Lessons Learned During In Situ Chemical Oxidation - Failure & Success?

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Background

- In situ chemical oxidation products are being sold as broadly applicable for hydrocarbon remediation.
- We tried one of these products, RegenOx™, at two sites.

Our Findings from Site Trials:

- Some key characteristics should be known about a site before using chemical oxidation
  - in order to understand both the target effects and the side effects
- This will help determine if in situ chemical oxidation is the correct approach.

Presentation Outline

- Theory of Chemical Oxidation
- Case Studies & Results
- Discussion of Key Characteristics
- Conclusion

Theory of Chemical Oxidation

- Range of products
  - Persulfates, percarbonates, peroxides, permanganates
  - RegenOx™ is a chemical formulation of
    - an oxidant complex: sodium percarbonate, $2Na_2CO_3 \cdot 3H_2O_2$, sodium carbonate (Na_2CO_3), sodium silicate and silica gel; and
    - the activator complex: ferrous sulfate ($FeSO_4$), sodium silicate and silica gel.

Theory of Chemical Oxidation

- Stoichiometry (how much do we need?)
  - for oxidation of benzene:
  - $C_6H_6 + 15H_2O_2 \longrightarrow 6CO_2 + 18H_2O$
  - RegenOx (oxidant)/benzene (wt/wt) = 20.1
- Reactions occur in aqueous phase

Theory of Chemical Oxidation

- Slurry Mixture
  - manufacturer recommended percent of oxidizer in solution: 9% to 4%
    = 5 L to 10 L water per kg RegenOx (oxidant+activator)
  - to oxidize 1 kg benzene requires 40 kg RegenOx (oxidant+activator) in approximately 200 L to 400 L water
- By-products
  - Sodium (Na), Iron (Fe), Sulfate (SO_4)…

Theory of Chemical Oxidation

- Delivery methods
  - Slurry injection, injection into existing wells, powder “socks”
- The objective is to achieve contact with affected soils.

Delivery Methods: slurry injection

Delivery Methods: injection into existing wells

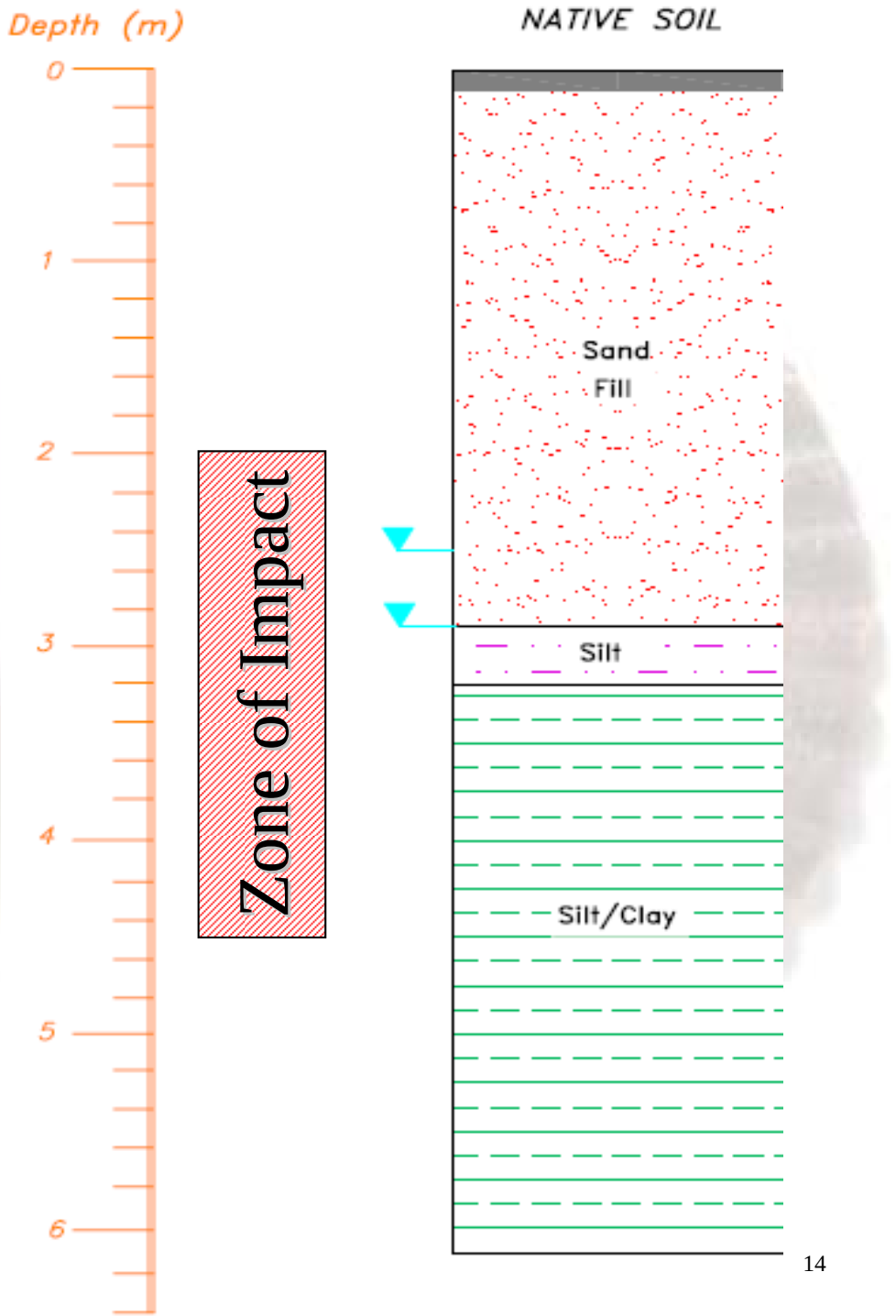
Delivery Methods: powder “socks” or “tubes”

Case Studies

- Two sites:
  - Both former service stations in central Alberta with coarse-grained soil
- Results of Field Trials of RegenOx™
  - Ability to deliver the slurry
  - Observed hydrocarbon degradation
  - Production of undesirable by-products

“P” Site

“P” Site Stratigraphic Column



“P” Site

- Contaminant concentrations in soil (**mg/kg**):
  - **B:** up to 63
  - **T:** up to 550
  - **E:** up to 200
  - **X:** up to 1900

  F1 - BTEX: up to 8900
  F2: up to 1000
  F3: <10
  F4: <20

  - total mass of contaminants (geometric mean):
    300 kg initial estimate
    (1000 kg post-injection estimate)
  - volume of soil affected ~600 m^3

“P” Site

- RegenOx prescription:
  - total mass = 12,250 kg (oxidant & activator) *
  - diluted into at least 61,250 L of water
  - 2 m x 2 m injection spacing
  - maximum pumping rate was 3.8 L/min, with actual rates decreasing due to formation pressure at each injection point

