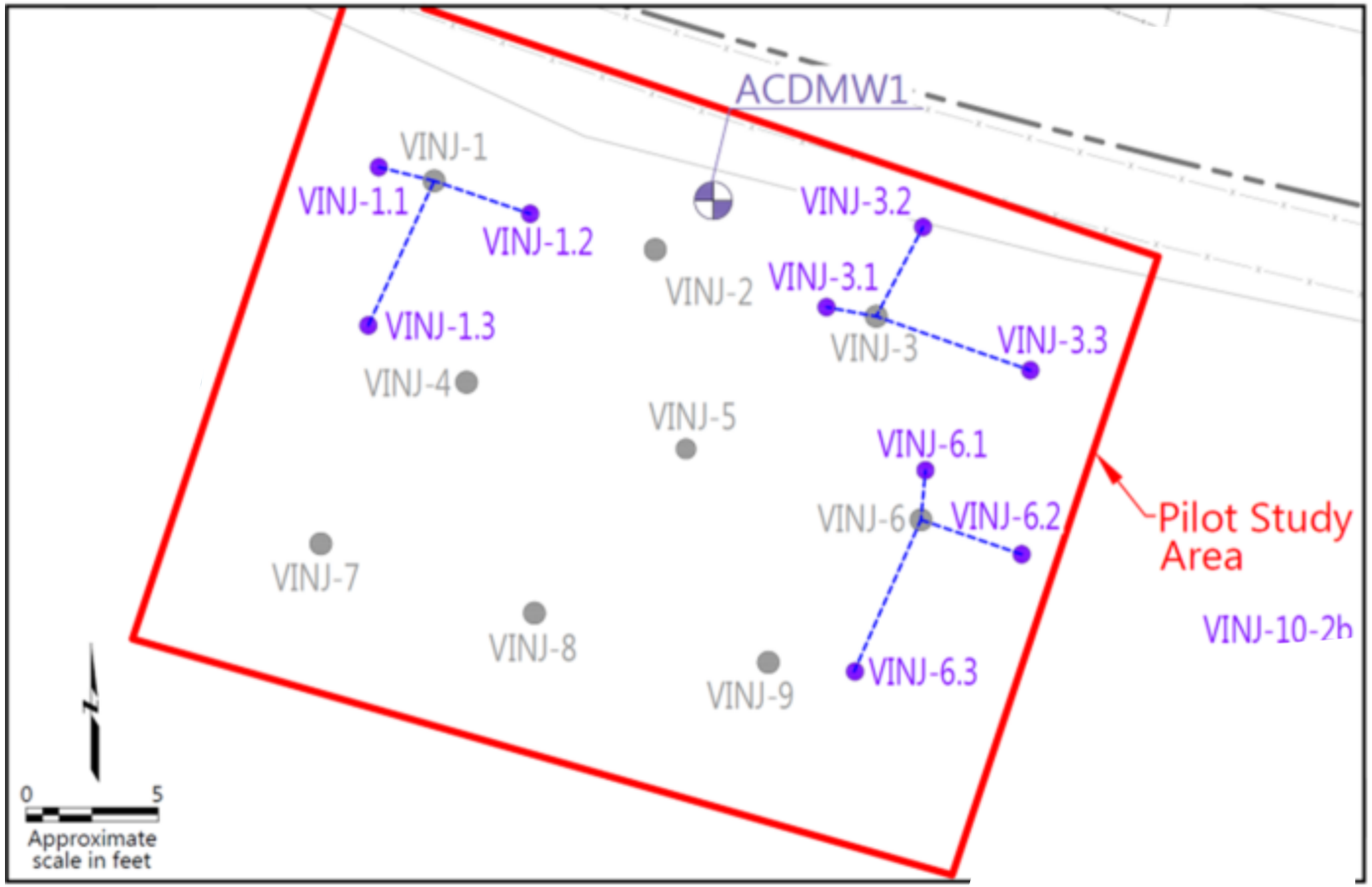
- Soil washing/flushing
- In situ bioremediation if electron donor can be delivered and anaerobic conditions achieved

Emulsified Vegetable Oil (EVO) injections selected for pilot testing – a relatively novel application of a well proven saturated zone technology

