15 Years of Experience with Klozur® CR

Webinar
April 13, 2022

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Persulfates | Soil & Groundwater
Evonik Active Oxygens

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Leading Beyond Chemistry

Our Presenter

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Webinar Outline

- Fundamental Chemistry
- Design and Applications Considerations
  - Lessons Learned
- Case Studies

Sold in:

45 lb (20.4 Kg) pails

1,800 lb (817 kg) super sacks (made to order)

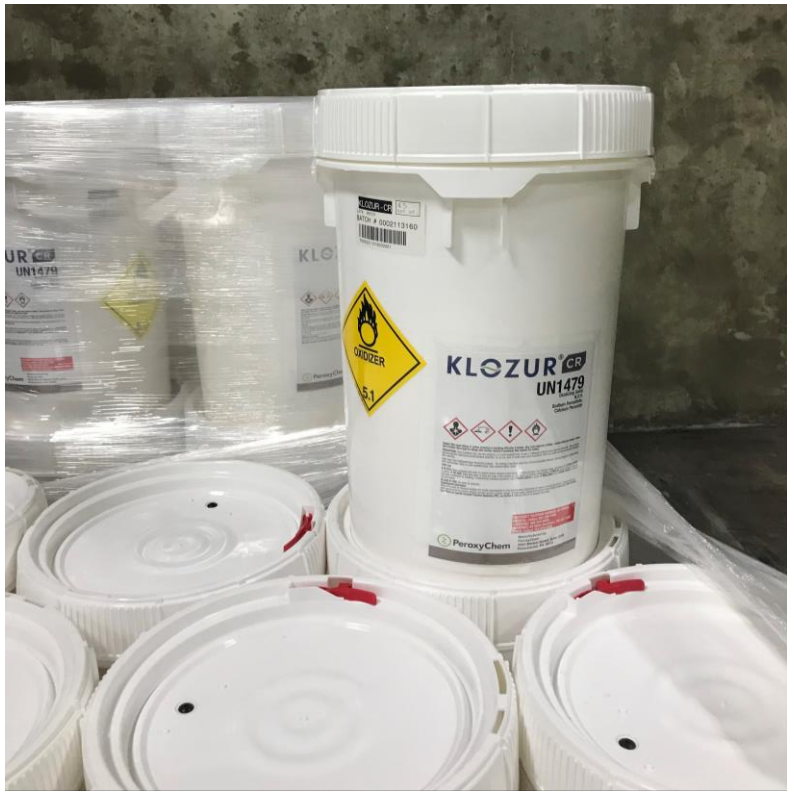
Klozur® CR

- Released in 2006 – Over 15 years of experience

- "CR" = Combined Remedy
  - In situ chemical oxidation (ISCO)
  - Aerobic bioremediation
  - Anaerobic oxidation

- Klozur® CR is a blend of Klozur® SP and PermeOx® Ultra
  - Typical blend is 50:50 ratio
  - PermeOx® Ultra activates the sodium persulfate

Three remedial pathways in single application



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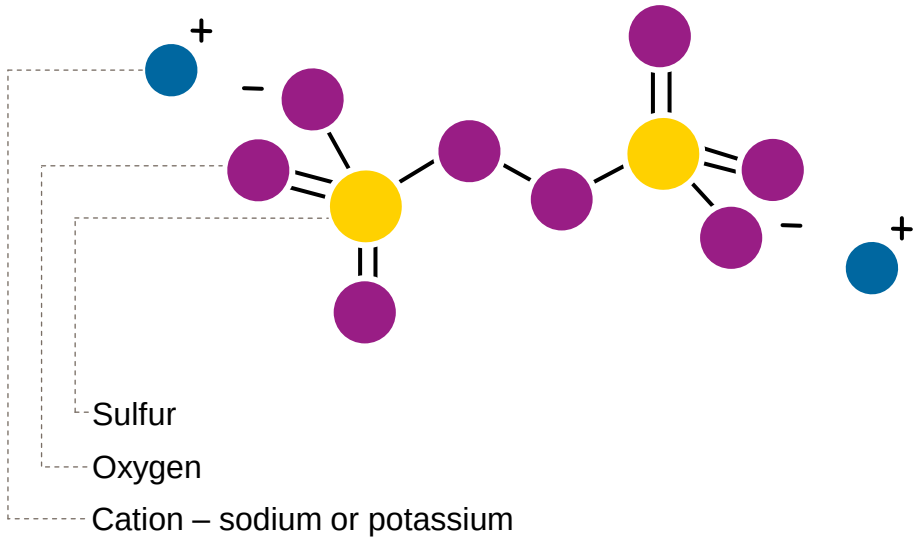
Klozur® Persulfates Chemistry

- Sodium and potassium persulfate are used in environmental remediation applications
- A strong oxidant
- Activation results in the formation of oxidative and reductive radicals
- Applicable across a broad range of contaminants
- Extended subsurface lifetime (weeks to months)
- Little to no gas evolution



Free Radical Chemistry:
Persulfates produce free radicals in many diverse reaction situations

$S_2O_8^{-2}$ + activator ⟶ $SO_4^{\bullet -}$, $OH^{\bullet}$ or O_2^{-}

Activation produces a radical which is more powerful and kinetically fast

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Contaminant Degradation Pathways

Petroleum Hydrocarbons

MGP Residuals

BTEX

PAHs

Oxygenates

1,4-Dioxane

PCE, TCE, DCE and VC

Chlorobenzenes

Chlorophenols

Select Pesticides

Select Fluorinated Compounds

PCBs

Select Energetics

Carbon Tetrachloride

1,1,1-Trichloroethane

Dichloroethanes

Select Pesticides

Select Energetics

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PermeOx® Ultra Chemistry

- PermeOx® Ultra
  - Calcium peroxide
  - Proprietary stabilizer
  - Hydrated Lime

Primary Pathway:

$$CaO_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2O_2$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O$$

Secondary Pathway:

$$CaO_2 + H_2O \rightarrow Ca(OH)_2 + \frac{1}{2}O_2$$

- Key Characteristics:
  - >18% active oxygen is typical
    - Higher or highest AO of calcium peroxide products
    - ~180 mg O_2 formed per g PermeOx® Ultra applied
    - ~90 mg O_2 formed per g Klozur® CR applied
  - pH 10.2 to 10.6 (1% slurry at 25 C)
  - PermeOx® Ultra has a very low solubility
    - Applied as a solid-slurry
    - Persistence of many months typical
  - Rate of solid slurry dissolution increases with decreasing pH

Wang et al, 2016, Chem Eng J, 303, 450-457

Klozur® CR/PermeOx® Ultra Reactive Pathways: Direct Oxidation and Aerobic Bioremediation

- Direct Oxidation (Northup & Cassidy, 2006):
  - Hydrogen peroxide generated from calcium peroxide
  - Expected to be in close proximity to solid slurry

- Aerobic bioremediation:
  - Extended release of oxygen
  - Supported with ~5 mg O_2/L in GW
  - Pure oxygen can support ~60 mg O_2/L in GW
  - Oxidative pathway
  - Typically occurs directly down gradient of solid slurry location
    - Transport distance will depend on fate mechanisms, but short to moderate distances is typical

