Petroleum Remediation Using In-situ Activated Carbon
(A review of results)

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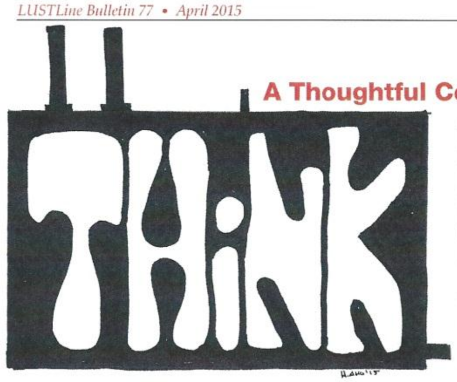
Supplement to recent LUSTLINE article--

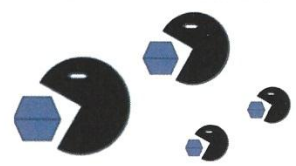


A Thoughtful Column Engineered by Mahesh Albuquerque

Mahesh Albuquerque, Director of the Colorado Division of Oil and Public Safety, is on the lookout for articles from creative thinkers and experts willing to share ideas, insights, and stories on a wide variety of issues related to underground storage tanks. Topics include policy, strategy, successes, failures, and lessons learned. "Now that we have been regulating USTs for 30 years," says Mahesh, "my hope is that this column will help stimulate readers to 'think outside the tank,' to ponder why we do what we do, and to consider and share creative ways to improve our effectiveness—as we strive toward environmental protection." Mahesh can be reached at mahesh.albuquerque@state.co.us.

Hello Carbon, My Old Friend

Petroleum Remediation Using Activated Carbon



by Tom Fox

Many readers may recall the early days of petroleum storage tank remediation when pump-and-treat (P&T) systems were commonly employed to move contaminated groundwater through above-ground treatment systems. Activated carbon (AC) filtration vessels were often used as a final treatment step prior to water discharge. As P&T systems fell out of favor due to their ineffectiveness in reaching the cleanup goals required for closure, likewise, AC seemed to fall out of favor as a remedial tool. But the beneficial properties of AC have not changed and still have a place in petroleum remediation.

Over the past decade, a new market has developed for AC; it involves direct injection into the subsurface to treat dissolved-phase contamination. This in-situ remediation technique uses AC in a two-step process—sequestration and then biodegradation. During this process organic compounds are sorbed to AC so strongly that it is almost certain that the contamination will be stable and unavailable for leaching for at least 50 to 100 years (Norwegian Research Council, 2011), an ample time for natural anaerobic biodegradation processes to occur. The Colorado Division of Oil and Public Safety (OPS) refers to this process as "carbon-based injection" (CBI).

To our knowledge, four AC products currently on the market can be used specifically for remediating petroleum hydrocarbons via injection: pure powdered AC; Trap & Treat BOS 200 by Remediation Products, Inc. (RPI); COGAC by Remington Technologies, LLC; and PlumeStop Colloidal Biomatrix by Regenesis. (OPS does not endorse any particular product.) The brand name products have patented or patent-pending additives that are intended to promote hydrocarbon degradation after injection. Some of these products are also available in granular form.

OPS has approved CBI at more than 200 LUST sites. The success we have noted in sequestering and immobilizing dissolved hydrocarbon contamination to reduce environmental and health risks makes AC an option to consider as part of our remediation toolbox.

How successful has CBI been? If success is defined as achieving site closure, approximately 15 percent of the CBI sites have satisfied OPS criteria to achieve site closure conditions (full disclosure: we have not evaluated the "success" of other remedial technologies with this criteria, but typically sites that require remediation have multiple remedial technologies employed to achieve closure). Furthermore, if success is defined as achieving a significant reduction in dissolved-phase contaminant concentrations, then we are glad to report that the vast majority of injection sites experienced >95 percent reduction in BTEX within six months.

As with any remedial technology, observations may take years to make themselves apparent. The purpose of this article is to share our observations with you. With that, we will present you with the three C's of our observations as they relate to the implementation of a successful CBI application—characterization, contact, and confirmation.

Step 1: Characterization

As with any remedial project, success is due in large part to good site characterization. OPS typically requires a thorough characterization of the proposed treatment area prior to full-scale design to precisely target the horizontal extent and vertical zones of contamination. We recommend the use of continuous soil sampling and/or Membrane Interface Probe (MIP) technologies. The effort expended in this site characterization improves the effectiveness of the design, and often reduces the total project cost as assumptions associated with the contaminant-bearing zone are reduced.

Estimations of the masses of hydrocarbon by phase (LNAPL, dissolved, and adsorbed) allow us to target an adequate amount of AC where

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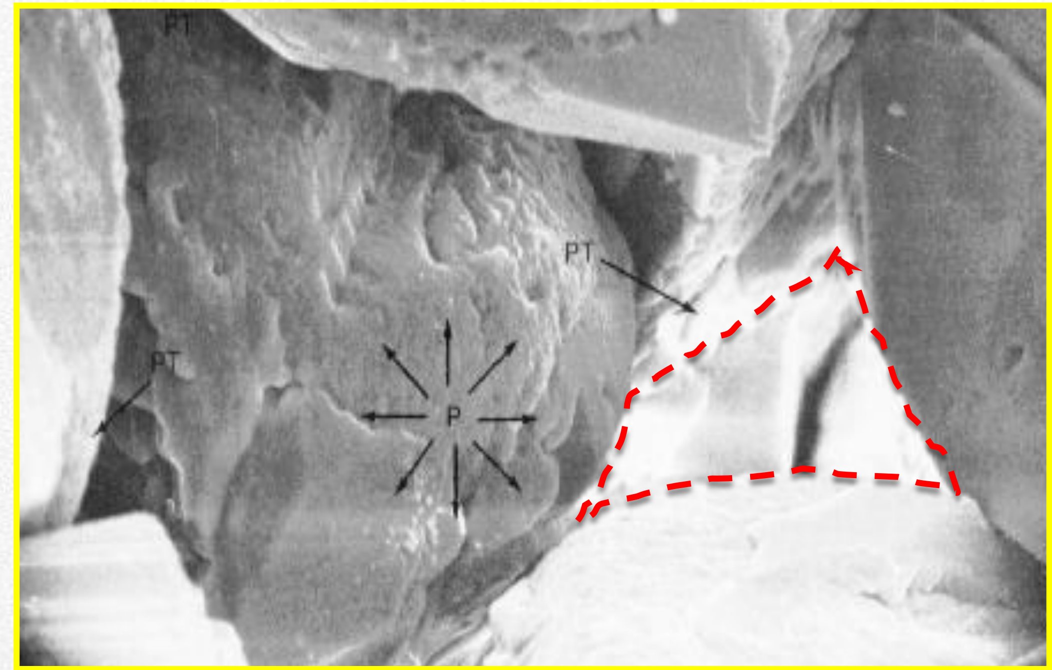
What we'll cover

- Background on activated carbon properties and injection technique.
- Colorado's experience with carbon-based injection.
  - Characterize---contact---confirmation.
- Preliminary results of new confirmation efforts.
- What next?

Properties of powdered activated carbon:

- Sourced from coal, wood, or nut shells. Activation process increases surface area by creating pores in a carbon matrix.
- One pound has ~100 acres surface area.
- Apparent density ~0.5 g/cc (30 lbs/cu ft).
- Absorbs 10-35% of its weight in hydrocarbons.
- Indefinite retention of contaminants.
- Inhalation hazard, but non-toxic if ingested.

Properties (cont.)



- Particle size <40 microns (μ)
  - 10-slot screen = 256 μ
  - 200-mesh sieve (clay) =75 μ
  - Bacteria = 0.5 - 2 μ
  - Pore throats (*Nelson, AAPG Bull., 3/09*):

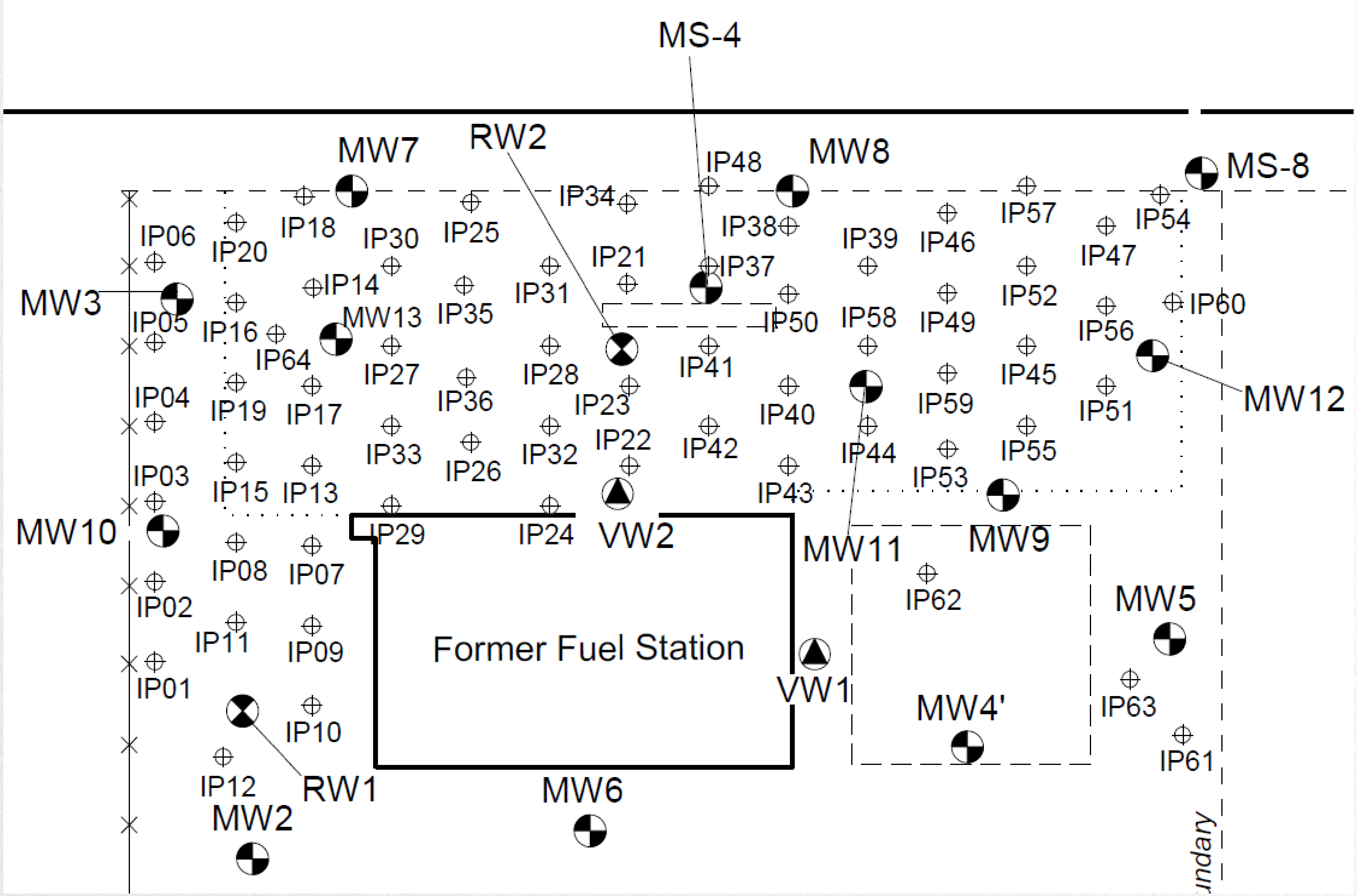
    sand >2 μ *silt* 0.03 – 2 μ *clay* 0.005 – 0.1 μ
  - BTEX molecules = 7 Angstroms (Å) = 0.0007 μ
  - Water molecule = 3 Angstroms (Å) = 0.0003 μ

