

Enhanced Physical Recovery of Petroleum Hydrocarbons from Groundwater



ADVANCED TECHNOLOGIES FOR GROUNDWATER RESOURCES



- Evaluation of a New Reagent for Increasing Pump-and-Treat Efficiency -



About Regenesis

- Environmental technical products company
- Founded in 1994 in California
- Ca. 20.000 projects to date
- 26 countries – 6 continents
- Free application designs and technical support
- Continuous product development and innovation





This Talk

- **New Remediation Product**

- Why?
- What?
- How?
- Show me

RegenOx[®]
PetroCleanze[™]

**Frees Bound Hydrocarbons For
Enhanced Recovery and Treatment**



Background – statement of the problem

- Pump-and-Treat
 - Widely employed for groundwater remediation around the world
- Can be an effective means of:
 - plume containment
 - mass reduction
- Clean-up to regulatory standards is often challenging
 - recovery frequently becomes asymptotic – diminishing efficiency
 - rebound post shut-down is common – within weeks or months
 - operation may be necessary for many years – often open-ended

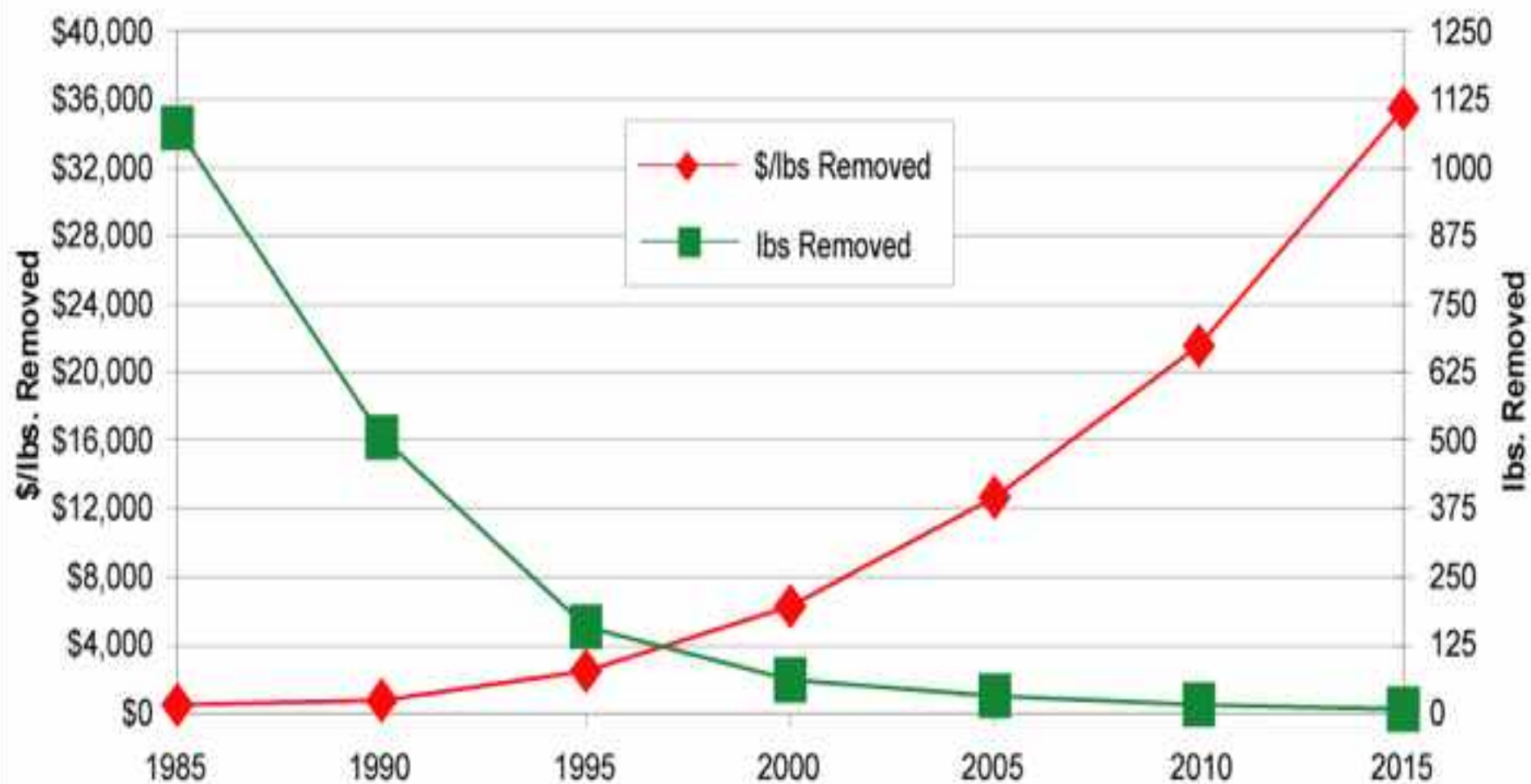


Extractive Remediation (P&T): **asymptote**

concentration

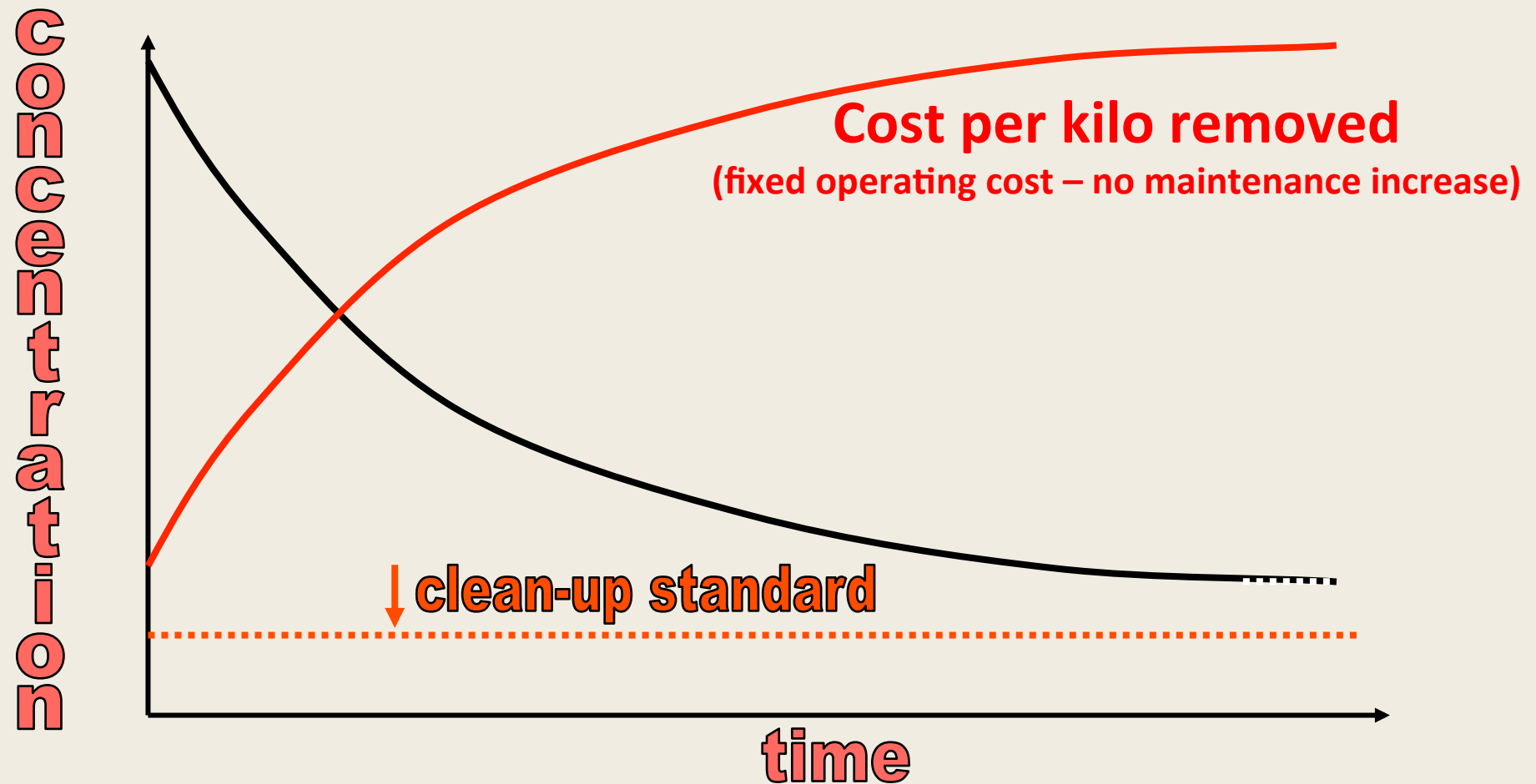


P&T System Cost and Effectiveness





Extractive Remediation (P&T): **asymptote**





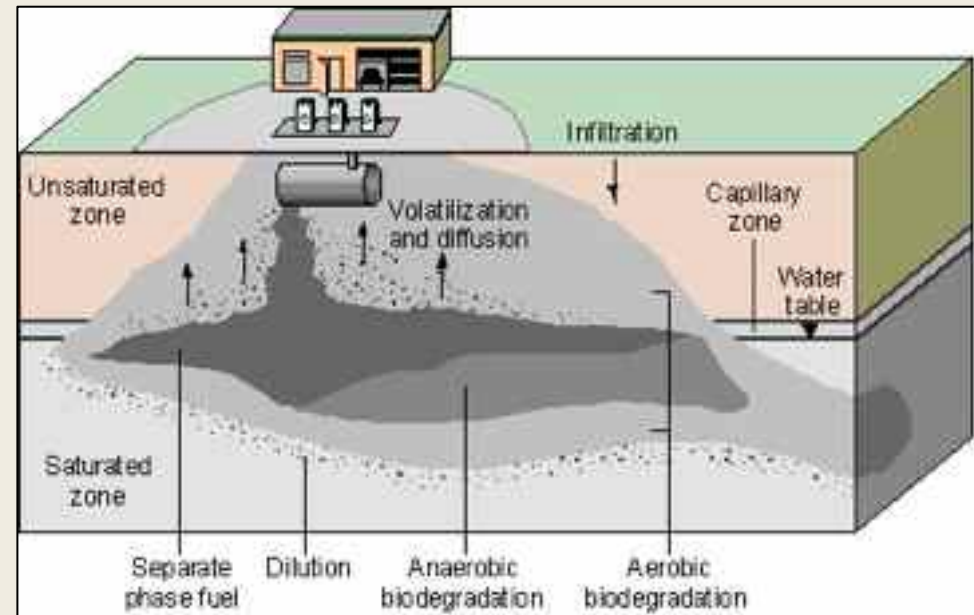
Background – statement of the problem

- P&T performance and efficiency governed by:
- Recoverable vs. non-recoverable mass
 - ☑ – Mobile mass - **recoverable**
 - ⊘ – Sorbed mass - **non-recoverable**, source of rebound
 - ⊘ – Low permeability zones - **non-recoverable**, source of rebound
- Requirement for multiple technologies
 - Mobile mass - P&T / extraction technologies
 - **Sorbed mass** - **this talk**
 - Low permeability zones - diffusive technologies (ORC[®], HRC[®])



Sorbed Mass – Source of ongoing groundwater contamination

- **Former spill areas**
 - Smear zone at water table
 - >90% of weathered TPH mass is typically on soil
- **System attempts Equilibrium**
 - Sorbed mass slowly partitions into groundwater
 - Replenishes removed GW mass
- **Sorbed mass is difficult to quantify**
 - Cannot be directly measured via wells – requires soil samples
 - Cannot be monitored over time – would need multiple intrusive (drilling) events
 - Spatially heterogeneous – requires statistically meaningful data sets





RegenOx[®] ISCO – Incidental Desorption Experience



- The Regenesiis proprietary ISCO product **RegenOx[™]** has consistently demonstrated a strong desorptive effect on soil-bound TPH mass



Example Field Observations – Kent, UK





Example Field Observations – Liguria, Italy





Example Field Observations – USA

- Same effect repeatedly observed around the world





