Long Term Challenges: EVO Biobarrier Wells

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Project Team

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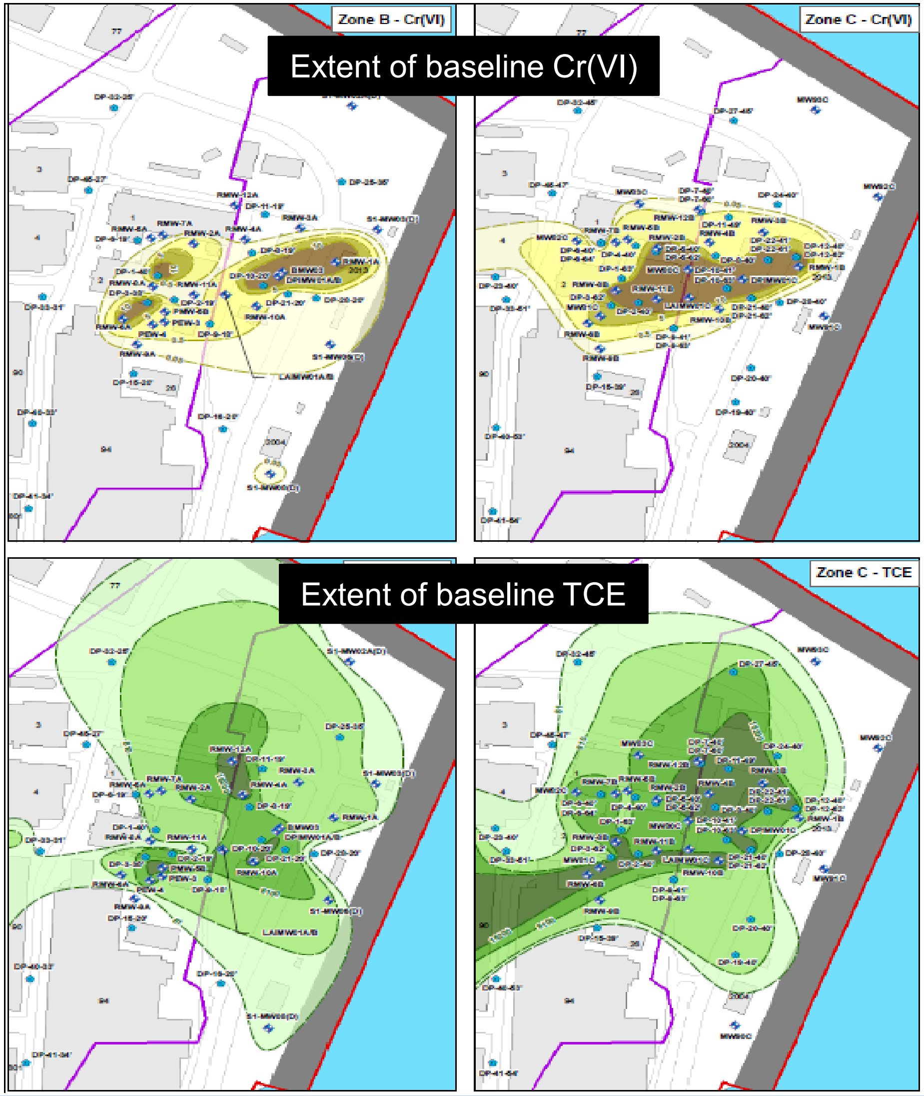
Presentation Overview

1. Background
2. Objectives
3. Approach for Removal Action
4. Results
5. Mitigating the Challenges
6. What Next?
7. Summary and Conclusions

