Comparison of Thermal Methods for Quantifying Natural Source Zone Depletion (NSZD) Rates Overlying a Shallow Petroleum Hydrocarbon Source Zone

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HERS Environmental Consulting, Inc.

OUTLINE

1. Why is NSZD important and Conceptual Site Model
2. Field research site: Instrumentation and temperature monitoring data
3. Thermal NSZD data analysis methods (background-corrected analytical model, single-stick and numerical model)
4. Analysis results
5. Summary and key learnings

Context is multi-year field research on methods for evaluation of NSZD rates, we hope this research will be published in GWMR later in 2023

Groundwater Monitoring & Remediation NGWA The Groundwater Association

Cutting-Edge Technical Paper

Multiple Lines of Evidence for Estimating NSZD Rates Overlying a Shallow LNAPL Source Zone

Anne Wozney, Ian Hers, Krista Stevenson, Calista Campbell, Nick Nickerson, Colleen Gosse

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David Epstein in his book "***Range Why Generalist Triumph in a Specialized World***" describes wicked problems as full of uncertainty, ill-defined, with few rules, and rapidly changing.

Solving wicked problems requires conceptual reasoning skills that can connect new ideas and work across contexts

RATIONALE AND MOTIVATION

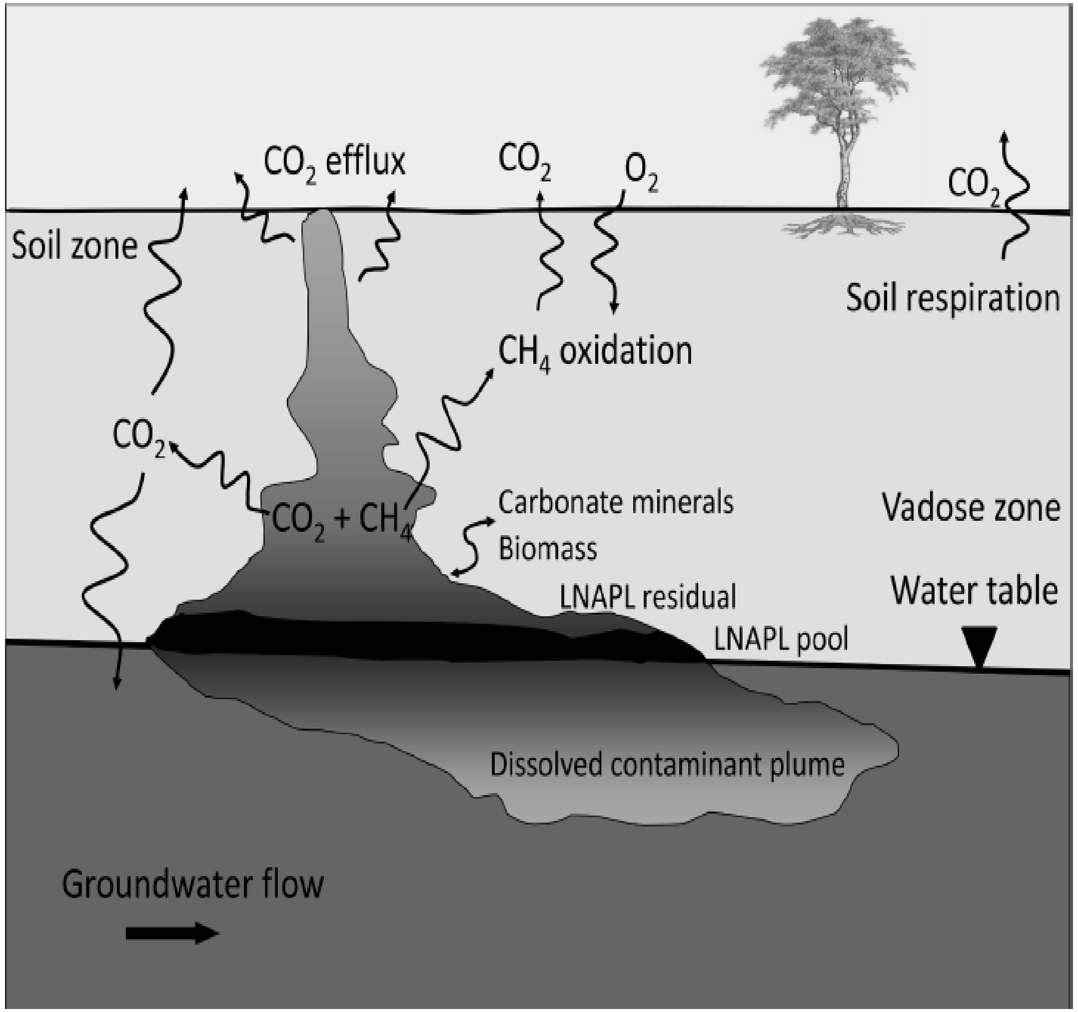


Figure from Sihota et al. 2011

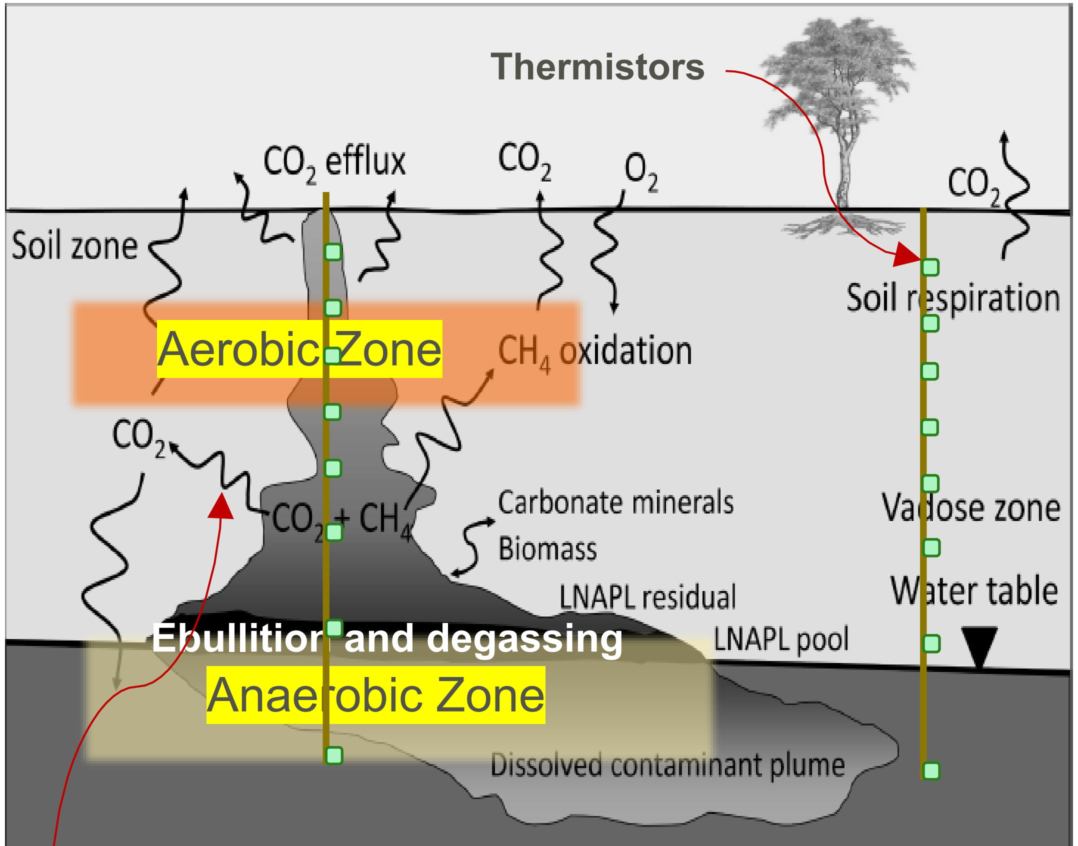
- Natural depletion rates of petroleum hydrocarbons (PHCs) can be relatively significant
- Conceptual models and rates can improve site management and support transition to passive remediation
- Both bulk NSZD rates and compositional change are important
- Thermal NSZD methods described in several guidance (ASTM, ITRC, API) but there are few detailed evaluations of analysis methods
- Learnings on technology potentially can be incorporated in other applications (e.g., heat enhanced biodegradation)

RESEARCH SITE

- Field trial conducted in area of former refinery
- Petroleum hydrocarbon (PHCs): weathered middle distillate with lesser amounts of lube oil
- Silty sand and silt over coarse sand, pockets of peaty soil
- Depth to corrected water table: 2.7 - 4.7 m
- Free and residual LNAPL
- Highly variable contamination from near surface to below water table, soil gas regime also highly variable