RegenOx[®] ISCO – Incidental Desorption Experience

RegenOx[®]

- The Regenesiis proprietary ISCO product **RegenOx[™]** has consistently demonstrated a strong desorptive effect on soil-bound TPH mass
 - Side feature of its design and purpose, but helpful all the same
 - This has been built upon to develop a **new reagent**
 - We are a commercial organisation therefore it has a trade-name

RegenOx[®]
PetroCleanze[™]





Why not simply use a surfactant?

- Surfactants have a high Biological Oxygen Demand (BOD)
 - Significant surfactant residues remain in the formation
 - These present a barrier to contaminant biodegradation
 - Compete with contaminants for available oxygen
- At low concentrations (sub-CMC), surfactants *increase* sorption
- Surfactants are expensive
 - And are ineffective unless at substantial concentrations
- Surfactants clog formations
 - Counterproductive to primary objective
 - barrier to other activities
- They have been known about for years but are seldom used
 - There is a reason for this!



Development of PetroCleanze™

- Repeated observations of dissolved-phase TPH increase post RegenOx®
 - Especially sites with *high adsorbed TPH* mass (e.g. soil 100 mg/kg)
- Regenesis enhanced these properties specifically to address “banked” (soil bound) TPH mass
 - **Target contamination:**
 - **Weathered, highly adsorbed hydrocarbons**
 - e.g. petroleum filling stations, home heating oil spills and manufactured gas plants (MGPs)
 - **Product function:**
 - **To enhance recoverable mass**
 - shorter pump-and-treat (P&T) duration - elimination of post P&T rebound – increased removal of higher molecular weight (lower solubility) hydrocarbons – removal of smear-zone – *in situ* vadose zone treatment (including low v/p TPH inaccessible to SVE)





PetroCleanze™ - Product Function

To enhance *recoverable* mass

- shorter pump-and-treat (P&T) duration
- elimination of post P&T rebound
- increased removal of higher molecular weight (lower solubility) hydrocarbons
- removal of smear-zone
- *in situ* vadose zone treatment (including low vapour-pressure TPH inaccessible to SVE)





PetroCleanze™ Contaminant Desorption



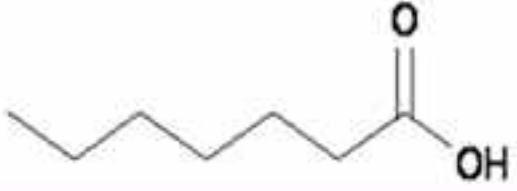
- **Driven by:**
 - Detergent-like reagent ingredients (silicates, carbonates)
 - Alkaline conditions
 - Formation of surfactants from the TPH
 - Formation of more soluble organic species from the TPH
- **Soil bound contamination is transferred into recoverable phases**
 - dissolved phase
 - free-phase

May then be captured / removed by a variety of means



Partial Oxidation → Higher Solubility

Alkane + [O] → Alcohol + [O] → Organic Acid → CO₂ + H₂O

Chemical Name	Chemical Structure	Solubility in H ₂ O(g/L)
Heptane		0
Heptanol		3.3
Heptanoic Acid		241.9