* estimate based on initial PHC mass estimate

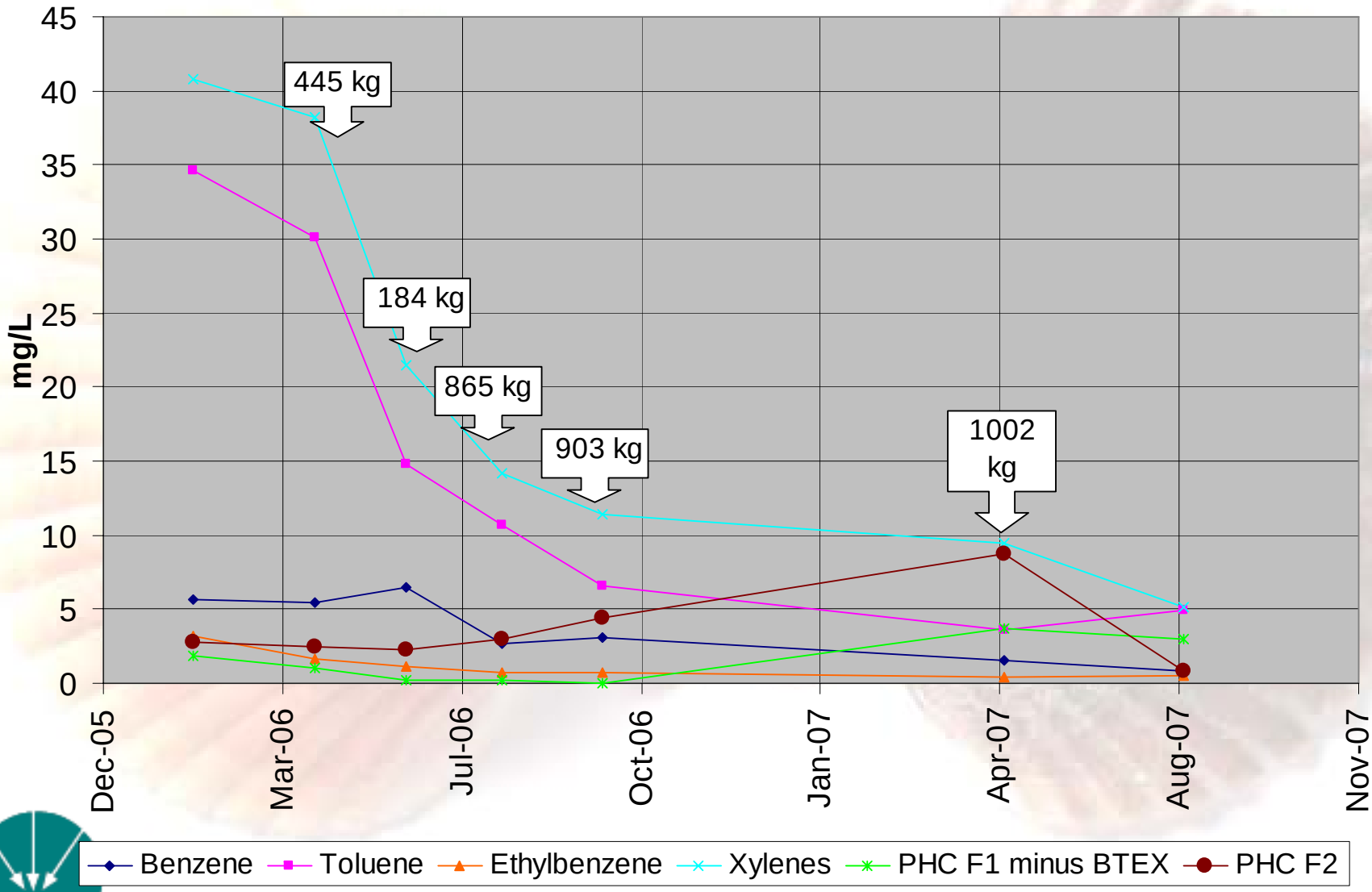
“P” Site

- Approximately 50% of recommended mass was delivered over 1-year period
- Actual amount of RegenOx delivered to subsurface: ~ 6,000 kg (~51,000 L of water)
- consisting of 6 injection events
  - each injection event lasting 1 to 3 days

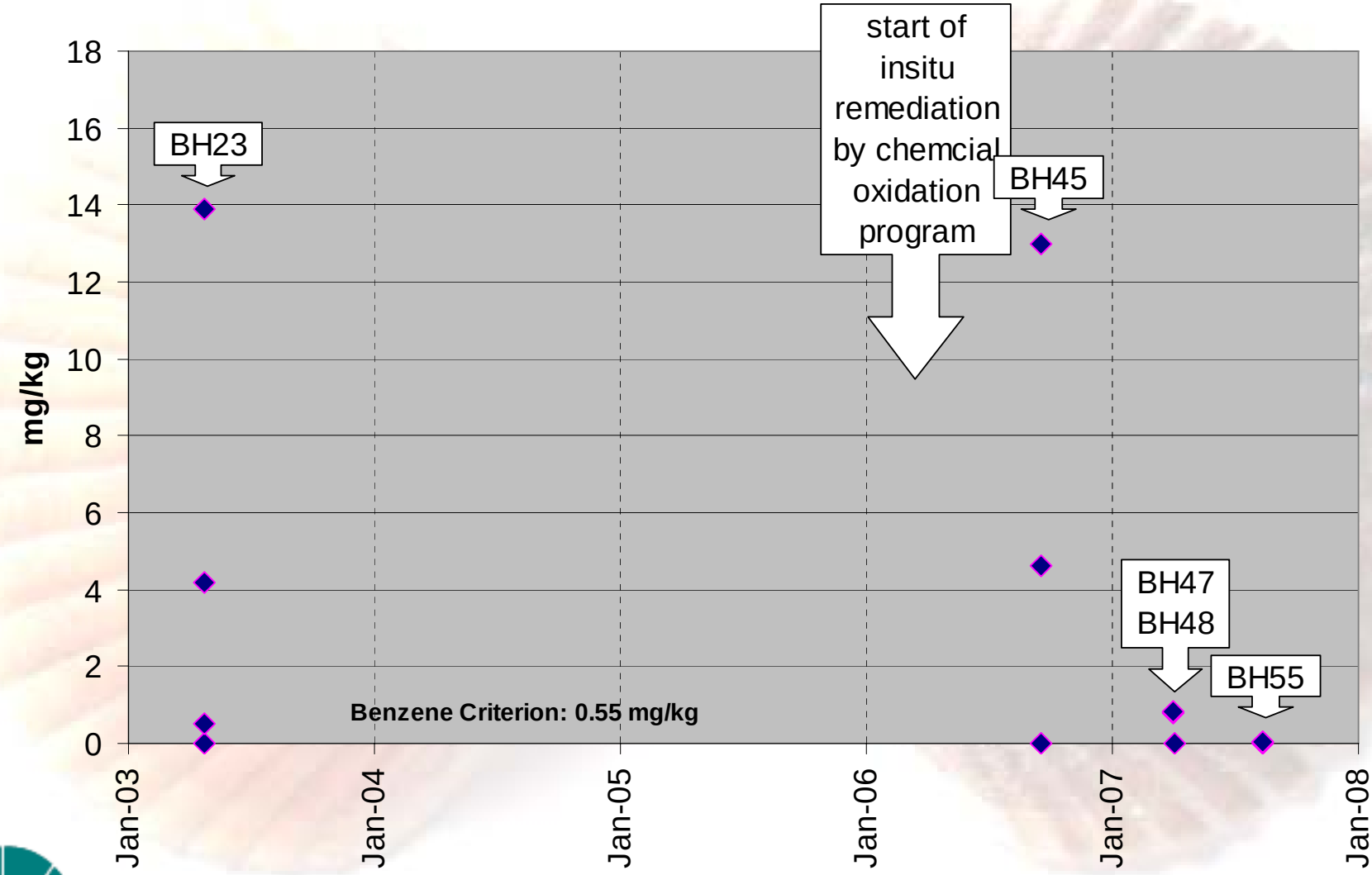
“P” Site: Approximate Plume Area (before and after)

With 50% of recommended mass of RegenOx injected there was no definitive change in the lateral extent of impacted soil or groundwater plume, although concentrations within the plume had reduced.