Carbon-based injections (CBI)—

- Usually 10-foot hexagonal grid spacing
- 0.3 - 2 lb/gal slurry
- Pressures <1000 psi. (minimum 1 psi/ft)
- Flows <1 to >30 gpm
- Surfacing and well infiltration always a concern

- Usually has nutrients, oxidants or bacteria added

Typical injection plan



CBI in Colorado

- Over 225 facilities treated since 2005.
- Usually tried when other methods unsuccessful / impractical (clay or bedrock; offsite).
- Significant reductions (>90%) in dissolved BTEX noted.
- Visible carbon usually in wells.
- Rebound and/or additional treatment often occurred.
- About 15% of sites treated with CBI reached NFA.
    - ❑ Small areas
    - ❑ <700 ug/L benzene (usually <200 ug/L)

CBI Guidance

1) Detailed CHARACTERIZATION:

- Conceptual Site Model (CSM)
- MIP or continuous soil samples for lab analysis
- Estimate mass by phase
  (LNAPL, dissolved, adsorbed)
- Use an experienced design team
  (mass calculations are critical)
- Pilot test for pressures/flows

CBI Guidance

2) CONTACT:

- Use an experienced injection crew
- Closely spaced injection points
- Target the entire vertical extent of contamination
- Use short (1-2 foot) injection intervals
- STOP if surfacing or well injection occurs

CBI Guidance

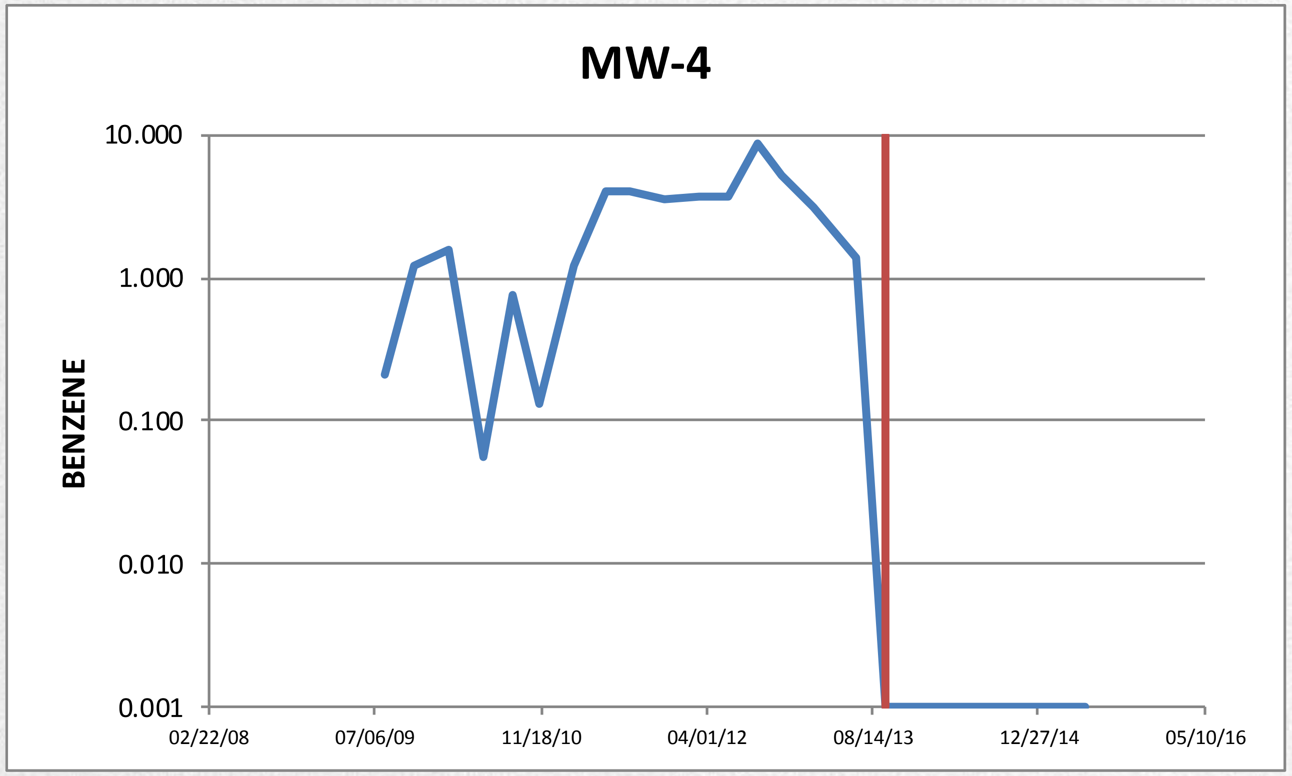
3) CONFIRMATION:

- Extended closure monitoring from 4 to 6 quarters for injection techniques due to lingering effects of injectates (e.g. carbon, oxidants, bio-nutrients)

BUT…

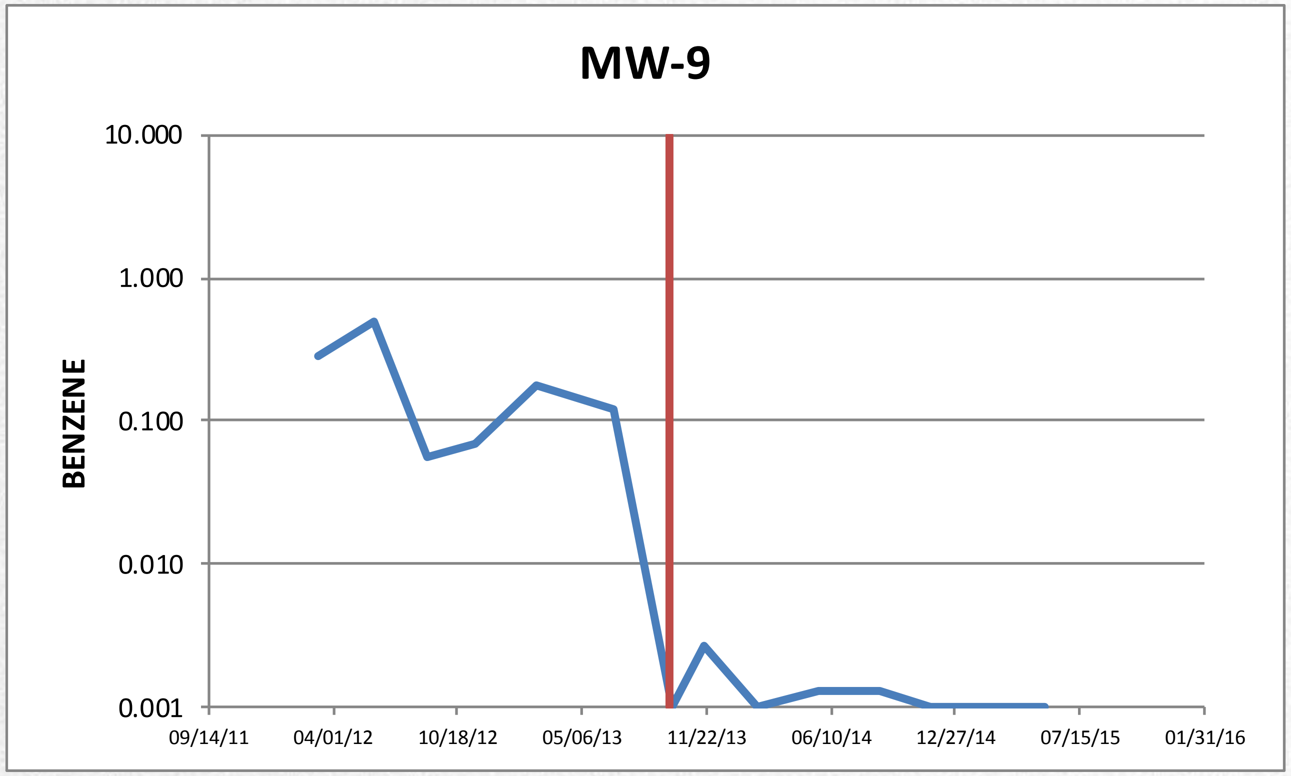
Is this a representative groundwater sample?

Typical well responses after CBI:



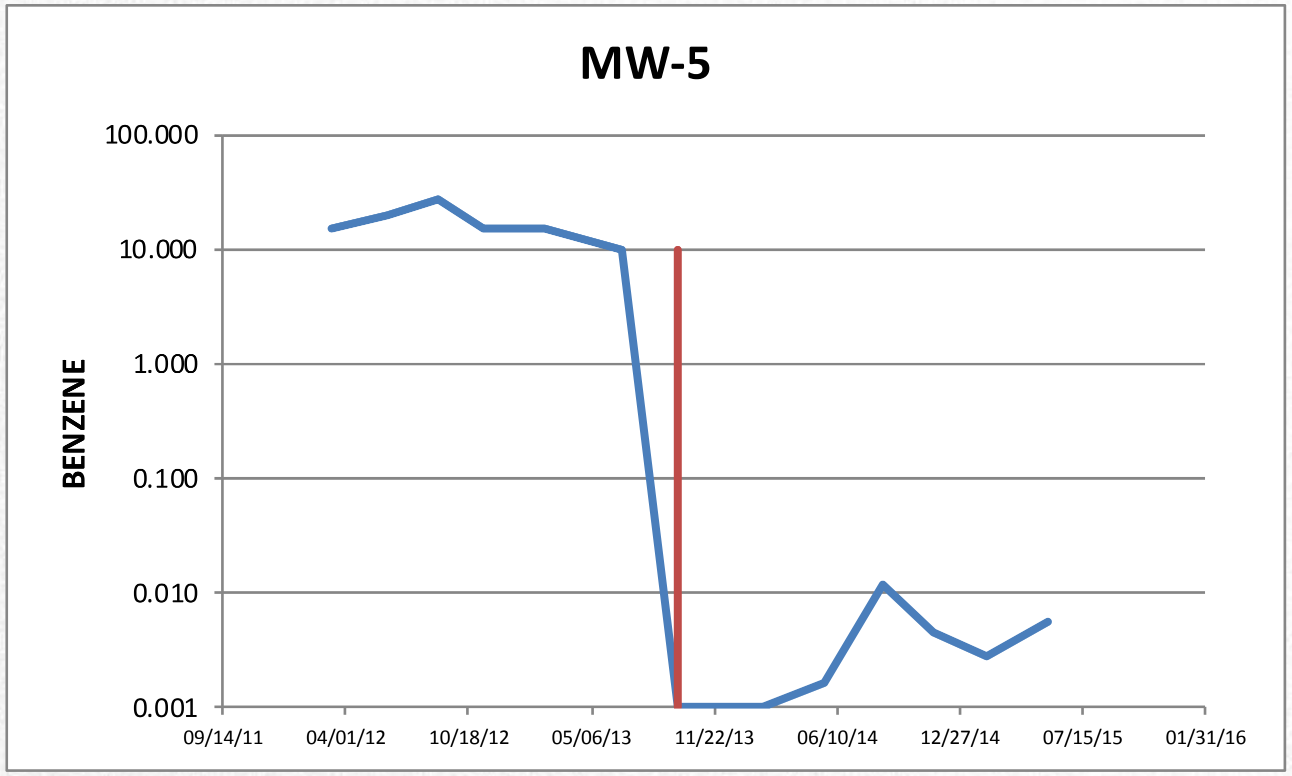
Instant response

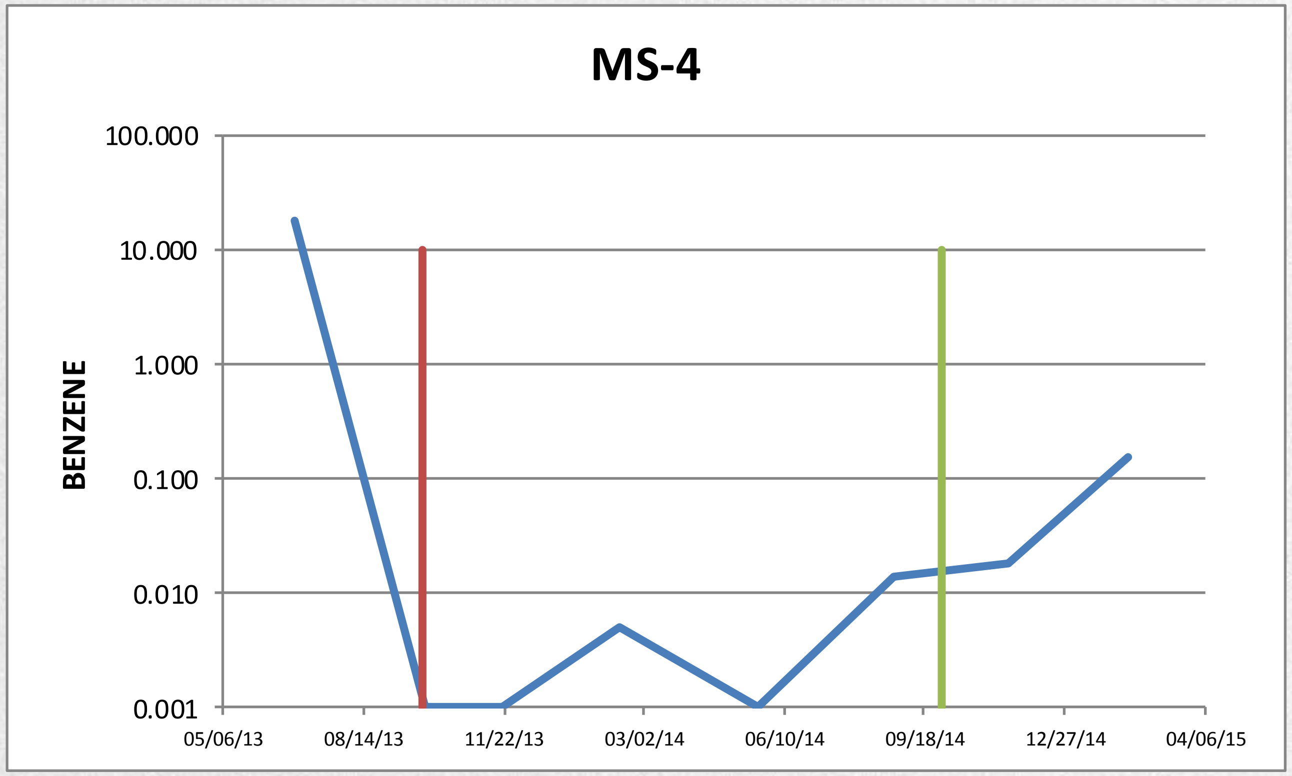
Slower response



Typical well responses after CBI:

Rebound



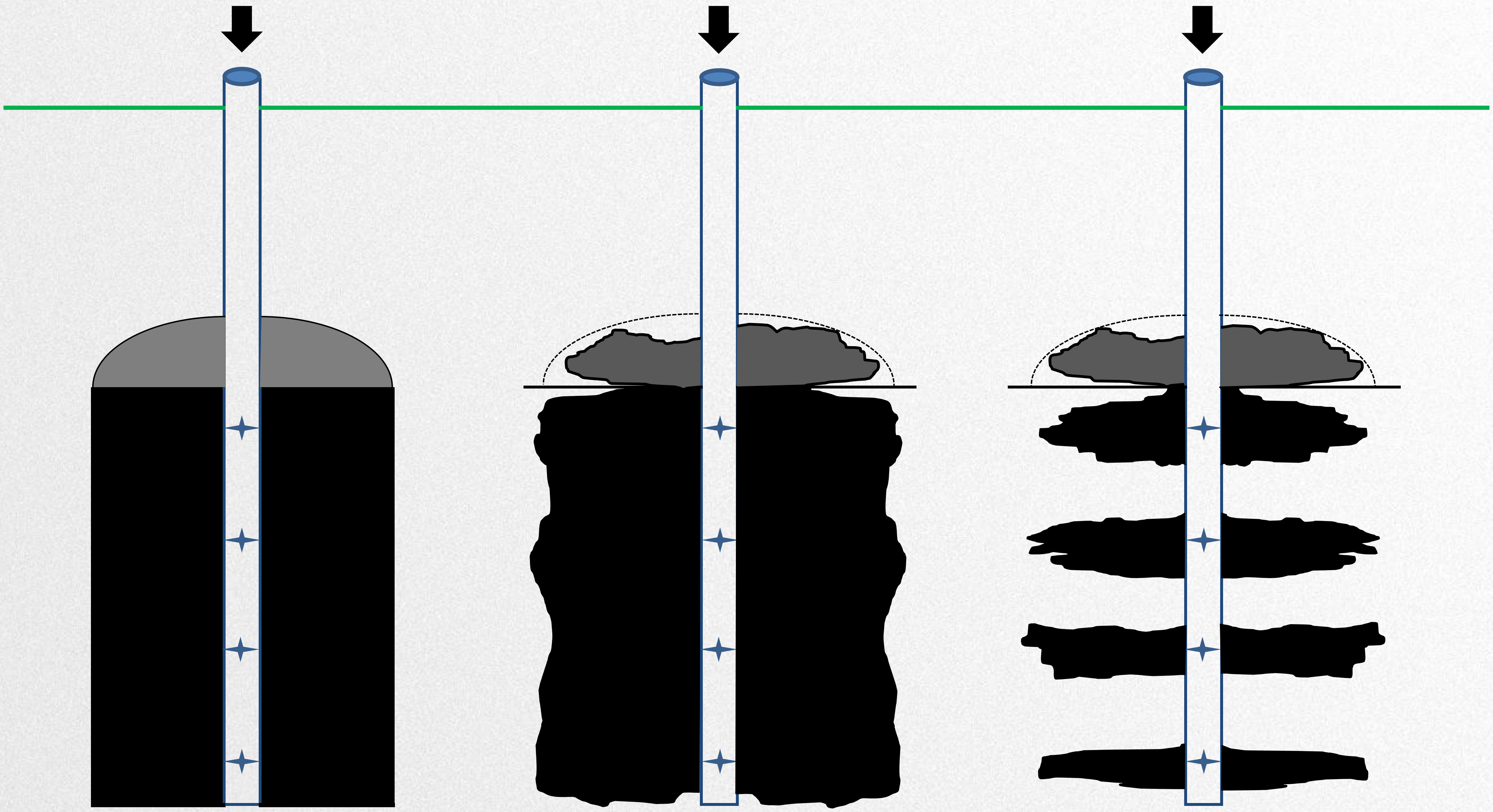


Rebound after pilot plus second injection

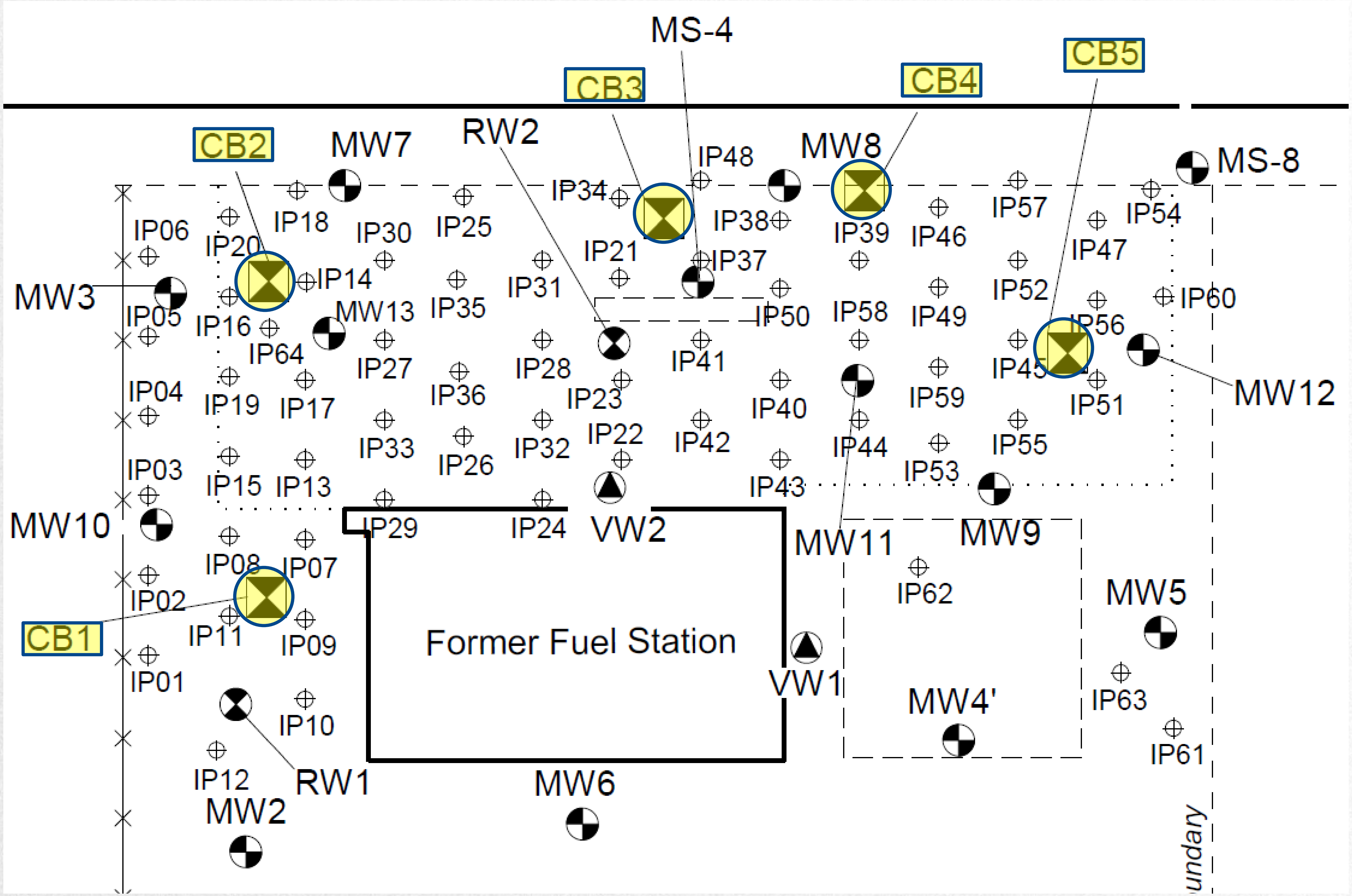
OPS wants to confirm:

1. How is carbon distributed by injection?
2. Is the aquifer remediated?
3. Any evidence of continuing degradation?

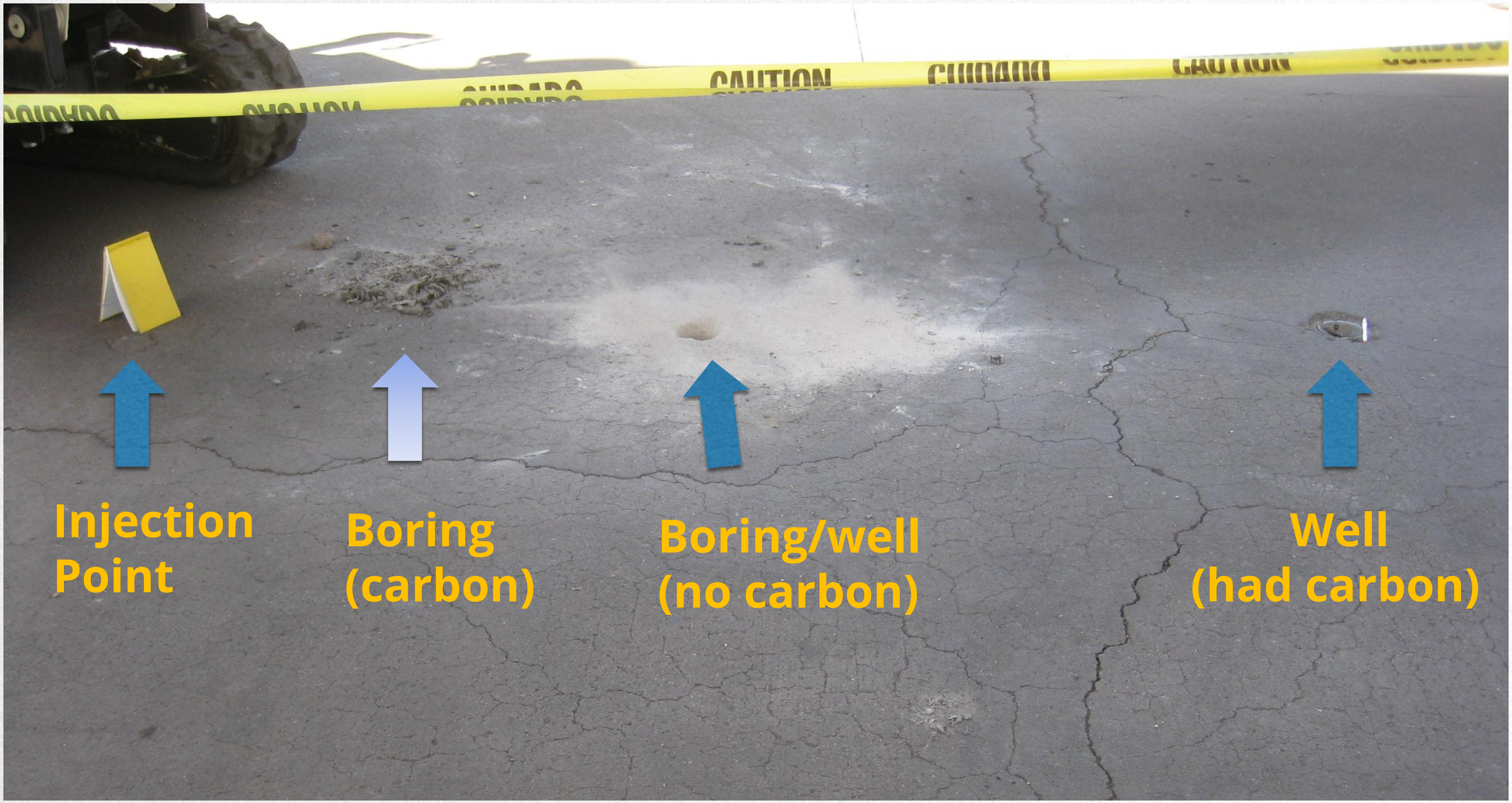
Concepts of CBI Distribution



Confirmation points

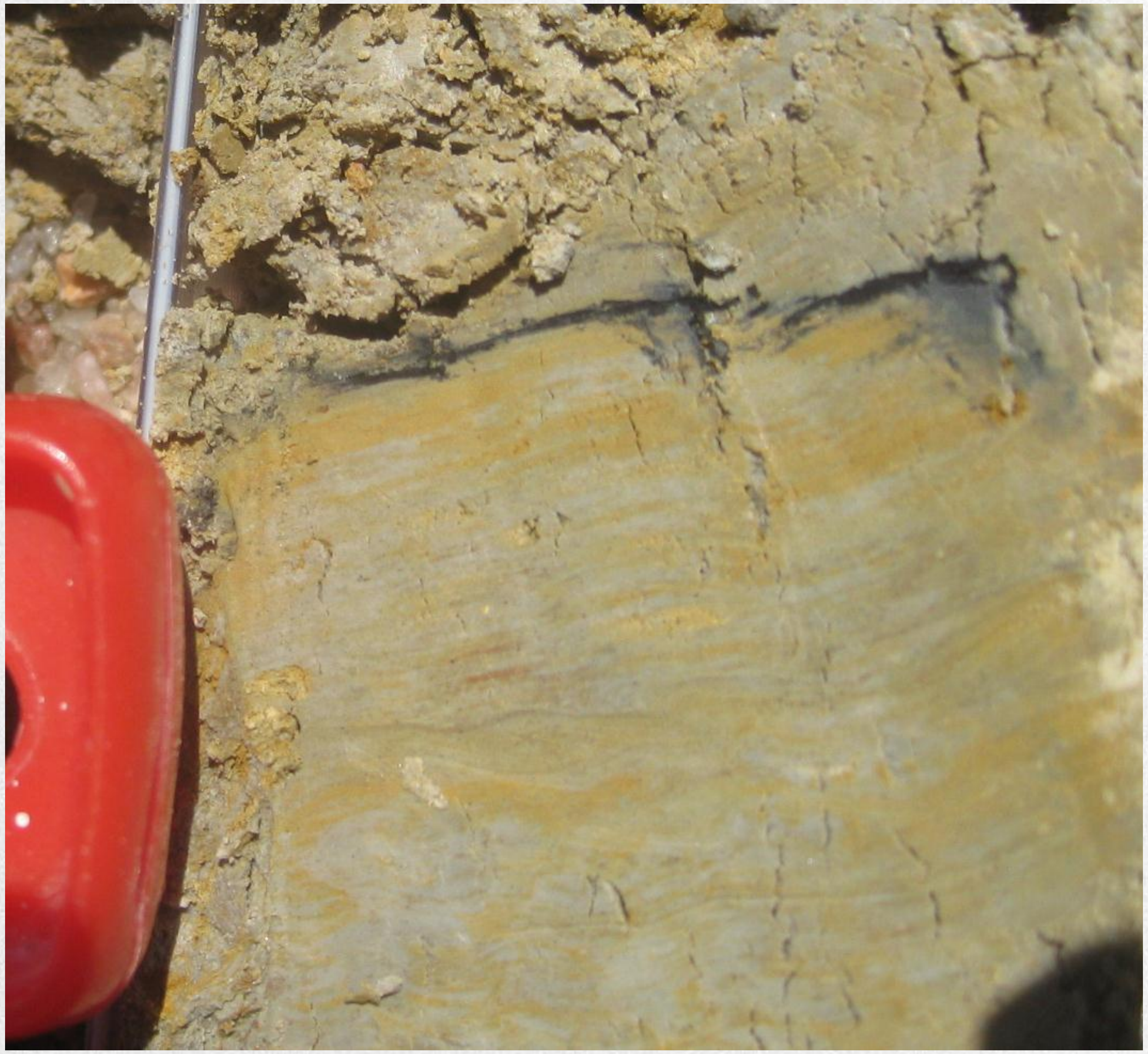


Confirmation borings