Study Area

THERMAL NSZD CONCEPTUAL MODEL



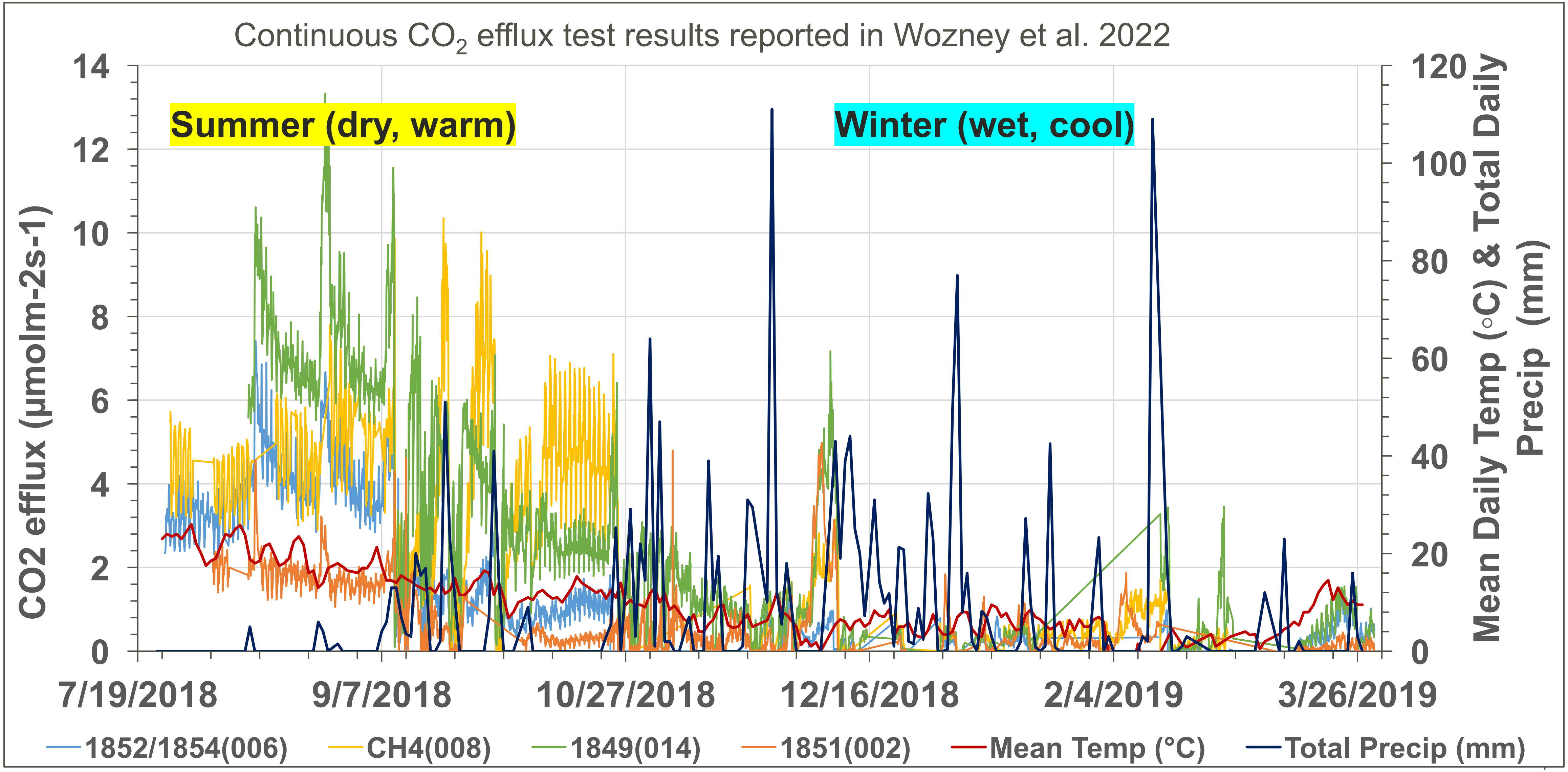
$$6.25\,CH_4 + 12.5O_2 \rightarrow 6.25CO_2 + 12.5H_20$$

$$\Delta H_{MethOx} = 765 \text{ KJ/mole (for } CH_4)$$

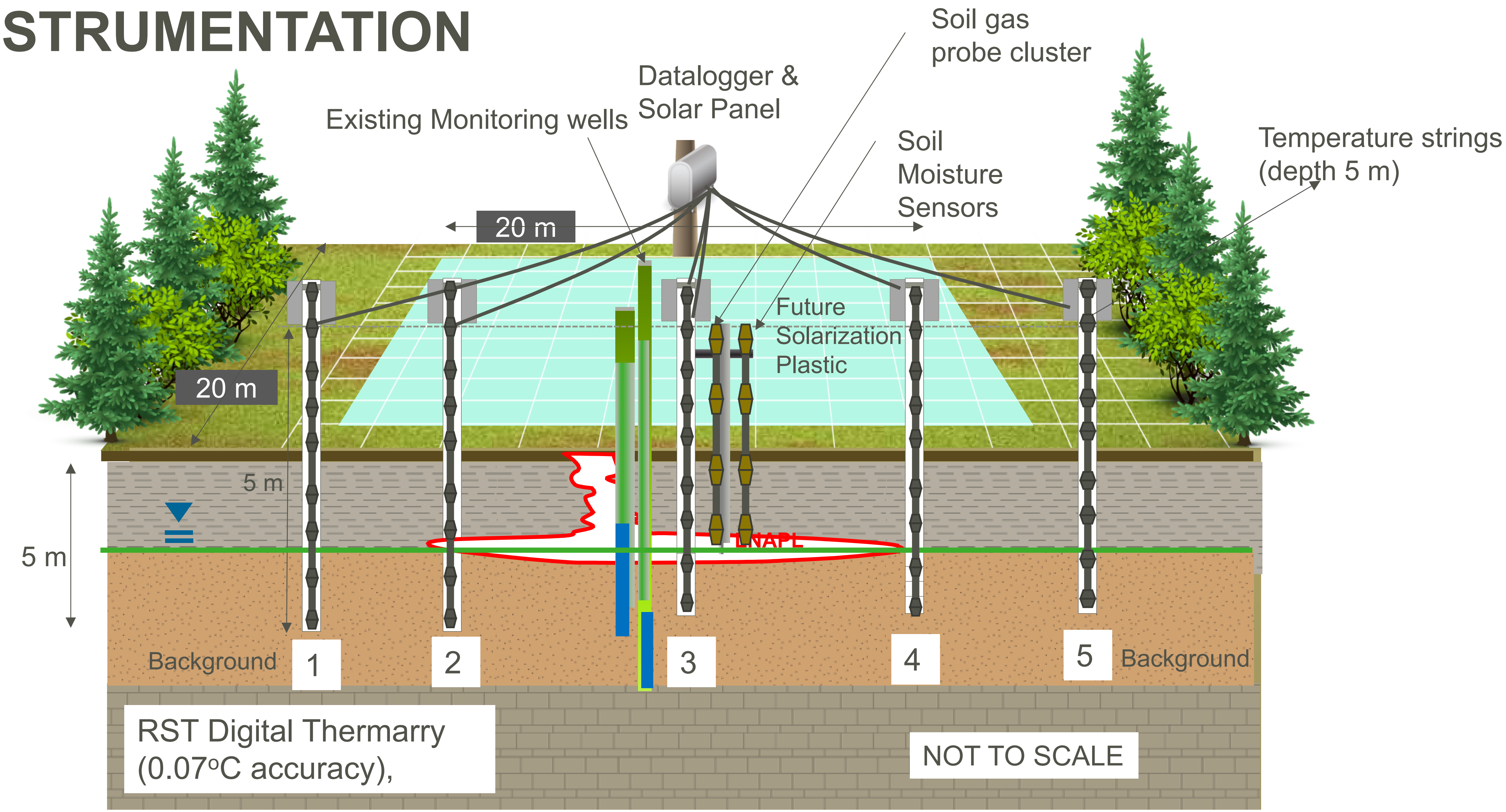
- Aerobic biodegradation of PHCs produces CO_2 and heat
- CO_2 efflux is routinely measured to assess NSZD rates
- From known heat of reaction monitoring of soil temperature can also be used to resolve NSZD rates
- Thermal methods potentially advantageous in terms of long-term rates and bulk measurements