Sample of Compounds Treated by Aerobic Bioremediation
Petroleum hydrocarbons (BTEX, PAHs, etc)
Oxygenates (MTBE and TBA)
Vinyl Chloride and dichloroethene
Chloromethane and methylene chloride
Cometabolic:
Trichloroethene

Anaerobic Biological Oxidation/Sulfate Reduction

- Biological oxidation where residual sulfate from Klozur® SP serves as electron acceptor
  - Sulfate reducing bacteria (SRBs)
  - Reducing conditions (ORP: -150 to -200 mV)
    - Need to have sufficient residual electron donor to push conditions reductive
  - Less energetic process
    - Slower process (months to years)
    - More limited compounds treated

Sample of Compounds Treated by Anaerobic Bioremediation/Sulfate Reduction
BTEX
Smaller PAHs (Naphthalene)
Other readily oxidizable petroleum hydrocarbons
Cometabolism of some chlorinated compound

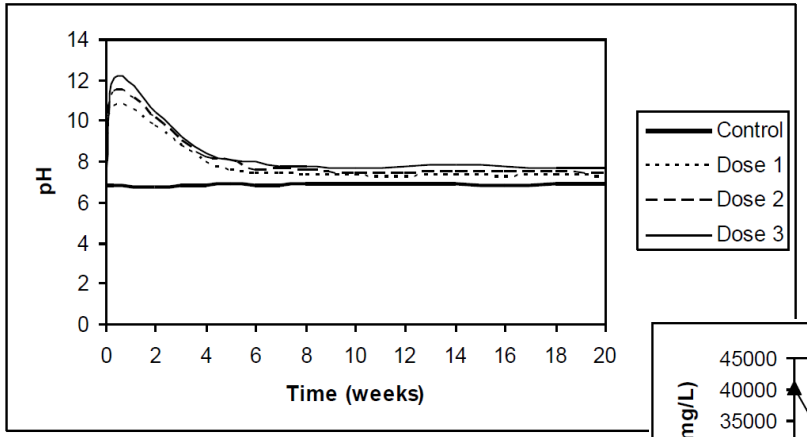
Miao et al (2012) Environ Geochem Health, 34, 539-550

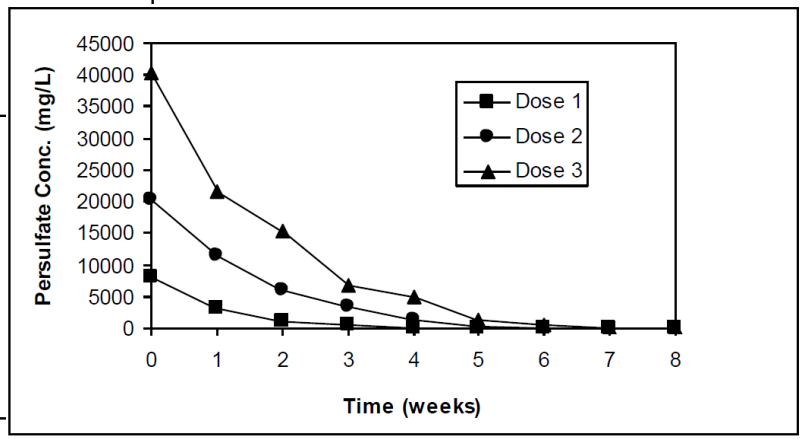
Boll et al (2002) Chem Biol, 6, 604-611

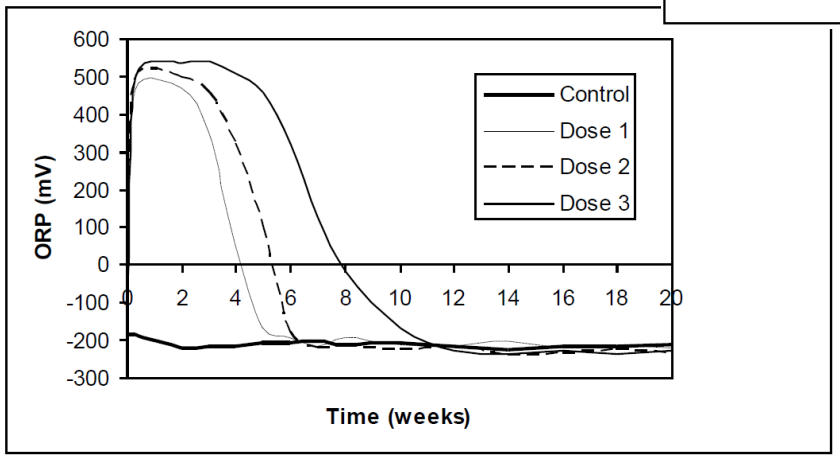
Lee et al (2016), Battelle Chlorcon, Palm Springs, E-006

Western Michigan University Bench Study: PAHs in Sediments

- Lab Study with Dan Cassidy/Western Michigan University
- Contaminated sediments
- Three dosages of Klozur® CR tested
  - 4 g/Kg, 10 g/Kg and 20 g/Kg
  - Reactors maintained in anoxic chamber at 15 C for 20 weeks







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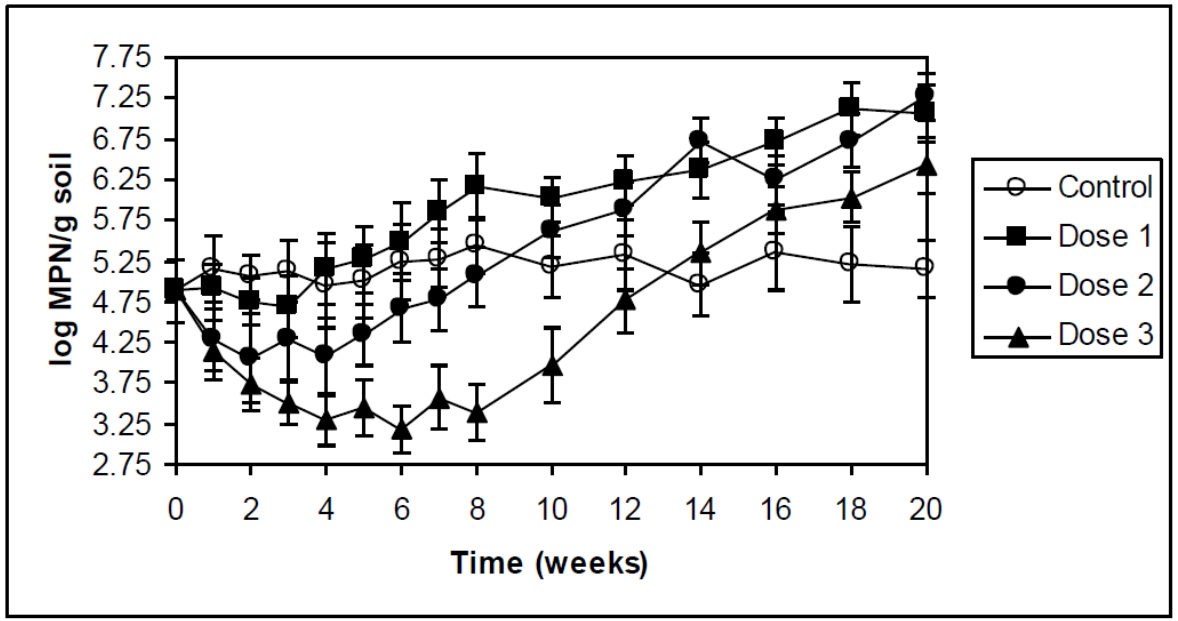
Western Michigan University Bench Study: PAHs in Sediments