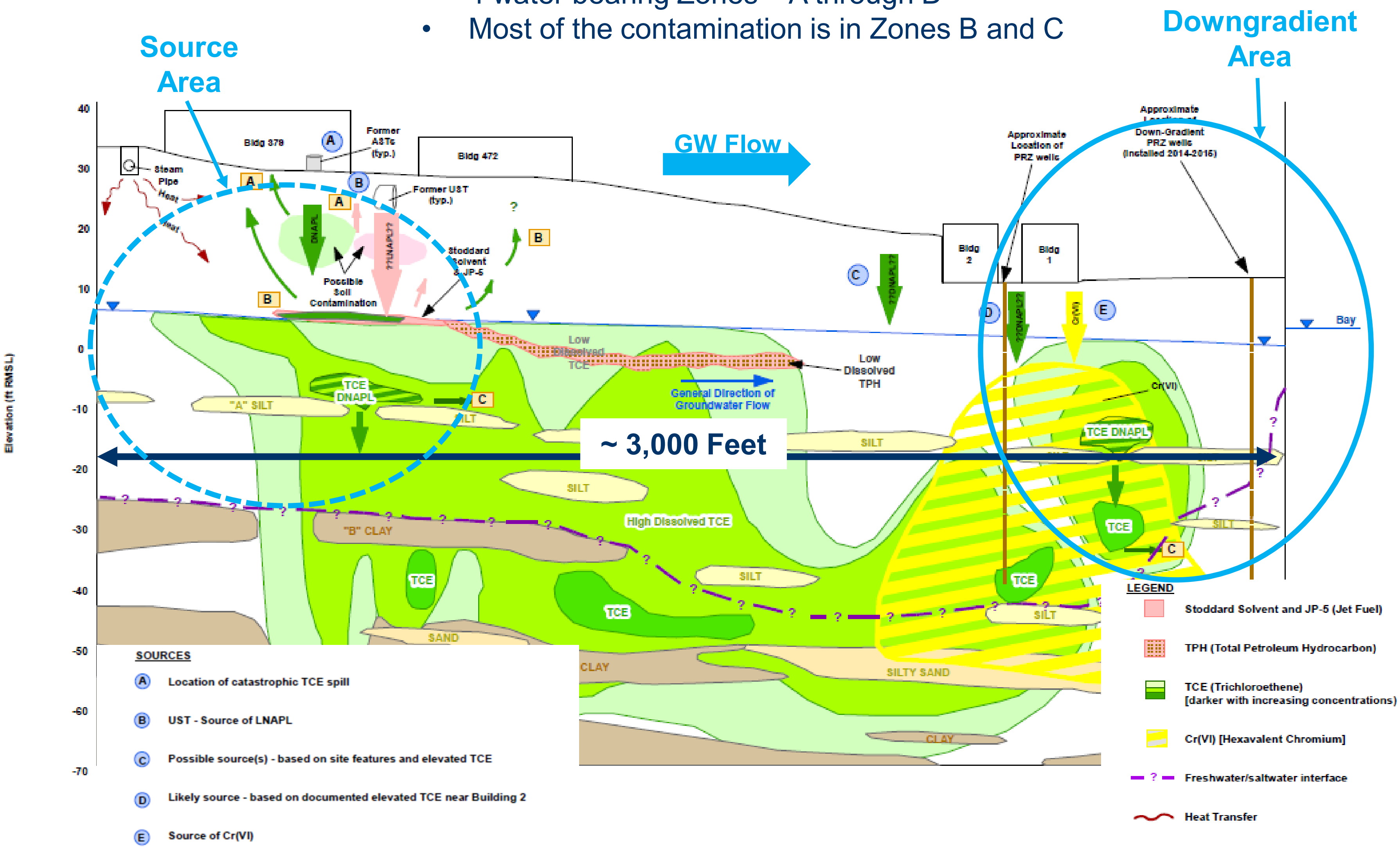
1. Background – NASNI OU 20

- Elevated levels of Cr(VI) > 140 mg/L and TCE >100 mg/L in brackish groundwater, at multiple saturated zones (A, B, C, and D)
- Cr(VI) and TCE plume present in close proximity to San Diego Bay
- A Time Critical Removal Action was implemented, using EISB for groundwater remediation



1.1 Background: OU 20 Conceptual Site Model

- 4 water bearing Zones – A through D
- Most of the contamination is in Zones B and C



2. Objectives

Present an overview of lessons learned from implementation of multiple bio-barriers used to remediate the downgradient edge of a long and diffuse plume:

- Elevated levels of multiple contaminants [>100 mg/L for TCE and >140 mg/L for Cr(VI)] in brackish water with high TDS
- Significant methane generation, lasting several years
- Blockage in injection wells, makes replenishment challenging

3.1 Overall Approach for Removal Action