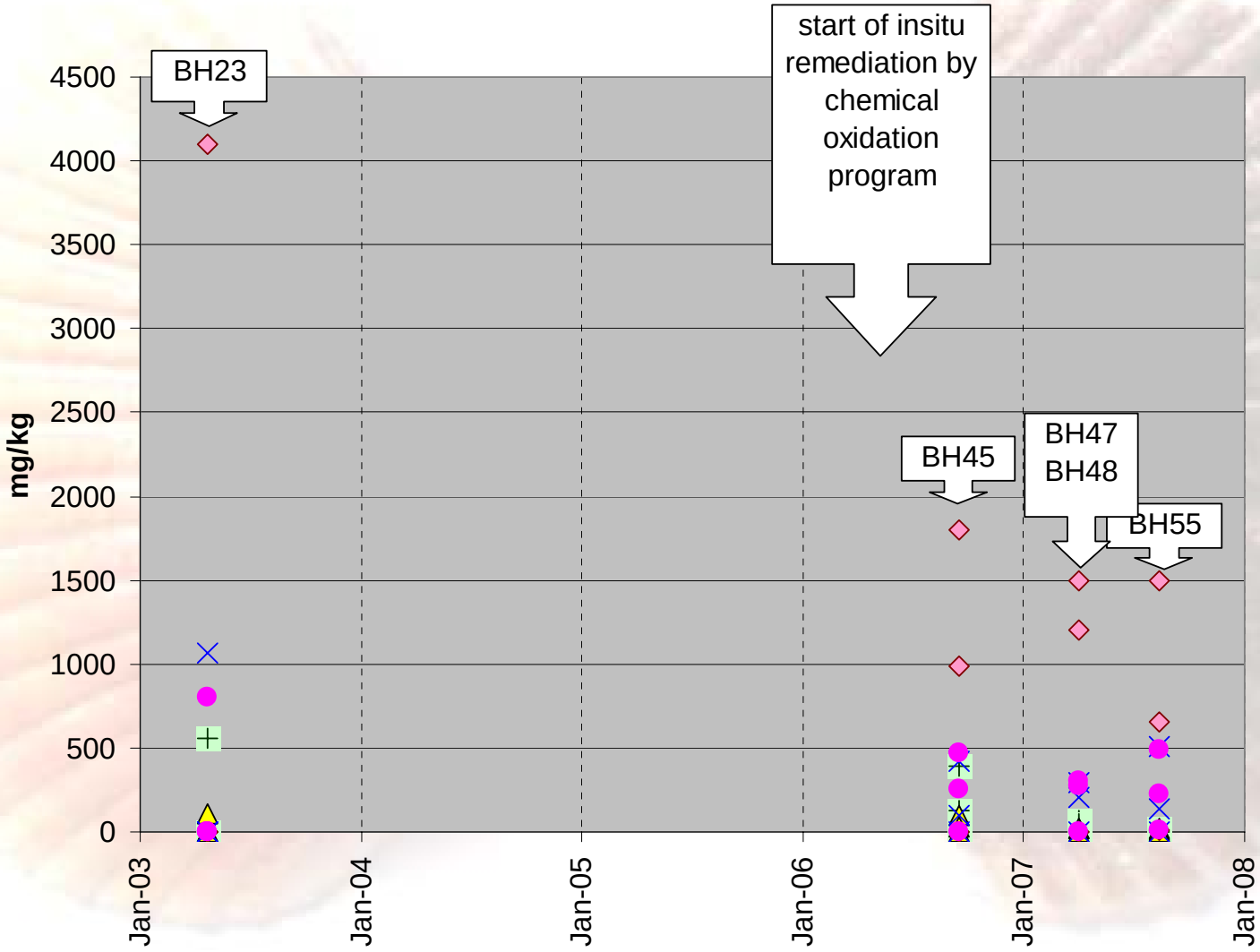
“P” Site: Dissolved Hydrocarbons in BH23



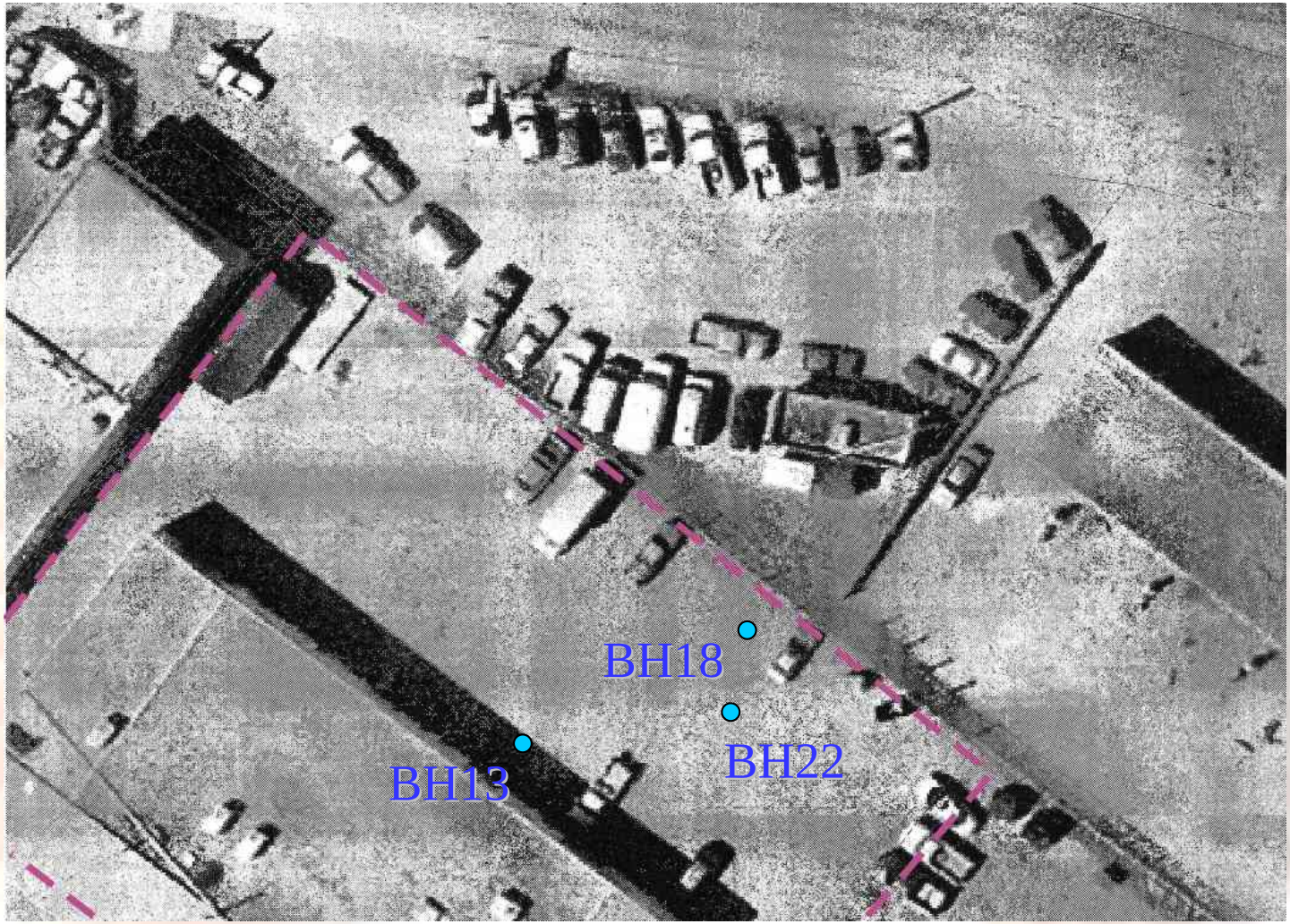
“P” Site: Soil Benzene in the Vicinity of BH23