Figure from Sihota et al. 2011

CO_2 EFFLUX, TEMPERATURE AND PRECIPITATION

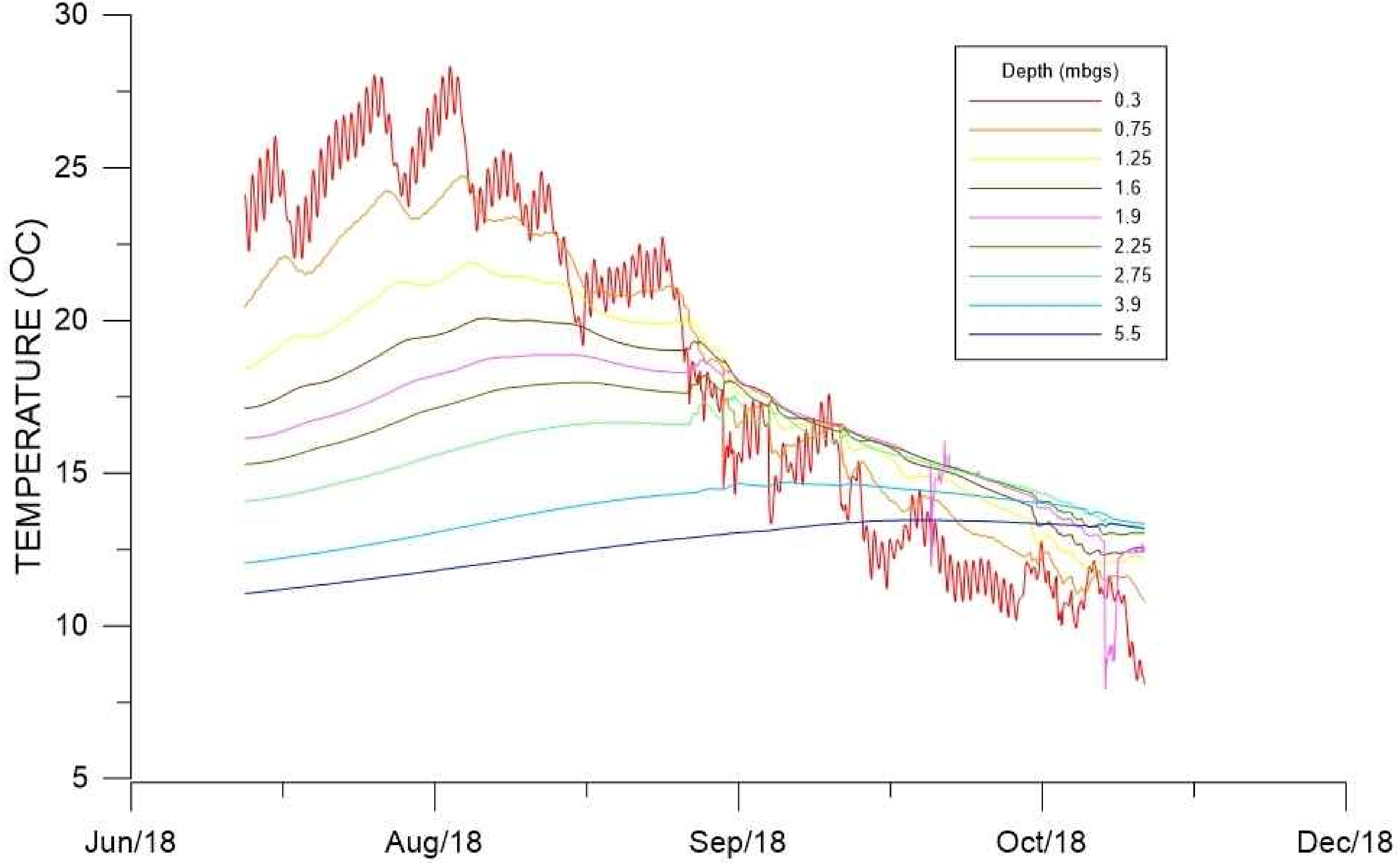


INSTRUMENTATION



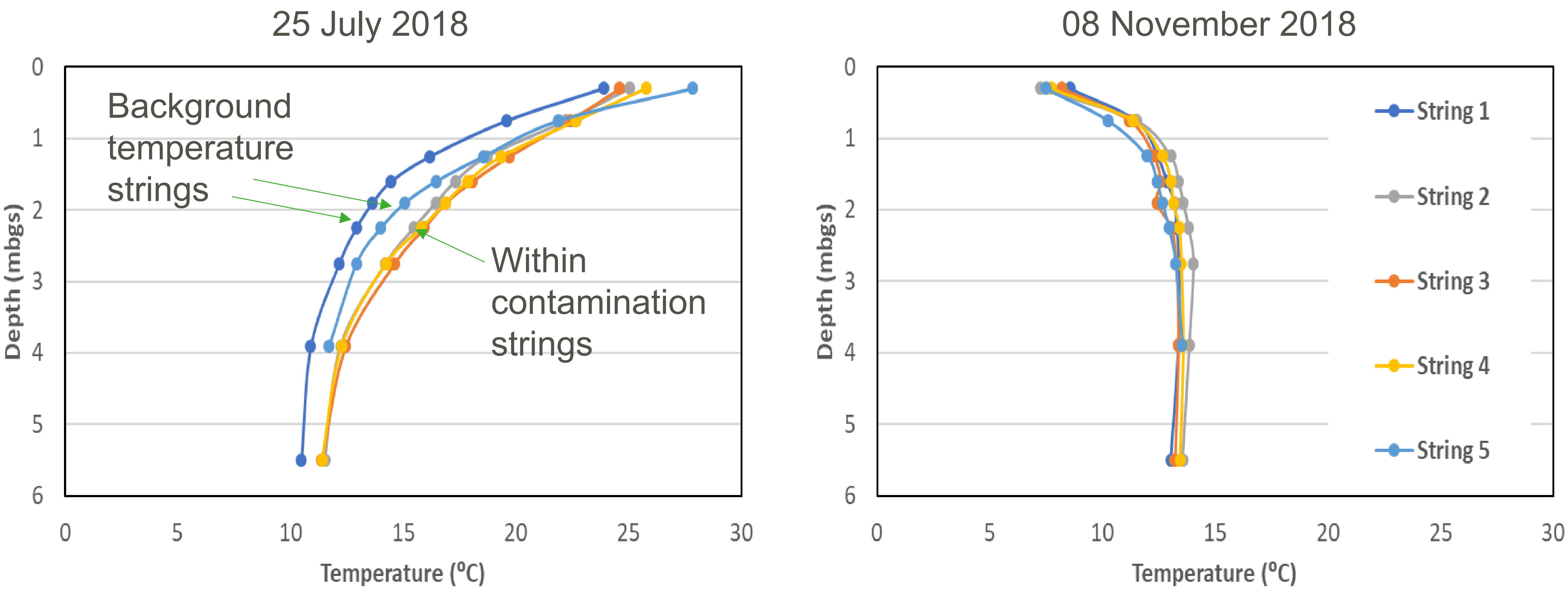
SOIL TEMPERATURE MONITORING DATA

TEMPERATURE STRING 3

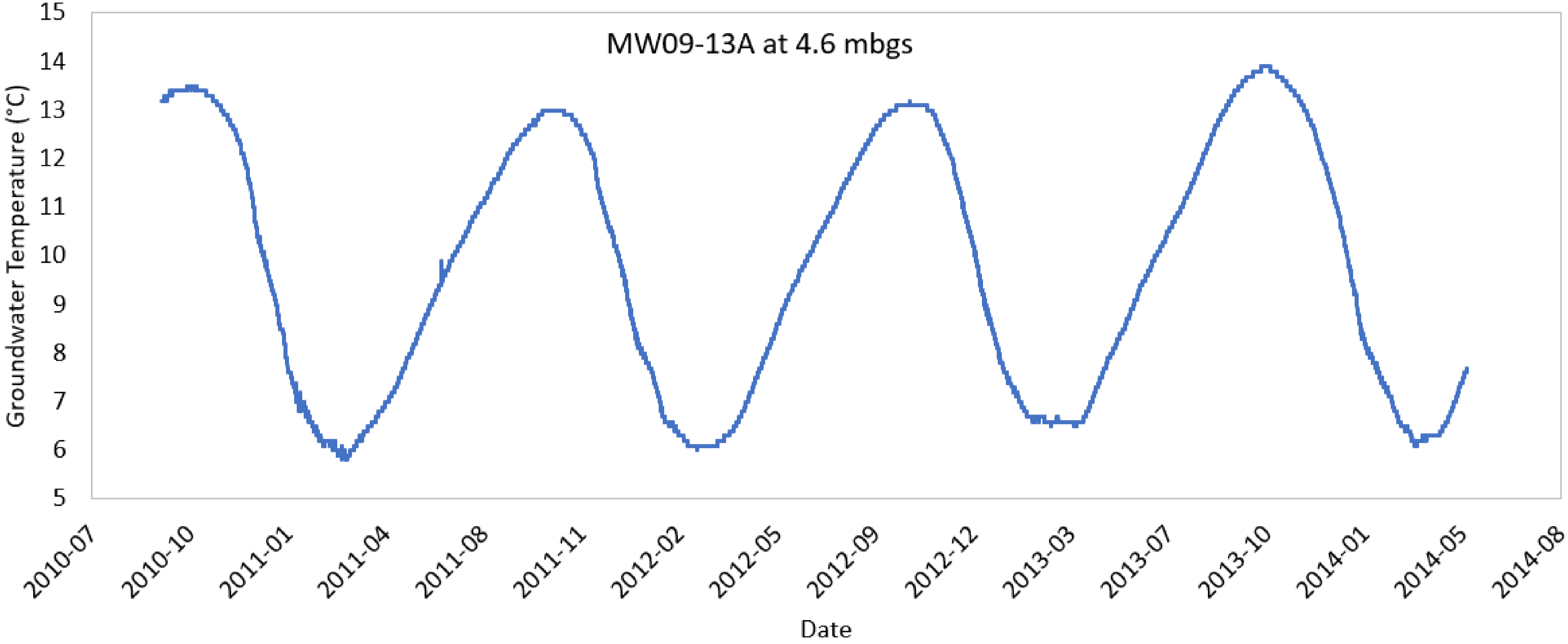


SOIL TEMPERATURE MONITORING DATA

SNAPSHOT TEMPERATURE PROFILES



SHALLOW GROUNDWATER TEMPERATURE MONITORING DATA



Site is at base of small hill in likely groundwater recharge area – variability complicates analysis

THERMAL NSZD MODELS