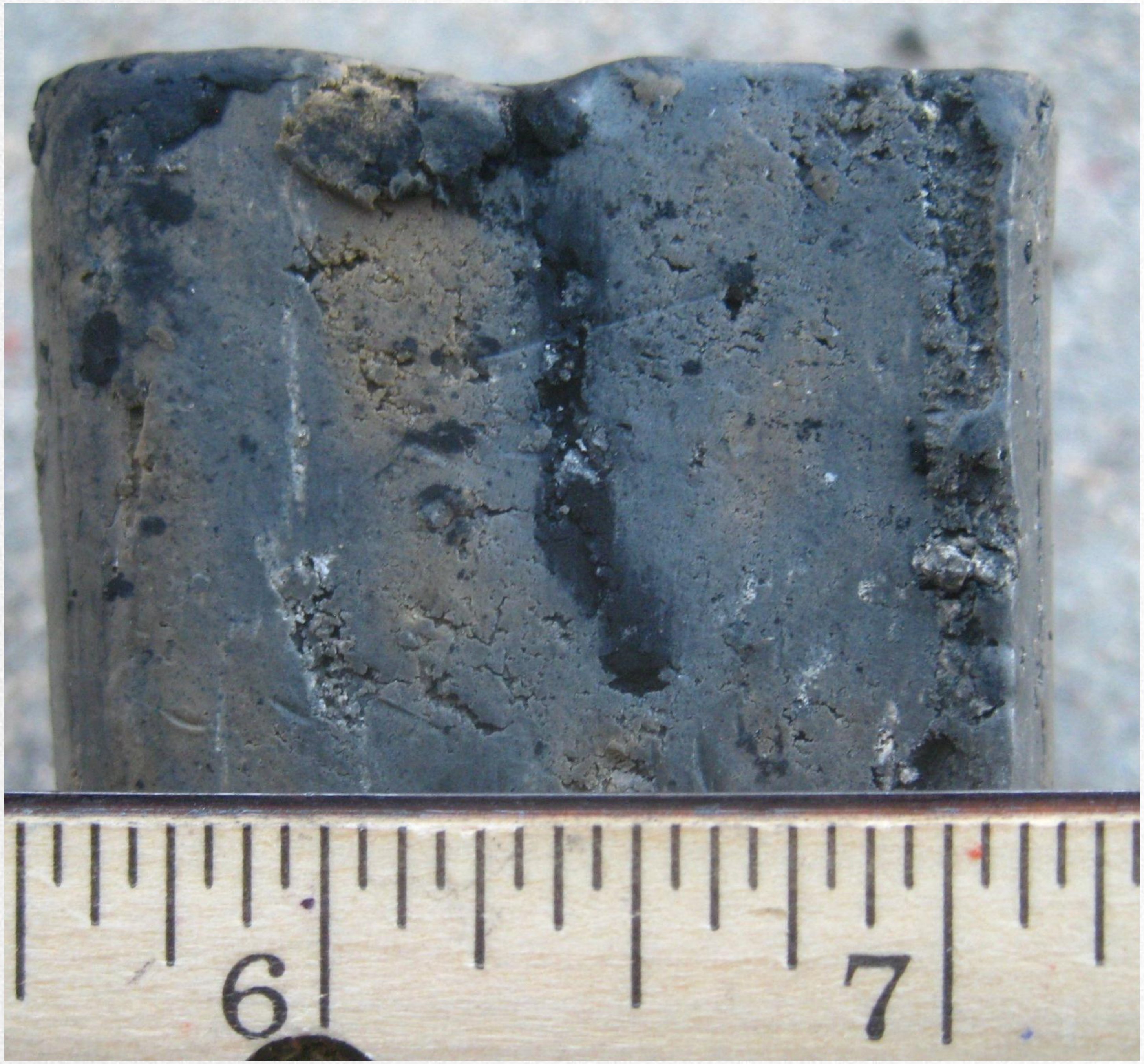


Identifying carbon

Emplacement-thin veins

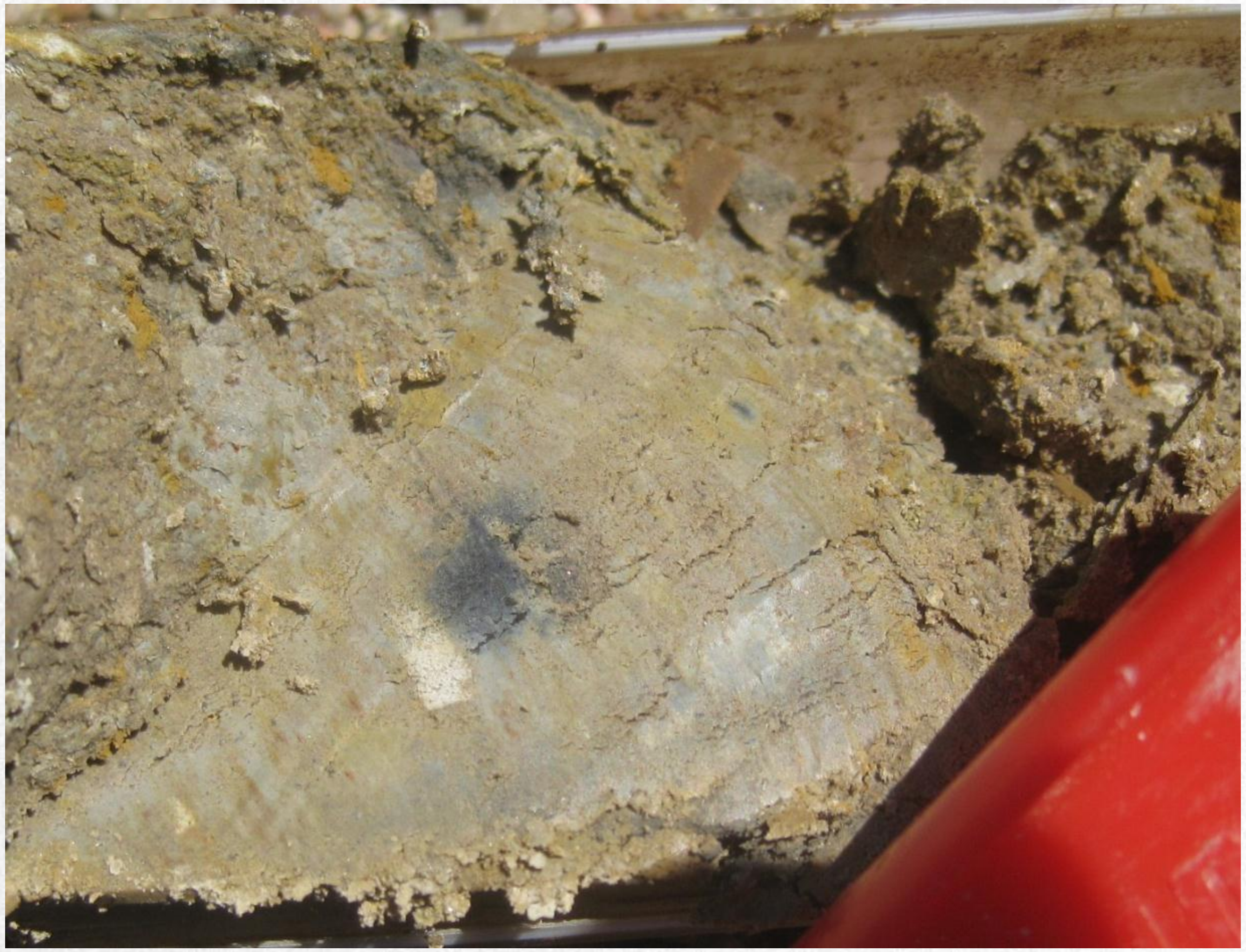


Emplacement-thin veins



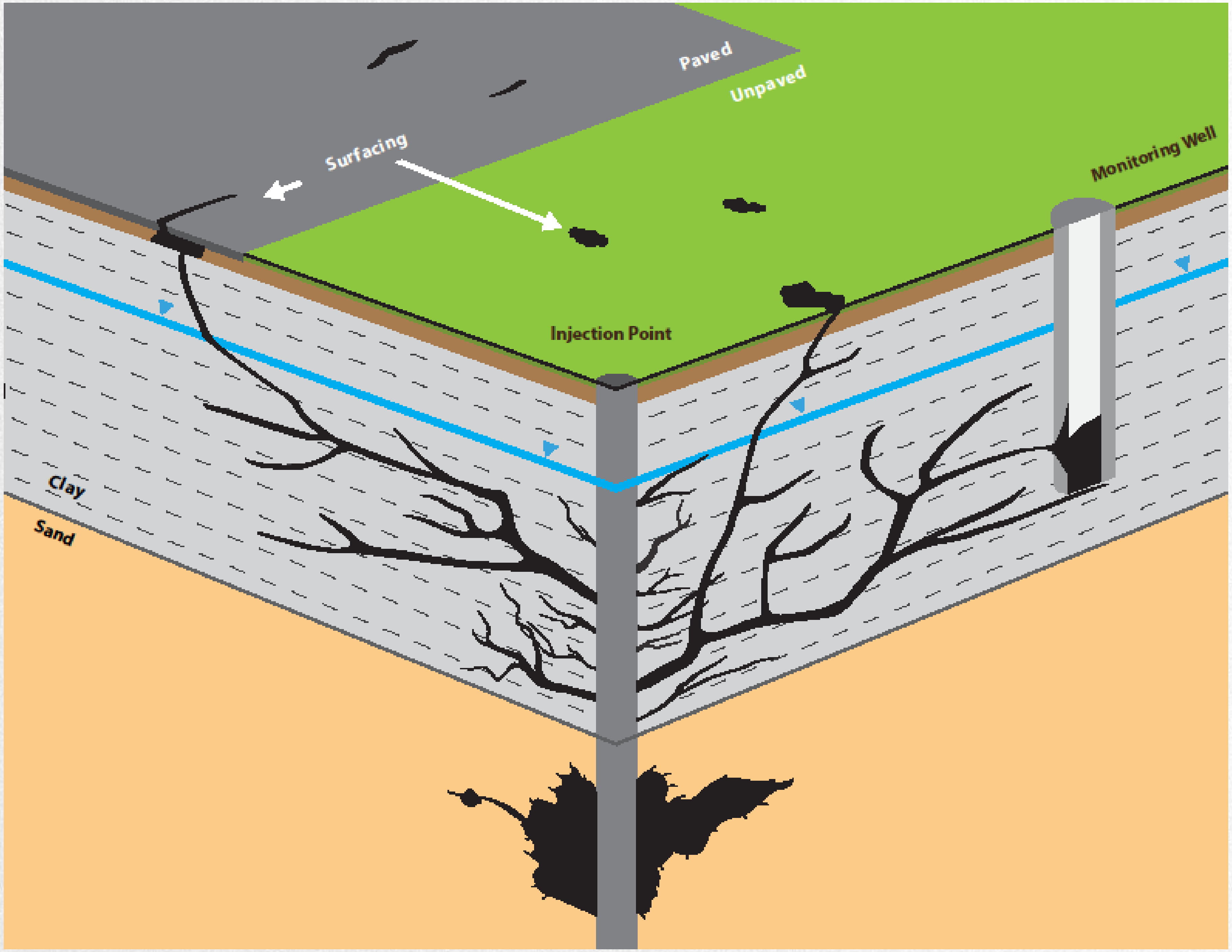
Emplacement-veins/spots

Emplacement-diffused



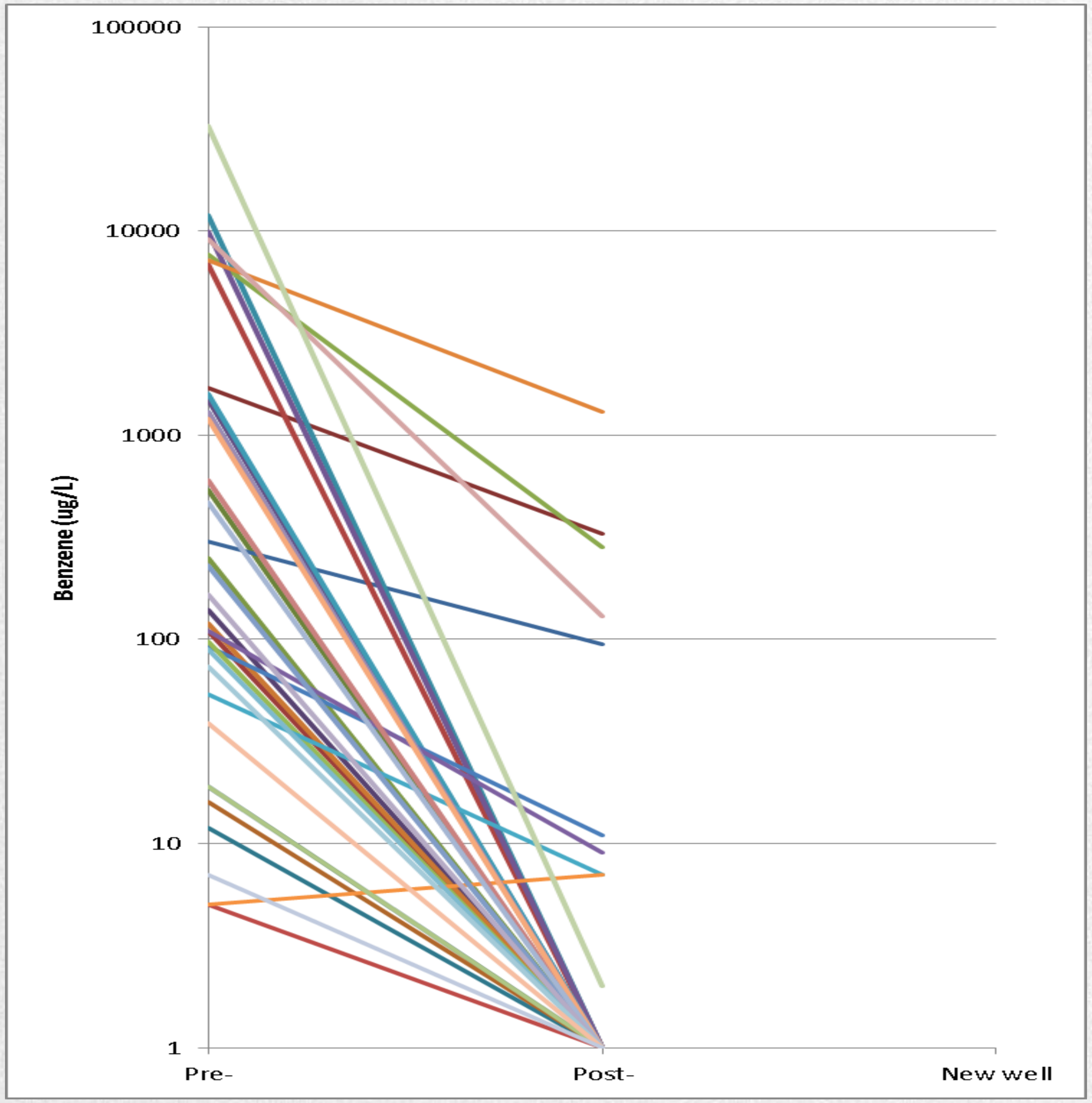