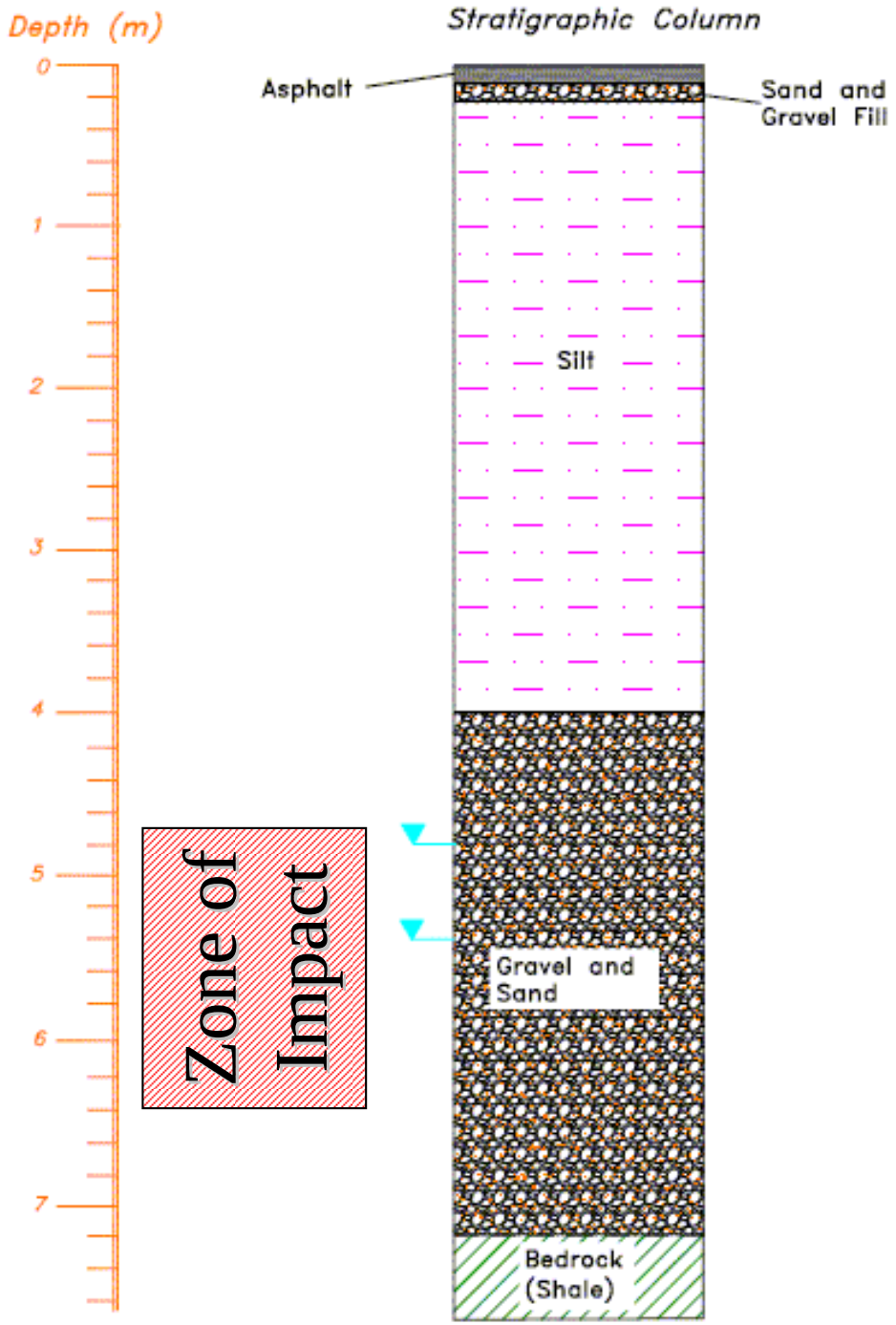
“P” Site: Soil TEX, F1 and F2 in the Vicinity of BH23



“S” Site



“S” Site Stratigraphic Column



“S” Site

- Contaminant concentrations in soil (**mg/kg**):
  - **B:** up to 0.2
  - **T:** up to 0.55
  - **E:** up to 11.0
  - **X:** up to 37.2

  F1 - BTEX: up to 400

  F2: up to 3670

  F3: up to 2430

  F4: up to 2790

  - total mass of contaminants (geometric mean): 300 kg (initial estimate)
  - volume of soil affected ~500 m^3

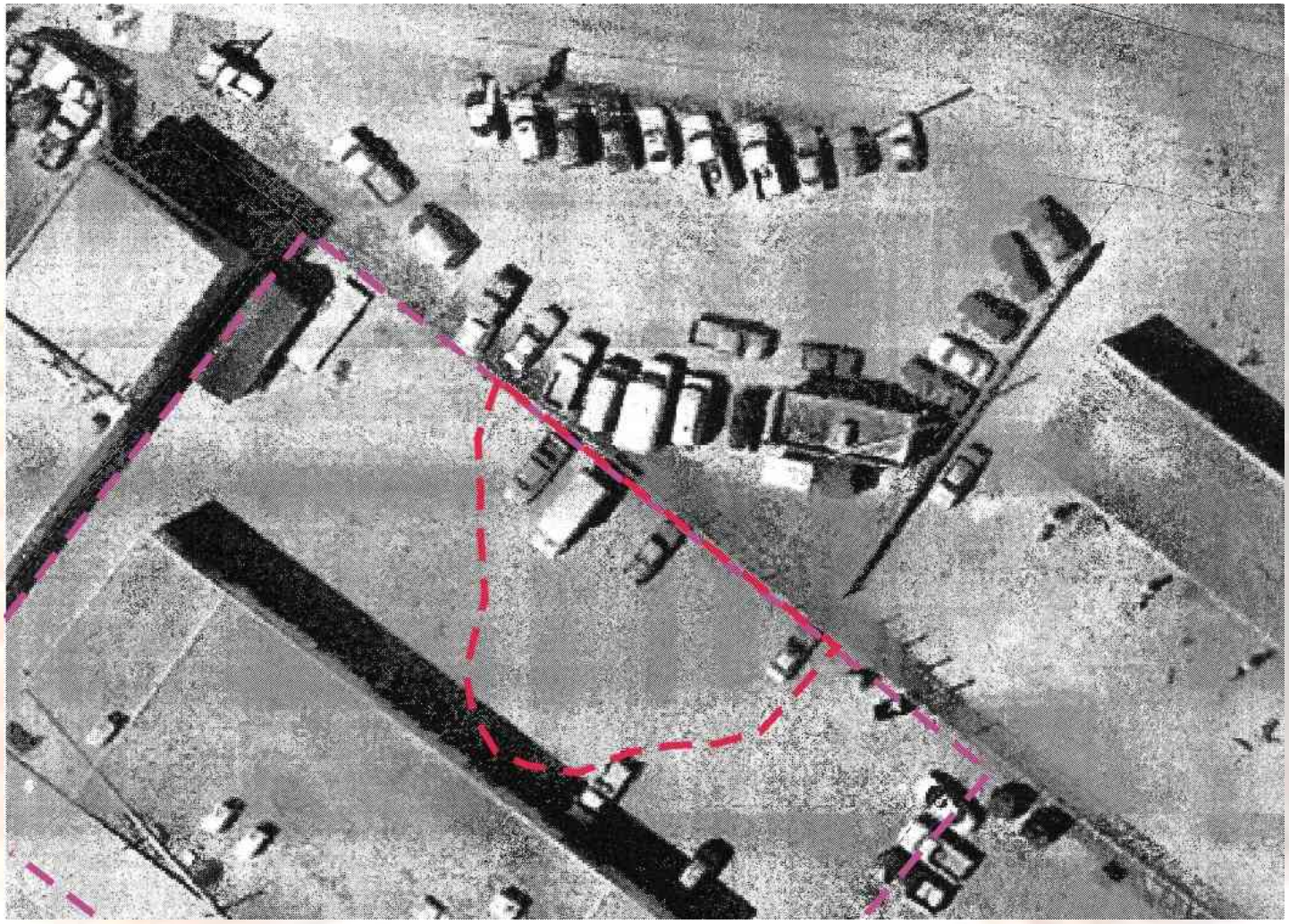
“S” Site

- RegenOx prescription:
  - total mass = 12,200 kg (incl. oxidant & activator)
  - diluted into 122,000 L of water
  - 2 m x 2 m injection spacing
  - injection rate was 1.9 to 3.8 L/min per pump at each injection point

