In Situ, Low Temperature Thermal Remediation of LNAPL with Pesticides and Other Recalcitrant Compounds

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The business of sustainability

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Background

- The Site has been used since the late 1960's for the manufacture of wood preservatives, damp proofing chemicals and specialist coatings
- The Site comprises two main buildings (offices and laboratory, which remain in use and a central area comprising mainly storage and disused offices)
- The Site is bounded by a railway line to the south beyond which lie residential properties. A river is located approximately 500m downgradient of the site.

The clients goals for the Site include:

- Establish the current environmental status with respect to the presence and significance of historic soil and groundwater contamination; and
- Manage potential liabilities associated with these impacts in the context of UK contaminated land legislation

Geology and Hydrogeology

- The Site is underlain by Made Ground (typically <1m thickness), sands and gravels, and Chalk.
- Both the sands and gravels and Chalk form unconfined aquifers with relatively high permeability.
- Lower permeability silts and clays are present towards the top of the sands and gravels in some parts of the Site.
- Soil source zones appear to correlate well to the main areas where chemicals were previously used, stored or disposed.
- Multiple overlapping plumes are present, beneath and downgradient of the source areas, although impact from a more limited range of compounds has been identified within the Chalk.
- Likely that the recent channel identified within the centre of the Site may be influencing contaminant migration towards the south-west corner of the Site.
- The dominant controlling mechanism for contaminant migration into the Chalk is likely to be contaminant properties (those which sink) or be related to preferential flow through soakaways.

Properties and Distribution of Selected Contaminants

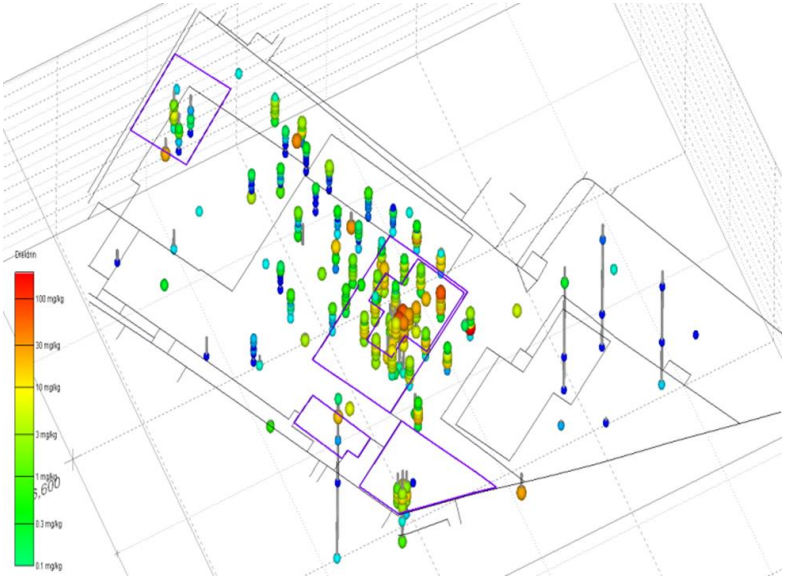
Contaminant	Physical state	Molecular weight	Water solubility	Log KOC	Vapour Pressure	Henry's Law Constant
			mg l-1 25oC	cm3 g-1	Pa	Pa m3 mol-1 (25oC)
Aldrin	solid	364.91	0.02	5.34	1.35E-02	50.3
Dieldrin	solid	380.91	0.2	3.59	4.18E-08	5.88
gamma HCH	solid	290.82	7.3	3.07	3.70E-03	0.375
>C10-C12 Aliphatics	liquid		3.40E-02	5.40	63.83	
>C12-C16 Aliphatics	liquid		7.60E-04	6.70	4.86	
Benzene	liquid	78.11	1780	1.83	6240	557
Tetrachloroethene	liquid	165.83	225	2.43	1010	1730

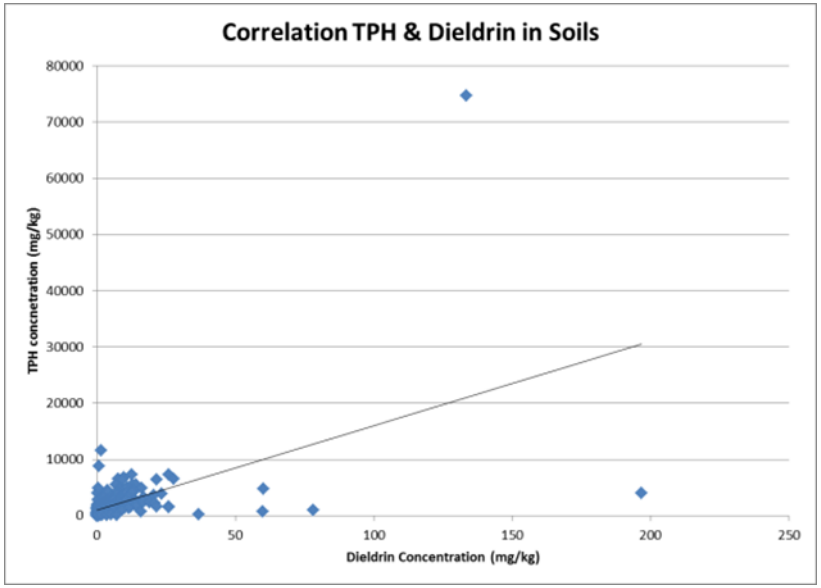
Environment Agency 2008 SR7 Compilation of data for priority organic pollutants for derivation of Soil Guideline Values

PPDB: Pesticide Properties Data Base http://sitem.herts.ac.uk/aeru/projects/ppdb/index.htm