Vadose Zone Pilot

Injection Design and Application

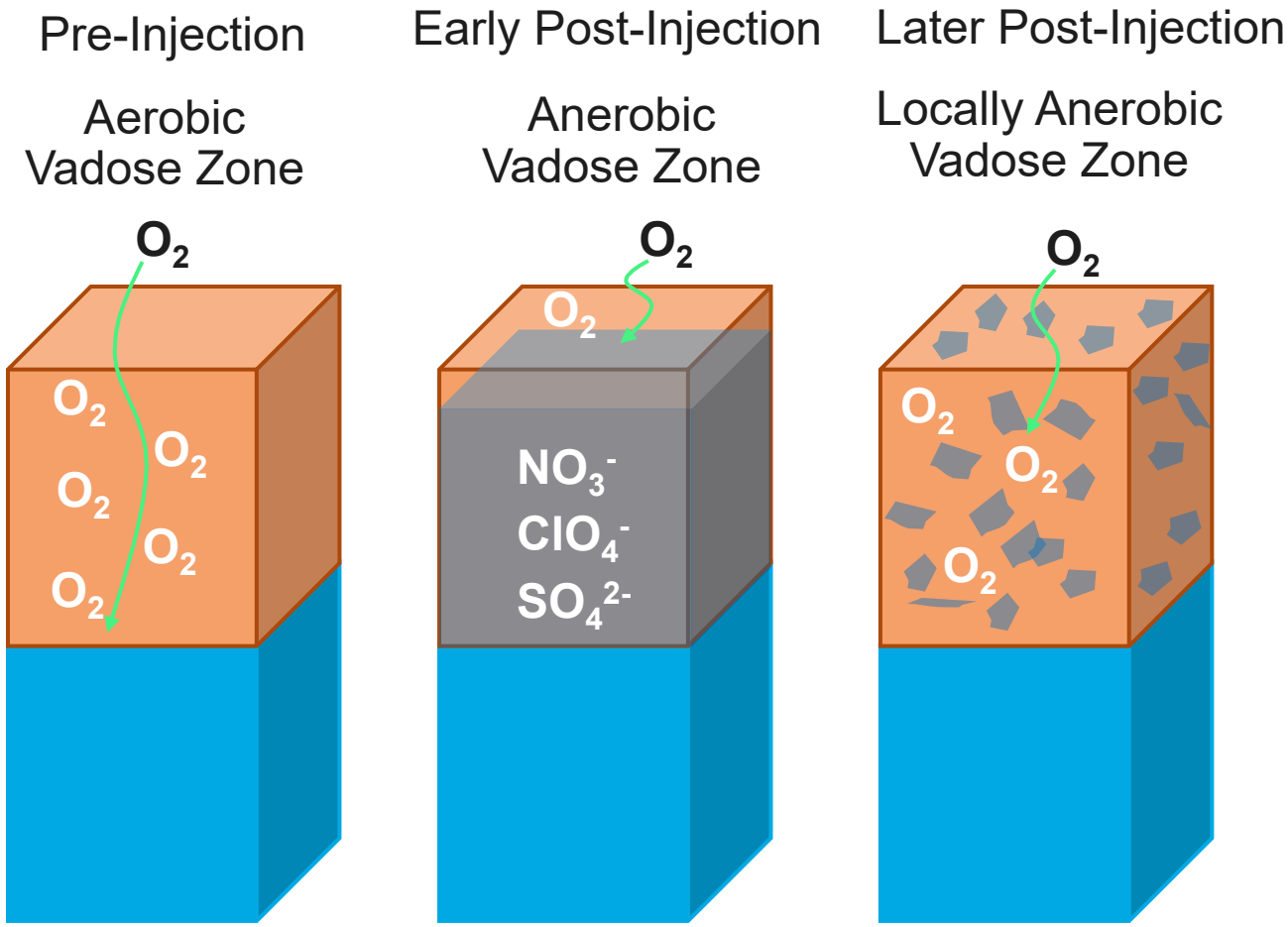
- 9 locations (VINJ-1 through VINJ-9)
- 9-ft spacing, 5-ft ROI design
- Depth interval 5’-15’ bgs
- Pressure ≤ 1 psi/foot of depth
- 47 gallons of solution per foot of depth
- Injections performed from bottom to top with injections at 2’ vertical intervals
- EVO was applied at 3% of product strength (~60% soybean oil in product)
- Injection flow rates ranged from 1.1 to 2.0 gpm
- Post injection samples taken within ~1’ of baseline samples
- Samples collected pre-injection and 30, 60, 180, 371, and 730 days