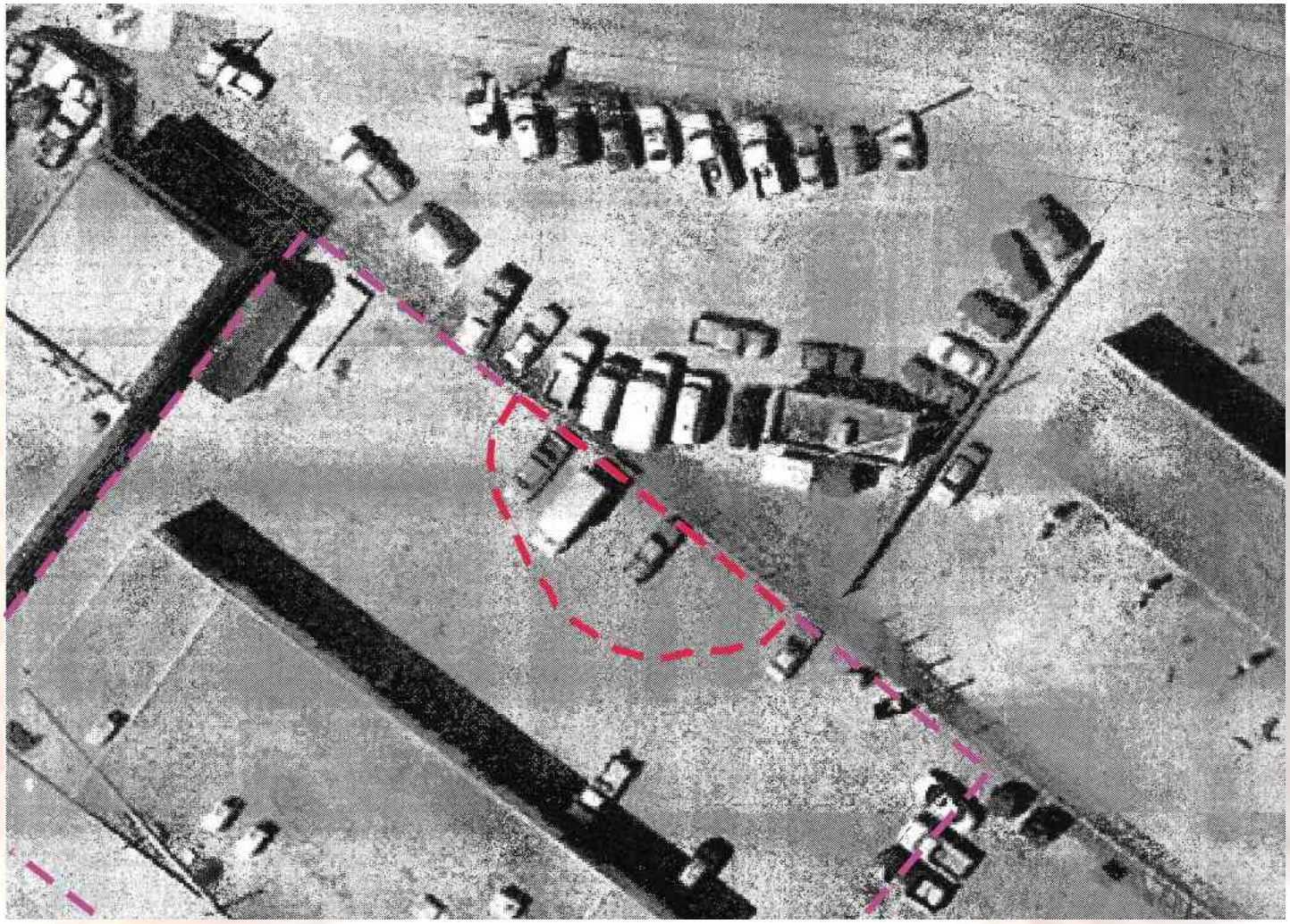
“S” Site

- Actual amount of RegenOx (oxidant) delivered to subsurface: ~ 4,980 kg (~60,000 L of water)
- Approximately 50% of recommended mass was delivered over 1-year period
- consisting of 2 injection events
  - each injection event lasting 2 to 3 days