TPHCWG Vol 3

KOC - organic carbon partition coefficient





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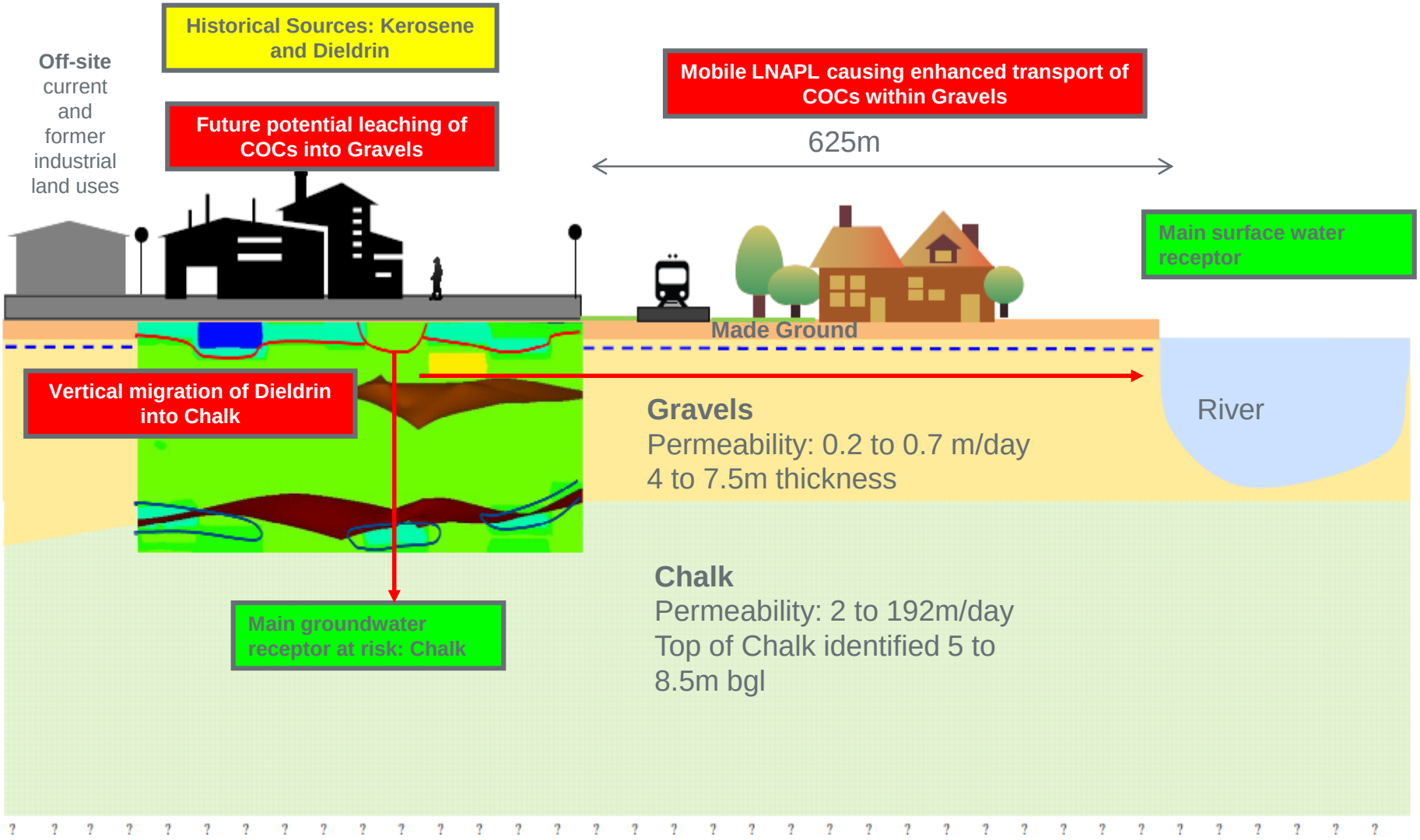
Conceptual Site Model



Not to scale

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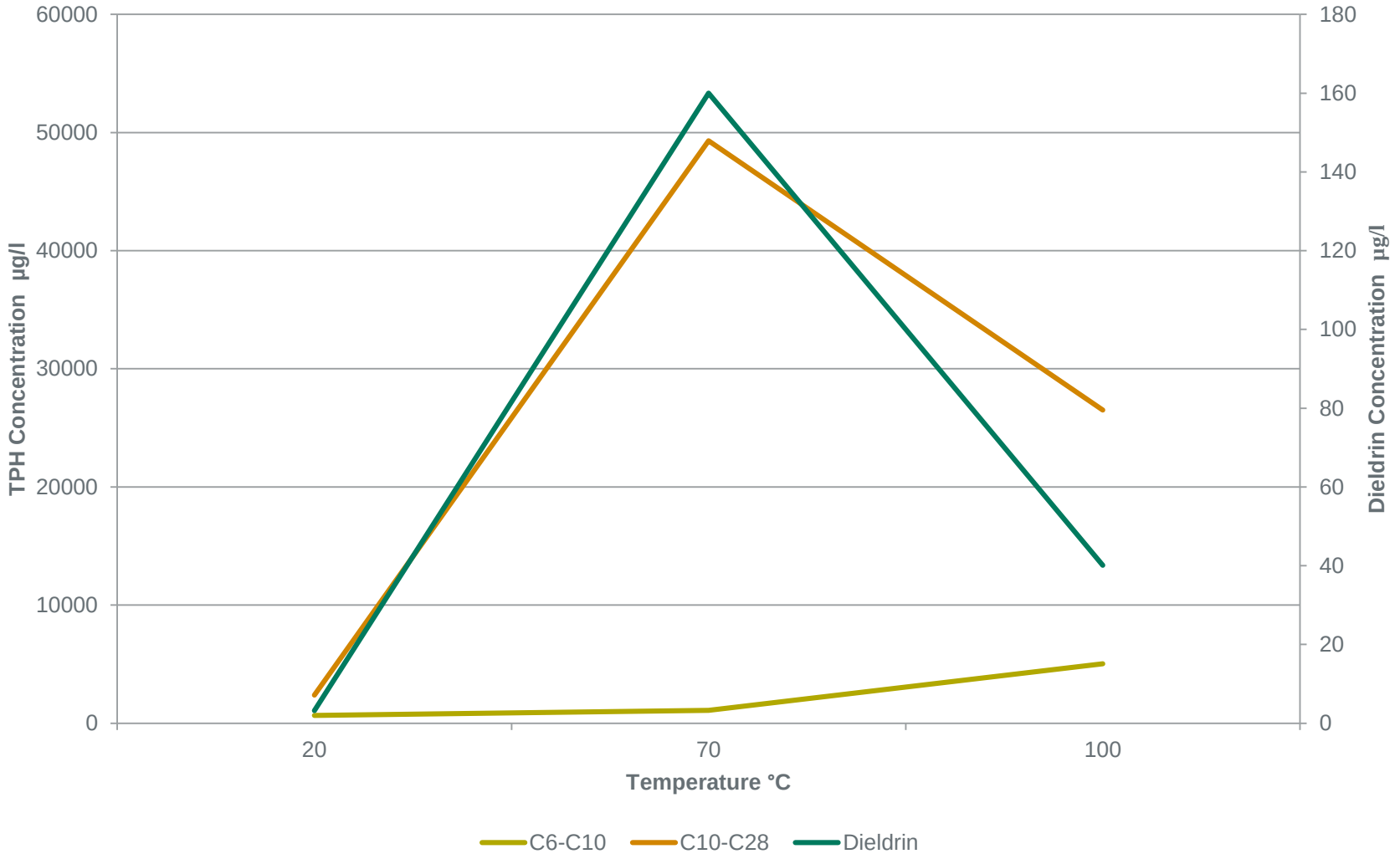
Initial Remedial Concept