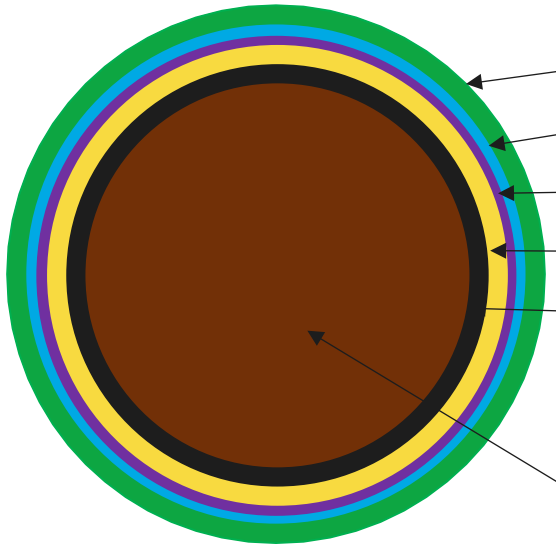
Vadose Zone Perchlorate Bioremediation

Bioremediation using EVO injections was piloted after testing combined bioremediation / soil washing approaches with acetic acid

Predominately fine-grained soils were expected to retain moisture and allow for formation of a temporarily saturated, anaerobic "vadose" zone that would allow for perchlorate reduction to proceed