Emplacement-diffused

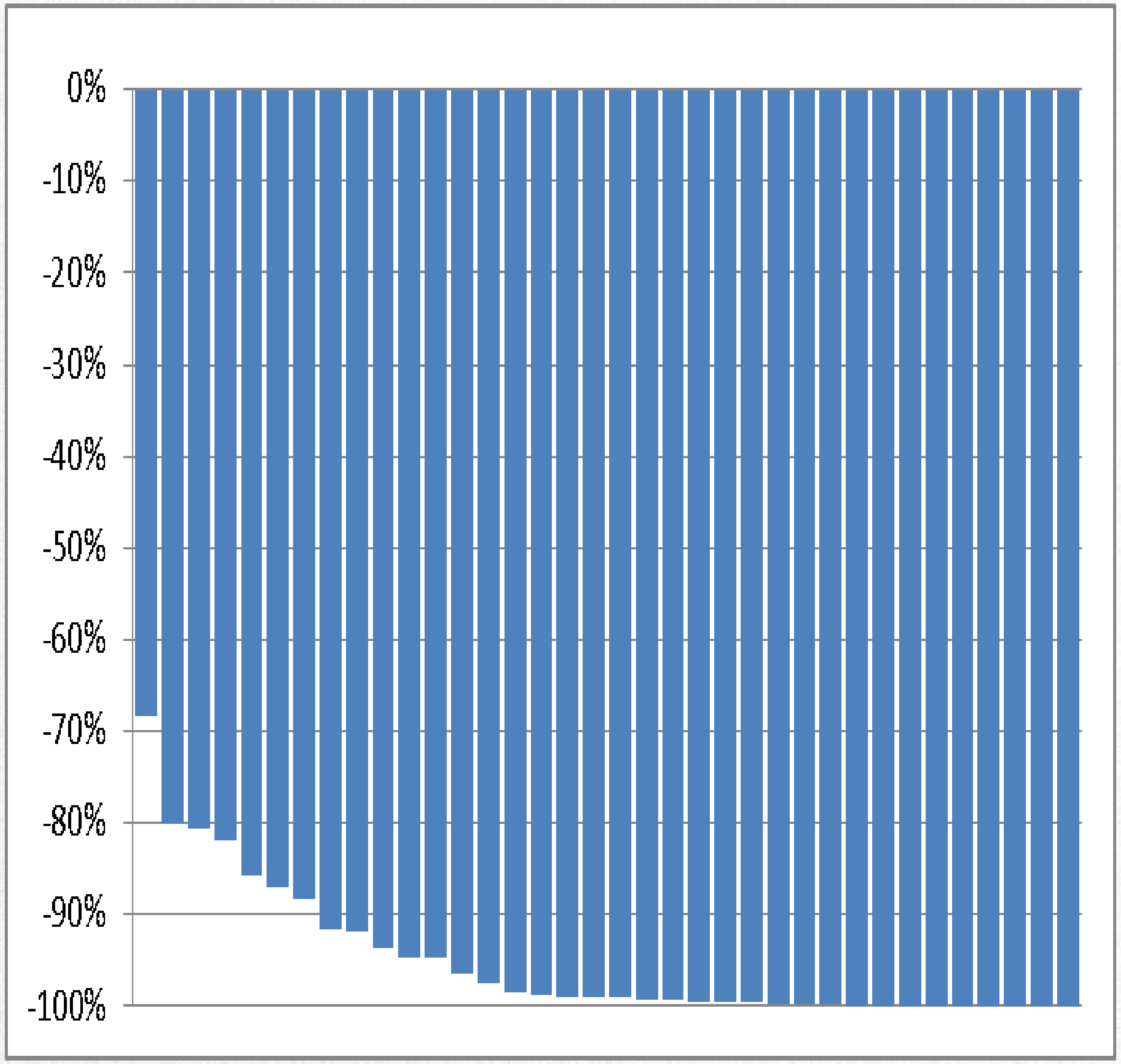
Distribution is based on lithology and unpredictable.



The aquifer...?

Rapid reduction in benzene (36 wells, 14 sites)…

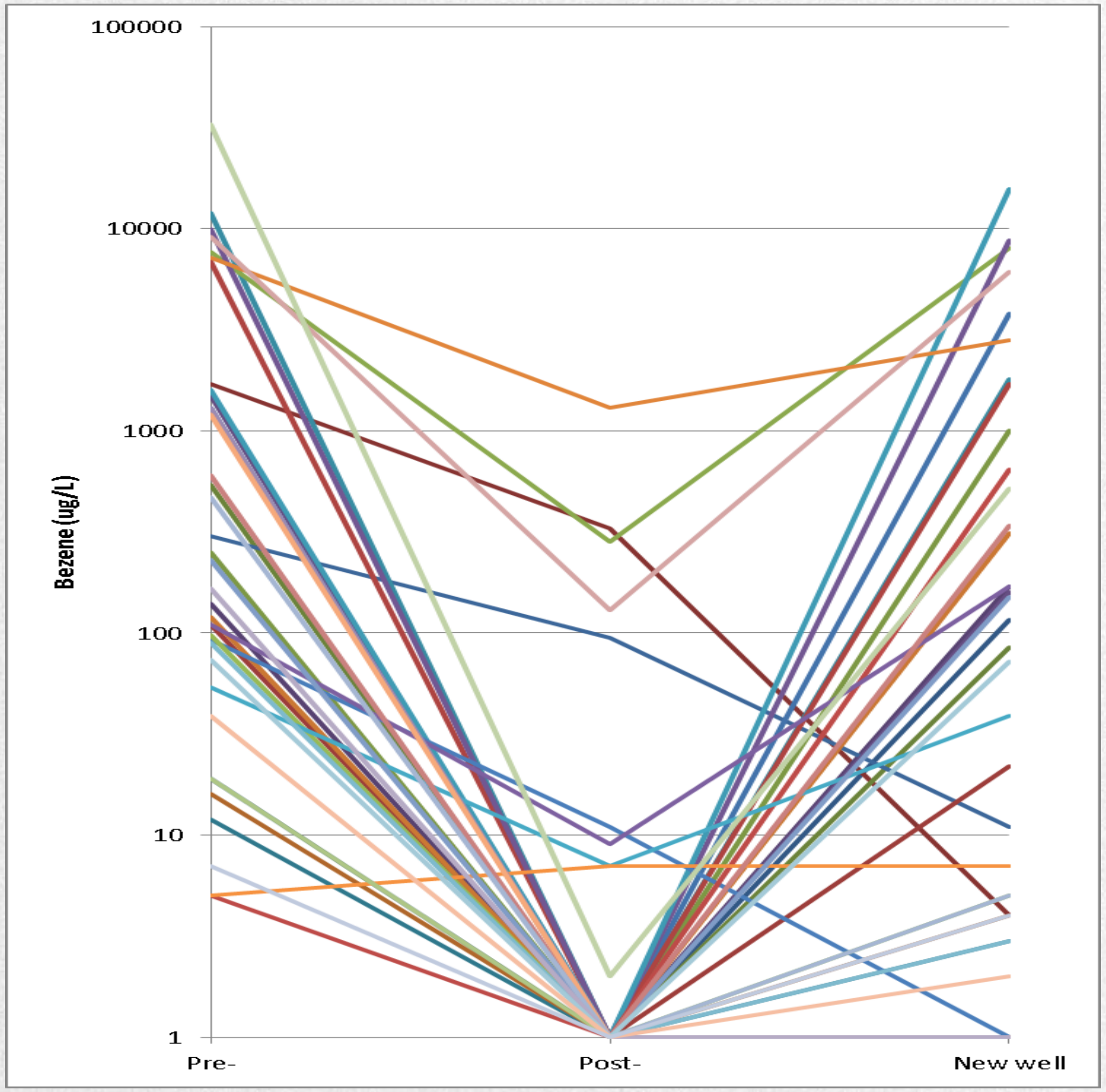


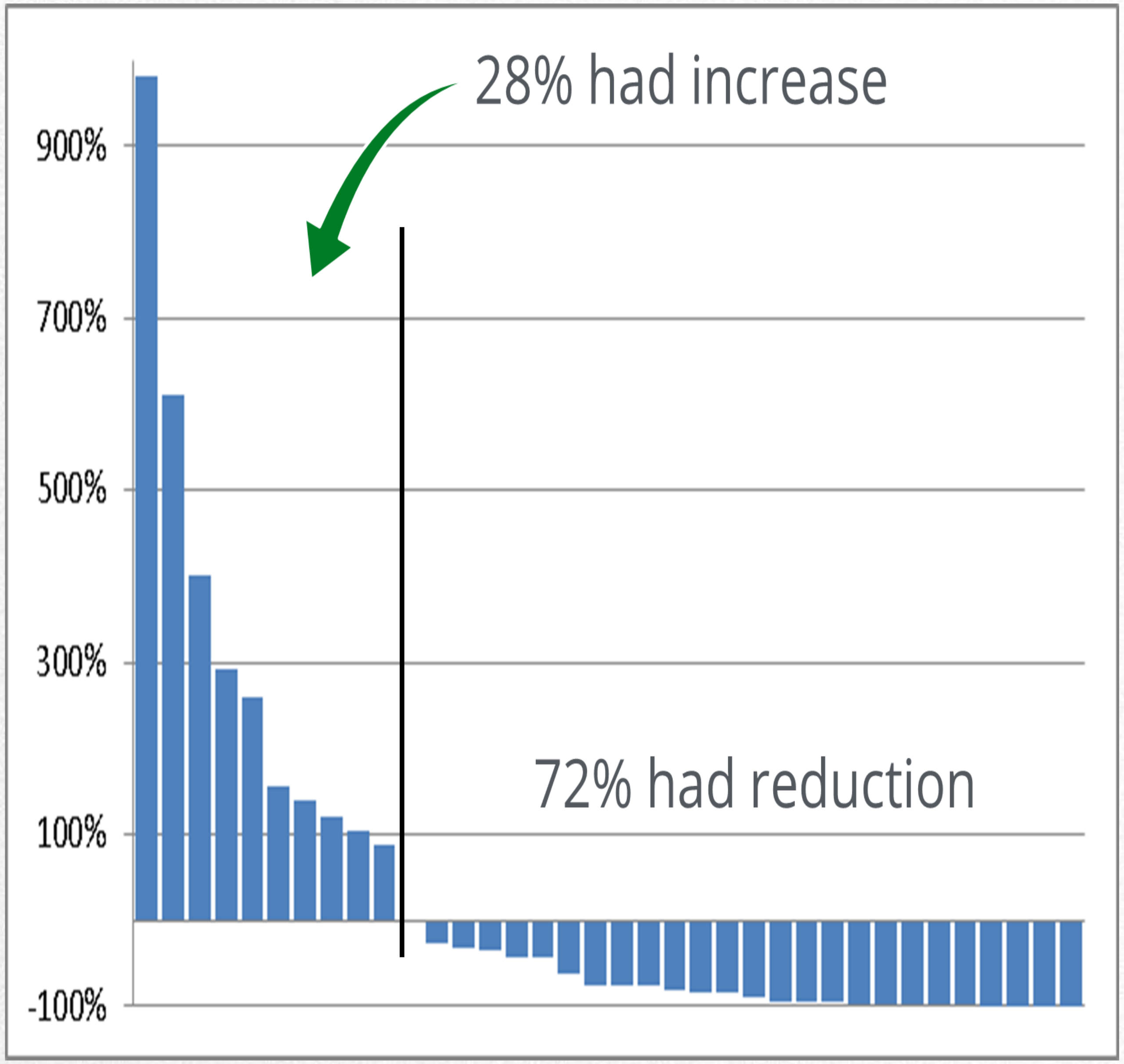


>80% reduction!