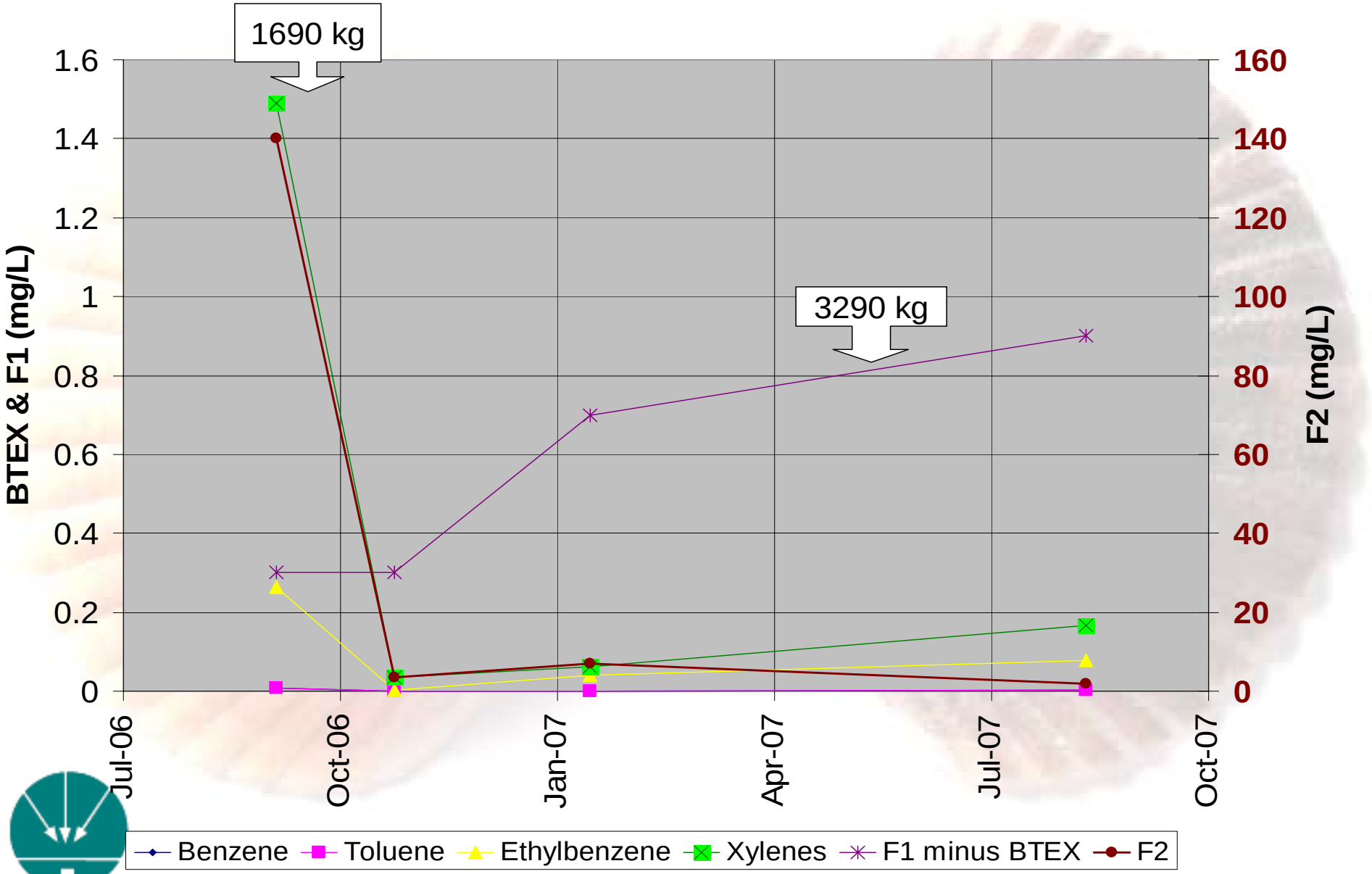
“S” Site – Plume Before Injection



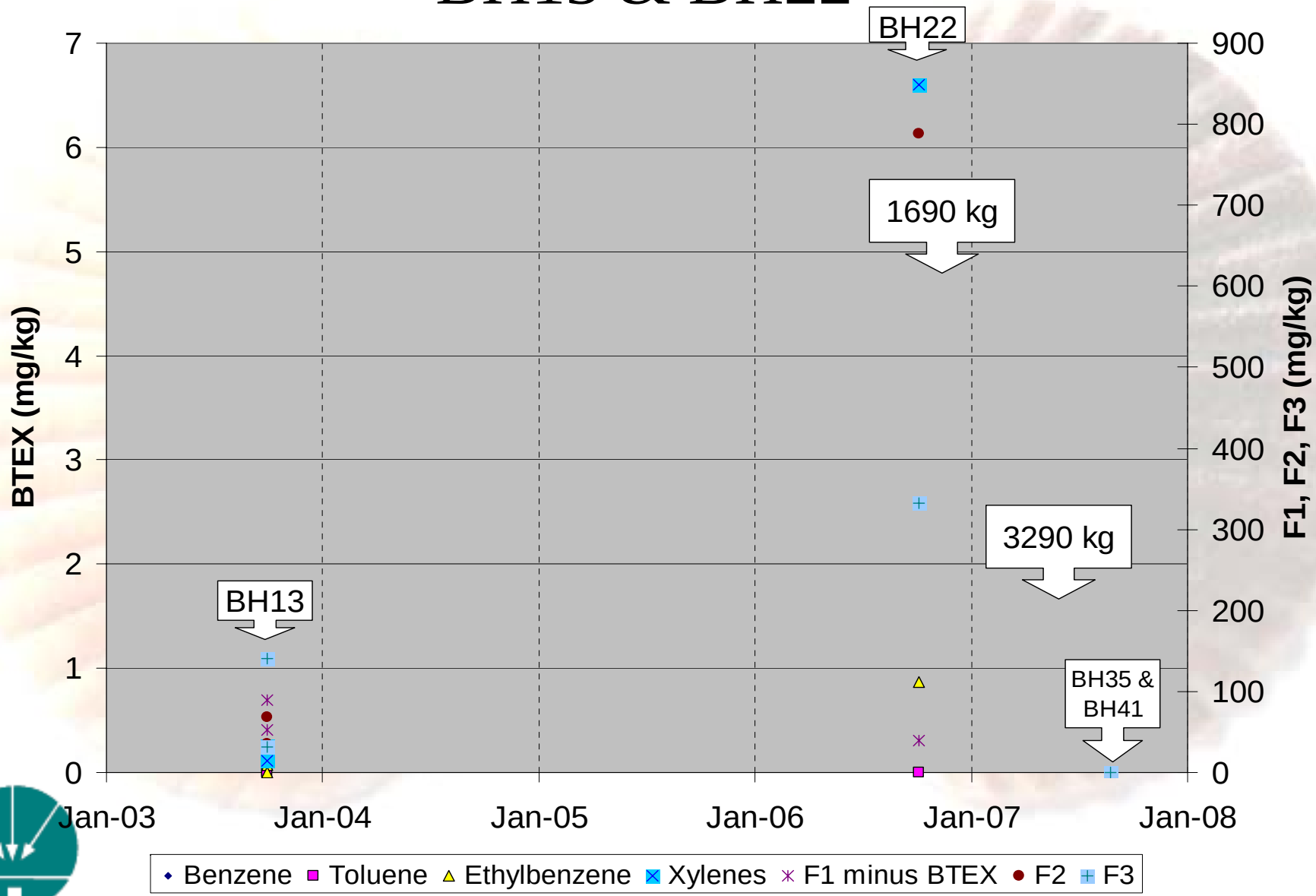
“S” Site – Plume After Injection



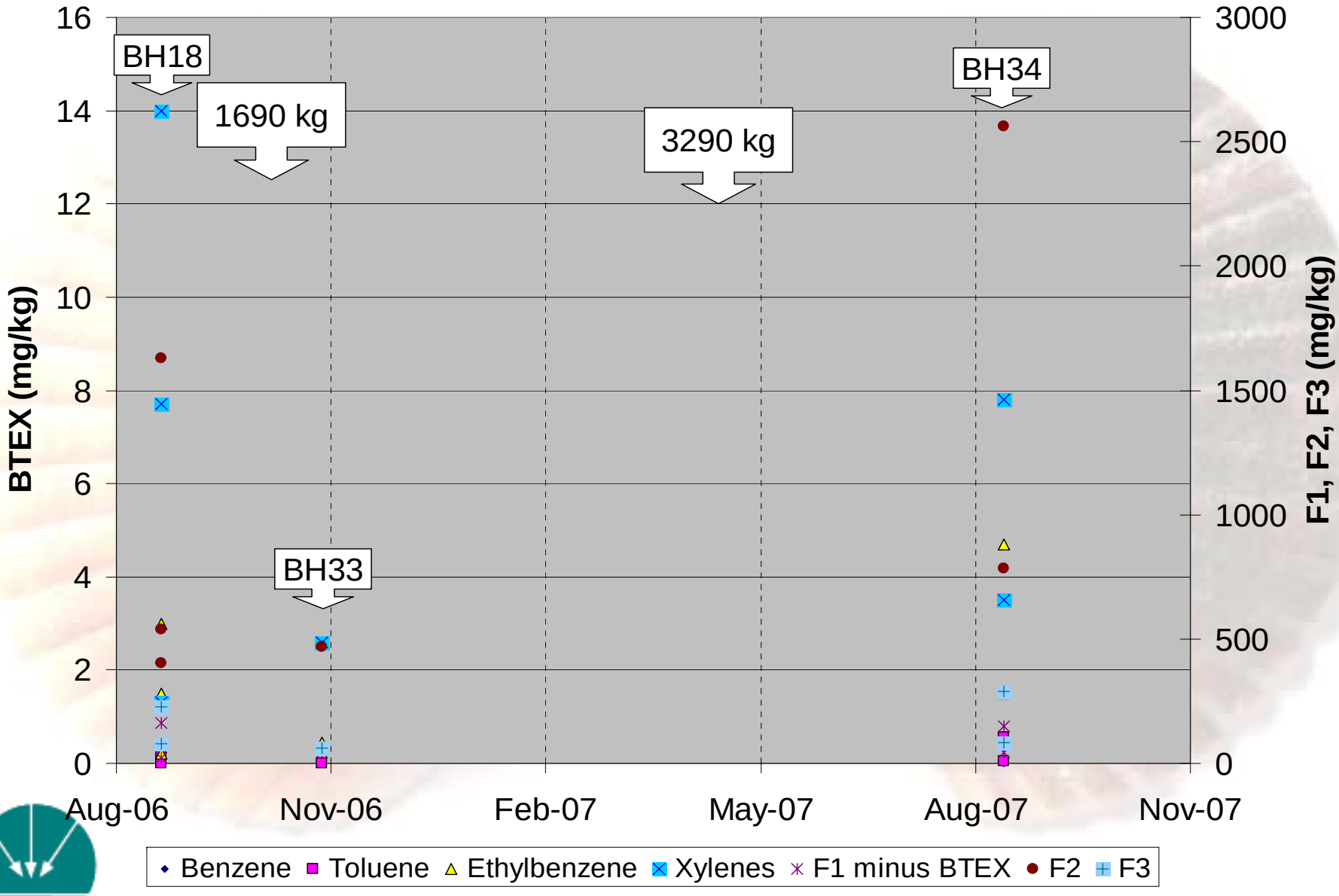
“S” Site: Dissolved Hydrocarbons in BH18