Microscale Redox and Soil Moisture

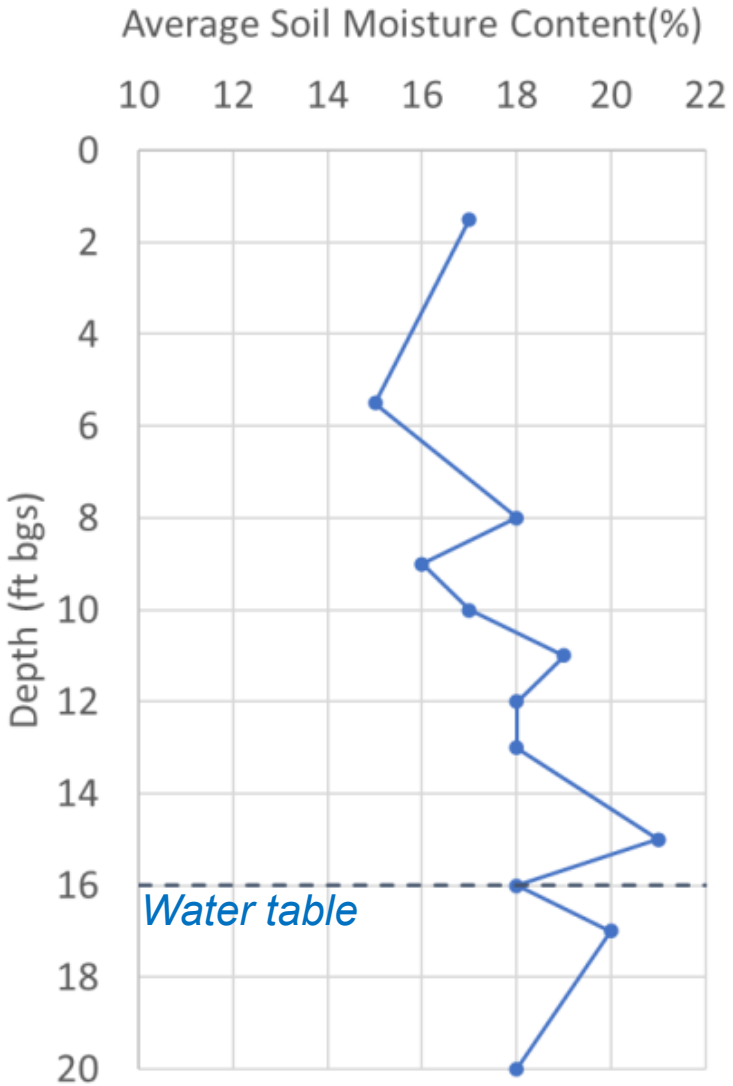


Soluble Terminal Electron Acceptor

- Oxygen
- Nitrate
- Perchlorate
- Sulfate
- Carbon Dioxide

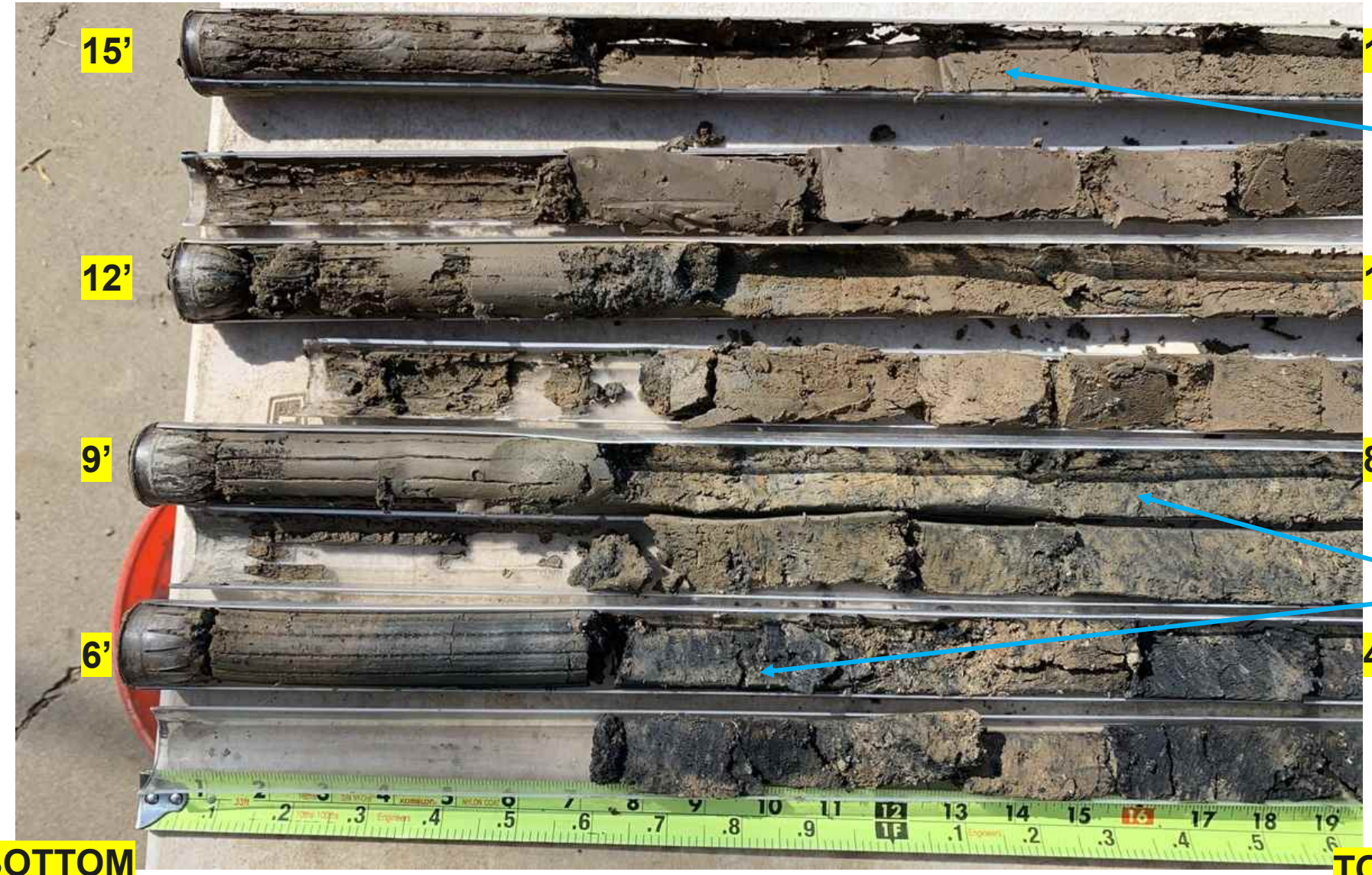
Surface reactions

- Fe reduction
- Mn reduction
- VFA and H_2 production



Fine grained vadose zone soils can hold significant water

Example Core - 30 Days Post Injection



Note: fine grained soils, no black materials

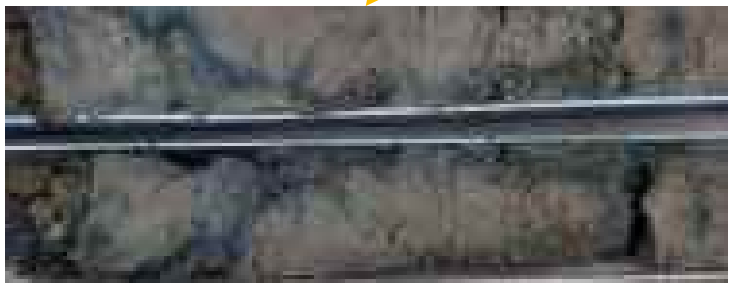
Note: visual heterogeneity, especially in distribution of black materials (presumptive iron sulfides)