- Due to proximity of contaminants to Bay, Navy elected to implement a Time Critical Removal Action
- Selected approach needed to:
  - Be effective for both elevated Cr(VI) and TCE – single technology
  - Account for high traffic/buried utilities
  - Minimize number of mobilizations
  - Minimize impacts to site activities
- Ultimately, Enhanced *In Situ* Bioremediation (EISB) was selected

3.2 Approach – Bench/Field Scale Testing/Delivery Design of EISB

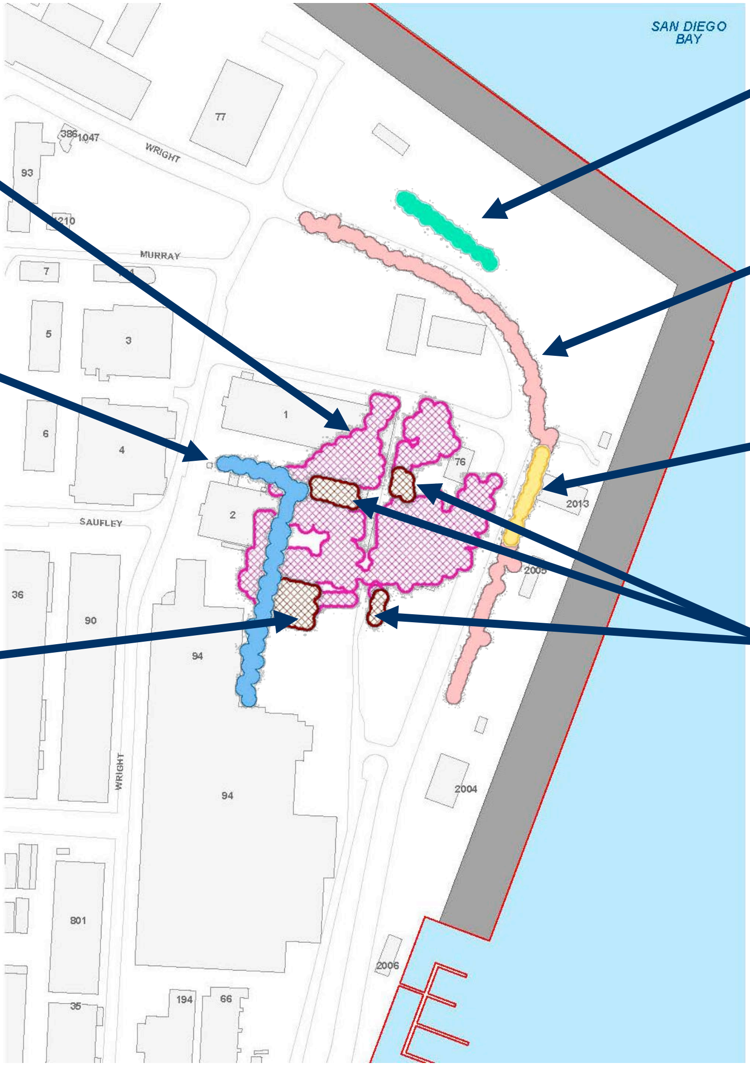
- Bench-scale Testing
  - Assessed several organic and inorganic amendments before identifying Emulsified Vegetable Oil (EVO) for bioremediation of COCs
- Field-scale Testing
  - Conducted liquid atomized injection (LAI) and direct-push injection (DPI)
  - DPI was selected
- Delivery Design consisted of:
  - DPI in areas of elevated COCs
  - Upgradient Permeable Reactive Zone (UGPRZ) – due to almost ½ mile long plume upgradient of DPI area
  - Downgradient PRZ (DGPRZ) – at the downgradient edge