New wells

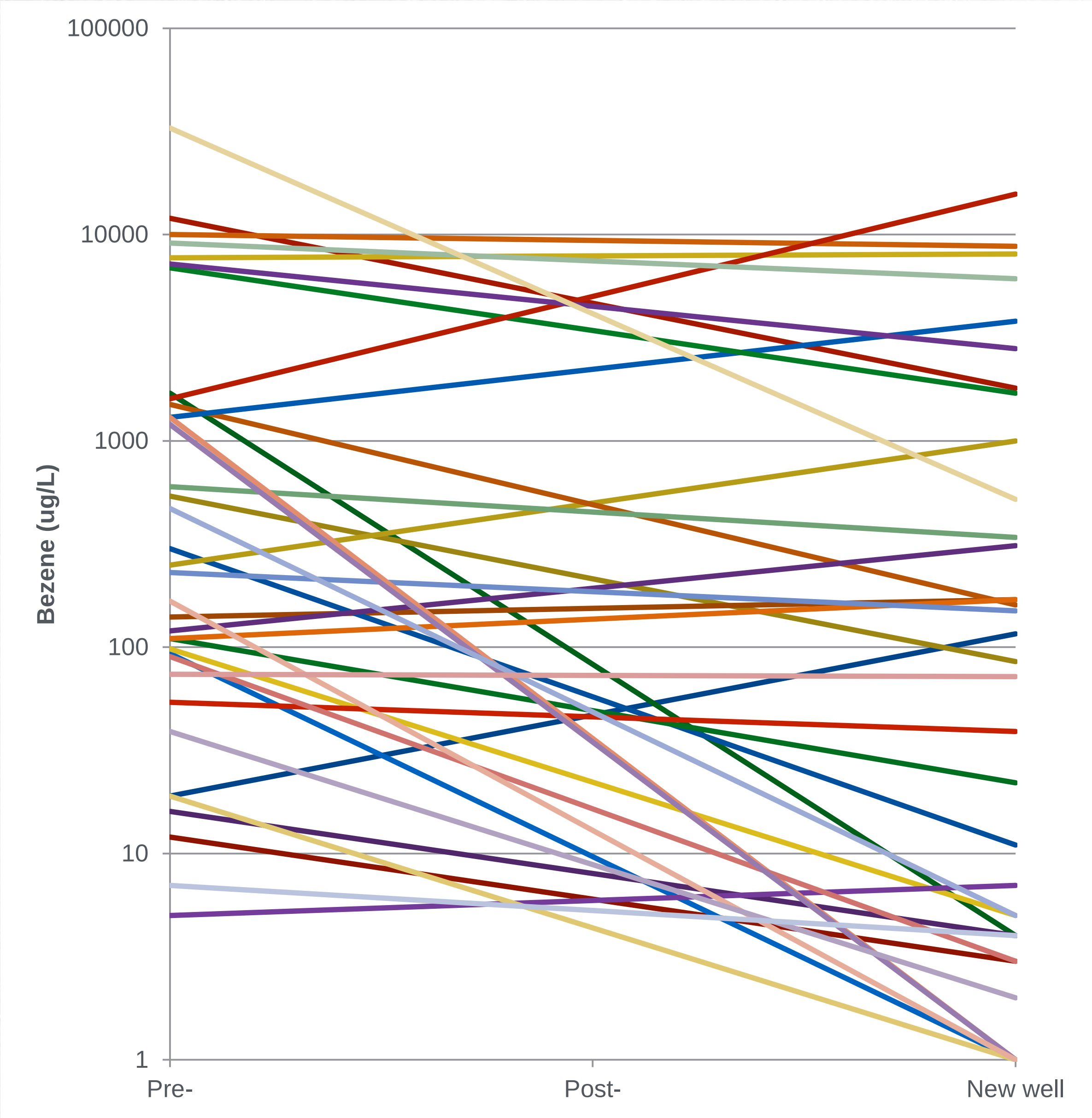
...but aquifer treatment incomplete.

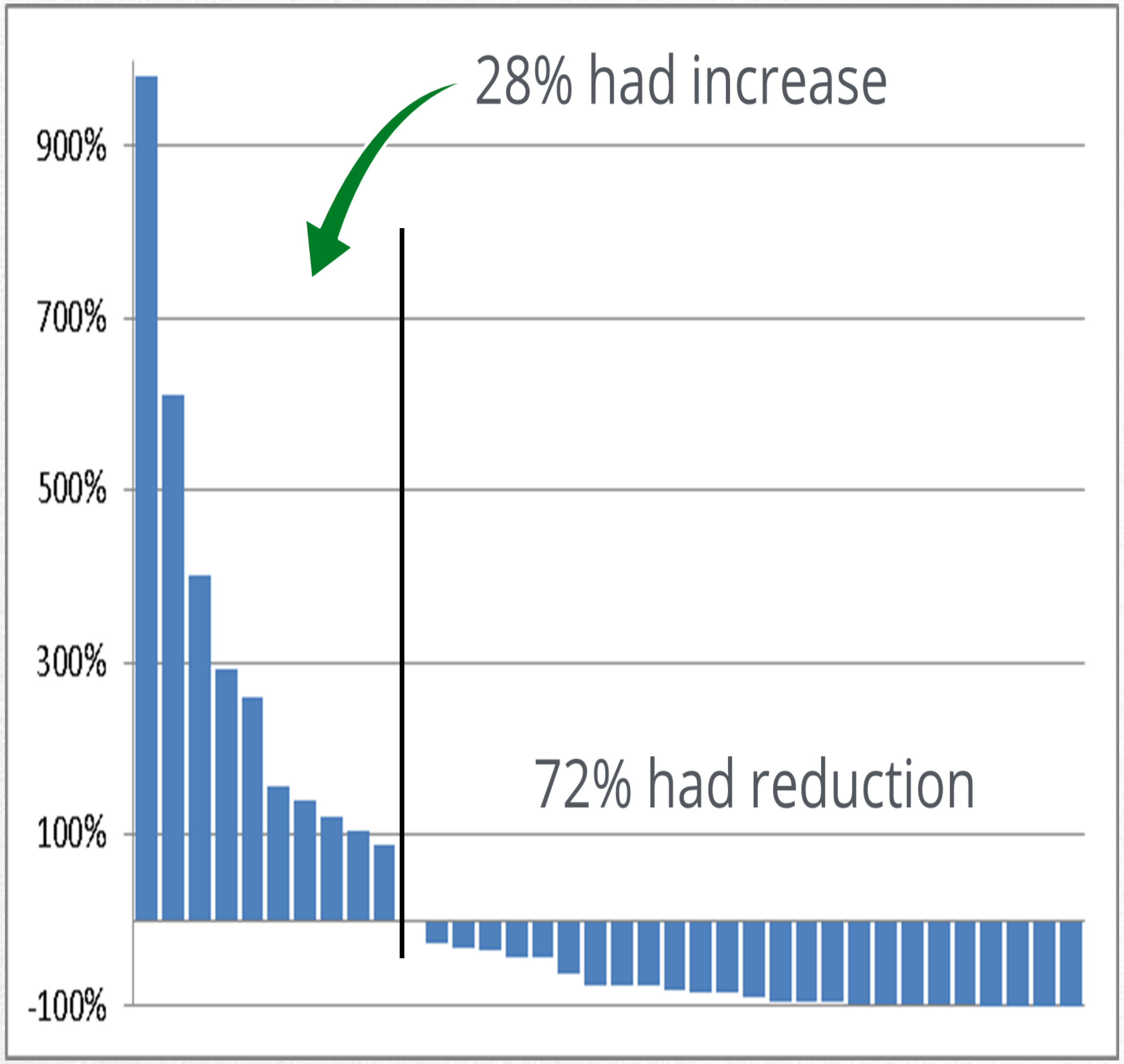




(36 well pairs)

…but aquifer treatment incomplete.





(36 well pairs)