- Mass removal
  - Limited LNAPL in wells
  - circa 8,000kg mass (mostly Kerosene).
  - Pesticides (dieldrin) solubilized in carrier oil
- Remedial options appraisal identified limited mass recovery options
  - Excavation requiring building demolition
  - Thermal considered most applicable, but target temperature challenges
    - Boiling points:
      - Kerosene 150ºC (minimum)
      - Dieldrin 350ºC!
    - Only applicable heating method to volatilize both ISTD
  - Thermal remediation questions for bench testing
    - Are temperatures even achievable?
    - Is there an alternate thermal mass removal mechanism

In-Situ Thermal Bench Test: *Results*

- Contaminant Mobility test
  - oil sheen appeared at temperatures of approximately 60°C after 24 hours of heating;
  - visual observations of contaminant release from the soil into the water
  - greater contaminant mobility observed at 100°C.
- Post heating, soil concentrations appeared to increase from baseline concentrations;
  - not expected;
  - likely due to pre-test concentrations being under reported due to analytical interference caused by the presence of both pesticides and hydrocarbons in the same sample.
- Results
  - At 70ºC Dieldrin and C_{10} - C_{28} TPH concentrations of liquids increase significantly, suggesting mobilization of both carrier oil and pesticide (solubilized) via the heating process.
  - At 100ºC concentrations of both compounds remain above baseline, but significantly lower.
    - The decrease may reflect a combined mass removal mechanism
      - Volatilization for the TPH compounds at 100ºC, since Dieldrin's boiling point is nearly four times the temperature attained during the test.
      - Mobilization of TPH and Dieldrin
  - Both compounds could be recovered at lower temperatures via mobilization of solubilized NAPL and limited volatilization of TPH.

Thermal Bench Test Results



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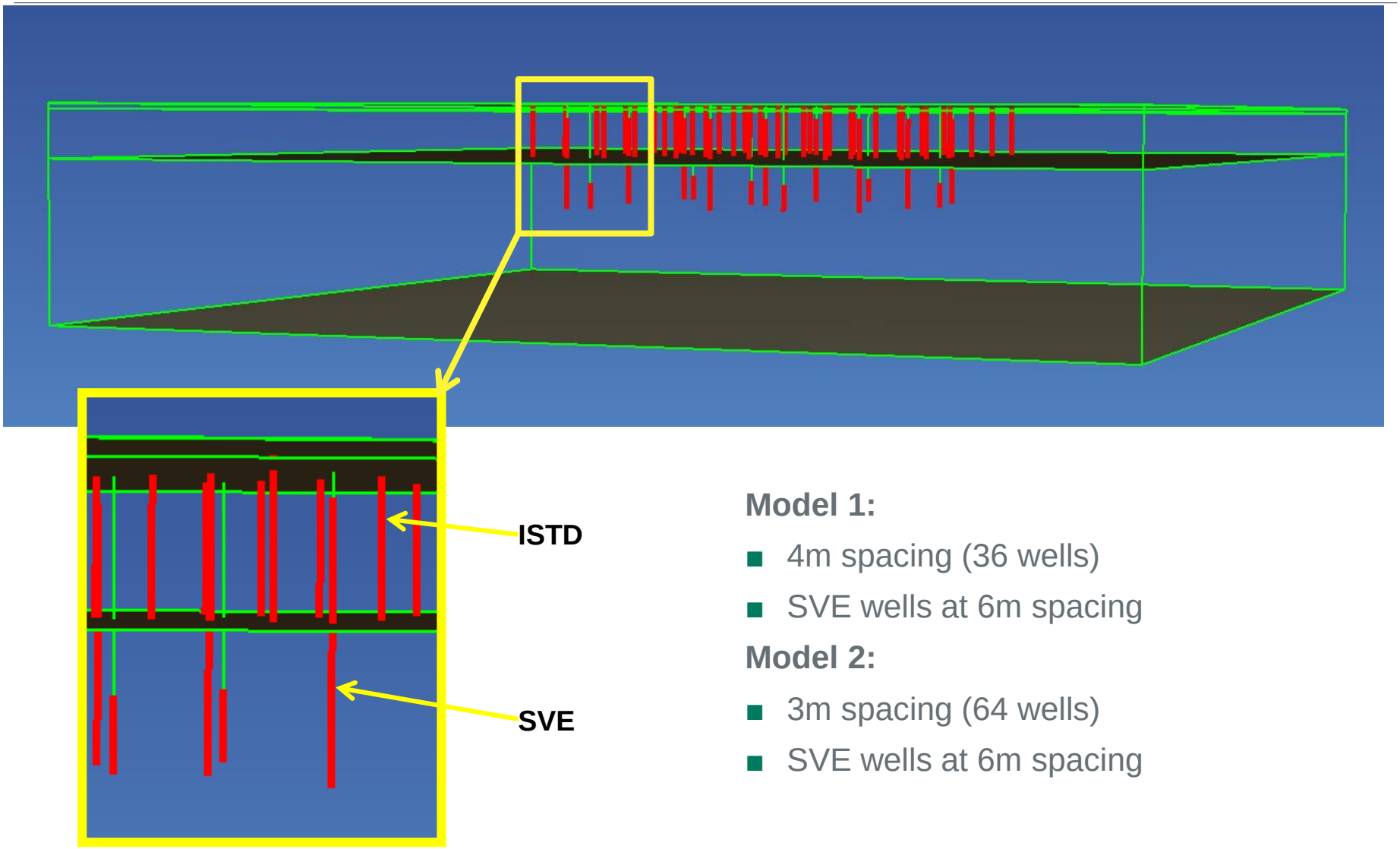
Thermal Model: *Methodology and Objectives*

- The results from bench test suggested that a target temperature of between 70ºC and 100ºC would be sufficient to remove the COCs.
- Temperatures can be accomplished via steam injection.
- A thermal model was created using PC based PetraSim™ software to estimate the following design parameters for implementation of steam injection system in the upper margins (contaminated area) of the saturated zone:
  - Mass and energy balance;
  - Energy consumption;
  - Prediction of heating duration;
  - Sensitivity to heating and extraction well spacing including number of heater wells, energy cost and duration.