3.3 Approach - TCRA Injection Design/Timeline

DPI – Phase I
(Q2/Q3 2012)

UGPRZ – Phase I
(Q2/Q3 2012)

DPI – Phase II (ZVI)
(Q4 2015)



DDPRZ – Phase II
(Q4 2015)

DGPRZ – Phase II
(Q4 2015)

DGPRZ – Phase II
(Lactate) (Q4 2015)

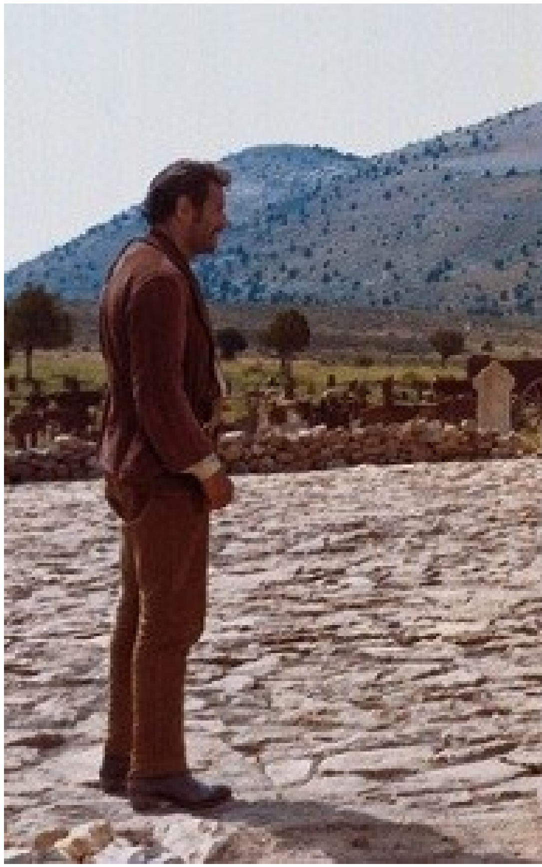
DPI – Phase II (Q4 2015)

3.4 OU 20 GW TCRA – By The Numbers (So Far)

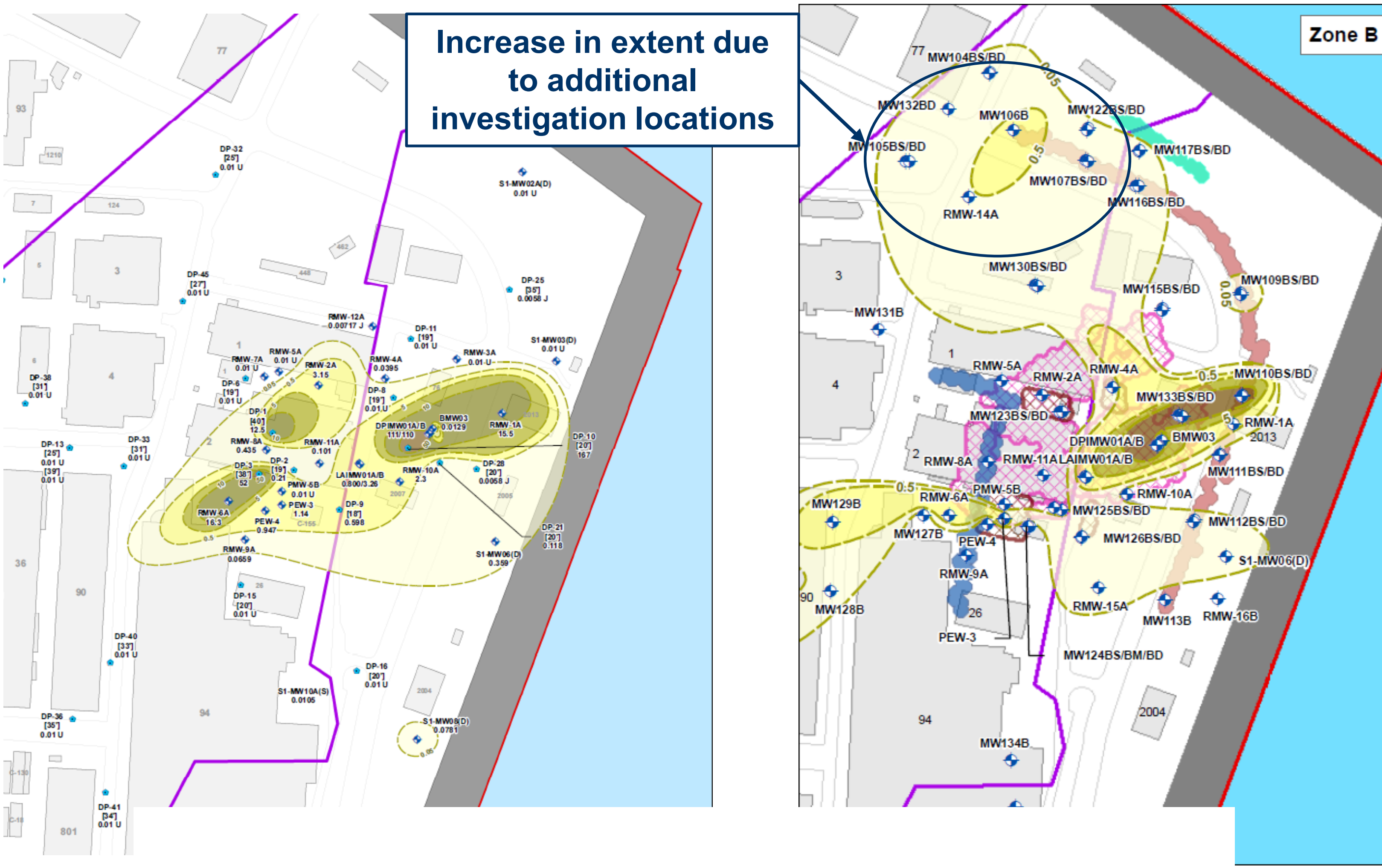
Parameter	Value	Unit
Length of Plume	3,000	Feet
Width of Plume	1,300	Feet
Total Length of PRZs	2,400	Feet
Monitoring Well Screens	217	Each
Injection Well Screens	378	Each
CPT/Hydropunch®	388	Sample Depths
DPIs	413	Locations
EVO	46,255	Gallons
Microbial Culture	1,121	Liters
Total Injectate Volume	697,150	Gallons