Model name and references	Background correction?	Model type	Model available?	Comments
Background-corrected analytical solution (Sweeney & Ririe 2014; Warren & Bekins 2015)	Yes	1-D, analytical, steady state	No, but can be programmed in spreadsheet	Varying approaches to estimation of thermal gradients and data analysis (e.g., varying time scales)
Background-corrected energy balance model[1] (Sale et al. 2015; Karimi Askarani et al. 2018)	Yes	1-D, semi-analytical[1], transient	No	Can be simplified to steady state equation
Single Stick semi-analytical model (Karimi Askarani & Sale 2020)	No	1-D, semi-analytical[1], transient	No	Complex code needed for computations is not publicly available
Numerical Geostudio Temp/W model (this study)	No	2-D, transient, numerical	Yes	Can simulate varying soil thermal properties

Note: 1. There is US patent for measuring thermal flux and rate estimates using this method (Sale et al. 2018); 2) described as semi-analytical because curve-fitting and/or iterative solution is needed.

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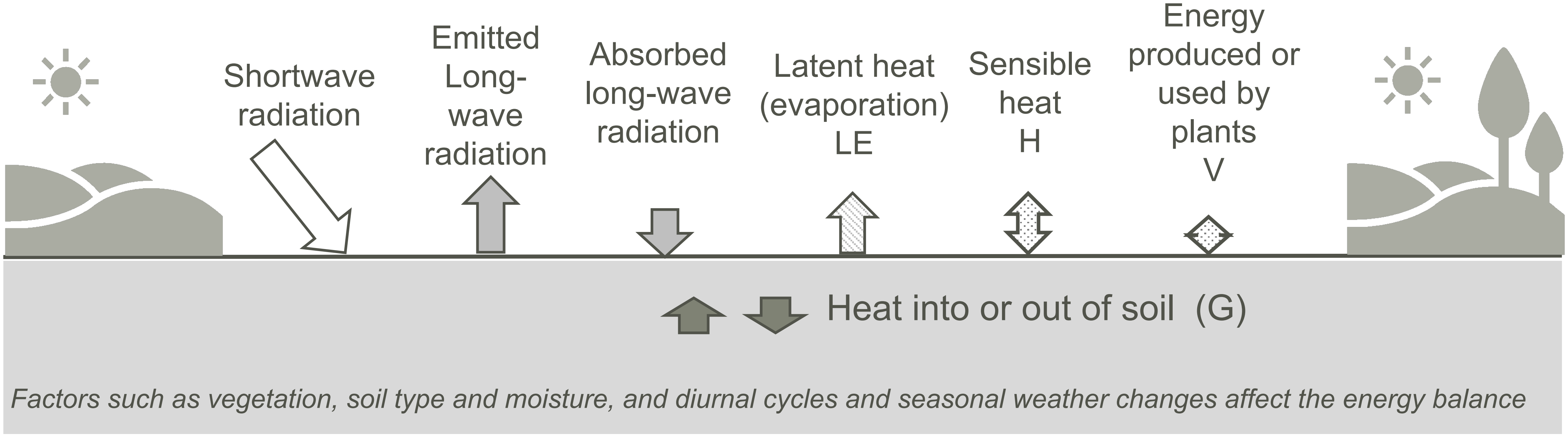
SURFACE ENERGY BALANCE