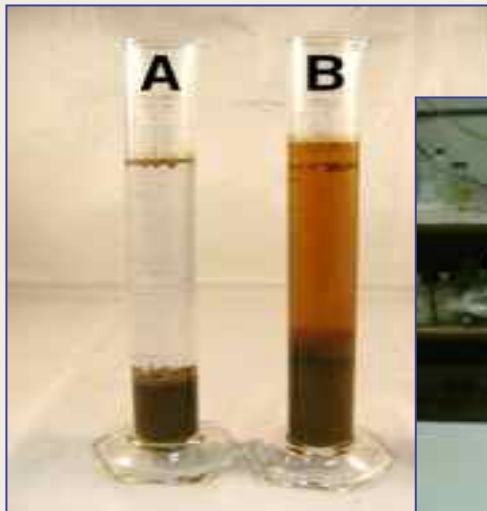


Laboratory Studies



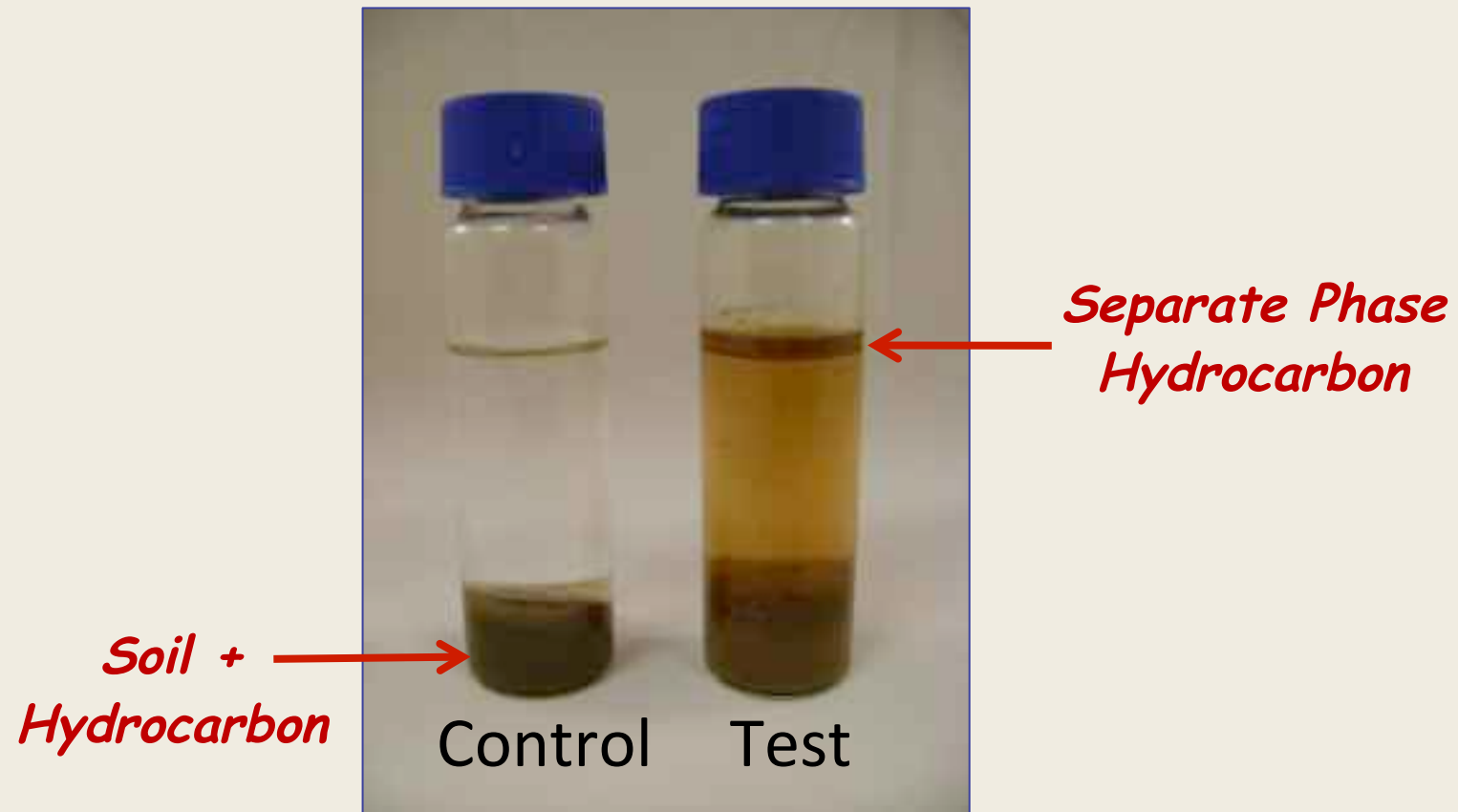
Laboratory Studies

- Range of formulation adjustments explored
 - Optimisation of performance, safety, cost...





Laboratory – influence visually evident





Formulation

- PetroCleanze™ - Two Part Product
 - Oxidizer complex
 - PetroCleanze activator
- Formulated to optimize desorption → physical removal of soil bound TPH
- Inorganic formulation eliminates residual BOD common to surfactant flush methods
 - Preserves the oxygen associated with RegenOx
 - Increases contribution of bioremediation
 - Post Application (back end of projects)





Case Studies



Case Study

- Commercial Yard, South East UK -

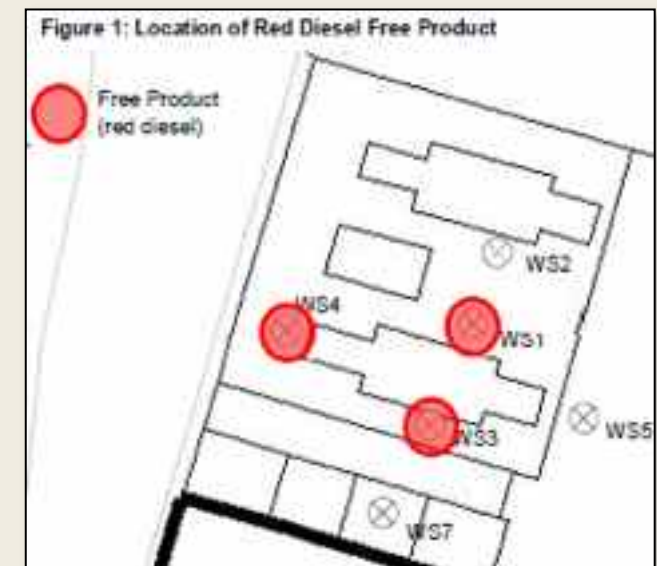




Commercial Yard, SE UK: Site Background



- Engineering Yard
 - Red Diesel plume – leak from back-up generator
 - Restricted access – plume extending under generator compound
 - Continuous use – high site traffic
- Remedial Requirements
 - No disruption of on-going site operations
 - Contaminant removal from below buildings
 - Compatibility with site infrastructure
 - Compatibility with calcareous formation (chalk)





Commercial Yard, SE UK: PetroCleanze Application

- Use of existing 50mm wells
 - no additional drilling
- Packer Push-Pull application
 - minimal time on site (hours)
- Freed mass recovered using vacuum tanker
 - **no resident equipment**



ADVANCED TECHNOLOGIES FOR GROUNDWATER RESOURCES

Commercial Yard, SE UK







Commercial Yard, SE UK – Remedial Performance

- Recoverable free product
 - increased from <10 mm to > 1000 mm
- Remedial targets secured
 - three push-pull cycles, two weeks apart
- Remediation completed
 - within **two months**

no resident equipment
a few hours on site
- No rebound
 - three months after last extraction and counting...



Case Study

- Northern UK -

Case Study, Northern UK

Pump-and-Treat Enhancement





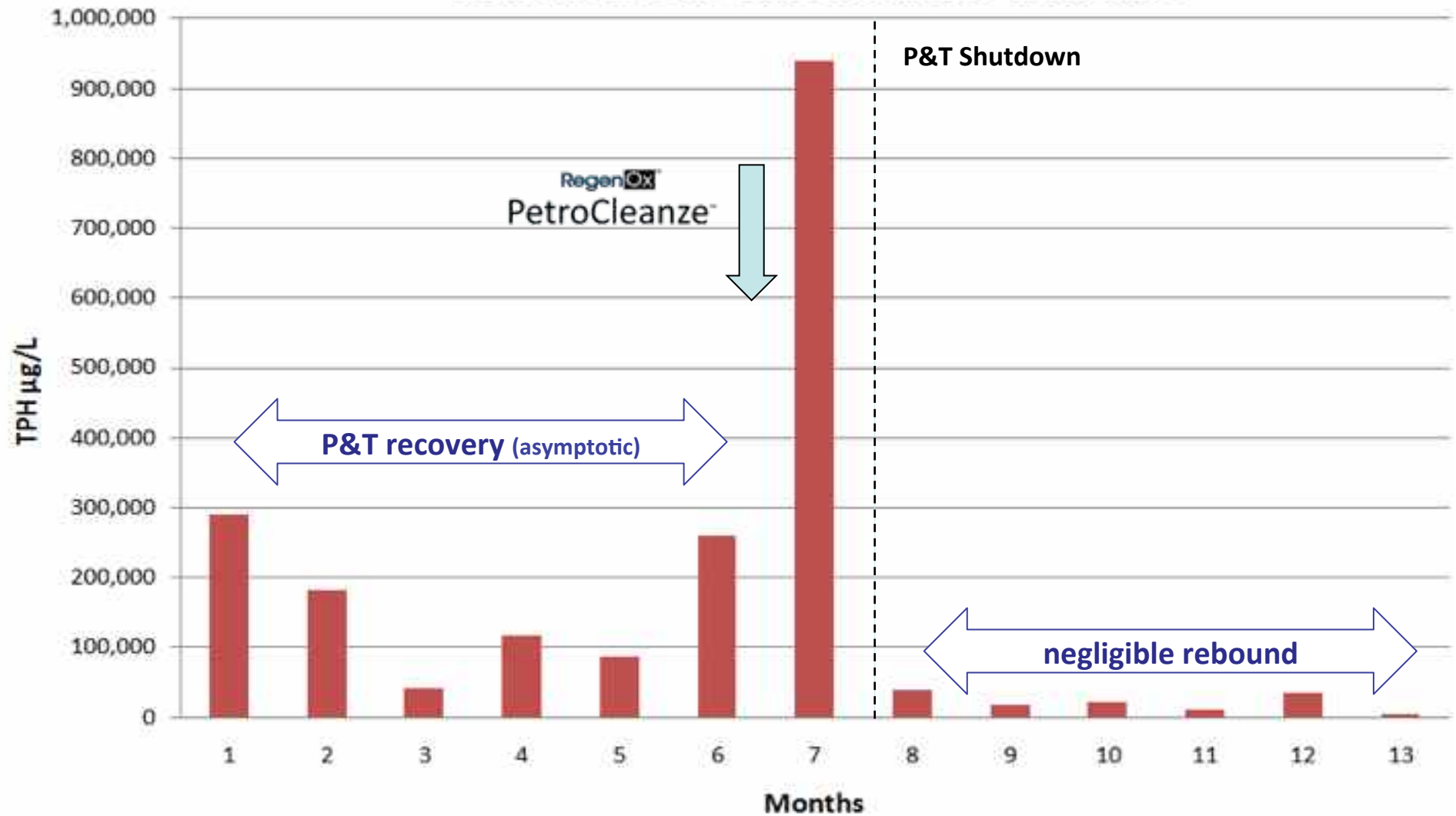
Northern UK: Site Background

- Residential redevelopment of former filling station
 - removal of underground storage tanks
 - removal of grossly impacted soils
 - Dual-Phase recovery of free product
- Highly time-sensitive project
 - Strict remediation deadline – with penalties