ISTD Heating Models



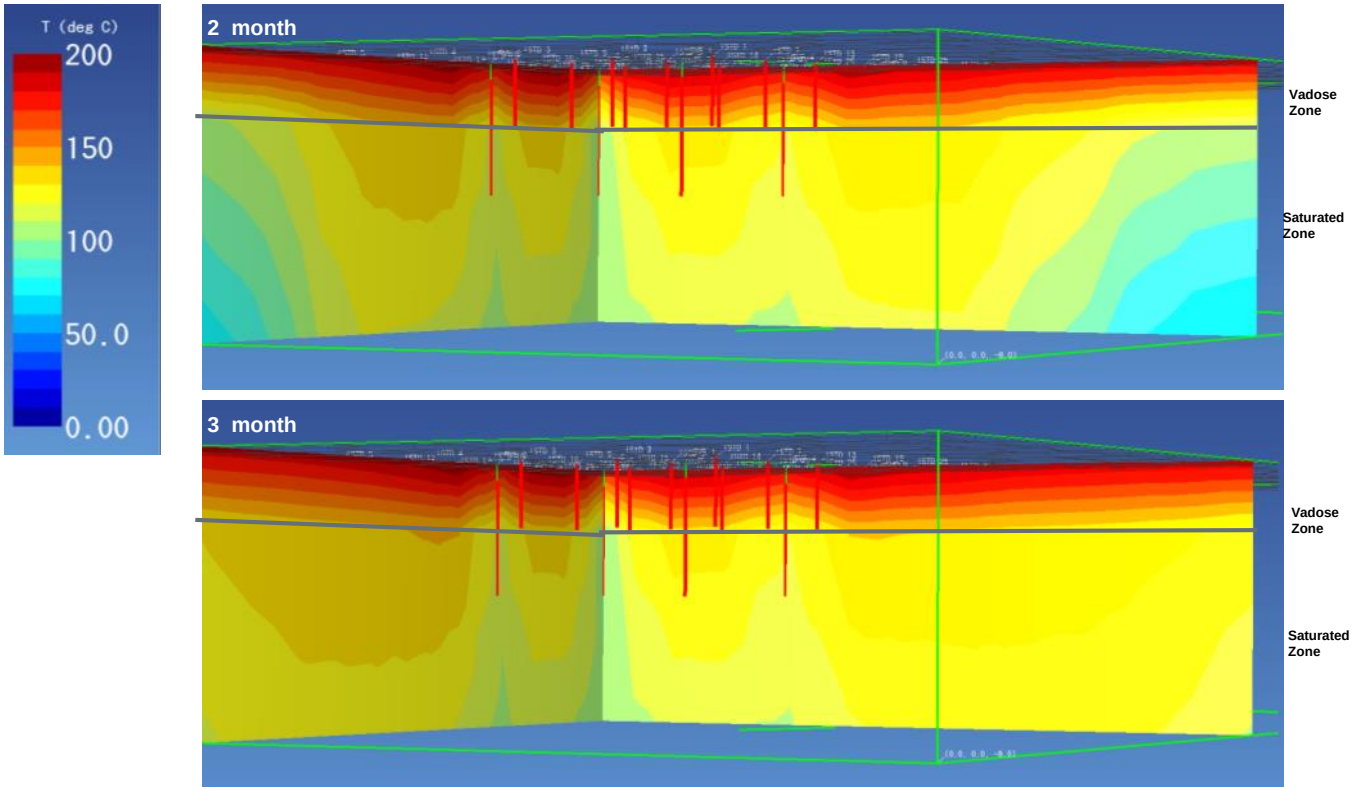
Model 1:

- 4m spacing (36 wells)
- SVE wells at 6m spacing

Model 2:

- 3m spacing (64 wells)
- SVE wells at 6m spacing

ISTD Model Results (3m spacing)



After 3 months:

- Range in target zone = 130 – 200°C
- Vadose zone = ~ 170°C
- Saturated zone = ~ 130°C