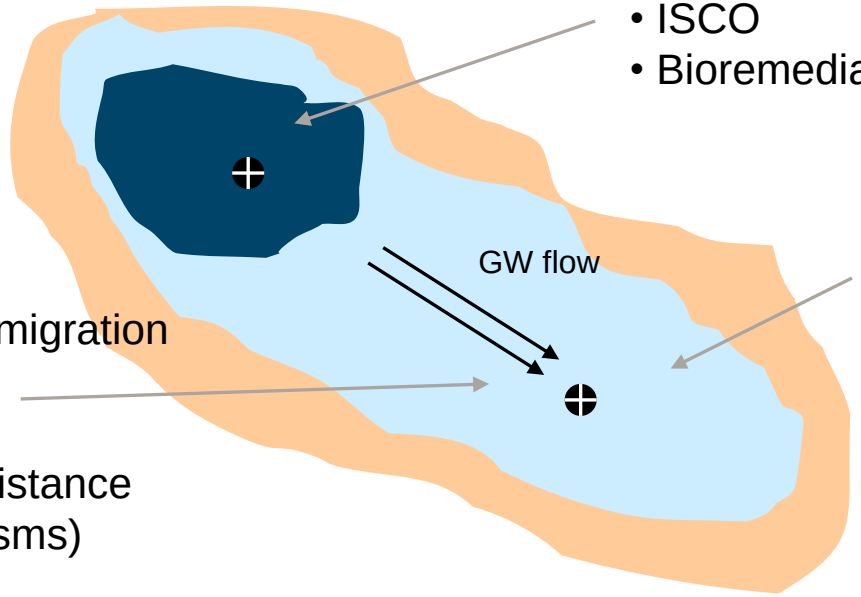
- Microbes: Sulfate Reducing Bacteria (SRB) counts did initially decline but rebounded once the persulfate was consumed and the ORP / pH returned closer to background.
- SRB counts increased beyond baseline levels, likely in response to the addition of sulfate and dissolved organic content
- Increasing treatment with increasing dose of Klozur® CR



Dose	PCB removal (%)	PAH Removal (%)	MeHg (%)
Control	0	0	0
Dose 1	31	27	>99.96
Dose 2	59	61	>99.96
Dose 3	91	88	>99.96

Klozur® CR: Chemistry Summary

Source Zone Treatment
- ISCO
- Bioremediation (aerobic and sulfate reduction)



Contaminant plume

Down gradient migration
- Dissolved O_2
- Sulfate
- Site specific distance (fate mechanisms)

Potential Combined Remedy Timeline

0 | 3 | 6 | 9 | 12 | 24+ Months

1) ISCO — **Source treatment**

2) Aerobic Bioremediation — **Source polishing and plume treatment**

3) Anaerobic Oxidation/Sulfate Reduction — **Plume polishing**

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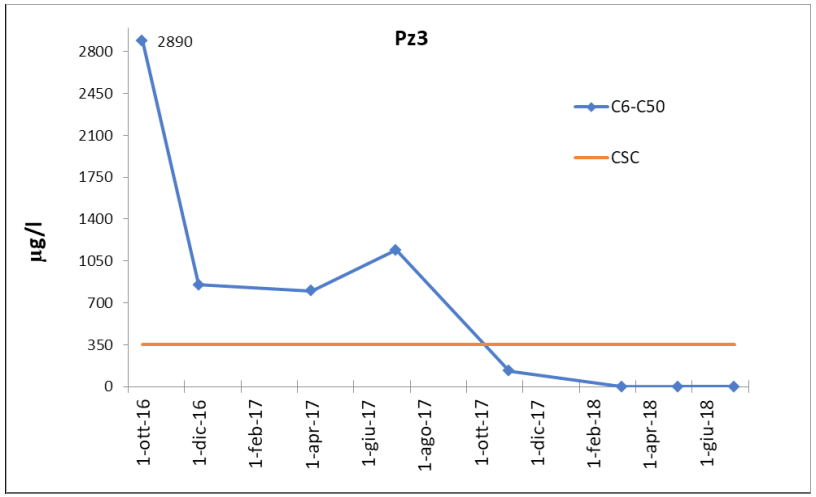
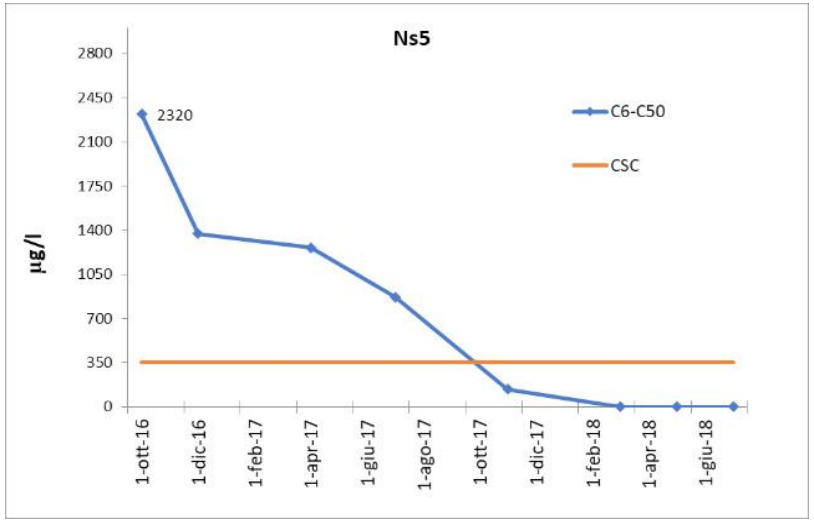
Klozur® CR: 50:50 Blend

- Our goal for Klozur® CR:
  - Powerful treatment with ISCO follow by extended aerobic and anaerobic bioremediation to achieve low remedial goals
  - In 50:50 blend:
    - Klozur® SP acid formation helps consume ~30% of PermeOx® Ultra (not accounting for soil alkaline demand)
    - Leaves ~70% of PermeOx® Ultra for extended release of oxygen
- Blend (50:50) allows for initial treatment with activated persulfate followed by extended oxygen release to stimulate aerobic bioremediation

Why Klozur® CR??