ADVANCED TECHNOLOGIES FOR GROUNDWATER RESOURCES

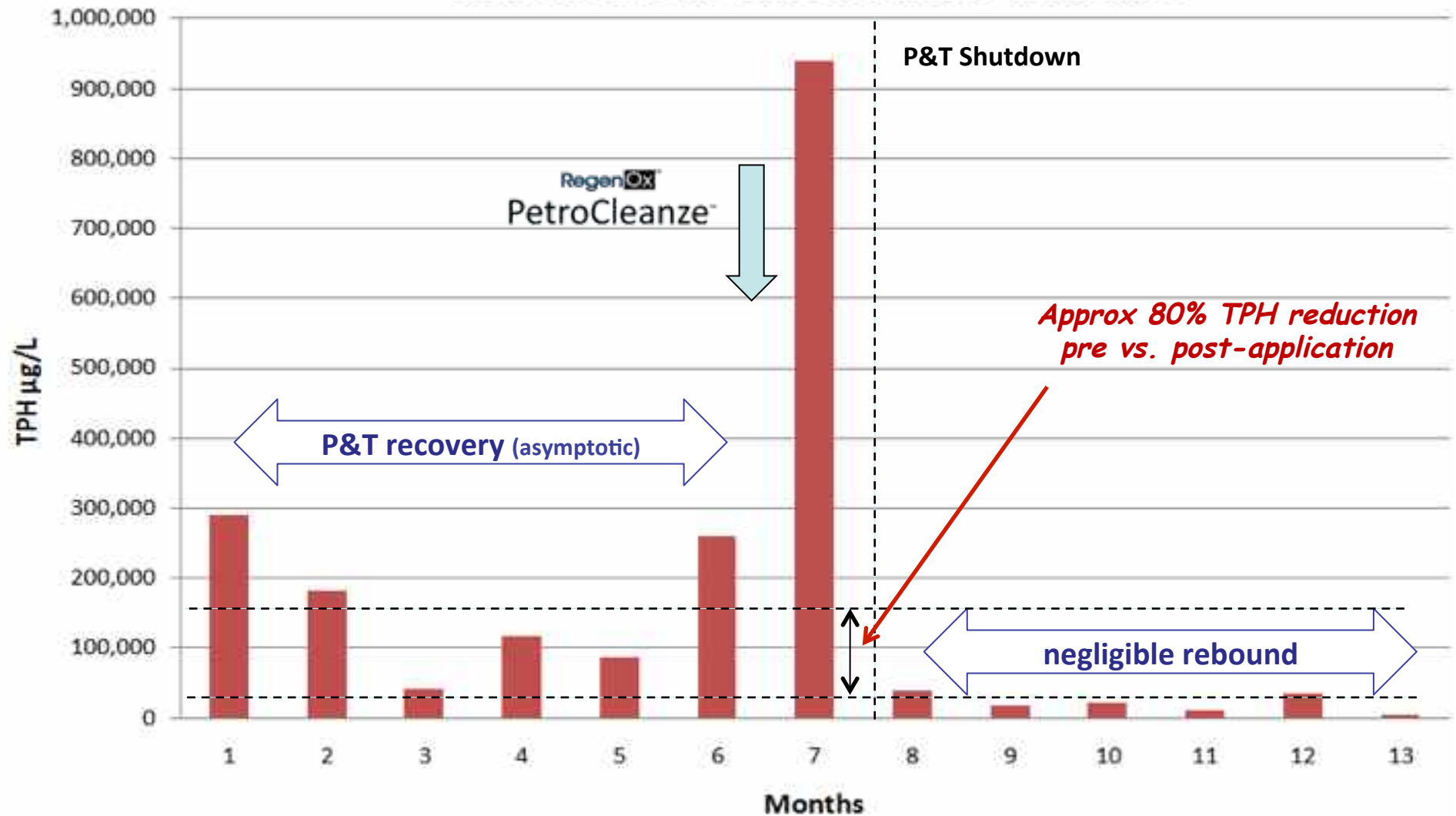
Core Area TPH Concentration - Yorkshire





ADVANCED TECHNOLOGIES FOR GROUNDWATER RESOURCES

Core Area TPH Concentration - Yorkshire



skip to close



Case Study Summary

- **>80% TPH reduction** achieved with two reagent applications augmenting DPVE recovery over **four weeks**
- **No rebound** due to augmentation process successfully removing sorbed-phase TPH and smear from the soil.
- **Ongoing enhanced biodegradation** / attenuation post reagent expiry and DPVE shut-off
 - elevated electron acceptors post ISCO
 - Increased contaminant bioavailability (RegenOx-enhanced desorption)
 - increased contaminant biodegradability (partial oxidation)
 - ~40% post-DPVE TPH reduction in core area in 4½ months (not enhanced with ORC-Advanced®)
- **Regulatory closure achieved** after three months post-DPVE with no rebound



Case Study

- Large Mixed Plume, Northern England -





Large Mixed Plume – Northern England

- Old chemical works
 - To be developed as an education center
- Town centre location
 - L-shaped site 70m x 20-40m
- Gravel formation
 - Slurry wall up-gradient; clay down-gradient
- Mixed contamination
 - **Monochlorobenzene (MCB)** (principal contaminant)
 - TCE, DCE, VC



Mixed Plume – Northern England: Remedial Strategy

- Contaminants and concentrations are amenable to bio
 - 10,000 – 20,000 $\mu\text{g/L}$ range
 - Good treatment record (both MCB and chlorinated ethenes)
- But biodegradation conditions are incompatible
 - Monochlorobenzene optimal aerobically
 - TCE requires anaerobic conditions
 - (MCB had likely been electron donor supporting TCE bio)
- Selected strategy:
 - MCB mass reduction followed by anaerobic bio of TCE, DCE, VC
 - Any MCB residuals then consumed as co-electron donors



Mixed Plume – Northern England: Remedial Strategy

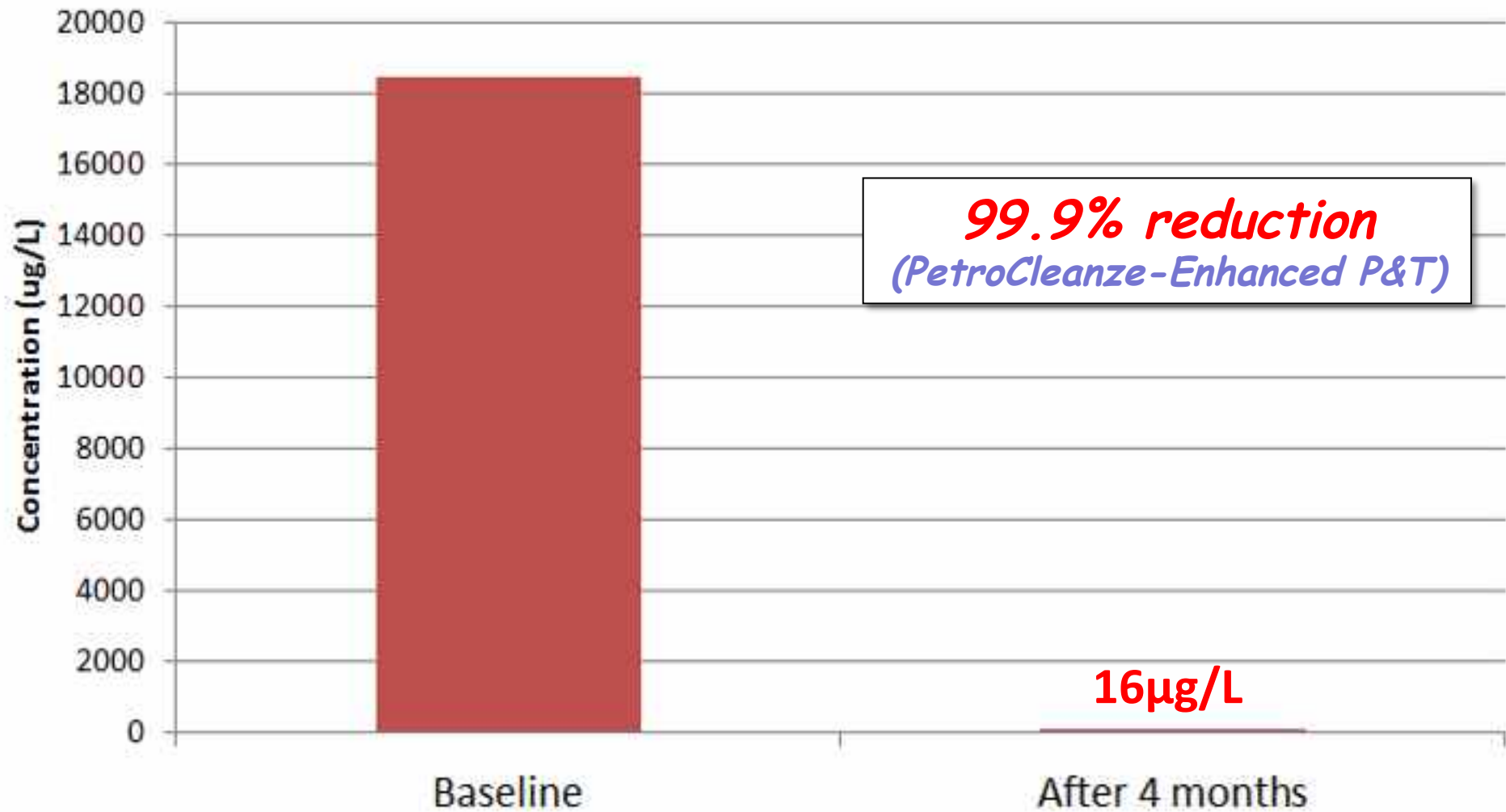
- Phase I
 - P&T on 10m grid
 - PetroCleanze on 5m grid
 - Two treatment cycles
- Phase II
 - Anaerobic bioremediation
 - 3DMe electron donor