10 Rounds of Post Injection Monitoring since 2012

4.0 Results

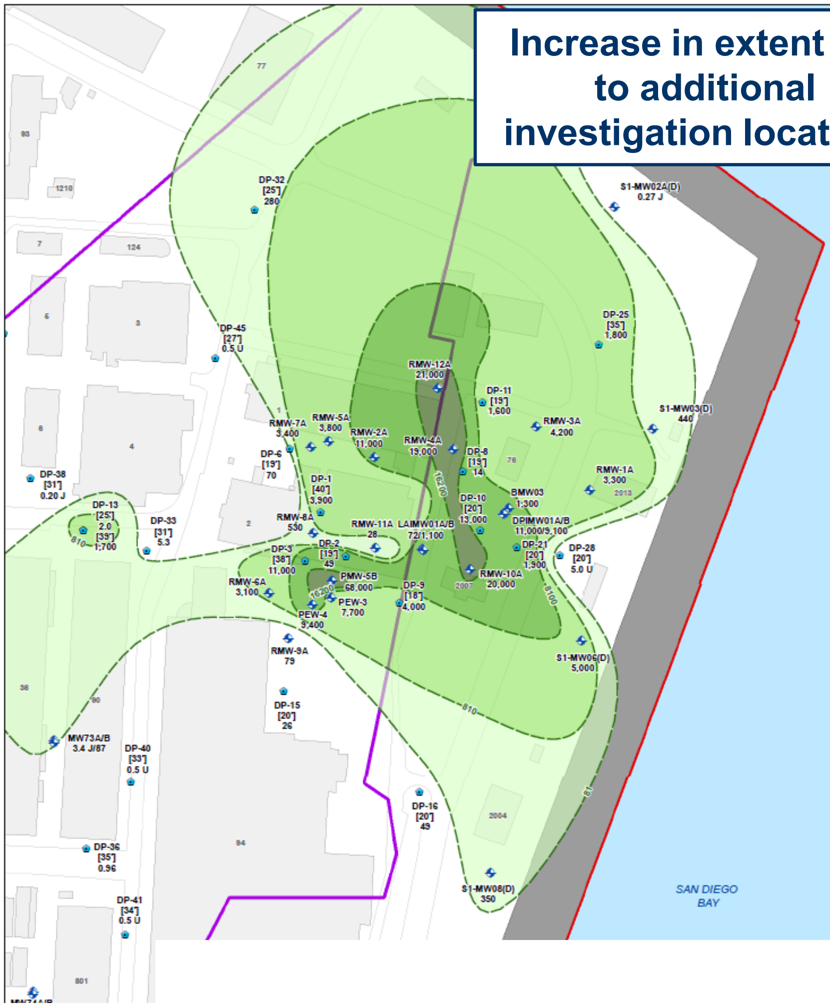


4.1 (The Good) Decrease of Extent of Cr(VI) Since 2012 – Zone B

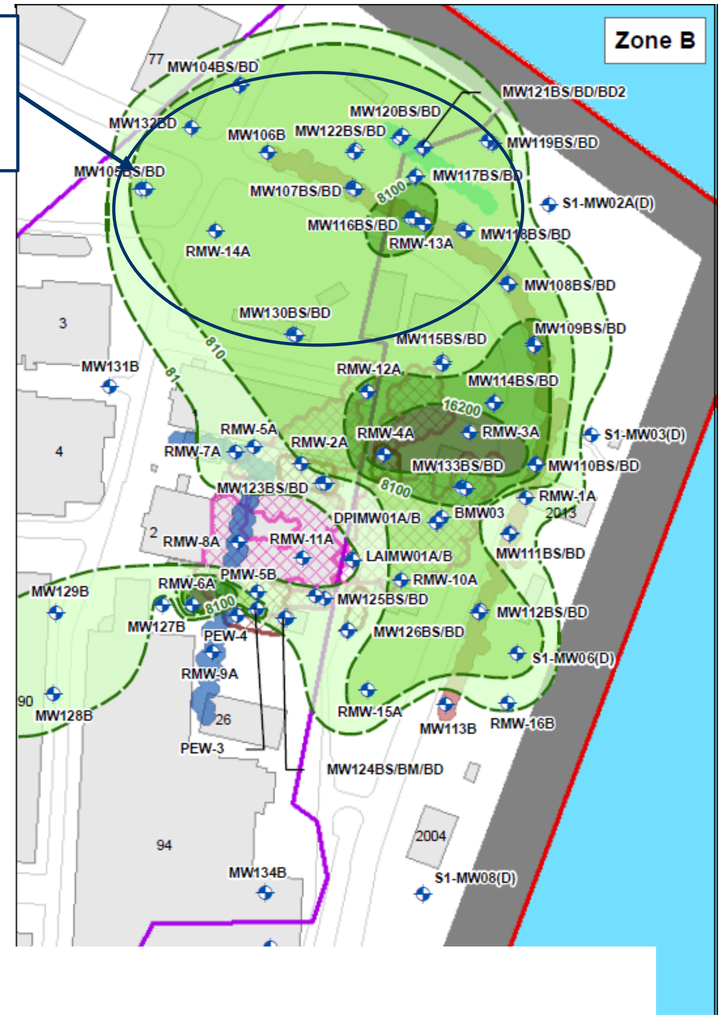


Levels and areal extents of Cr(VI) have decreased significantly

4.1 (The Good) Extent of TCE since 2012 – Zone B



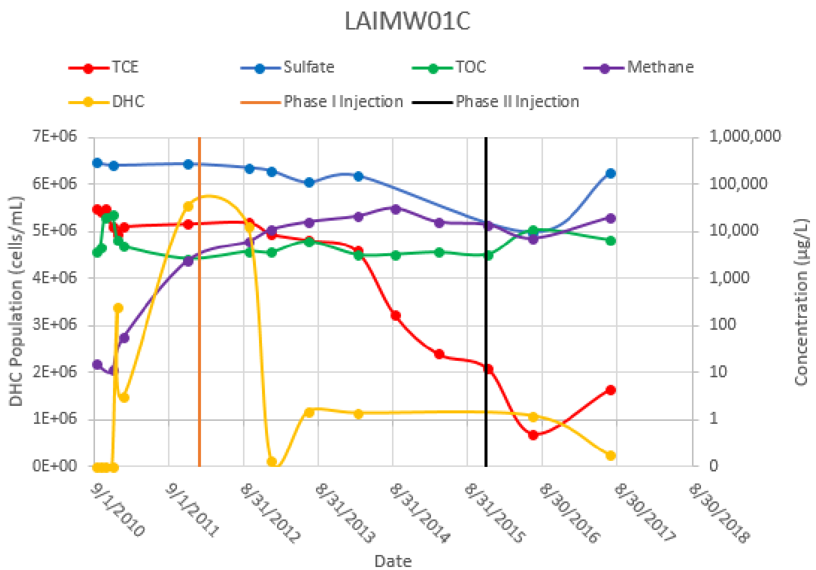
Increase in extent due to additional investigation locations