Sample location VINJ-3-1

Example Cores 30 & 60 Day Post-Injection

30-day Post-injection

60-day Post-injection



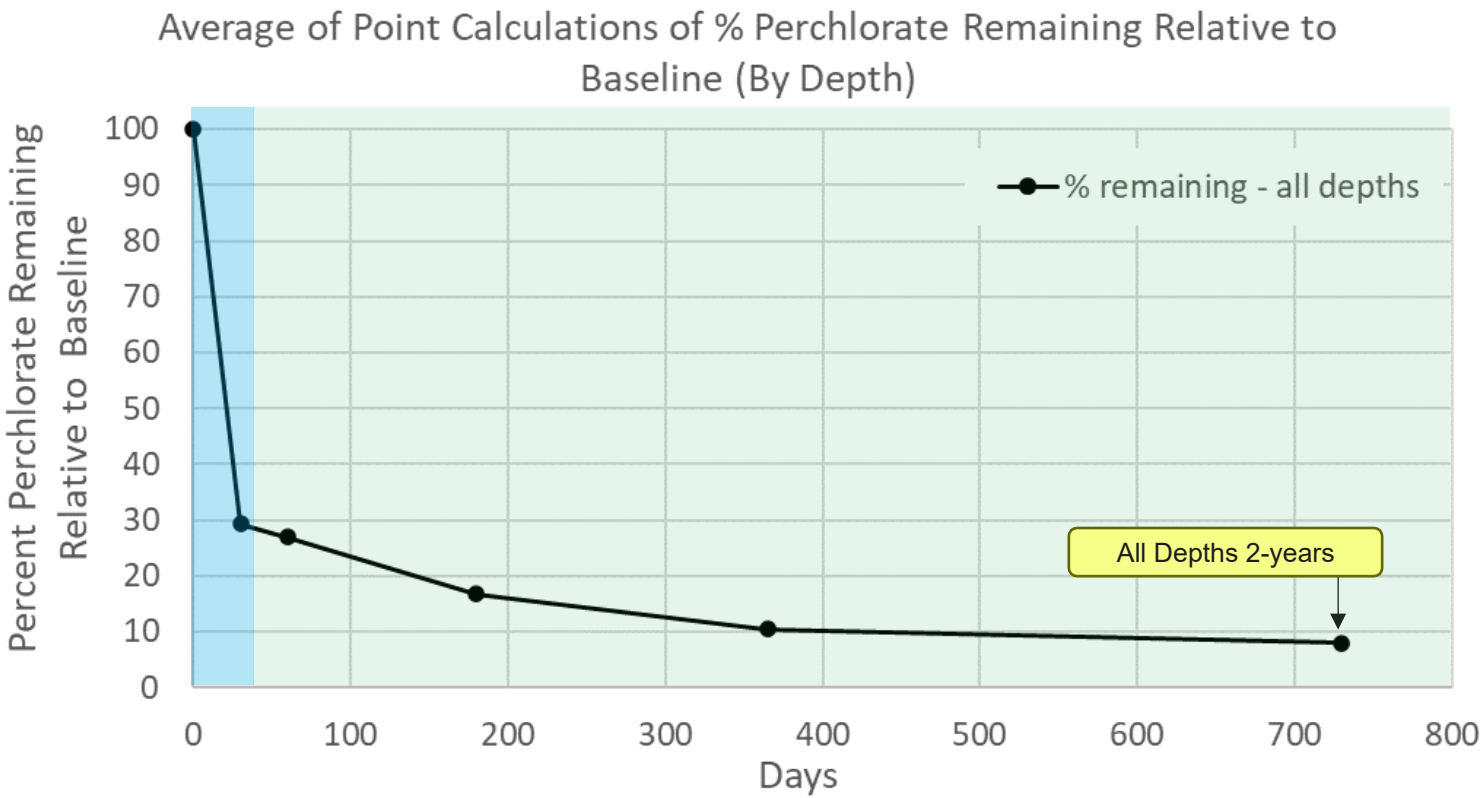
Diffuse presumptive iron sulfides

Note: More visually abundant black materials from 30 to 60 days, particularly in 12’ and 15’ samples