- Ease of use
  - Single product; single application = 3 treatment pathways
    - Two of which can persist for extended periods of time
- Three treatment pathways make it ideal for:
  - Low remedial goals
  - Low to moderate levels of TPH with low remedial goals out of a single application
    - <100 mg/Kg of contamination
- A backfill amendment to treat residual contamination after an excavation
- Primarily treating petroleum hydrocarbons or lightly chlorinated compounds
  - But can treat low levels of moderately chlorinated compounds





Leombruni & Mueller, 2020, J Mari Scie Res Ocean, 3.3, 117

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Design and Application Considerations

Courtesy of ERM-Australia

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Klozur® CR: Dosage

- Design and dosage estimates very similar to ISCO and bioremediation:
  - Account for target demand
  - Account for non-target demand (SOD or KDT test)
  - Apply a safety factor to account for variability in assumptions, contaminant concentrations, reagent distribution, etc

- Klozur® CR: Follow procedure for each reagent
  - Klozur® SP: 50% of Klozur® CR applied
  - PermeOx® Ultra: 50% of Klozur® CR applied with ~180 mg O_2/g PermeOx® Ultra (~90 mg O_2/g Klozur® CR)
  - Anaerobic oxidation: Sulfate will be ~40% of Klozur® CR applied
    - Requires specific geochemical conditions
      - Often not assumed in design calculations

Application of Klozur® CR

- Solid Slurry
  - Klozur® SP (Highly soluble)
  - PermeOx® Ultra (Low solubility; Solid)

- Slurries have alkaline pH
  - Protects carbon steel

- Typically applied:
  - Injected as a solid slurry
  - Excavation backfill amendment

Application of Klozur® CR: Injection

- Klozur® CR is often injected as a solid slurry
  - 10 percent to 30 percent Klozur® CR solid slurries are typical
  - PermeOx® Ultra is settleable, even if slowly (small particle size)
    - Slow in line velocities or stagnant slurry may have settling
  - Usually injected under pressure
    - Most formations require injection pressures that fracture the formation
      - PermeOx® Ultra is typically <100 μm
  - Radius of influence are typically:
    - Clay (fine material): <5 ft (1.5 m)
    - Sand (permeable material): <10 ft (3 m)

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Application of Klozur® CR: Injection

- Typically injected via direct push technologies using large orifice ports
  - Fixed wells with slotted screens not recommended
  - Fixed well alternative: TAM tubes with larger ports
- Issue with typical fixed well screens:
  - Opening size for solids to flow through
    - PermeOx Ultra typically <100 μm
    - Bridging of several particles common when injection through well screens attempted
  - Ability to withstand necessary injection pressures
    - Failure creates preferential pathway

Well Screen Slot Size	Opening Size		
	(inches)	(mm)	(mm)
10 slot	0.01	0.254	254
20 slot	0.02	0.508	508
30 slot	0.03	0.762	762
Port	0.25	6.35	6,350
Port	0.5	12.7	12,700

Recommended

Application of Klozur® CR: Excavation backfill

- Klozur® CR is commonly used as a backfill amendment
  - Used to treat residual contamination following excavation

- Health & Safety:
  - Dust control
    - Open bags near excavation floor
    - Apply as a solid slurry

Confidential Client-Alaska

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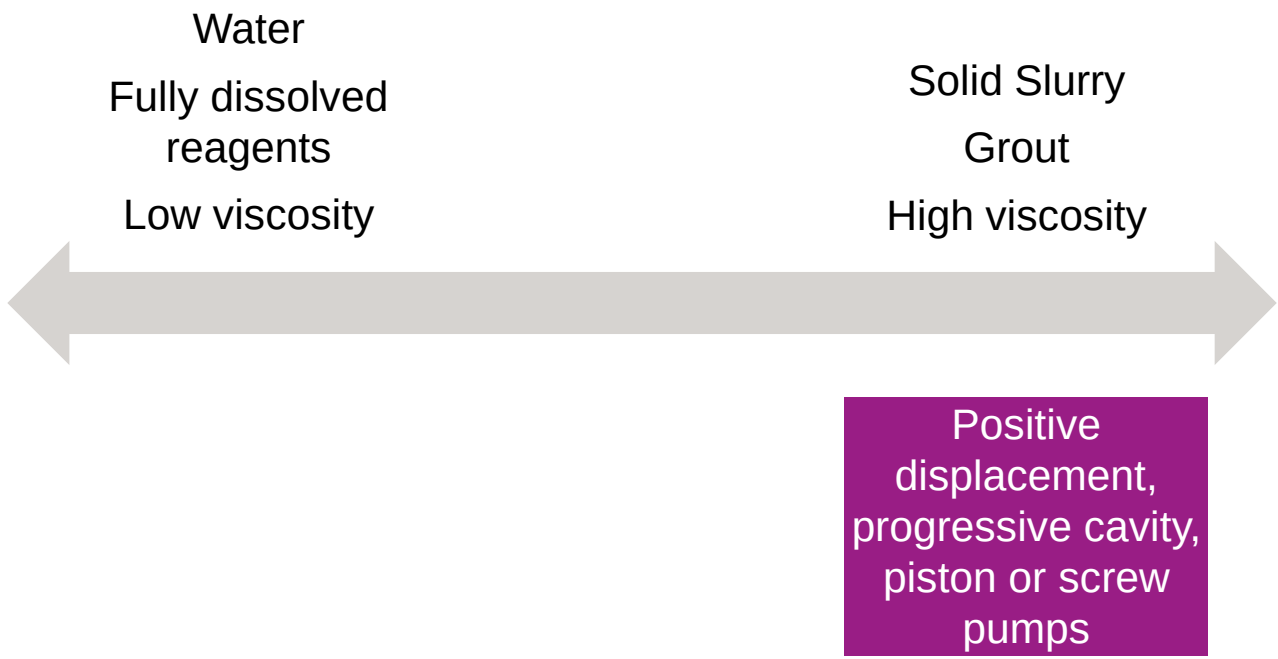
Application of Klozur® CR: Pumps

- Specifically need a pump that is intended to move a settleable solid-slurry. Key characteristics:
  - Low head if just transferring
  - High head if using to creating subsurface fractures for the solid slurry
  - Appropriate flow rate
  - Chemical compatibility (see guide)
    - All wetted parts
    - Even non-wetted parts often can come in contact with reagents under field conditions
  - Minimize shear points/heat build up



Application of Klozur® CR: Slurry Density

- Klozur® CR slurry densities of 10-30% Klozur® CR is typical
  - 5-15% PermeOx® Ultra and Klozur® SP
  - Select right pump to move reagent
    - PermeOx® Ultra: will be a very fine, but settleable solid
    - Klozur® SP: Will increase viscosity of the solution
      - Viscosity (cp at 25 C) = 0.8904 + 0.0043857 $conc^{0.5}$ – 0.0012218 conc + 0.00015146 $conc^{1.5}$
        - Conc = Concentration of SP in g/L
        - 5% SP = 51 g/L = 0.91 cp
        - 15% SP = 164 g/L = 1.064 cp
          - Lower than skim milk


Courtesy of Arcadis-Italy

Proper Storage

- Always store in a dry, cool, ventilated and clean facility (see SDS).