“S” Site: Soil Hydrocarbons in Vicinity of BH13 & BH22



“S” Site: Soil Hydrocarbons in Vicinity of BH18

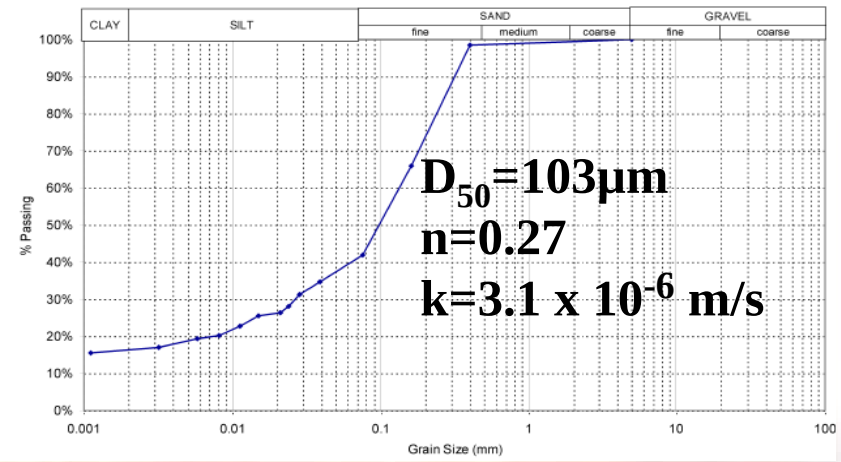


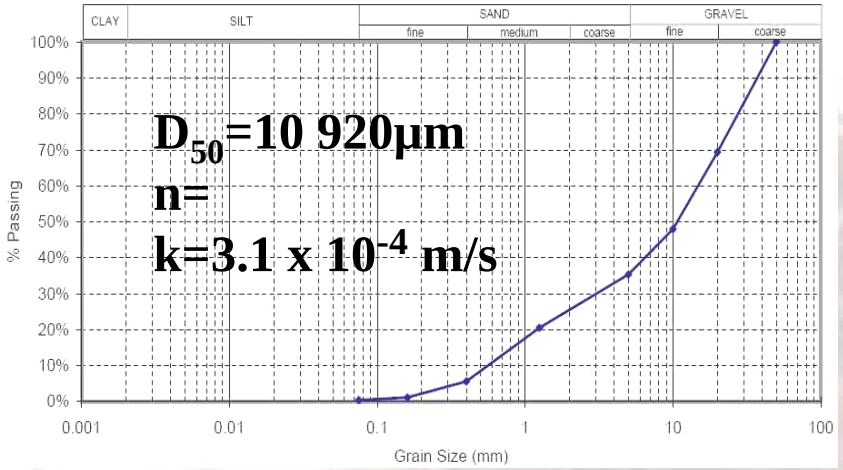
Success of Delivery

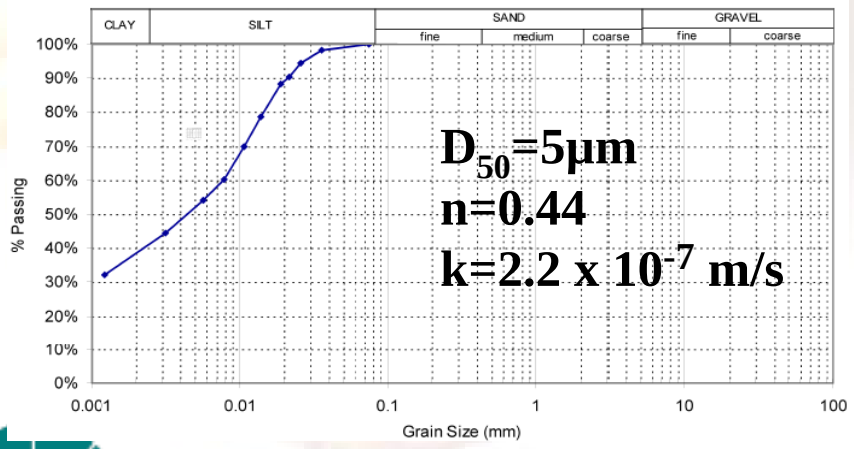
- Slurry was delivered easily at “S” site
  - there seemed almost no limit to what we could inject
- We had trouble injecting at “P” site
  - short circuiting to ground
  - low injection rates achieved
- Why?

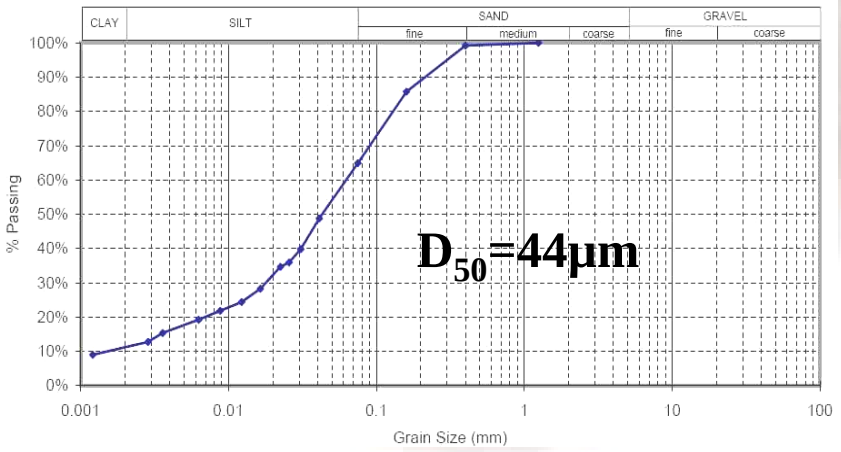
Success of Delivery

"P" Site versus "S" Site









Failure of Delivery

- Differences in hydraulic conductivity
- High initial injection pressure at “P” Site may have fractured the formation, creating preferential pathways
- Existing infrastructure at “P” Site created further alternative pathways