3-D MicroEmulsion™
HRC ADVANCED™



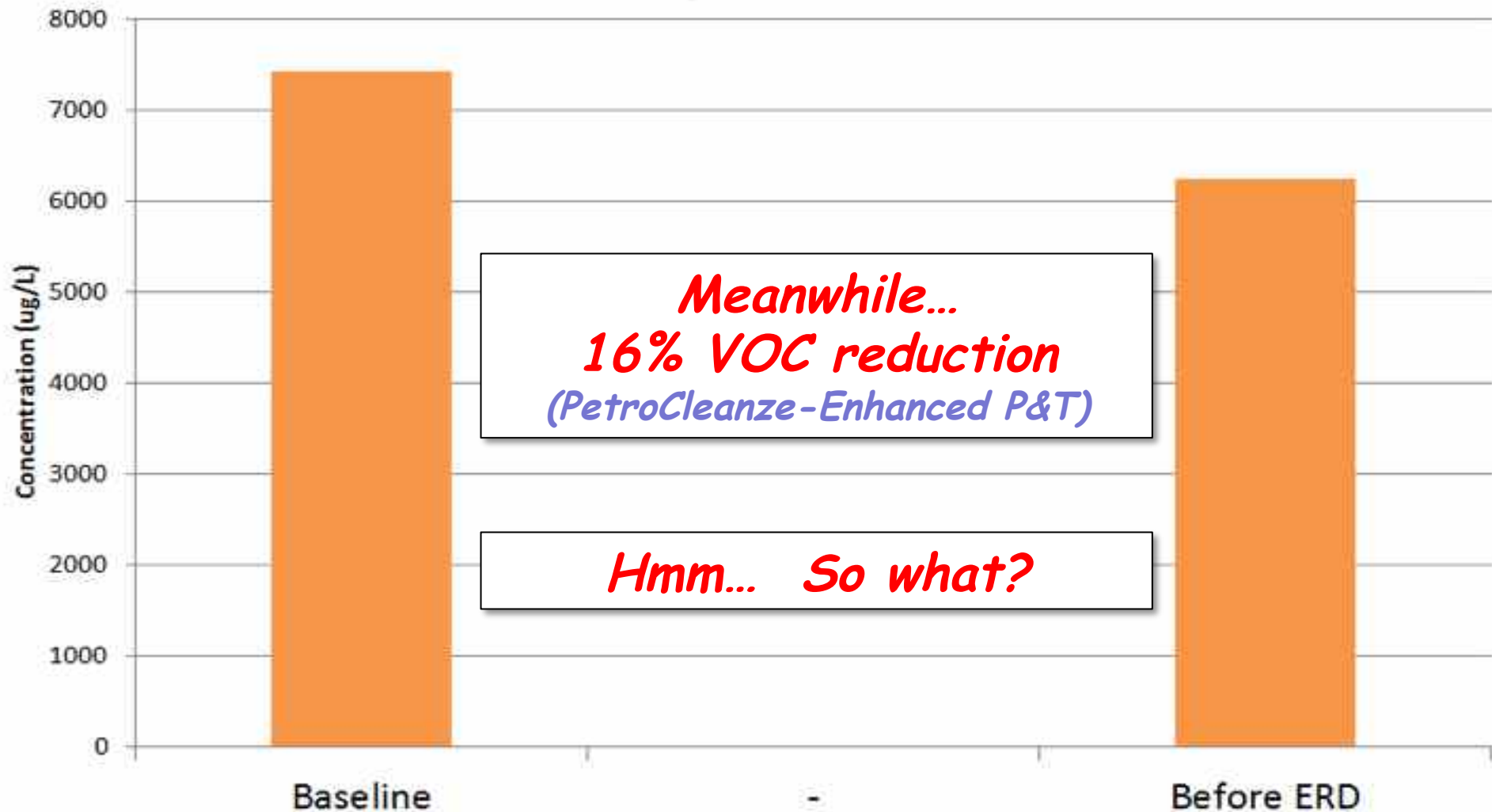


Mean Monochlorobenzene Concentrations



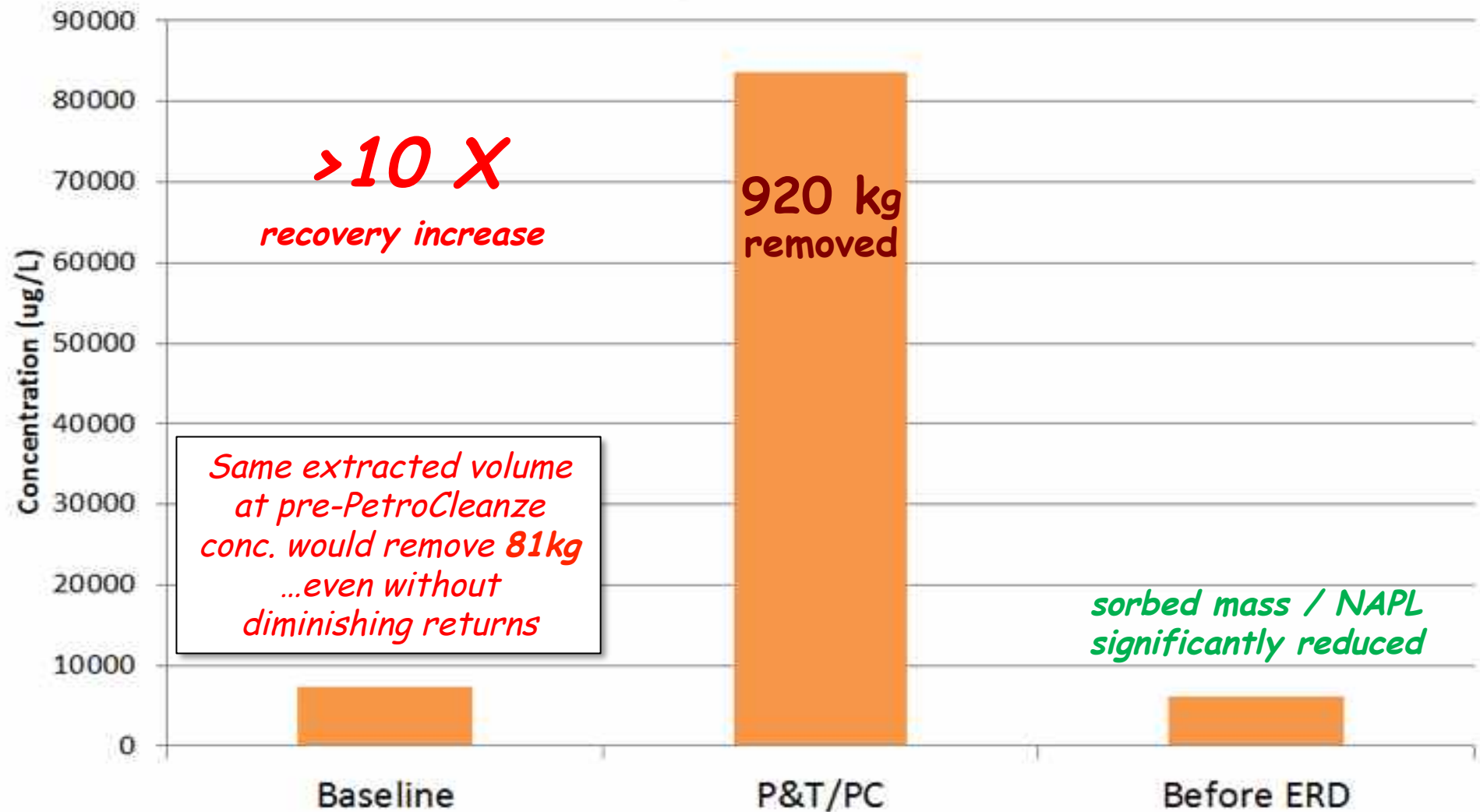


Mean Chlorinated Hydrocarbon Concentrations





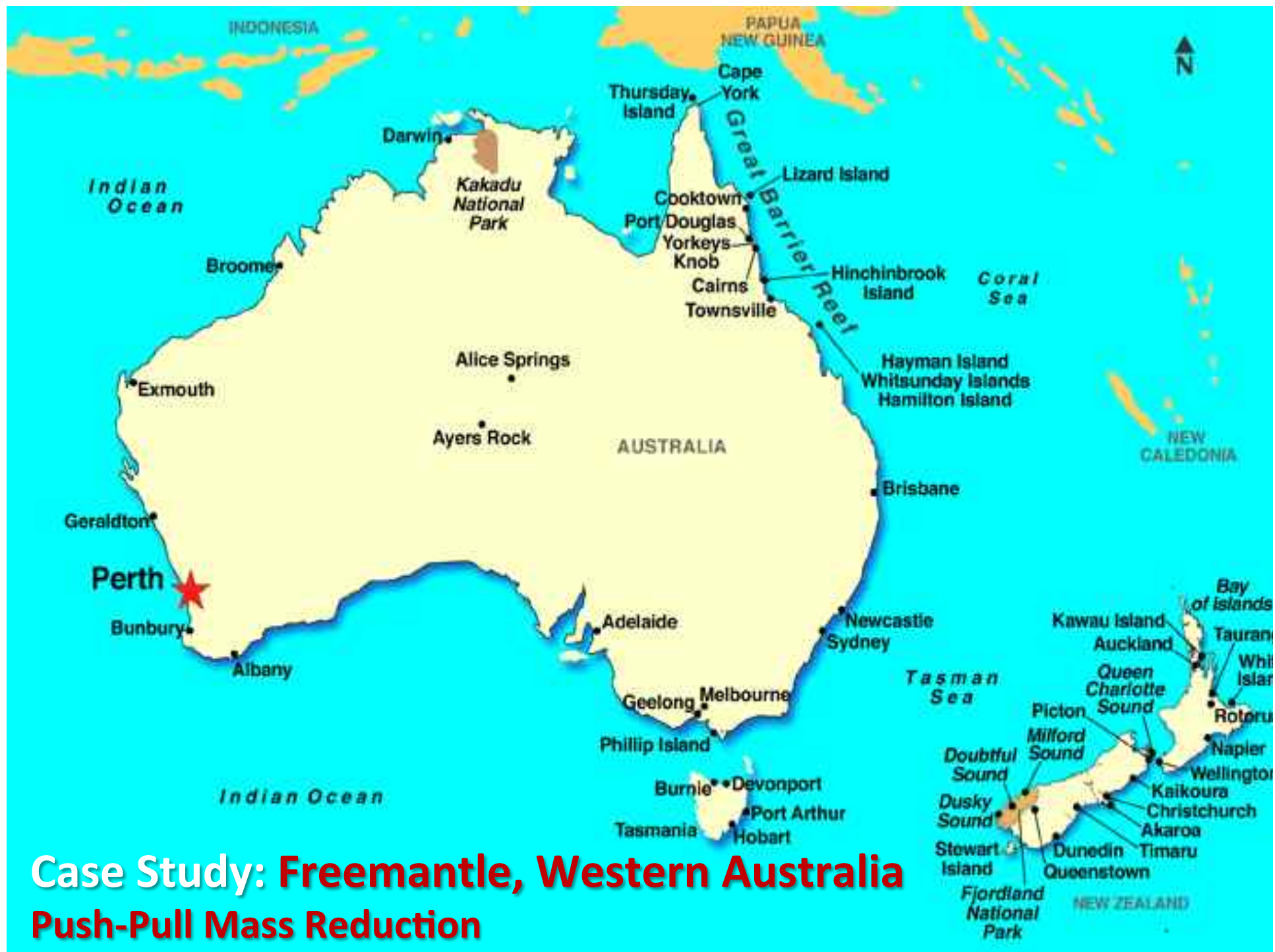
Mean Chlorinated Hydrocarbon Concentrations





Case Study

- Western Australia -



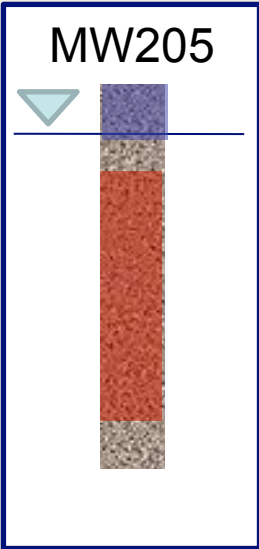


Freemantle, Western Australia: Site Background

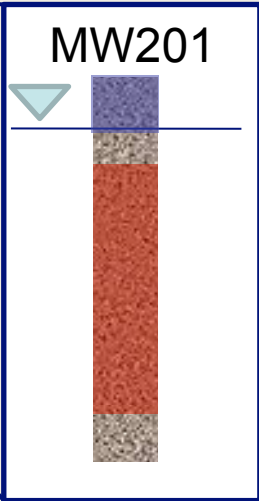
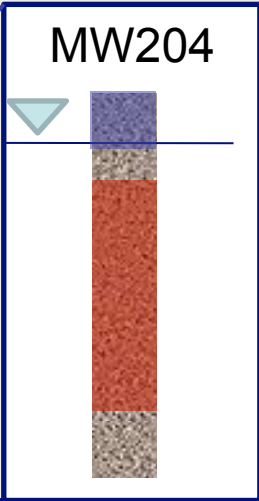
- Site: International Sea Port
- Remedial Driver: Redevelopment
- Source: Pipe Leakage
- Aquifer Type: Sand
- Contaminant: Diesel-Range TPH (weathered)
- GW Depth: Approx. 6 mbgs
- GW TPH Concentration: Range 10,000 -100,000 $\mu\text{g/L}$
- Soil TPH Concentration: >5,000 mg/kg



Visible Soil Staining (Borehole logs)



Approx. 3.5 m impacted thickness



Visible TPH Staining



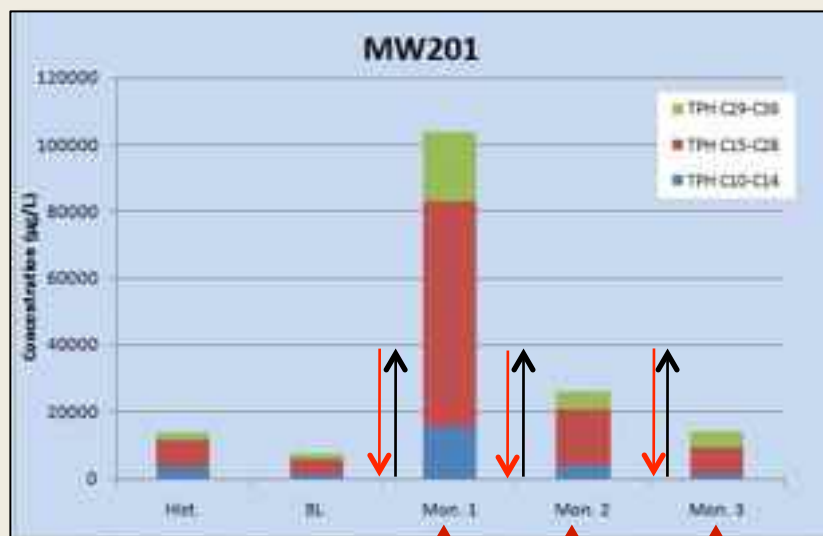
Remedial Approach