Sample location VINJ-3-2

Perchlorate Concentrations and Average Performance

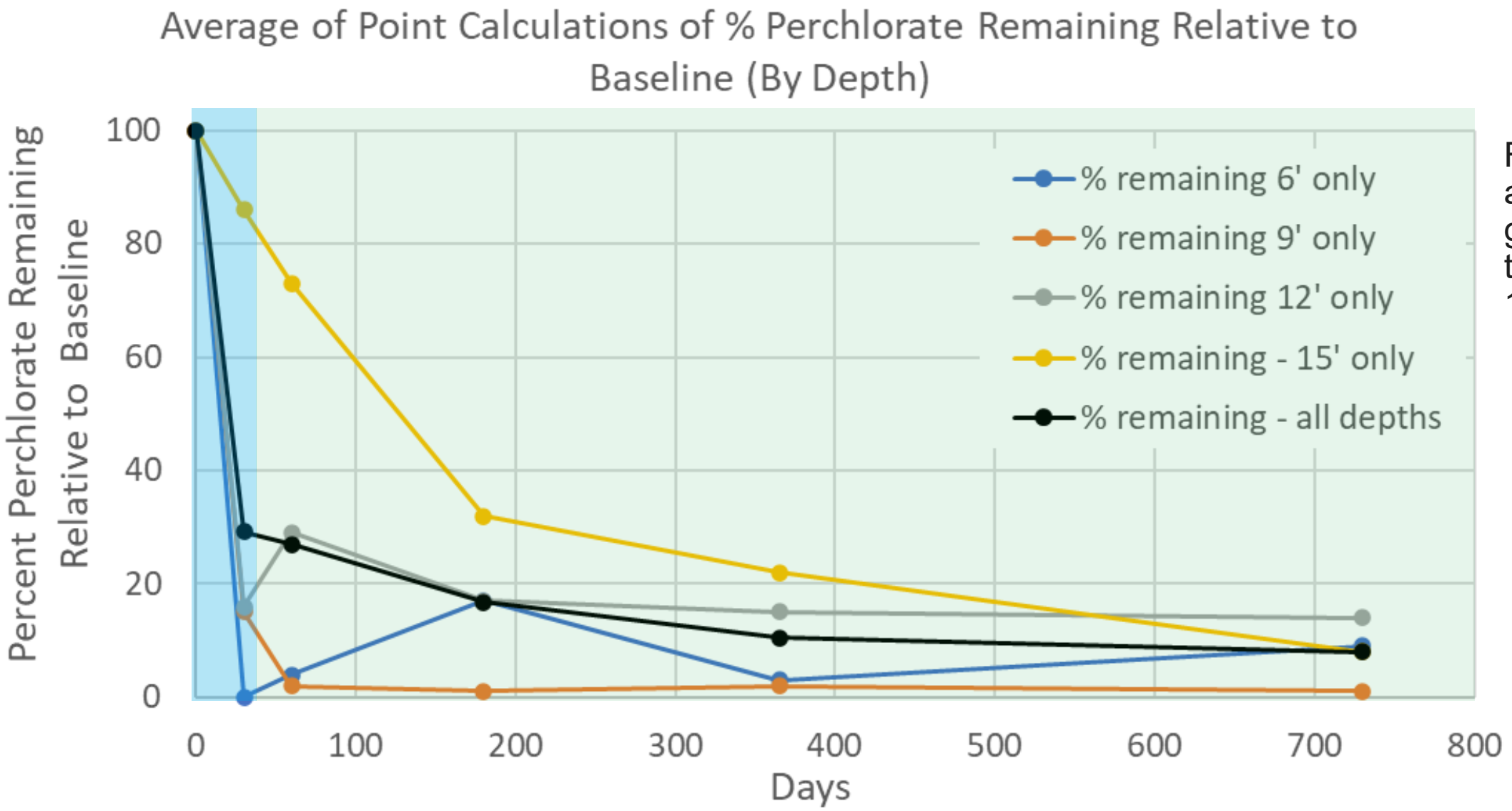
Pre	2-ft from inj point			4-ft from inj point				
ppb in soil	1-1	3-1	6-1	1-2	3-2	6-2	1-3	6-3
6-ft bgs	85	570	800	54	360	1,000	58	110
9-ft bgs	170	450	1,200	170	520	1,200	60	250
12-ft bgs	1,500	300	2,200	1,400	170	6,100	710	1,600
15-ft bgs	2,900	2,800	19,000	2,100	1,900	16,000	4,800	16,000
Post - 30 days								
6-ft bgs	-	-	-	-	-	39	-	-
9-ft bgs	210	-	-	-	-	-	-	-
12-ft bgs	1,600	-	75	220	-	-	-	-
15-ft bgs	2,900	2,400	28,000	2,200	-	15,000	5,500	7,300
Post - 60 days								
6-ft bgs	-	-	-	-	-	350	-	-
9-ft bgs	-	-	150	-	-	-	-	-
12-ft bgs	1,900	230	-	410	-	-	13	-
15-ft bgs	3,200	2,500	10,000	1,900	-	23,000	4,700	190
Post - 180 days								
6-ft bgs	28	-	-	-	-	1,000	-	-
9-ft bgs	10	-	-	-	-	-	-	-
12-ft bgs	1,600	-	-	11	50	-	-	-
15-ft bgs	3,800	2,900	440	-	-	2,400	-	700
Post - 371 days								
6-ft bgs	14	-	6	-	-	41	-	-
9-ft bgs	23	-	-	-	-	-	-	-
12-ft bgs	1,500	-	-	-	-	-	150	-
15-ft bgs	2,600	-	8,300	-	-	48	1,700	1,200
Post - 730 days								
6-ft bgs	3	-	49	-	-	14	3	21
9-ft bgs	3	-	-	-	-	-	3	-
12-ft bgs	850	-	11	54	-	-	360	-
15-ft bgs	310	9	540	-	-	5	2,400	-



Perchlorate reduction is “fast” but observed rates depend on:

- Provision of e- donor/delivery & growth of microbes – **blue region**
- Mass transfer via diffusion in low K soils – **green region**
- *Intrinsic microbial kinetics – probably not important in practice*