- Due to ability to generate oxygen, both PermeOx® Ultra and Klozur® CR come in vented packages
  - For drums/buckets, water can enter through ports on top of lids
    - Must prevent standing water on top of drums/buckets

- Klozur® CR is an all-in-one product: Contains activator and oxidant
  - Addition of moisture can initiate reaction
  - A few reports people that have stored Klozur® CR pallets outside, in rain which resulted in decomposition reactions
    - Off venting of gas has been observed. Expected to be oxygen.
      - PermeOx® Ultra decomposition is endothermic
      - Product often consumed and forms large solid blocks that will require disposal

Bench Testing

- Design parameters Klozur® SP still relevant (KDT/SOD)
- Most people progress to the field
  - Mechanisms are well established

- Bench Testing Klozur® CR:
  - Three treatment mechanisms
    - ISCO mechanism can be tested over weeks to months
    - Bioremediation
      - Potentially over 1-2 years
      - Alkalinity can interfere with bioremediation in a small batch reactor or with little soil (low Soil:GW ratio)
        - Neutralizing alkalinity would eliminate alkaline activation of persulfate and could release all O_2 at once

- Bench tests can be accomplished, but with careful consideration of experimental design

Case Studies

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Klozur® CR Leads to Site Closure in Urban Bologna, Italy Gas Station

Consultant: Confidential
Contractor: Confidential

Klozur® CR:	6,300 Kgs (13,885 lbs)
Activator:	Built into Klozur® CR
Injection:	Two DPT Events (18 IPs)
Spacing:	350 m^2 (3,800 ft^2)
Interval:	4 to 9 m bgs (13 to 30 ft bgs)
Soils:	Silty sands and silty clays

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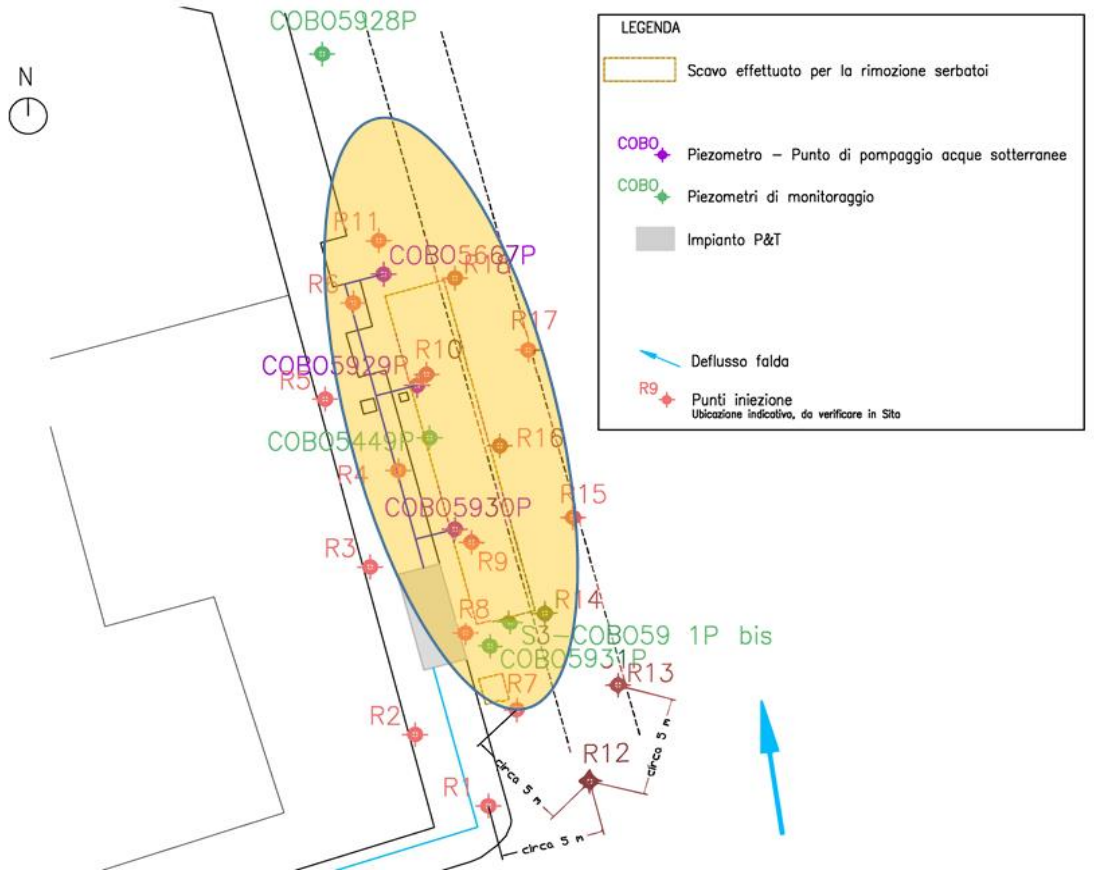
Klozur® CR Case Study - Petrol Station, Bologna, Italy
Site Background

- Former Petrol Station in Bologna, Italy

- Two applications of Klozur CR
  - 18 DPT points per application

- Contamination:
  - Total Petroleum Hydrocarbons (TPH): up to 2 mg/L
  - MTBE: Over 13 mg/L
  - Benzene: ~0.5 mg/L



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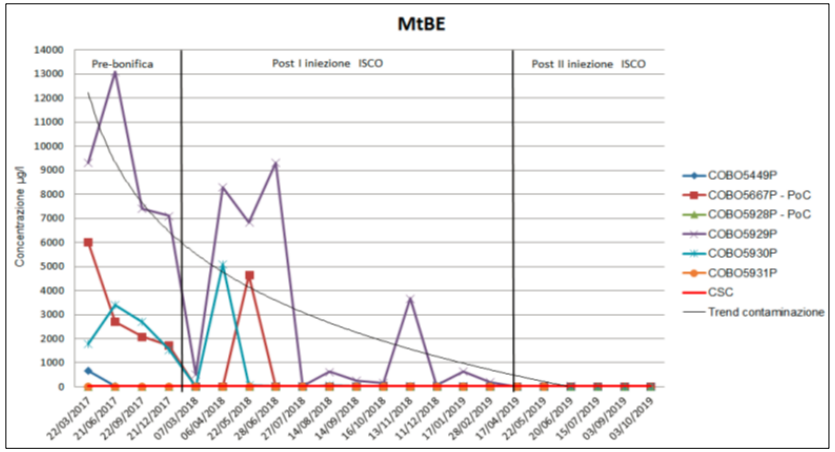
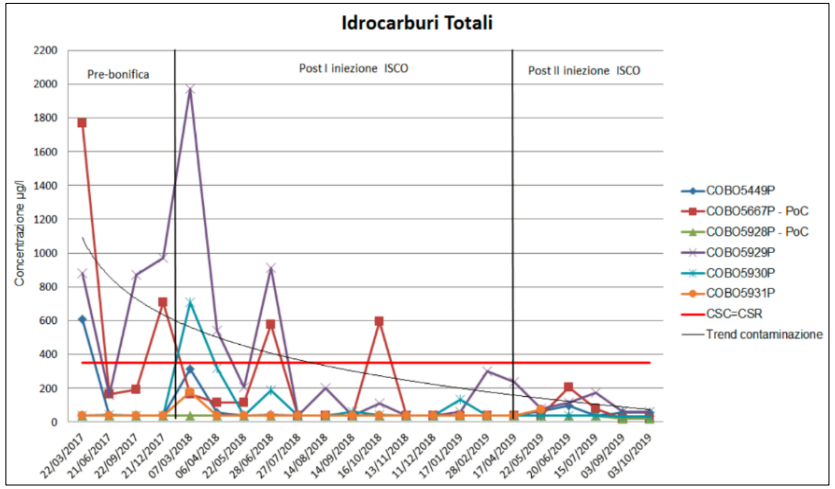
Klozur® CR Case Study - Petrol Station, Bologna, Italy
Results