Hydrocarbon Degradation

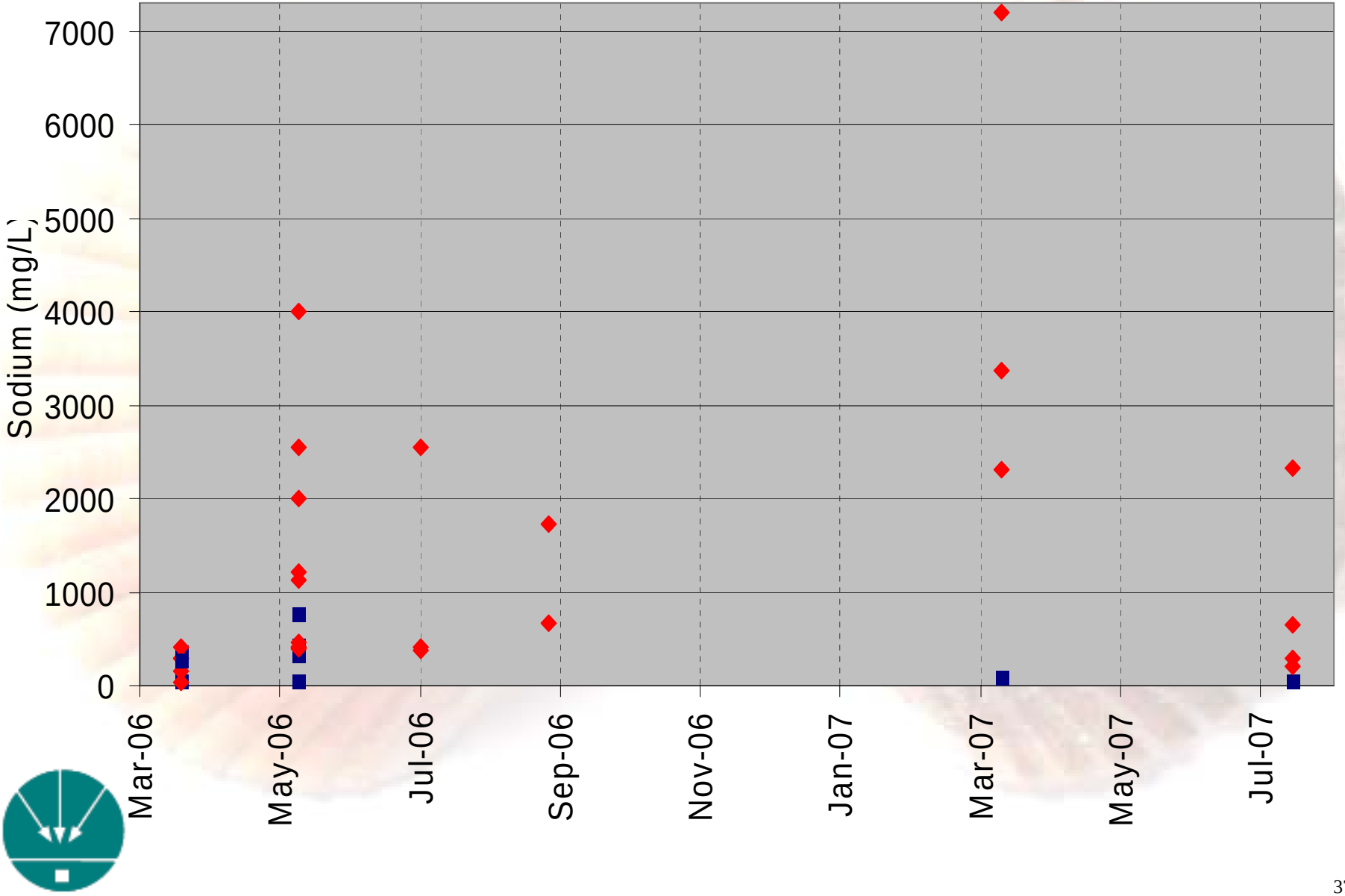
- Ability to deliver was different
- Natural TOC was similar
  - Both ranged from 0.5% to 0.6%
- Total hydrocarbon masses and maximum concentrations were different
- Different oxidant exposure to impacts, specifically, short circuiting due to injection pressures greater than formation would accommodate
- This all affects the amount of oxidant required.

Undesirable By-Products

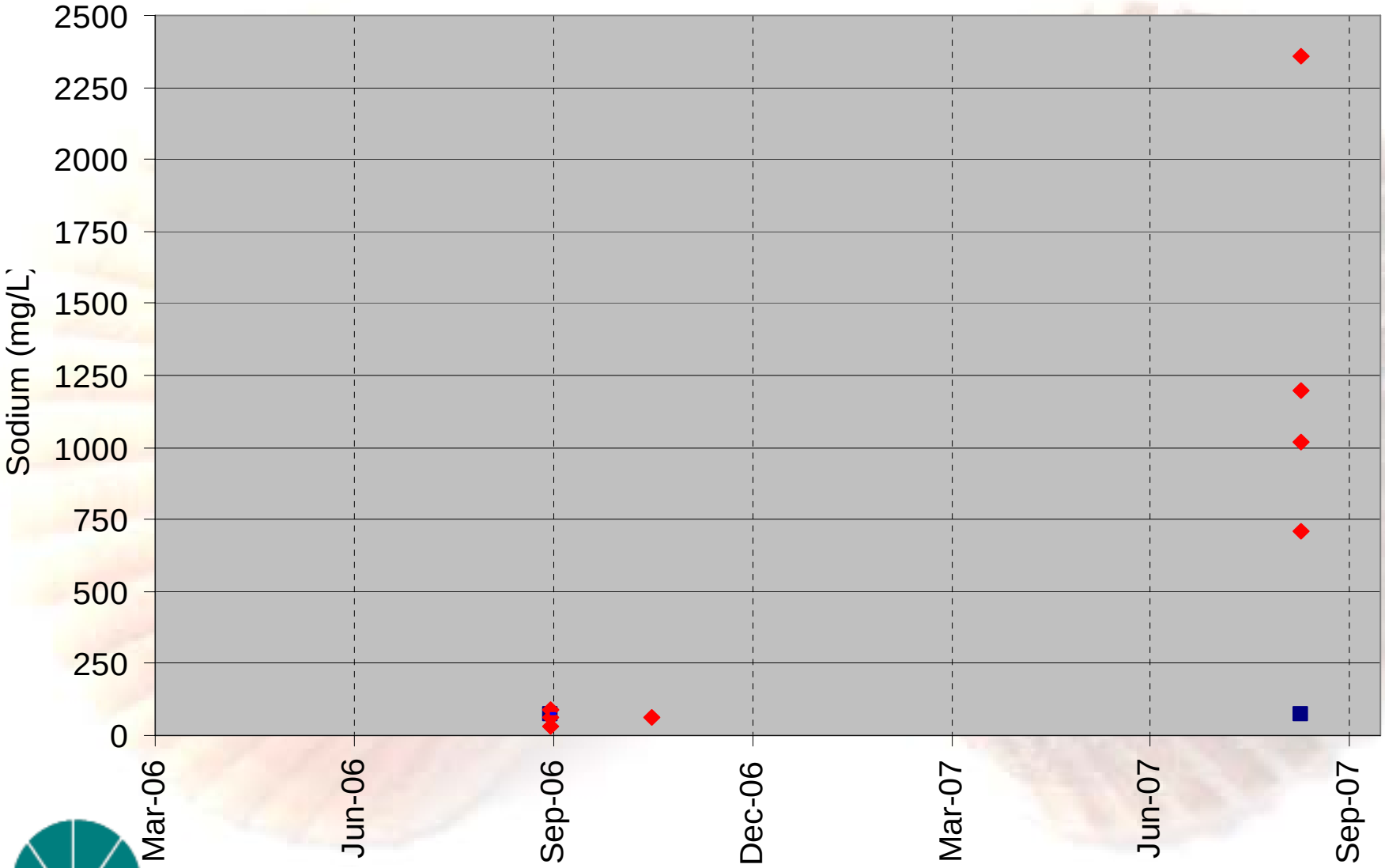
- Both sites had FAL and drinking water receptors
- Sodium is a major component of RegenOx

- Drinking water criterion for sodium is 200 mg/L

“P Site”: Sodium (Na) concentration in groundwater



“S Site”: Sodium (Na) concentration in groundwater versus time



Conclusions

- Practical considerations to in situ chemical oxidation:
  - How much oxidant will you need?
  - How long will it take?
  - Can you live with the side effects?
- Know these answers before you embark on a full-scale injection program.

Acknowledgements

- G & R Remediation
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