Levels and areal extents of TCE have decreased significantly

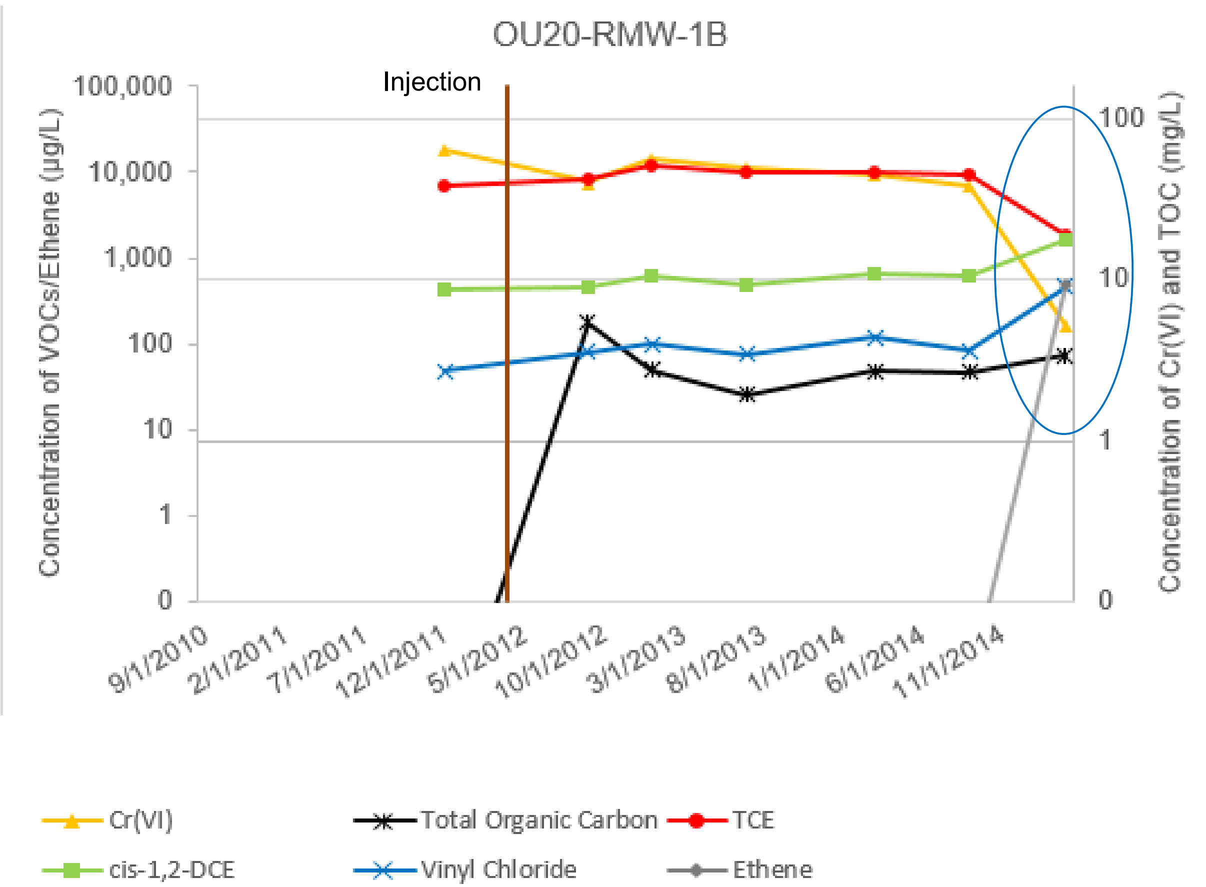
4.1 (The Good) Monitoring Results at a Typical Well

Summary of LAIMW01C - Geochemical Results



- TCE biodegraded with a robust microbial population (population >10^4 cells/)
- In a reducing environment, sulfate can be a terminal electron acceptor (reduced to sulfide)
- Good correlation between sulfate and TCE concentrations, as well as microbial population
- Strong correlation between increasing methane concentrations and decreasing TCE concentrations

4.1 (The Good) EVO Longevity



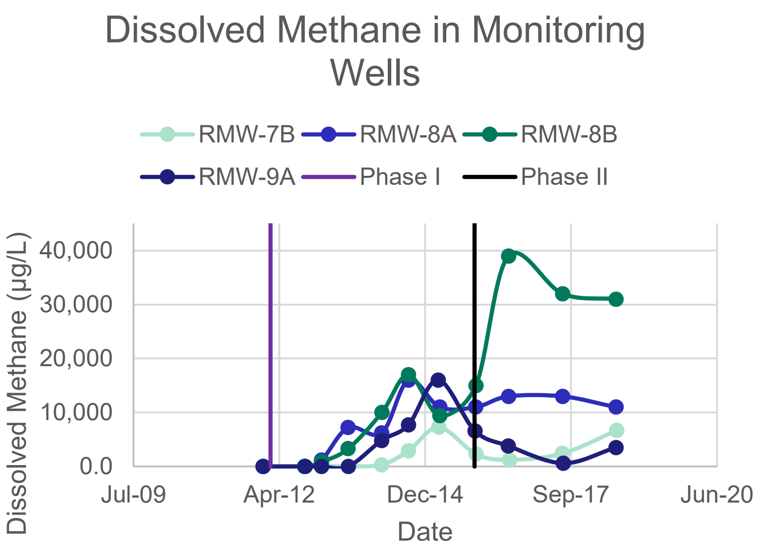
- RMW-1B is < 150 feet from the Bay
- Significant decrease in Cr(VI) and TCE, coupled with *cis*-1,2-DCE and VC increase in 2015
- Effects observed 3 years after injections, which occurred 60 feet upgradient

4.2 (The Bad) Methane Generation

Summary of CH_4/H_2S Results Within Select Monitoring Wells

Location	Dissolved CH_4 (µg/L)	CH_4 in Well Gas (ppmv)	H_2S in Well Gas (ppmv)
MW120BD	33,000	>4,268	99.9
MW110A	11,000	>4,268	11.5
MW116BD	--	1,017	2.2
MW107C	13,000	>4,268	99.9

- Methane readings were taken from monitoring wells within DGPRZ several months after injections
- Many wells showed >1,000 ppm CH_4 (gas in well head space) in zones where injection had occurred
- High levels of H_2S also detected in several wells



4.3 (The Ugly) EVO Coagulation in PRZ Wells

Coagulated EVO from UGPRZ Injection Wells

Has been described as "cheese", "butter", "wax", etc.