- Regulatory Limits:
  - TPH: 0.35 mg/L
  - MTBE: 0.074 mg/L
  - Benzene: 0.018 mg/L

- Results:
  - TPH > 80% Reduction
  - MTBE > 90% Reduction

Remedial goals achieved
Site Closed





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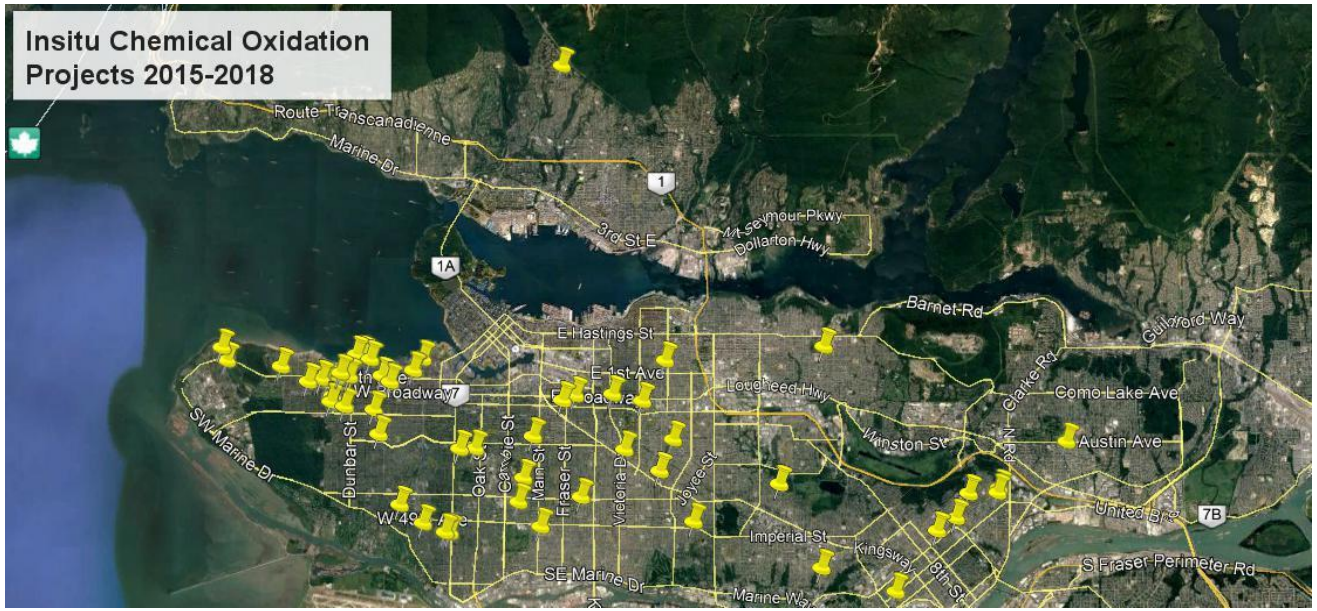
In Situ Chemical Oxidation and Bioremediation in the Complex Geologies of the Lower Mainland of British Columbia



Location: 150 in Vancouver, BC from 2015 to 2021

Lead Consultant: Ventus

Technical Support: Chemco

Contaminants:	Petroleum Hydrocarbons
Oxidant:	Klozur® CR
Strategy:	In Situ Applications of Klozur CR
	- Soil mixing
	- Filled via boreholes
	- Excavation backfill amendment

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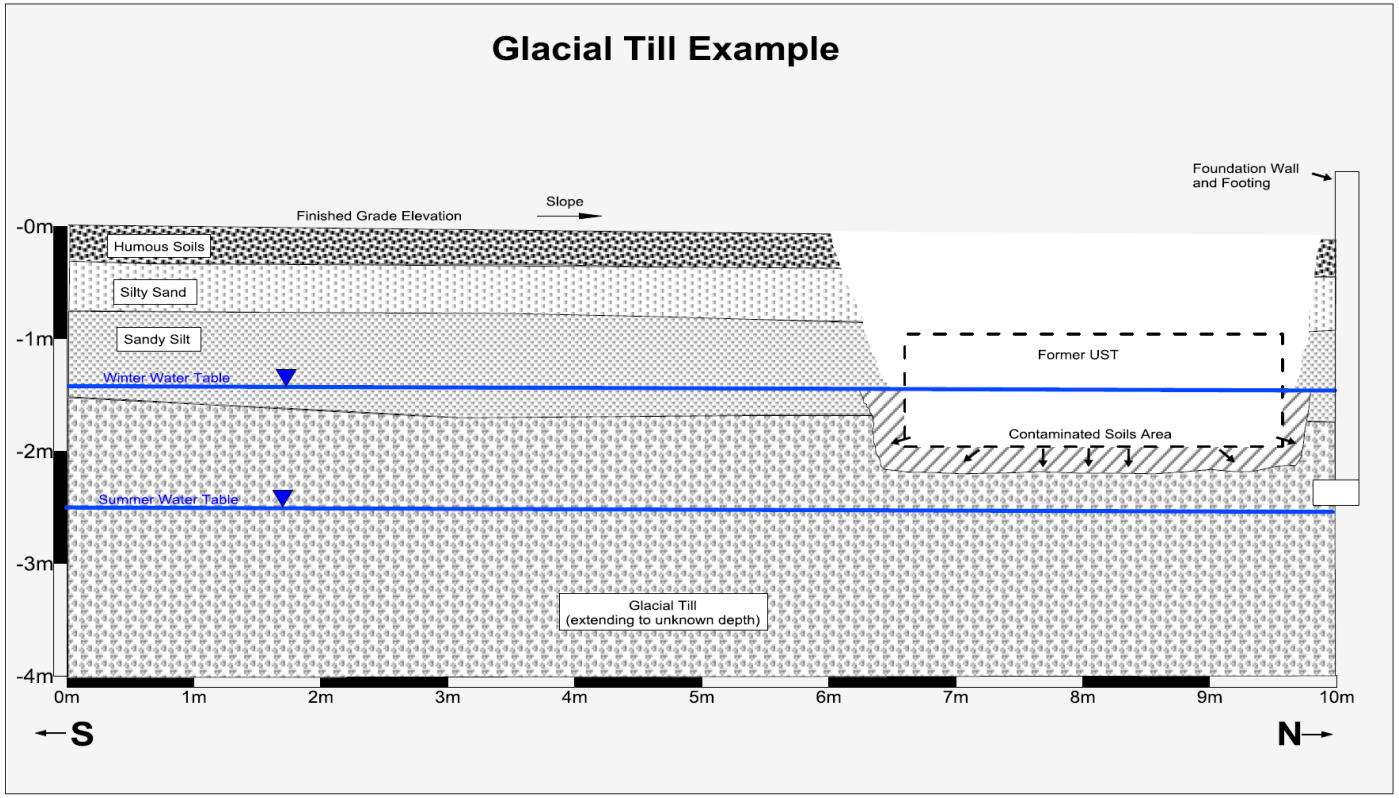
Klozur® CR Case Studies – British Columbia
Treatment of EPH C10-19 Contaminated Soils

- Given the yearly variation in water table depth there is often a small amount of contaminated soils that are above the water table.