Not high enough for ISTD

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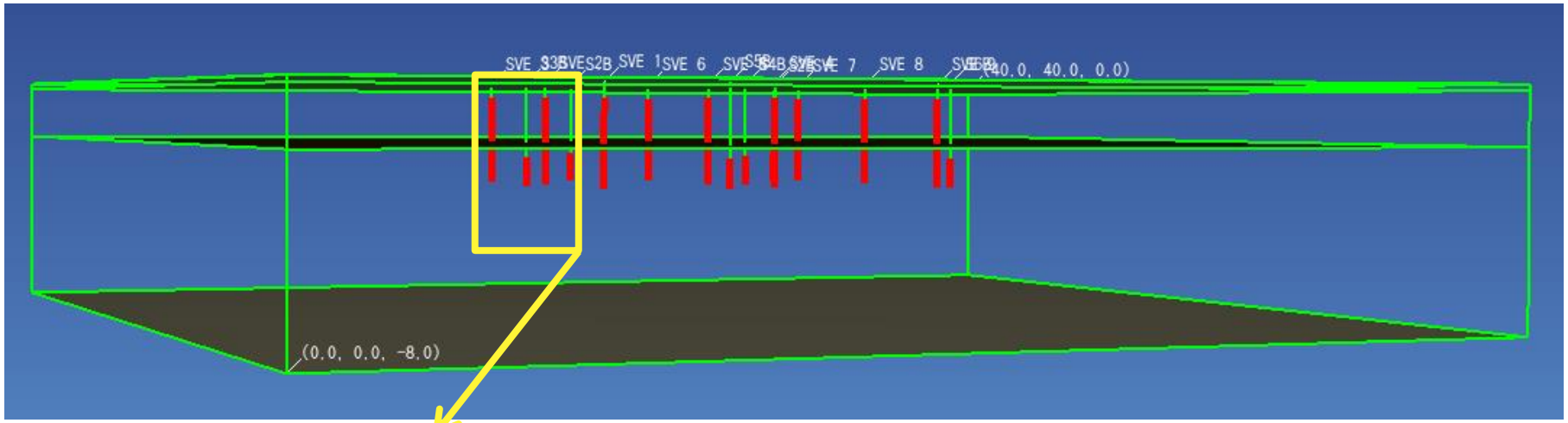
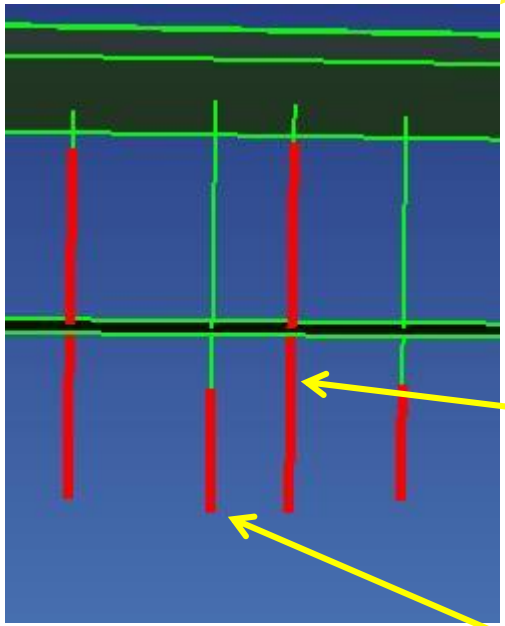
Model Input Parameters – Steam Injection Well Configuration

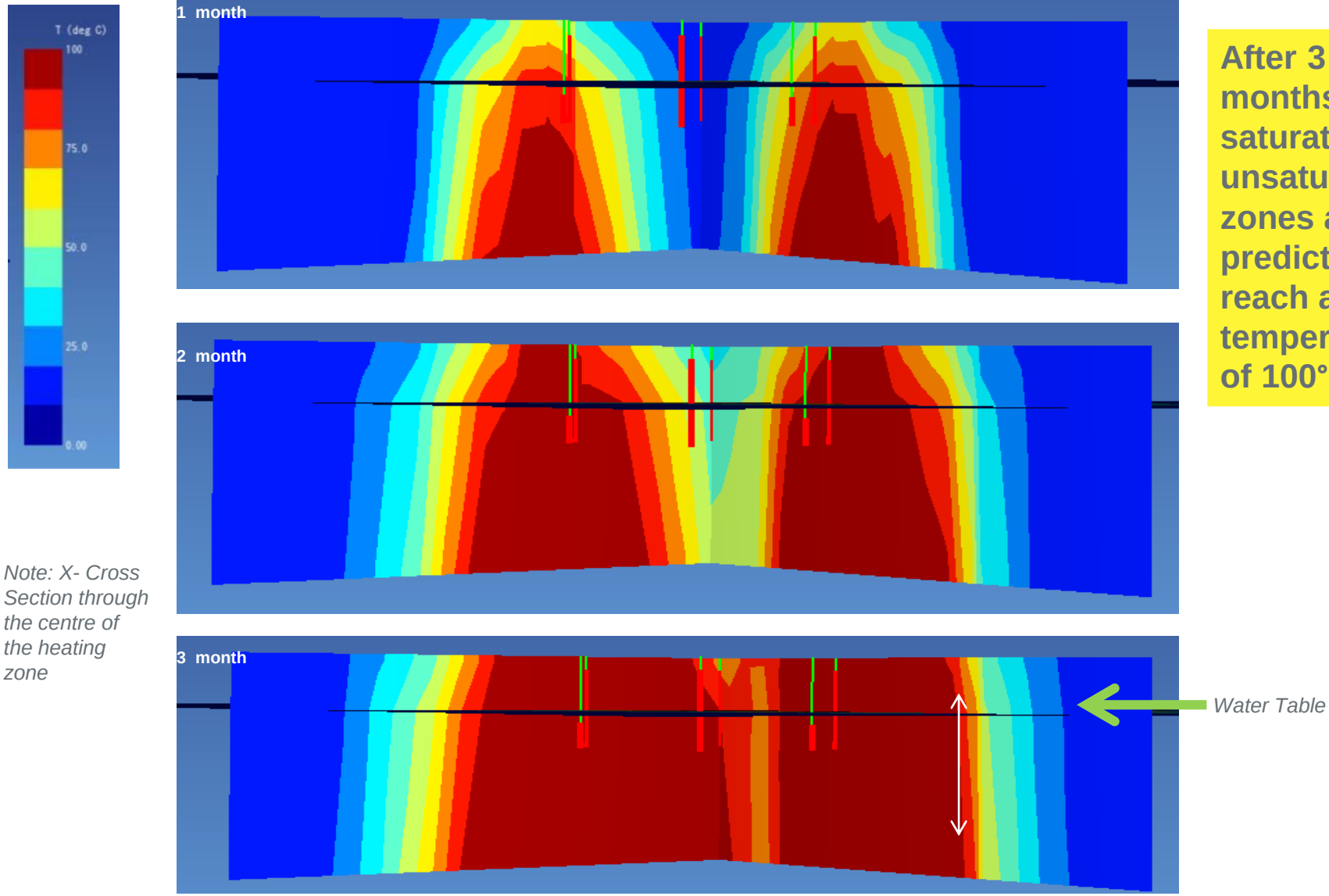




Remedial system well configuration:

- **Soil Vapour Extraction (SVE) well:**
  - 6 m Radius of Influence
  - 3.5 m depth
  - 0.5 – 3.5 m screened section (3 m)
- **Steam Injection Well:**
  - 6 m Radius of Influence
  - 3.5 m depth
  - 2.5 to 3.5 m screened section. (1 m)

Steam Injection Model Results



After 3 months the saturated and unsaturated zones are predicted to reach a temperature of 100°C