Staining from metals

- EVO can coagulate in an injection well ("crud") – appeared several years after initial injection, significantly hindering further replenishment
- UGPRZ Replenishment was planned for September 2018 – almost all (78) wells had white or grey crud – efforts to address are ongoing
- Of the 300 DGPRZ and DDPRZ wells, 213 have crud – replenishment planned next year
    - Most crud white to grey
    - Also observed orange, yellow, and red
- Effects are hypothesized to extend outside the well (but as a "scum" on soil matrix)

Crud + Scum = Scrud

4.4 (The Bad & Ugly) Crud in Wells with Elevated Methane

4.5 Is this Unique to NASNI?

- NASNI may not always be at the cutting edge of technology, but it is often at the cutting edge of problems
- Methane in soil gas is an issue at a lot of sites, with more attention to it in past few years given the intense spotlight on Vapor Intrusion
- Thickness of vadose zone is an important factor
- Scrud has been reported at other sites (less prevalent than methane)
- Issues such as these are not always reported (confidentiality concerns being the main reason)

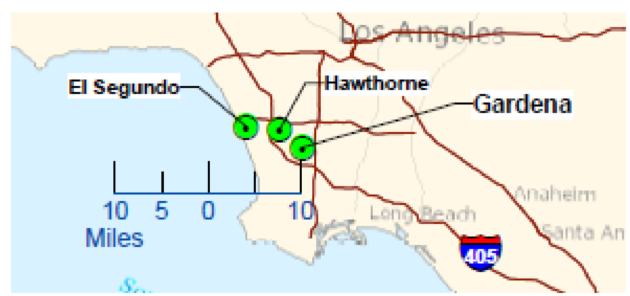
4.6 EVO Sites with (S)Crud

Other Sites (based on personal discussions):

1. One site in Nebraska (location unknown) – input from vendor
2. "At least 6 sites" – personal discussions with a leading consultant
3. "Several sites in the Northeast" – from another leading consultant
4. 3 sites in Southern CA, 1 in Northern CA, 1 at Edwards AFB (>60 miles inland)

So far, at least 20 sites

Southern California



Los Angeles Basin

5.1 Mitigating Methane

- Use electron donors that minimize methane production?
- Is mitigation system needed in vadose zone?
- Add antimethanogenic reagents (AMR) to injectate?
- Challenges –
    - How long will methane be generated?
    - Tenure of solution?

5.2 Mitigating Scrud

- Mechanical – well redevelopment
- Heat – water, steam (limited success)
- Chemical – potential use of solvents, acids, bases, detergents, etc.
    - Samples sent to two different entities to test options on bench scale (results were similar)

5.3 What is the Crud made up of?

- Crud was analyzed for metals and fat.

- In addition, the ash content (a measure of total salt of the crud) was analyzed for metals.
    - Crud is primarily a water insoluble fatty acid and salt.
    - The C14 to C20 fatty acids (hydrolysis of the EVO) represented greater than 98% of the total fats. There are also some shorter chain length fatty acids, indicating some fermentation
    - Calcium was the dominant metal in crud samples. Iron and manganese were higher in the samples with visible staining
    - Calcium, iron, magnesium and manganese made up about 20 to 30% of the ash, so there are more metals (and potentially halides) that are contributing to the total salt content in the crud

5.4 Scrud Mitigation Approaches (Bench-Scale Test)

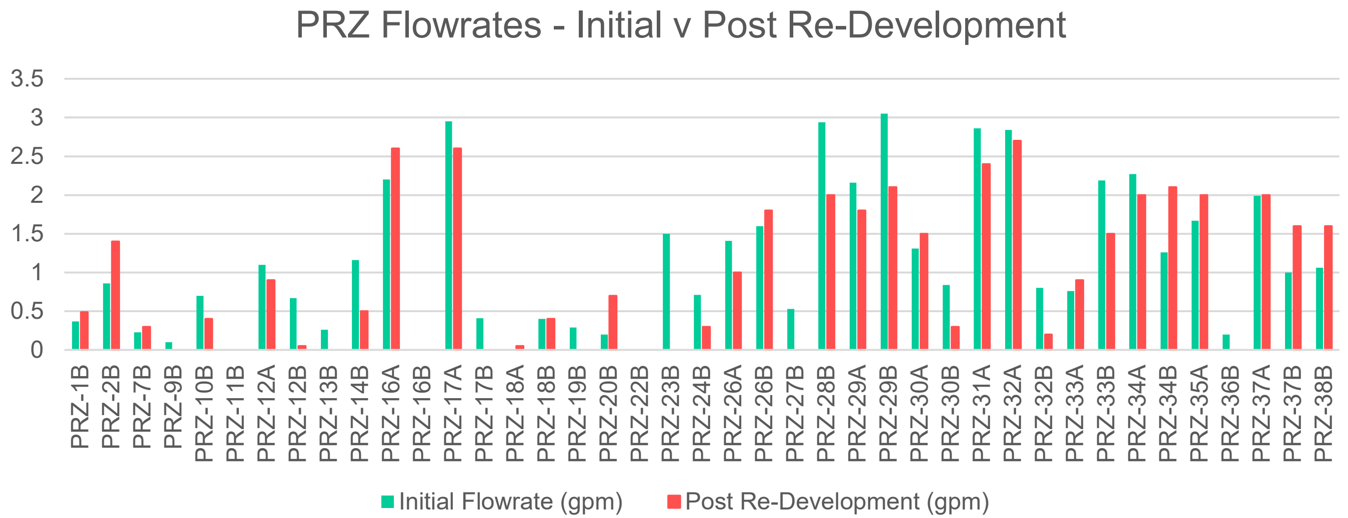
- Numerous commercially available options were tested
- Following are observations on the more successful approaches:
  - Both 91% isopropyl alcohol and 75% ethanol were effective at dissolving more than 75% of the crud.
  - Addition of surfactant to Isopropyl alcohol appeared to be a stable long-term solution.
  - Based on visual observations, isopropyl alcohol worked faster than the ethanol.
- Other observations:
  - Alconox at 1 weight percent and polyglycerol at 10 weight percent dispersed some of the crud but not enough to consider as a treatment option.
  - Crud melted at 50°C and typically formed a surface oil layer. When the material cooled, the oil often solidified or gelled depending upon the mixture used.
  - Acids, bases, detergents, heat showed little or temporary effect.
- Developed a two part approach:
  - Scrud Remover A (SRA) – mixture of alcohol and proprietary additives
  - Scrud Remover B (SRB) – polyphosphate and other additives – added to EVO on site