- Holes are drilled into the excavation area for injection after mixing or Klozur® CR can be mixed and poured directly into an open excavation.



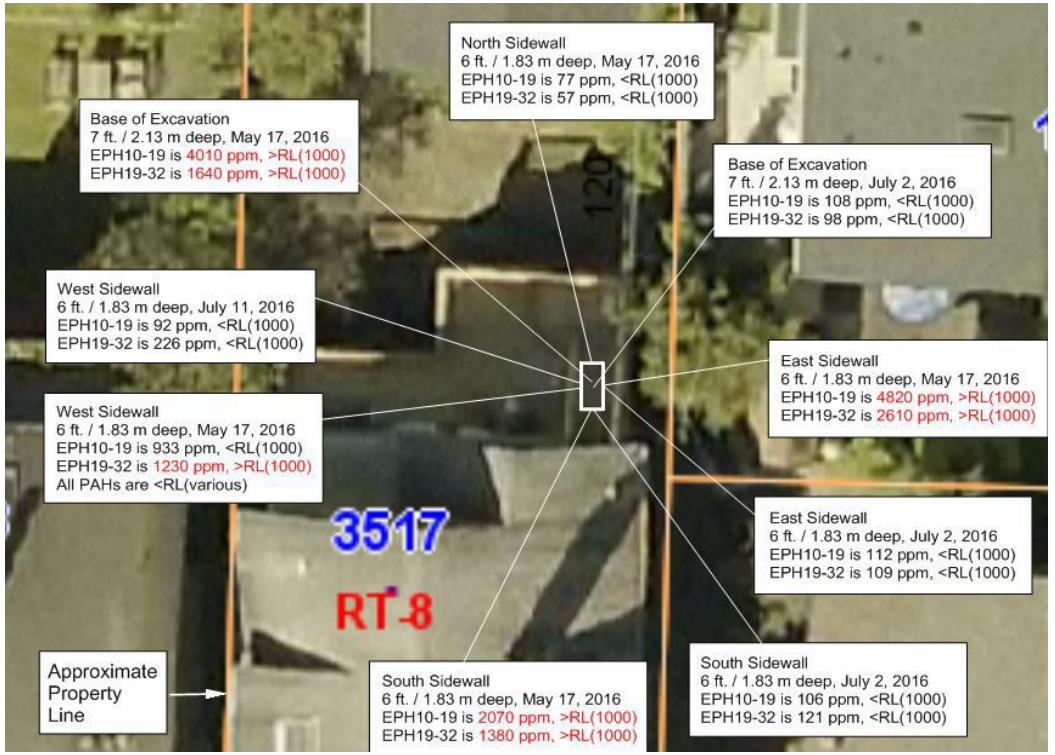
Klozur® CR Case Studies – British Columbia

- Thick slurries of Klozur® CR applied:
  - Into tightly spaced boreholes
  - Base of excavation of former USTs

Klozur® CR Case Studies – British Columbia
Treatment of EPH C10-19 Contaminated Soils

- In 8 to 9 weeks EPH (C10-C19) soil concentrations decreased:
  - Excavation base: 4010 ppm to 108 ppm
  - Sidewall: 4820 ppm to 112 ppm

- Dig and dump remediation would have required destruction of the deck (worth $18,000 CAD), making ISCO the safest easiest and cheapest approach to remediation. Remediation Cost was about $10,000.



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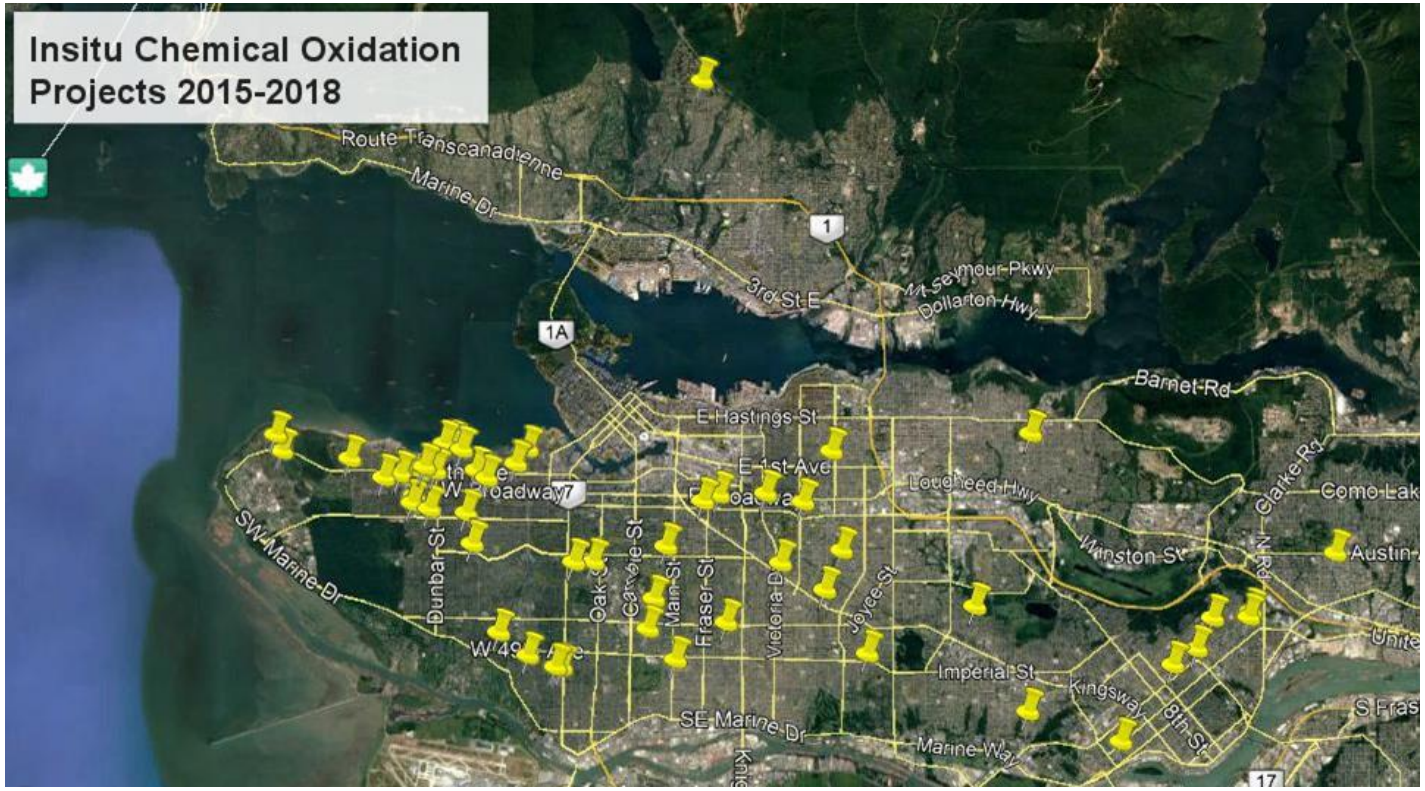
Klozur® CR Case Studies – British Columbia
Summary