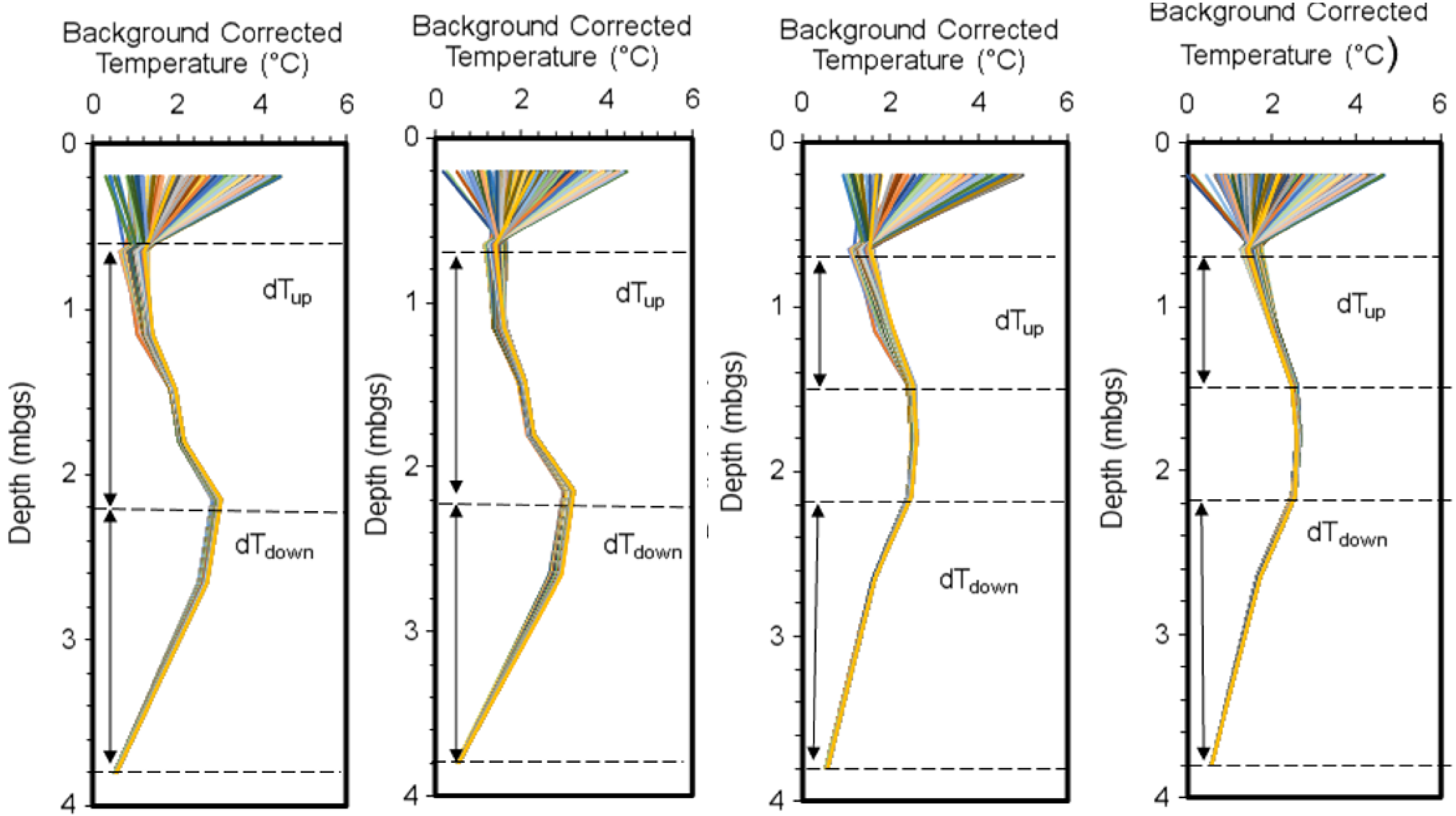
$$R_{NET} - G = LE + H + V$$

R_{NET} is the net downward radiative flux (longwave + shortwave).

BACKGROUND-CORRECTED ANALYTICAL SOLUTION

String 2 — July, August

String 4 — July, August



Sweeney and Ririe (2014)

$$_D = G_u + G_l = -K_u \left|\frac{dT}{dz}\right|_u - K$$

NSZD Rate = $G_{NSZD}/\Delta H_{RXN}$

Potential disadvantage in method area differences in contaminated and background area (surface energy balance, soil properties)

Hourly background-corrected data

SINGLE STICK METHOD

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\kappa}\frac{\partial T}{\partial t}$$