5.5 Scrud Mitigation Approaches – Field Tests (ongoing)

Round 1: Fresh water injections were conducted to establish a baseline performance for each well prior to re-development

- Flowrate and pressure were monitored during the test
- Flowrates varied from 0 to 7.3 gpm

Wells were subjected to robust re-development



5.5 Scrud Mitigation Approaches – Field Tests (ongoing)

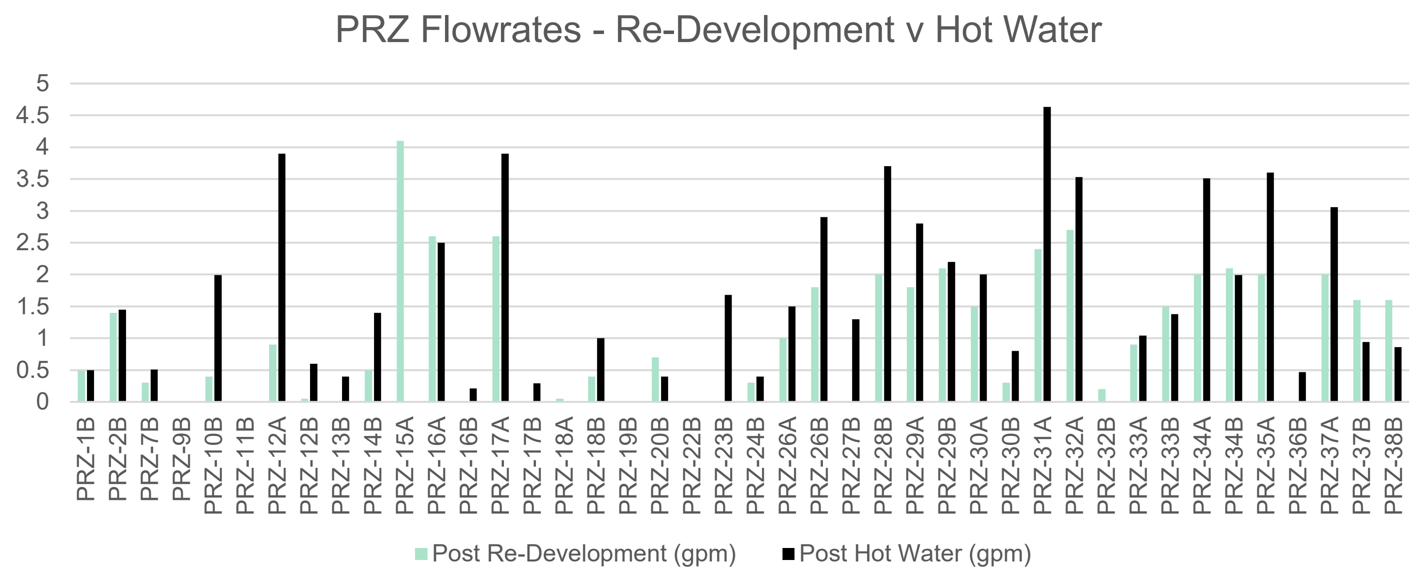
- Well Rehabilitation using SRA (ongoing)
  - Added SRA to the wells
  - SRA was left in wells for 2-3 weeks
  - Additional jetting of the well screen zone

- Round 2 of fresh water injection testing to determine efficacy of re-development efforts (ongoing)
  - Of 73 wells re-developed and tested, 20 showed appreciable improvement
  - Rhodamine dye added to a subset of injection wells to determine communication with surrounding monitoring wells.
  - A Rhodamine sensor was deployed into the PRZs and surrounding monitoring wells to measure concentrations over time (ongoing)

5.5 Scrud Mitigation Approaches – Field Tests (ongoing)

Hot water injections were conducted to test effectiveness for well rehabilitation

- Water was heated to 140 °F (the point at which PVC becomes malleable)
- The wells were pumped dry, then flooded with hot water
- Of 41 wells which received the hot water treatment, 28 exhibited improvement
- A number of limiting factors were experienced, making this method somewhat impractical



6.0 What Next?

- Continue testing of various approaches to overcome the challenges associated with scrud

- Investigate actual nature and extent of scum in formation

- Evaluate alternate approaches to PRZ Replenishment that do not use existing blocked injection wells

- Determine efficacy of AMR in alleviating methane from previous EVO injections:
    - ➢Measure dissolved methane (lab) and methane in well headspace (lab and field) over time
    - ➢Measure methane in soil gas (before and after AMR)
    - ➢Methanogens (before and after AMR)
    - ➢Testing a specialized in-well field meter for dissolved methane

7. Summary and Conclusions

- **The Good** – EISB has been successful at significantly decreasing CrVI and cVOCs; EVO longevity > 3 years

- **The Bad** – Significant Methane generation

- **The Ugly –** Scrud formation at several injection wells

- **Mitigating the Challenges -** Ongoing

Credits: Provectus, Redox-Tech, Tersus, John Sankey, several unnamed consultants

QUESTIONS?