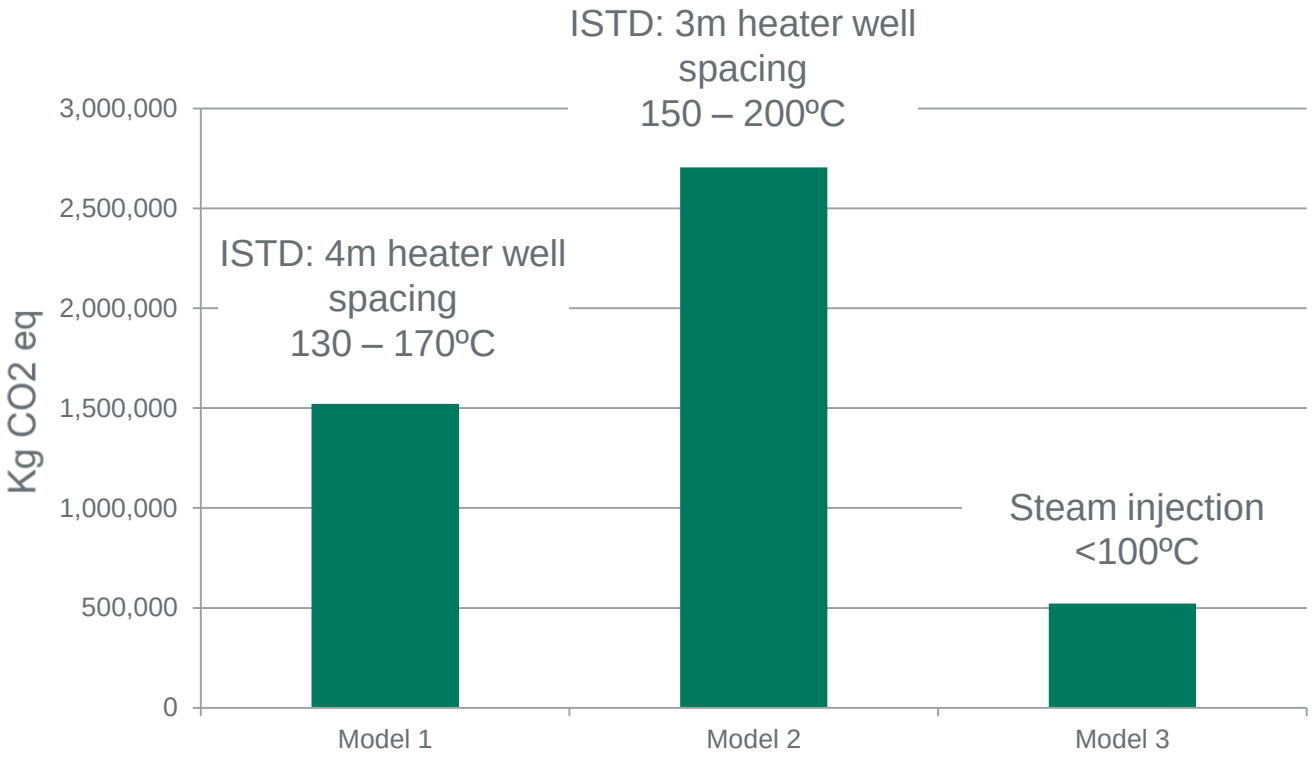
Note: X- Cross Section through the centre of the heating zone

Model Conclusions

- Maximum heat achievable in the unsaturated zone is 150°C (3m spacing)
- After 3 months, temperature stabilizes and does not increase above the maximum predicted
- **Implication: Kerosene can potentially be volatilized, but dieldrin cannot**
- Are there benefits to the closer spaced/higher temperature ISTD approach?

Effect on Remedial Strategy

- TTT reduced from 150°C to 70ºC
- Change in methodology meant steam rather than ISTD could be used to heat the subsurface (less wells and energy)
- Lowest carbon footprint heating approach developed using the model:



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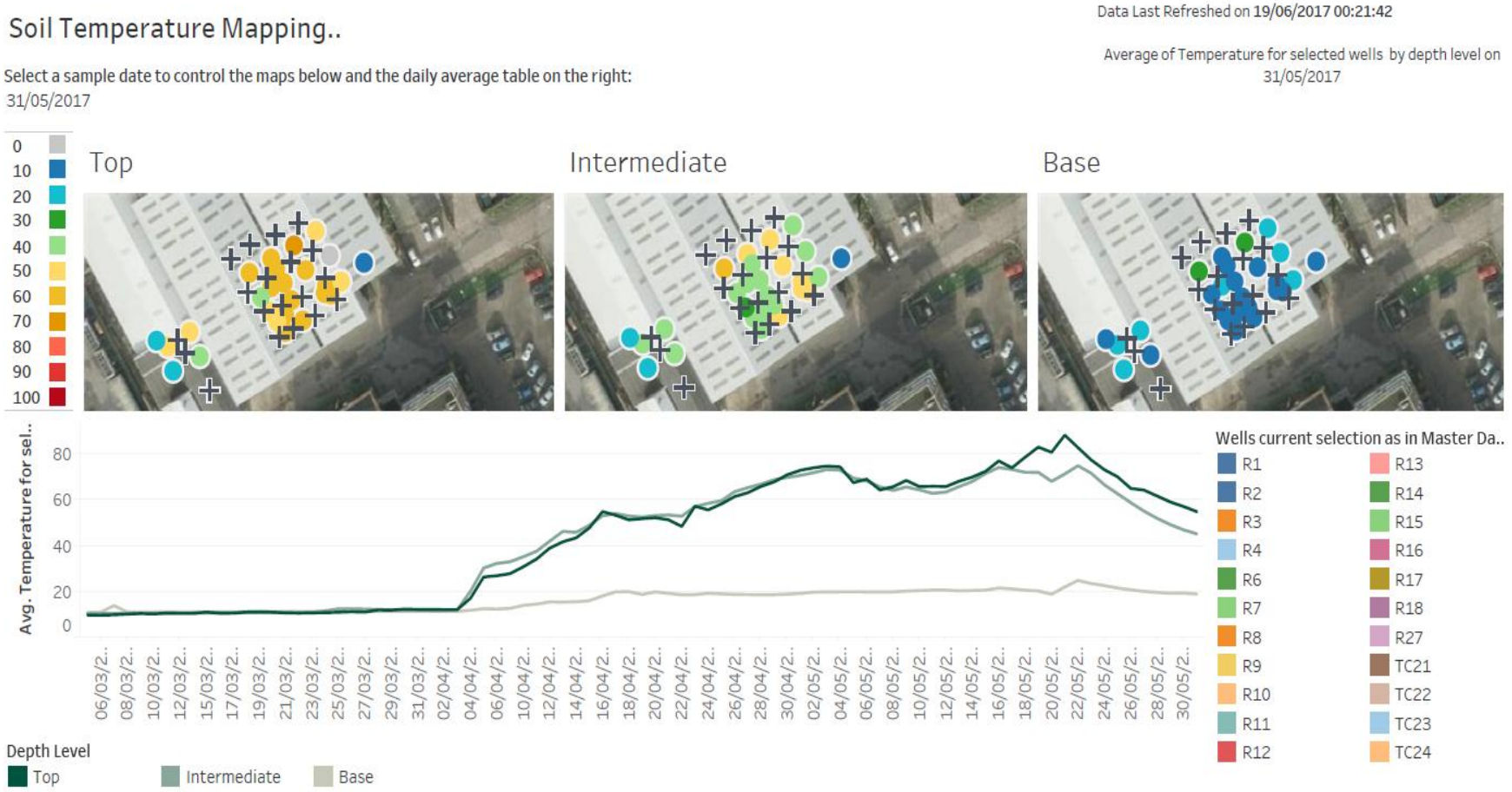
Enhanced ISTR Implementation