- 'Push-Pull' approach (reaction-extraction)
 - No resident equipment
 - No engineering installation
- Reaction phase
 - 17 wells
 - Application rate of 12 kg/m³ of treatment area at 5% solution
 - 14-21 days between injection and extraction
- Extraction phase
 - Vacuum trucks
 - Extracted from injection wells
 - Removed 20,000 – 40,000 L each event (3 events)





Contaminant Concentration Changes – core area of visual staining





Freemantle, Western Australia: Summary of Results

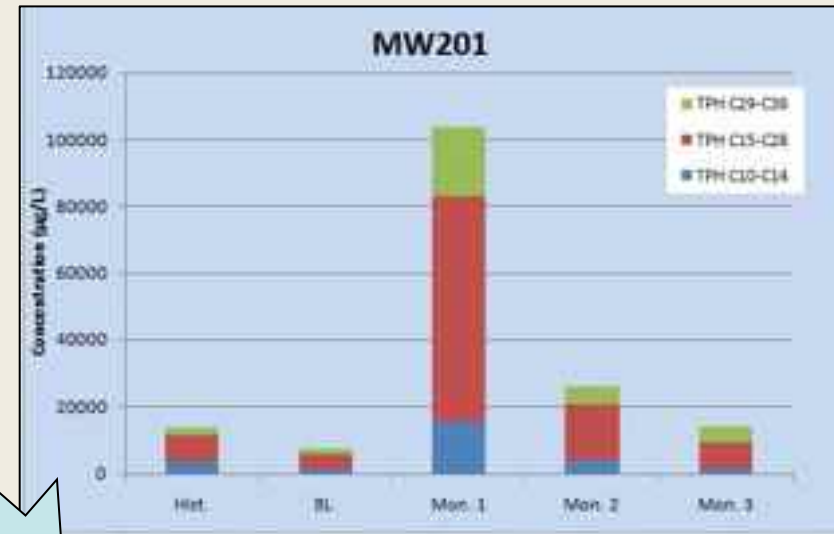
- **Average dissolved-phase reduction of 71%**
 - Representative reductions
 - High concentration well: 105,000 to 21,000 µg/L (80%)
 - Medium concentration well: 36,000 to 3,000 µg/L (92%)
 - Low concentration well: 7,000 to 2,000 µg/L (71%)
- **Remedial Performance**
 - 3 - 6 month campaign
 - 225 - 450 kg total hydrocarbon mass removed
 - Minimal rebound
 - GW remains below clean-up criteria 18-24 months post-treatment