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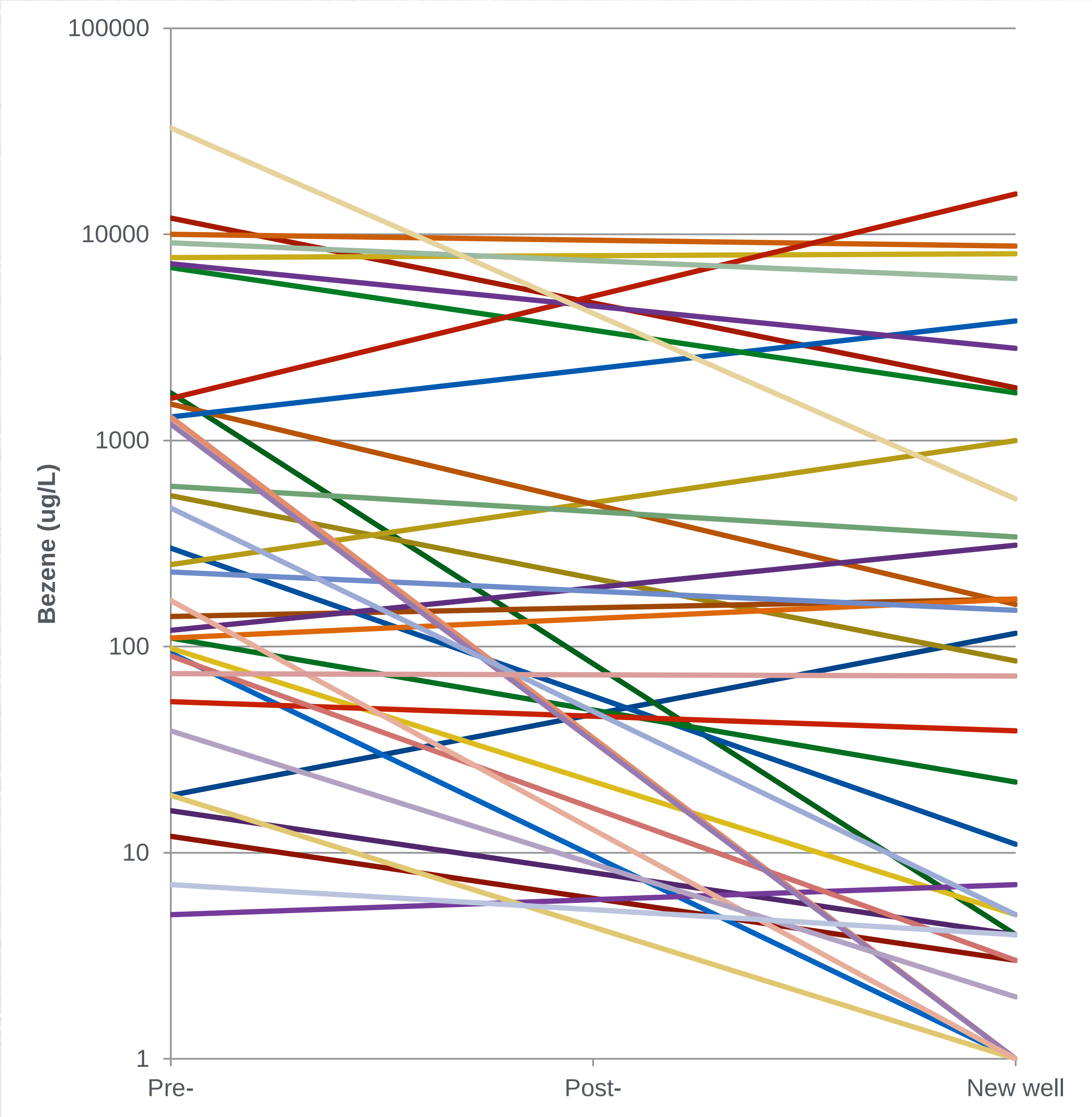
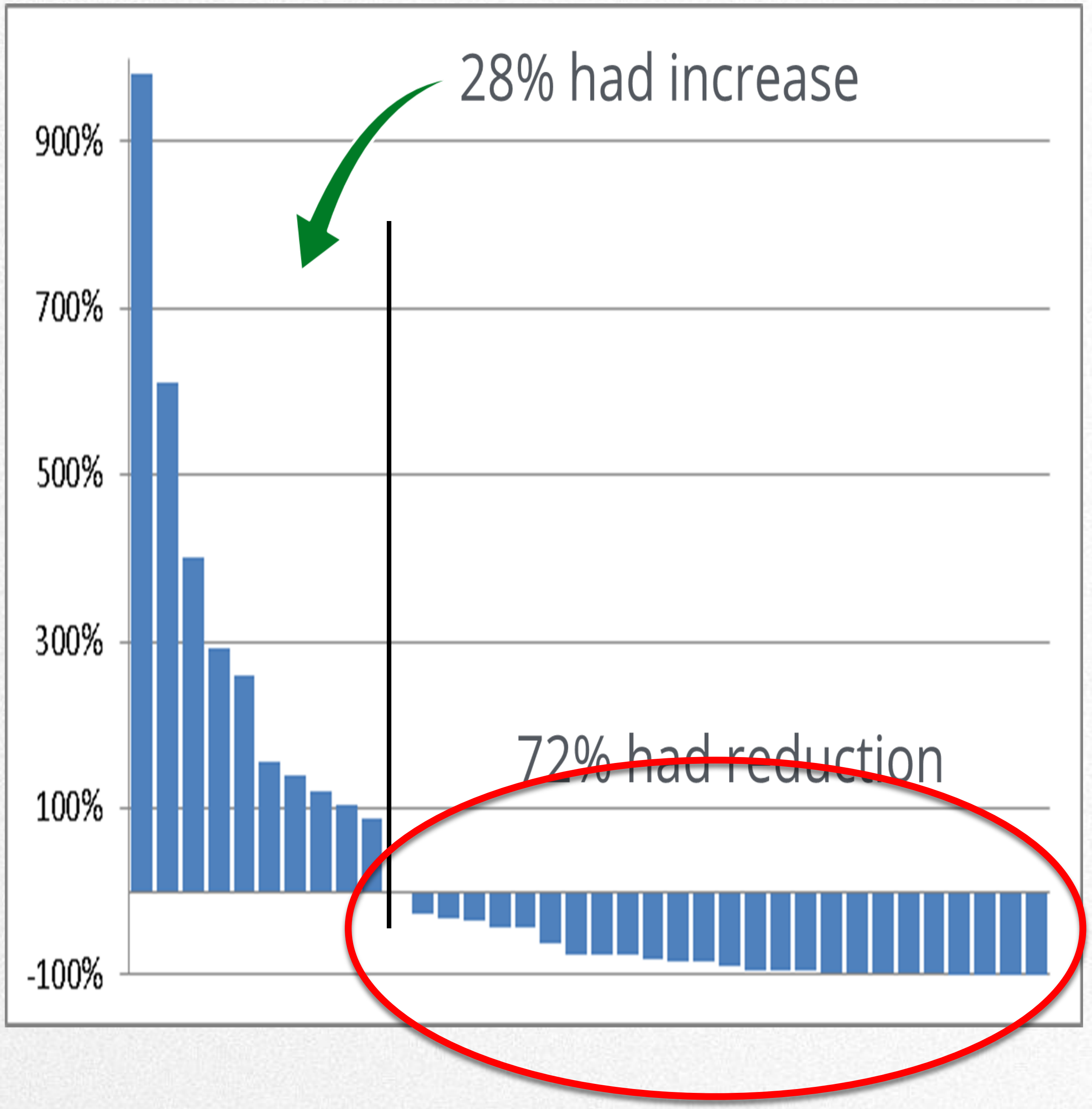
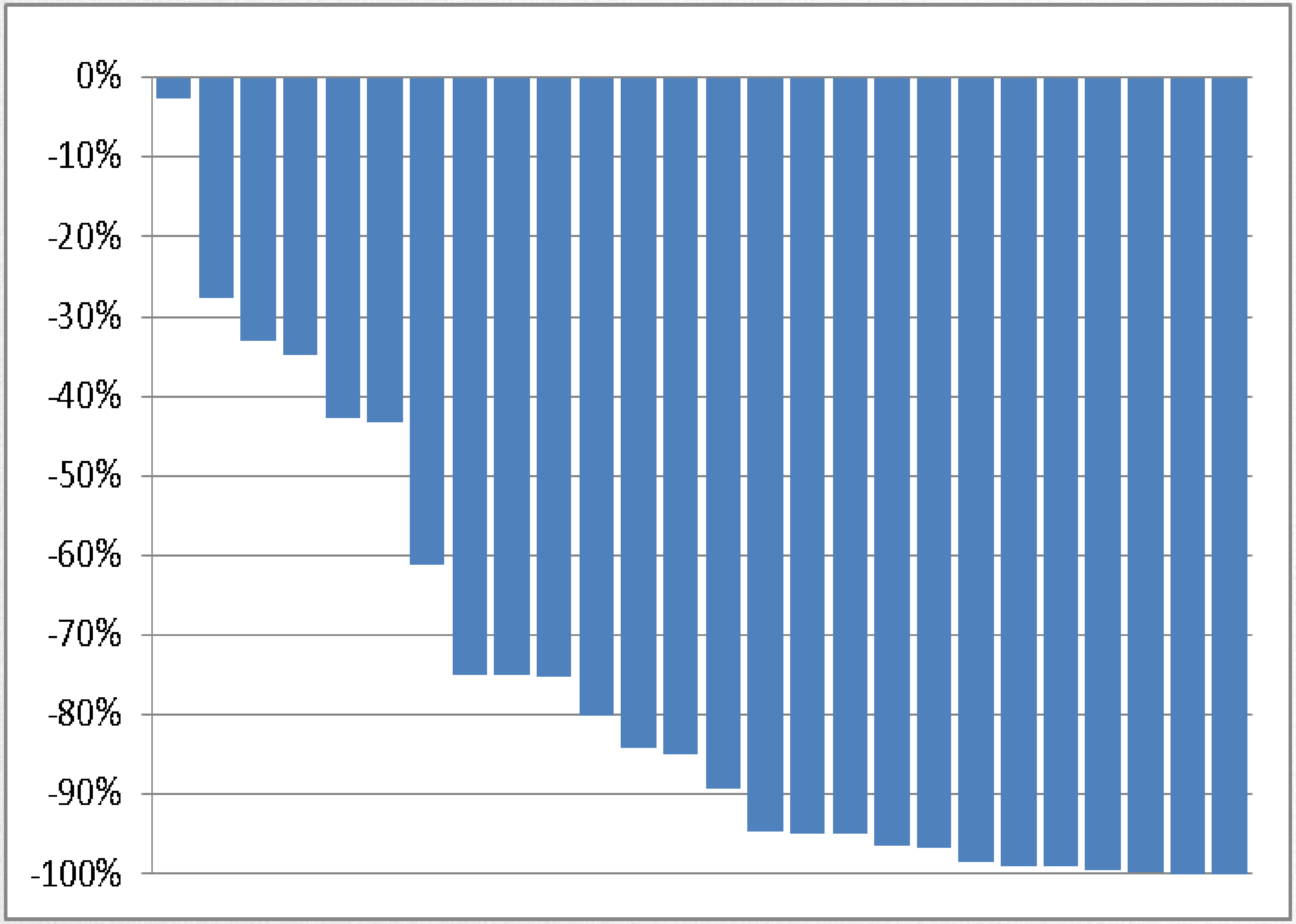




(36 well pairs)

Benzene reduction (new wells)



(26/36 well pairs—72%)

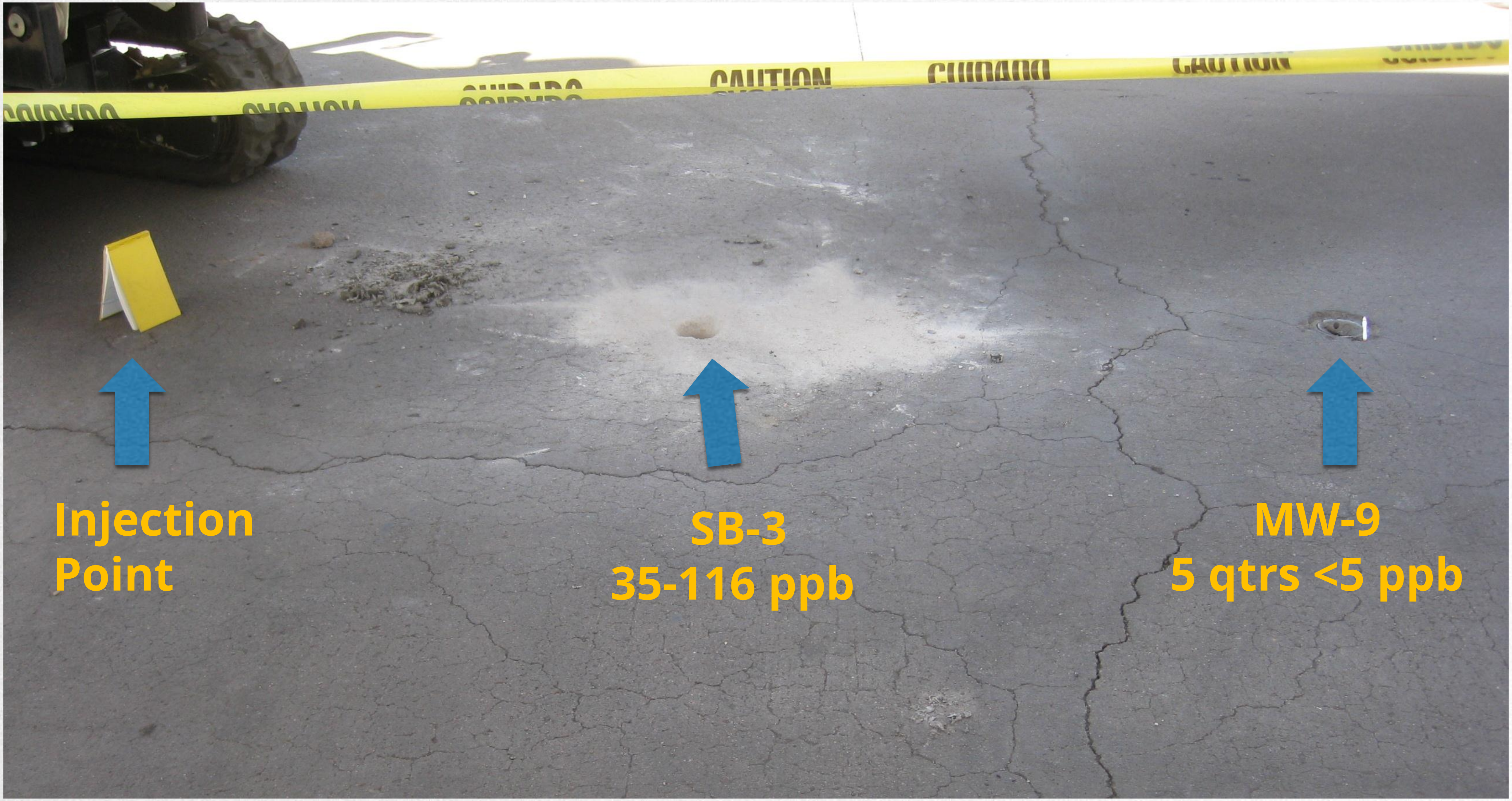
What causes an increase?

Most new wells were <10 feet from original ones---

Differing well construction (drilling method, well diameter, screen length) not a clear factor---

- ✓ Natural variations in contaminant distribution
- ✓ Inadequate site characterization
  - o Wells in the "wrong place"
  - o Inadequate number of (soil) samples
  - o Sampling methodology (soil and water)
- ✓ Injection process mobilizing contaminant

Groundwater samples



Conclusions

1. How is carbon distributed by injection?
   <5 feet, perhaps <3 feet laterally
   Surfacing and well impacts are not indicative of ROI
   Veins in clay, pockets in coarser materials
   Uneven distribution vertically and horizontally

2. Is the aquifer remediated? (at 10-foot spacing)
   reduction confirmed ~70% of the time (26/36 wells)
   >80% reduction ~45% of the time (16/36 wells)
   NFA ~10% of the sites?

3. Any evidence of continuing degradation?
   Not much evidence yet, to be determined

Moving onward…

1. Well rehabilitation doesn't work. Confirmation soil borings and wells needed.
2. More detailed site characterization needed to
    a) target injection zones,
    b) describe soils well, and
    c) identify impacted soil and LNAPL pockets (= long-term issues).
3. Possibility of contaminant displacement

Moving onward…

4. Pilot test / implement CBI on a 5-foot grid spacing
5. Best used for small plumes, low concentrations and sites with open access (for injection points)
6. Add more / continuous nutrients to boost biodegradation

Moving onward…

7. Evaluating if carbon in excavations/trenches, or injection used with sparging, is more effective


Thank you
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COLORADO
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