- Rental steam boiler
- Piping Layout
- Treatment compound
  - Vapor extraction system – Vapor phase GAC
  - GW extraction system - Liquid phase GAC
  - NAPL recovery

Heating Progress (3 April – 31 May 2017)



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Remediation Performance Evaluation (Area 4)

Project Endpoint	Evaluation	Endpoint Achieved?
Area 4: • The thermal system successfully operated for up to 20 weeks; • or until asymptotic mass recovery (of Total Petroleum Hydrocarbons (TPH) and/or total Drins) is demonstrated, whichever is the sooner	• Mass recovery has reached asymptotic conditions • Total system operational time was 20 weeks	Yes
Area 4: • In the event that Drin mobilisation is not reflective of the results of the pilot studies then conditions are created to enable the application of In-Situ Chemical Oxidation (ISCO) • ISCO success demonstrated through the creation of conditions conducive to oxidation processes and additional mass destruction of Drins is demonstrated to the extent reasonably practicable	• Dieldrin concentrations have been detected within the recovered NAPL and liquid at concentrations greater than detected during the bench scale testing, demonstrating success. • ISCO implemented in two isolated hot spots (Ara 3 and 4S). Conducive oxidation conditions demonstrated.	Yes

Total Mass Recovered/Removed (Area 4)

Steam Off
Steam On
Steam Off
Steam On
Steam Off
10000.0
1000.0
100.0
10.0
1.0
Mass Recovery (kg)
25/01/17
14/02/17
06/03/17
26/03/17
15/04/17
05/05/17
25/05/17
14/06/17
04/07/17
24/07/17
Date
Asymptotic recovery achieved
Mass composition is mainly TPH (kerosene) – 4,160kg recovery estimated.
Circa 7.5kg of mass is OCPs (recovered as free, dissolved phase and 'sludge')
Vapour Mass Recovery
Dissolved Phase Recovery
LNAPL Recovery
Total Recovery

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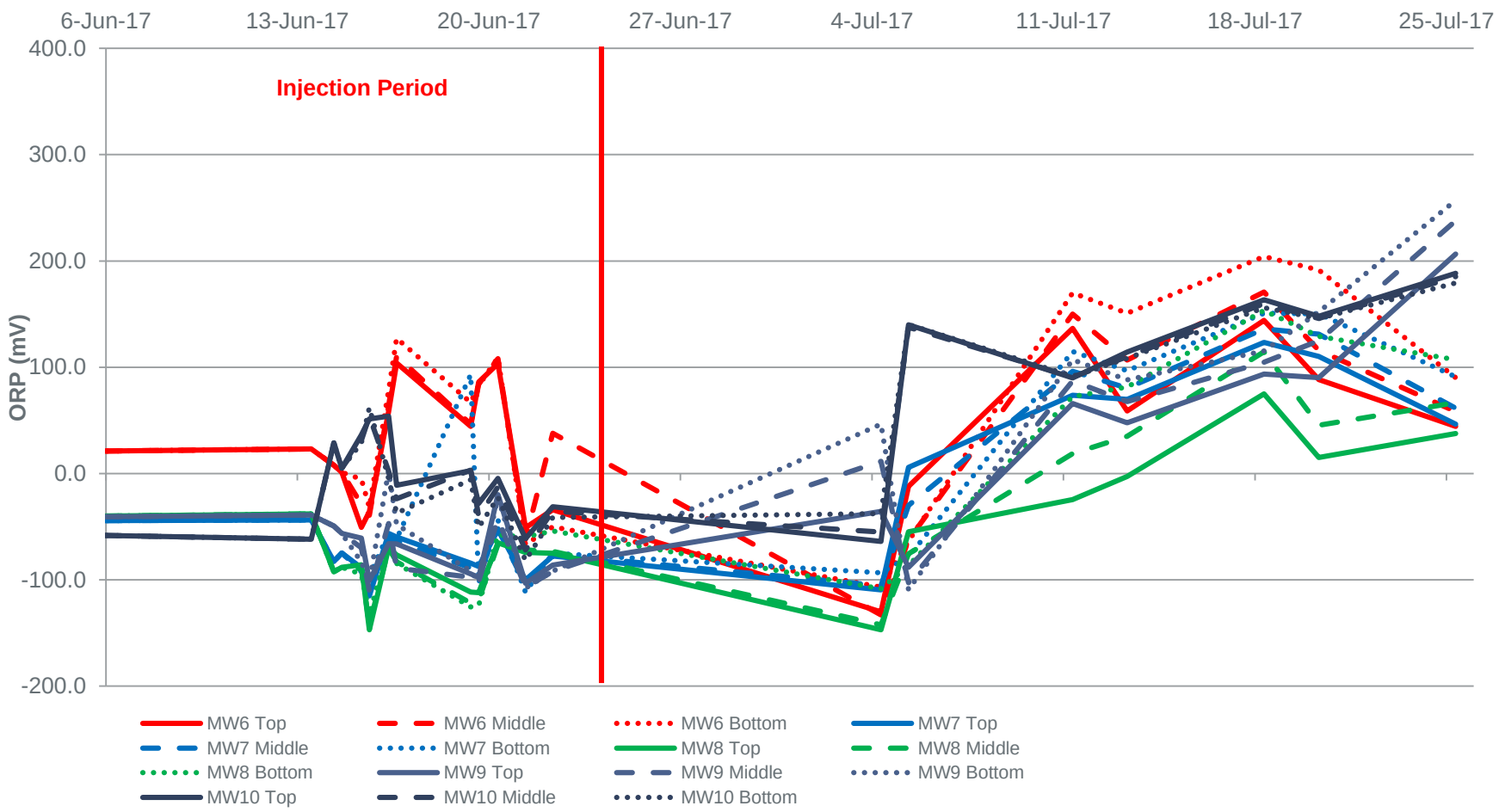
In Situ Chemical Oxidation – Activated Persulfate