Freemantle, Western Australia: Treatment Implications

- Coarse benefit illustration
 - Baseline pre-PetroCleanze = 5,000 $\mu\text{g/L}$
 - TPH mass recovered (3 events) = 5.6 kg
- 10 m³ Vacuum Truck (illustration)
 - Total PetroCleanze extractions = **12 truck movements**
 - Equivalent mass removal at baseline concentrations = **112 truck movements**
 - PetroCleanze requires <10% of effort

(conservatively assumes no diminishing returns at baseline)



- MW201
 - 40 m³ extracted each event
 - 3 events
 - 100,000 $\mu\text{g/L}$ - (4 kg TPH)
 - 25,000 $\mu\text{g/L}$ - (1 kg TPH)
 - 15,000 $\mu\text{g/L}$ - (0.6 kg TPH)



Case Study

- Florida, USA -



Florida, USA – mass-reduction in unsaturated zone



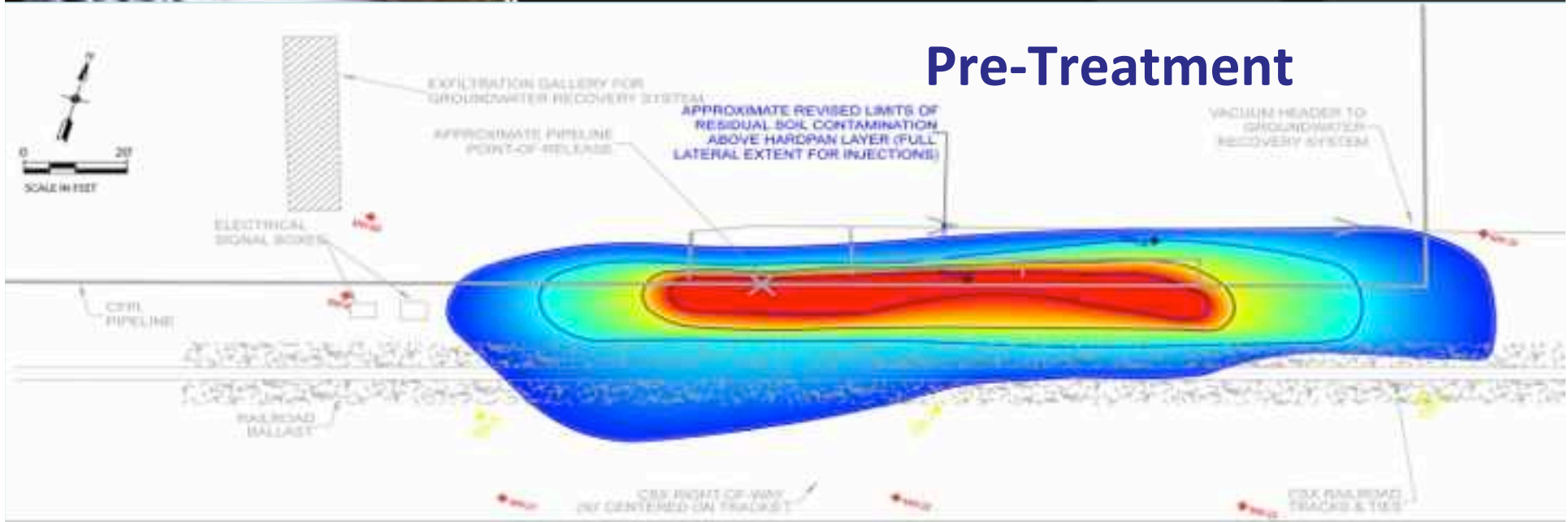
- Pipeline spill
- Residential area
- Diesel in soil $>10,000$ mg/kg
- 500,000 L product solution
- PetroCleanze™ prototype
- 3 push-pull applications

Not a shadow from a cloud!