- Over 150 Locations treated with Klozur® CR from 2015 to 2021
- 148 of the sites have been successfully closed
- Klozur® CR used:
  - In conjunction with excavation of the worst of the material
  - Treat more lightly contaminated soils



Klozur® CR Applied to Petrol Station in Residential Neighborhood

Consultant: ERM - Australia
Contractor: ERM - Australia

Reagent:	Klozur® CR and PermeOx® Ultra
Soils:	Silty sand
Area:	400 m^2 (4,300 ft^2)
Interval:	1 to ~4 m bgs (3 to ~13 ft bgs)

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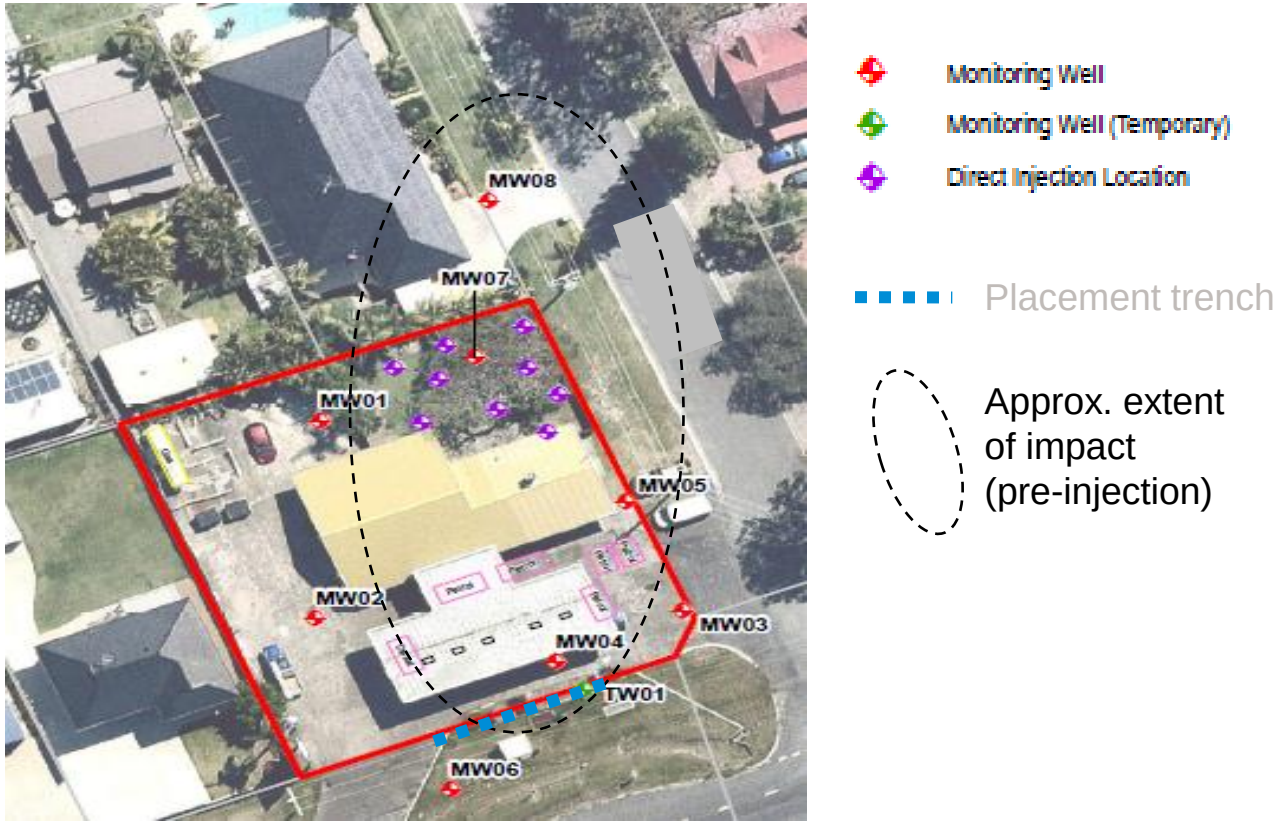
Klozur® CR Case Study - Petrol Station, Ningi, Australia
Site Background

- Petrol Station in Ningi, Australia
- Contamination:
  - Benzene
  - F1 (GRO)
- First application (Aug 2016)
  - Klozur® CR
    - 9 DPT points in back of station
  - PermeOx® Ultra:
    - Trench and 2 locations in front
- Second application of PermeOx® Ultra (Aug 2018)
  - 4 locations (Address MW-05 and MW-03)



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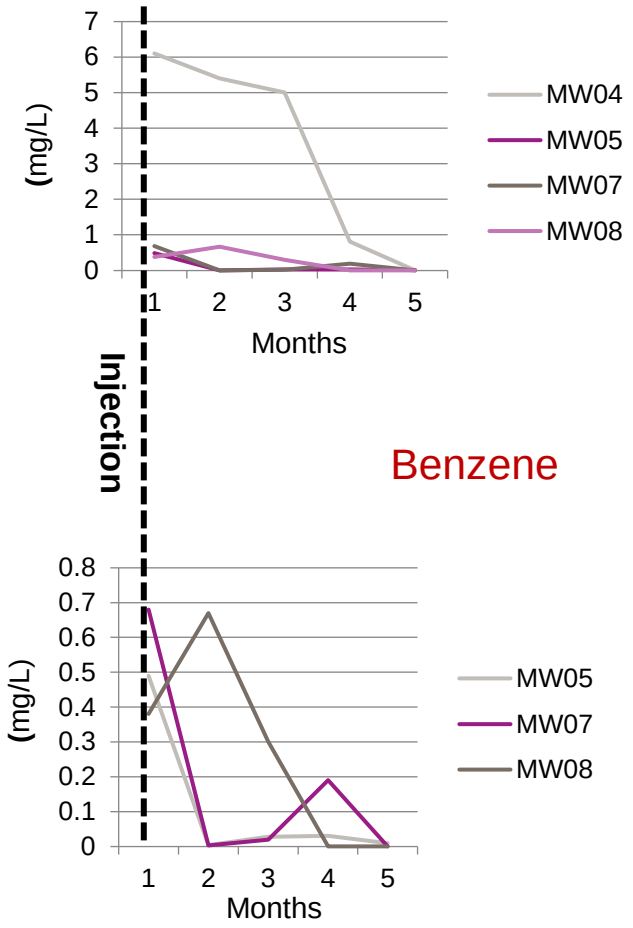
Klozur® CR Case Study - Petrol Station, Ningi, Australia
Results

Remedial goals achieved
Site Closed



Summary

- Over 15 years of experience with Klozur® CR

- Three possible treatment pathways from a single application
  - In situ chemical oxidation with activated persulfate and hydrogen peroxide
  - Aerobic bioremediation with extended release PermeOx® Ultra
  - Anaerobic biological oxidation (with specific geochemical conditions)

- Most cost effective when used to treat:
  - Low to moderately contaminated petroleum hydrocarbon sites
  - Can be used to treat some chlorinated solvents

Questions?

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