- In-Situ Chemical Oxidant (ISCO)
  - ISCO injection undertaken in northern site area (7 – 22 June 2017)
  - ISCO injection undertaken in southern site area (27 June – 12 July 2017)
  - Activation via sodium hydroxide
- Field monitoring (pH, conductivity, ORP, DO and temperature in observation wells) carried out during injection and into early August

Remediation Performance Evaluation (Area 3/4S)

Project Endpoint	Evaluation	Endpoint Achieved?
Area 3: • Where ISCO is deployed, groundwater conditions are demonstrated to be conducive to oxidation processes and mass destruction of Drins is demonstrated to the extent reasonably practicable	• Significant changes from pre-injection negative ORP to positive ORP recorded, proving effective oxidant injection.	Yes
Area 4S: • Where ISCO is deployed, groundwater conditions are demonstrated to be conducive to oxidation processes and mass destruction of Drins is demonstrated to the extent reasonably practicable	• Significant changes from pre-injection negative ORP to positive ORP recorded, proving effective oxidant injection (see measurements in observation wells MW1 – MW5, *Figure 3*)	Yes

ORP Field Monitoring Data (Area 3)



- ORP shows an increasing positive trend following ISCO injection in all monitoring wells (successful oxidant delivery)
- Low dieldrin concentrations detected both pre- and post oxidant injection. Concentrations remain at <0.005mg/l

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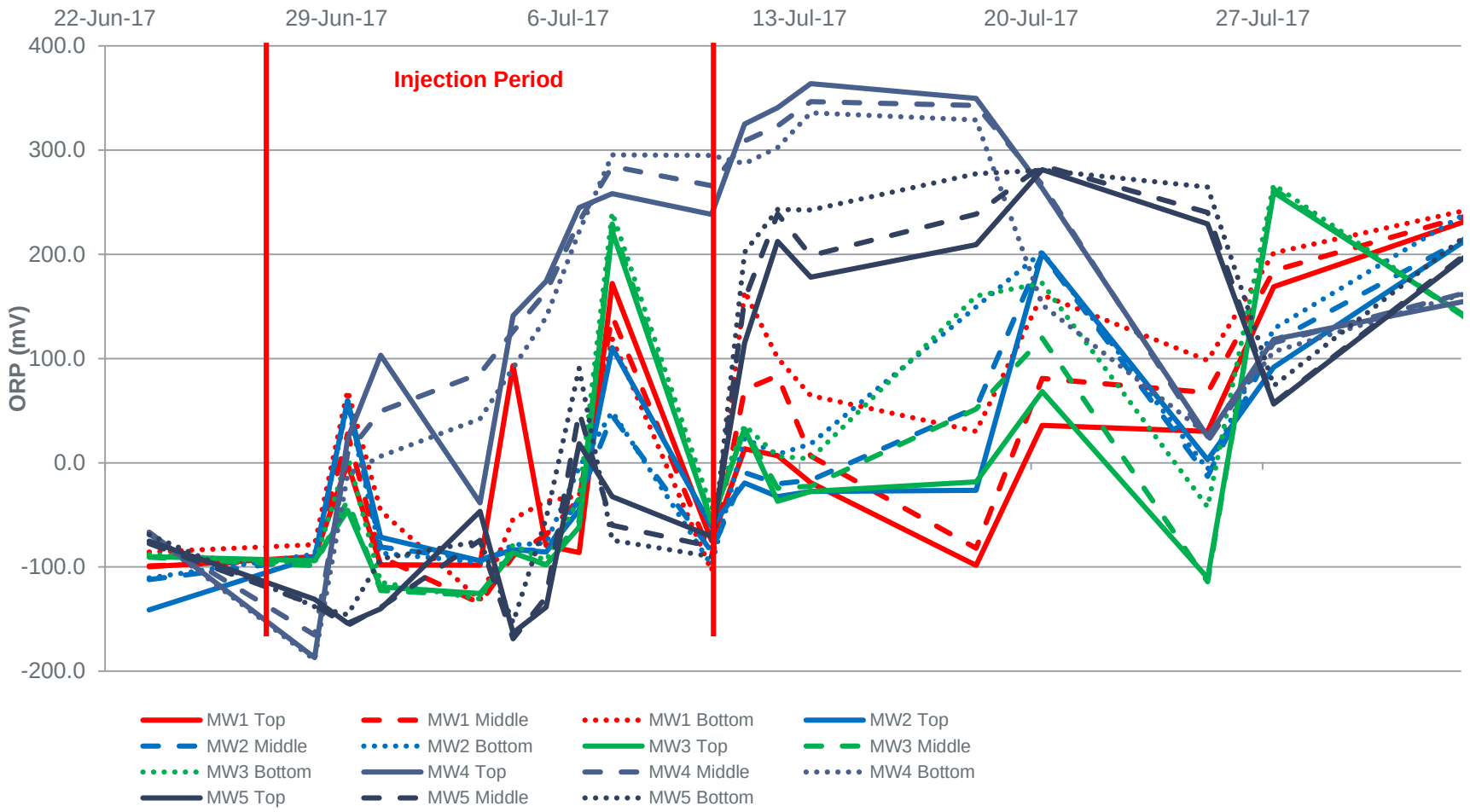
ORP Field Monitoring Data (Area 4S)



- ORP shows an increasing positive trend following ISCO injection in all monitoring wells (successful oxidant delivery)
- Low dieldrin concentrations detected both pre- and post oxidant injection. Concentrations remain at <0.03mg/l

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