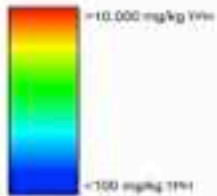


ADVANCED TECHNOLOGIES FOR GROUNDWATER RESOURCES

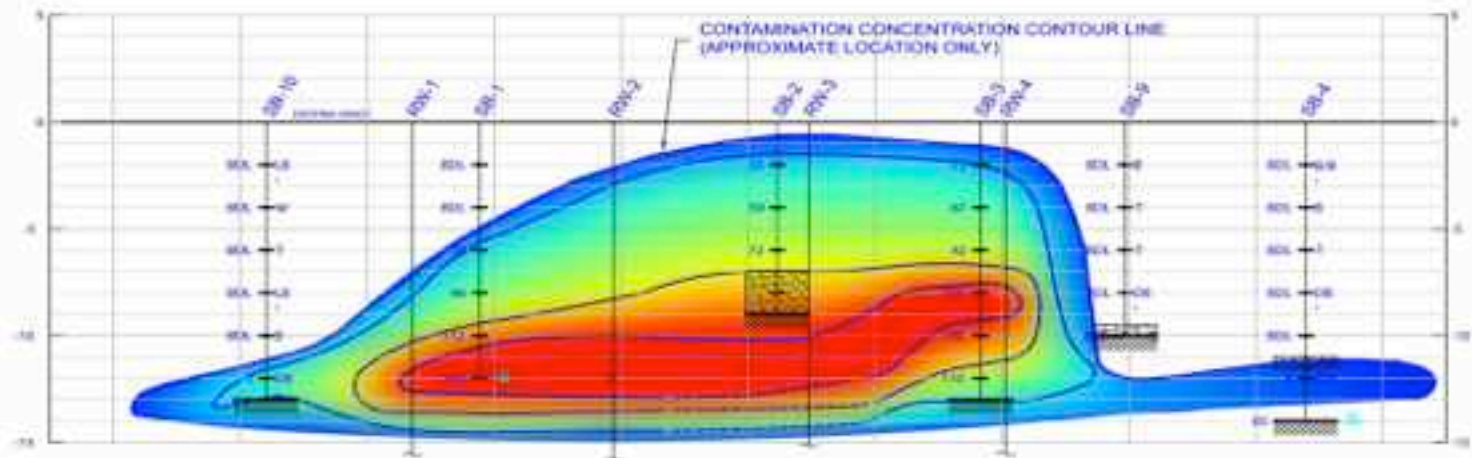
Pre-Treatment



> 10,000 mg/kg



< 100 mg/kg





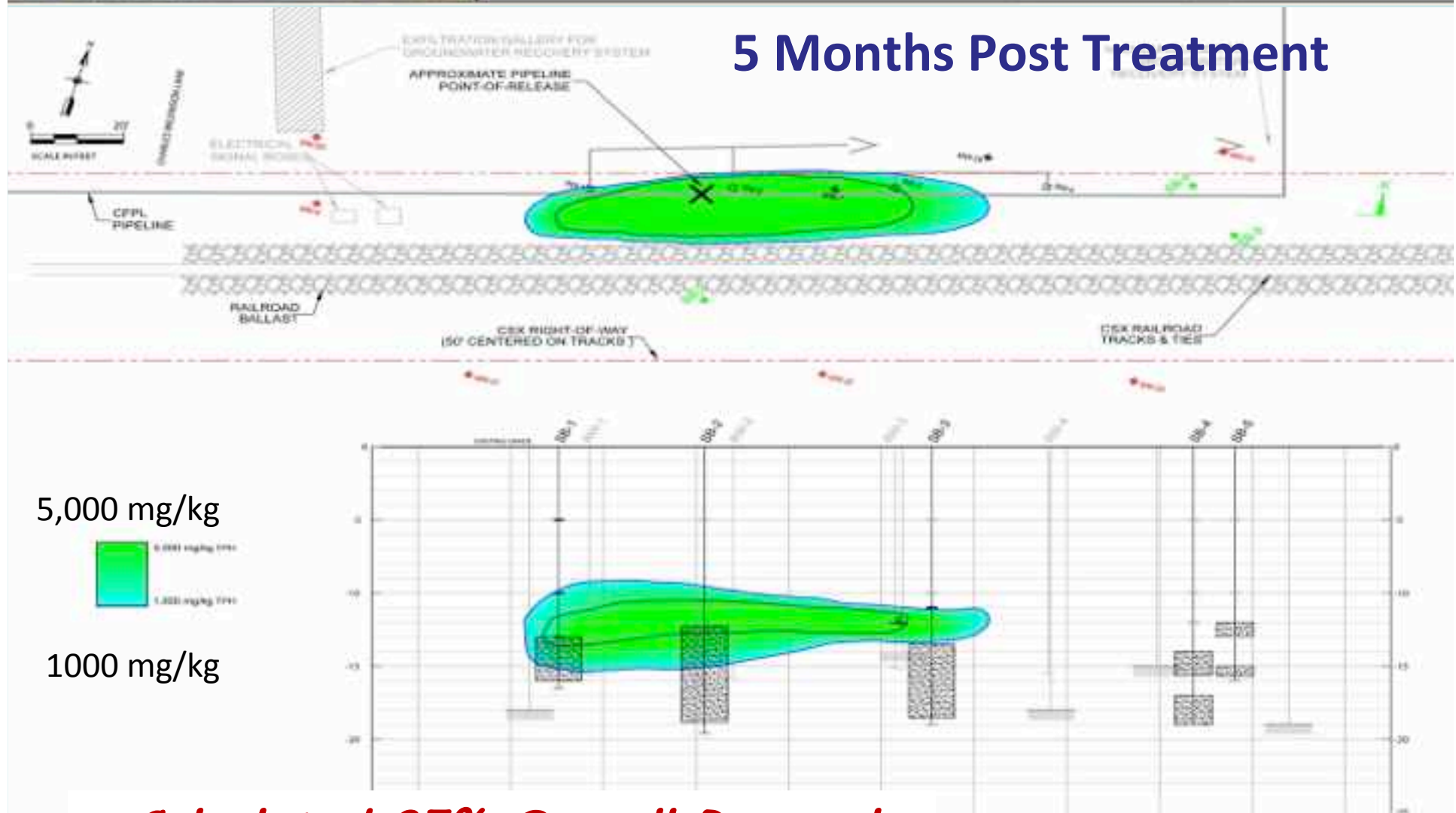
3 Months Post Treatment

The top map is a plan view showing the extent of a groundwater plume 3 months after treatment. The plume is elongated and oriented horizontally, with its center of mass located approximately 10-12 units from the left edge of the map. The plume is bounded by a green line, indicating a concentration of 5,000 mg/kg. The background is blue, indicating a concentration of less than 100 mg/kg. The map includes a scale bar (0 to 20 feet), a north arrow, and labels for 'EXPIRATION GALLERY FOR GROUNDWATER RECOVERY SYSTEM', 'APPROXIMATE PIPELINE POINT OF RELEASE', 'ELECTRICAL SIGNAL BOXES', 'CIVIL PIPELINE', 'RAILROAD BALLAST', 'CEE RIGHT-OF-WAY (30' CENTERED ON TRACKS)', and 'CEE RAILROAD TRACKS & TIE'. The bottom map is a cross-section showing the plume's depth and concentration profile. The plume is elongated and oriented horizontally, with its center of mass located approximately 10-12 units from the left edge of the map. The plume is bounded by a green line, indicating a concentration of 5,000 mg/kg. The background is blue, indicating a concentration of less than 100 mg/kg. The map includes a scale bar (0 to 20 feet), a north arrow, and labels for 'EXPIRATION GALLERY FOR GROUNDWATER RECOVERY SYSTEM', 'APPROXIMATE PIPELINE POINT OF RELEASE', 'ELECTRICAL SIGNAL BOXES', 'CIVIL PIPELINE', 'RAILROAD BALLAST', 'CEE RIGHT-OF-WAY (30' CENTERED ON TRACKS)', and 'CEE RAILROAD TRACKS & TIE'.



ADVANCED TECHNOLOGIES FOR GROUNDWATER RESOURCES

5 Months Post Treatment



Calculated 85% Overall Removal

skip to close

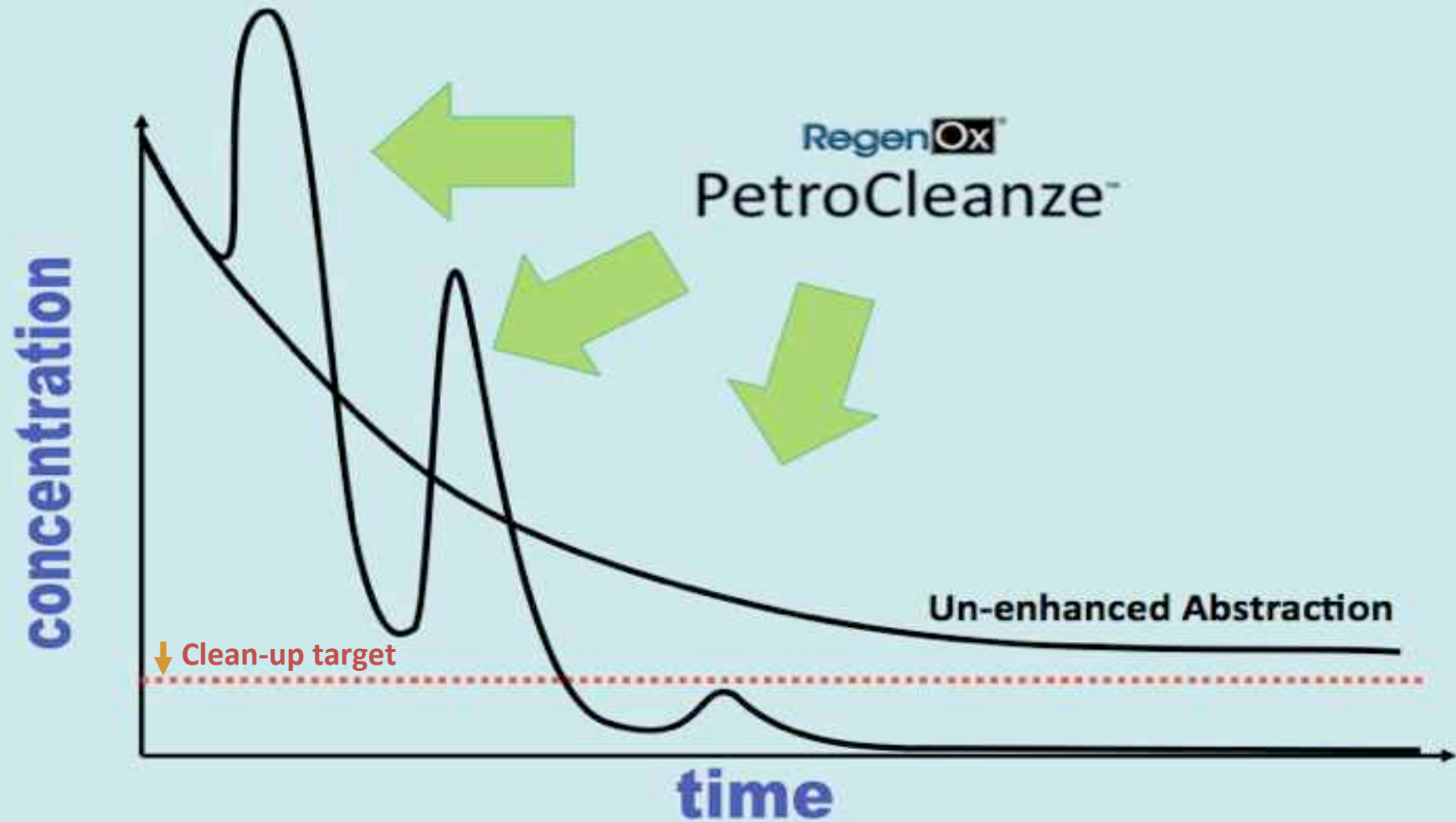


Case Studies Summary

- Sorbed TPH / Smear rapidly transferred to recoverable phase
 - Multiple options then available to engineers for mass recovery
- New means of addressing soil-bound TPH without excavation
 - Unsaturated zone / smear zone clean-up
- New means of rapid mass recovery without P&T installations
 - Vac truck 'push-pull' recoveries
 - Quickly reduce contamination to levels amenable to bioremediation
- Addresses contamination otherwise poorly accessible to P&T
 - Means of **increasing performance** of existing installations
 - Means of **expediting closure** of existing systems



ADVANCED TECHNOLOGIES FOR GROUNDWATER RESOURCES



[skip to contact info](#)



Regenesis Support

free of charge



- **Specialist Technical Assistance**

- ‘walking library’ of design and project experience
- On-line library of technical information and case-studies
- Comprehensive website www.regenesis.com
- Field support / application oversight
- Meeting support

- **Training**

- Lunchtime Talks
- In-House Seminars / Seminar Programmes

- **Application Design Service**

- Feasibility Checks – Strategy Options – Application Designs

- **Data Review Assistance**

- Project after-care
- On-going technical support through to project completion





Thank you



REGENESIS



REGENESIS



ADVANCED TECHNOLOGIES FOR GROUNDWATER RESOURCES

You have been watching....



Jeremy Birnstingl

Ph.D B.Sc. MSEE, CEnv

Vice President – Env. Tech.

+44 1225 731 446

Bath, UK

jbirnstingl@regenesisis.com



www.regenesisis.com