Perchlorate Concentrations and Performance by Depth

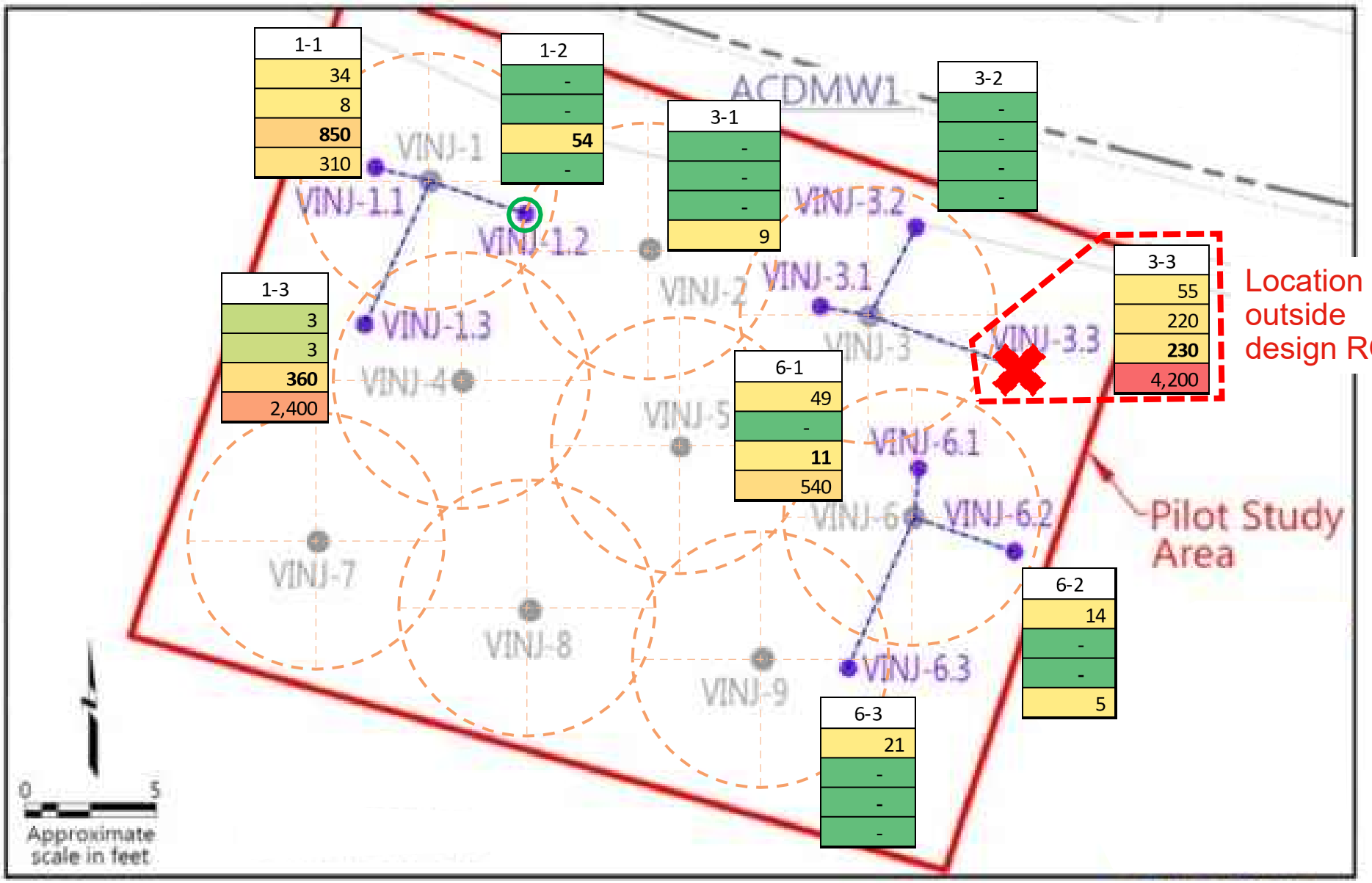


Reduction in 6' and 9' intervals generally faster than in 12' and 15' intervals

Soil Concentrations at 2 years

All values in µg/kg (ppb) in soil at 6', 9', 12', 15' bgs (top to bottom)

- ○ Within 2 different design radii
- ✖ Outside any design radii



Location 3-3 outside design ROI

Design Modifications

Modification	Rationale
Inject deeper	Improve EVO distribution. Target saturated as well as vadose zones.
Inject along periphery	Improve overlapping injections at periphery to fully cover target area.
Closer spacing of injection points	Improve distribution of EVO to account for soil heterogeneities.
Increase to 6% EVO	Potential additional EVO longevity and enhanced distribution.

Conclusions

EVO injection for remediation of perchlorate in the vadose zone is a viable approach for fine-grained soils

Perchlorate reduction occurs over an extended time period, likely becoming mass transfer controlled

Iron sulfides provide visual evidence of local sulfidogenic conditions and complete perchlorate reduction

Questions