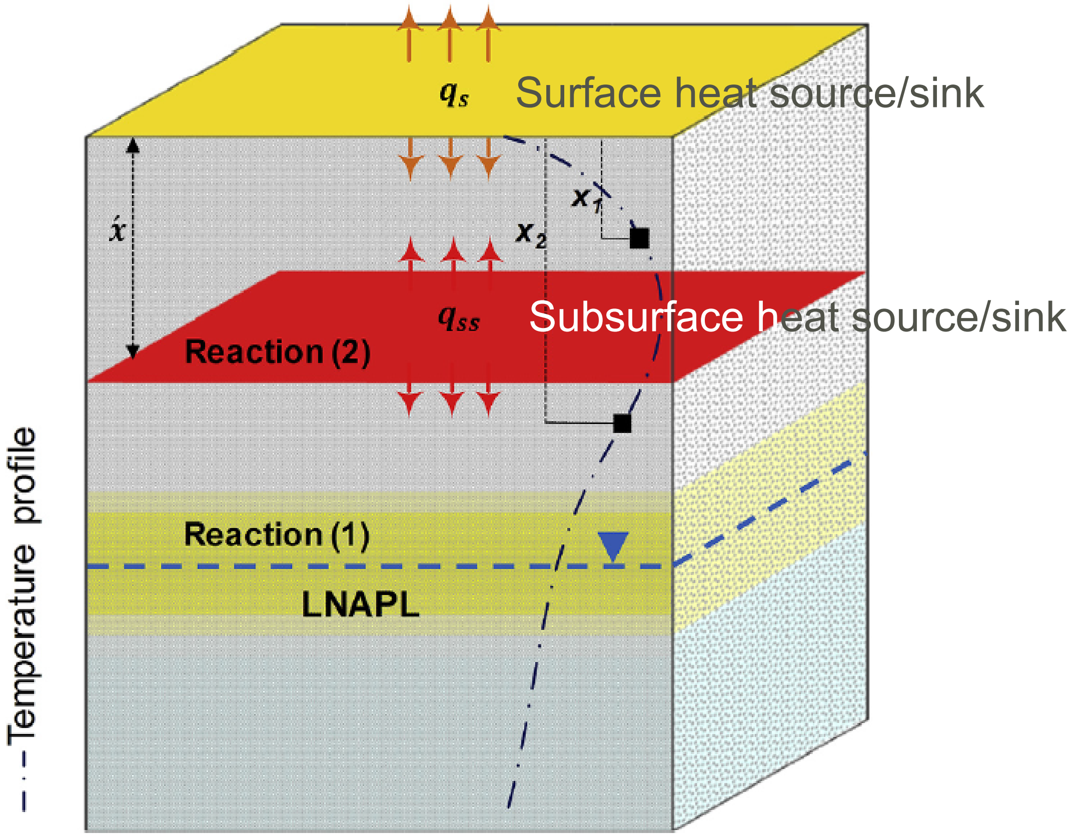


Fig. 2. Conceptual model for heat sources and one-dimensional heat flow in a LNAPL-impacted zone.

- Solution for 1D transient heat conduction equation obtained by superimposing separate solutions for temperatures associated with qs and qss
- Depth to NSZD heat source (Reaction (2)) solved iteratively to achieve optimal solution on daily basis
- Assumes uniform soil

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Thermal estimation of natural source zone depletion rates without background correction

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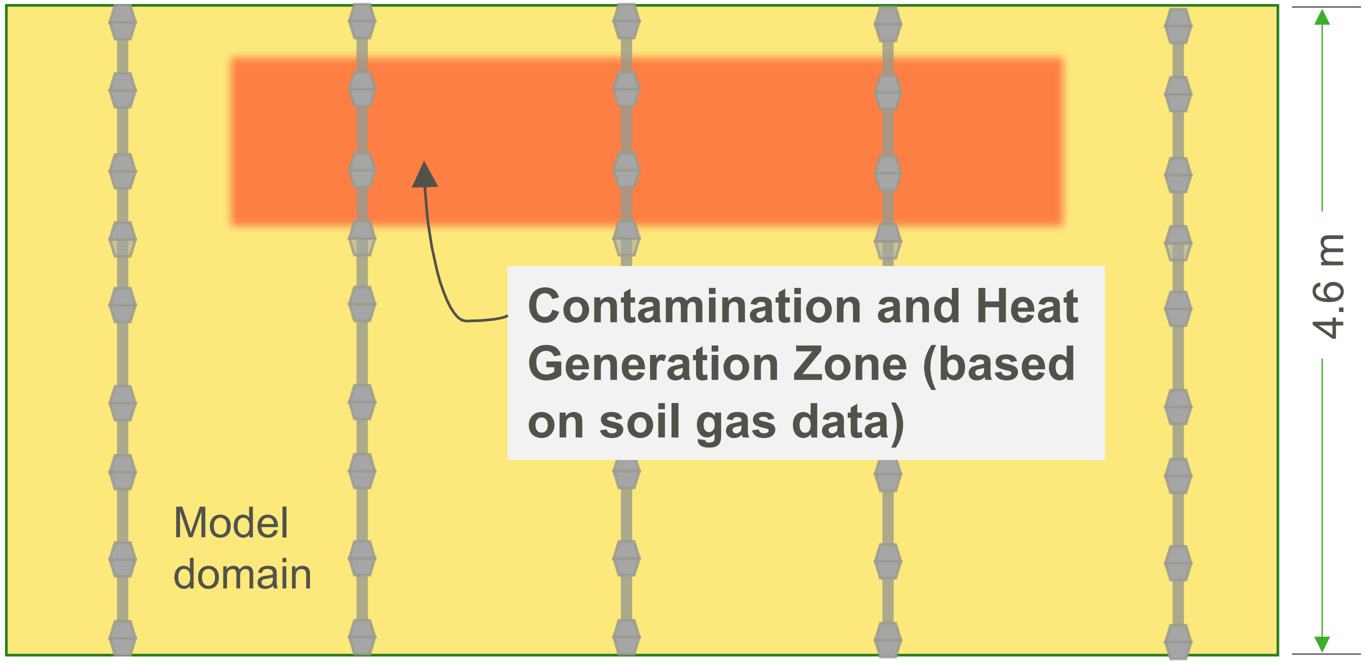
TEMP/W 2D HEAT CONDUCTION EQUATION AND MODELLING PROCESS

Heat transport **Heat Generation**

$$\frac{\partial T}{\partial t} = a_h \left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right] + \frac{q}{pc}$$

$$a_h = \frac{k}{pc}$$

Top b.c. = time-varying measured temperature at 0.05 m depth (n-factor method and energy balance considered)



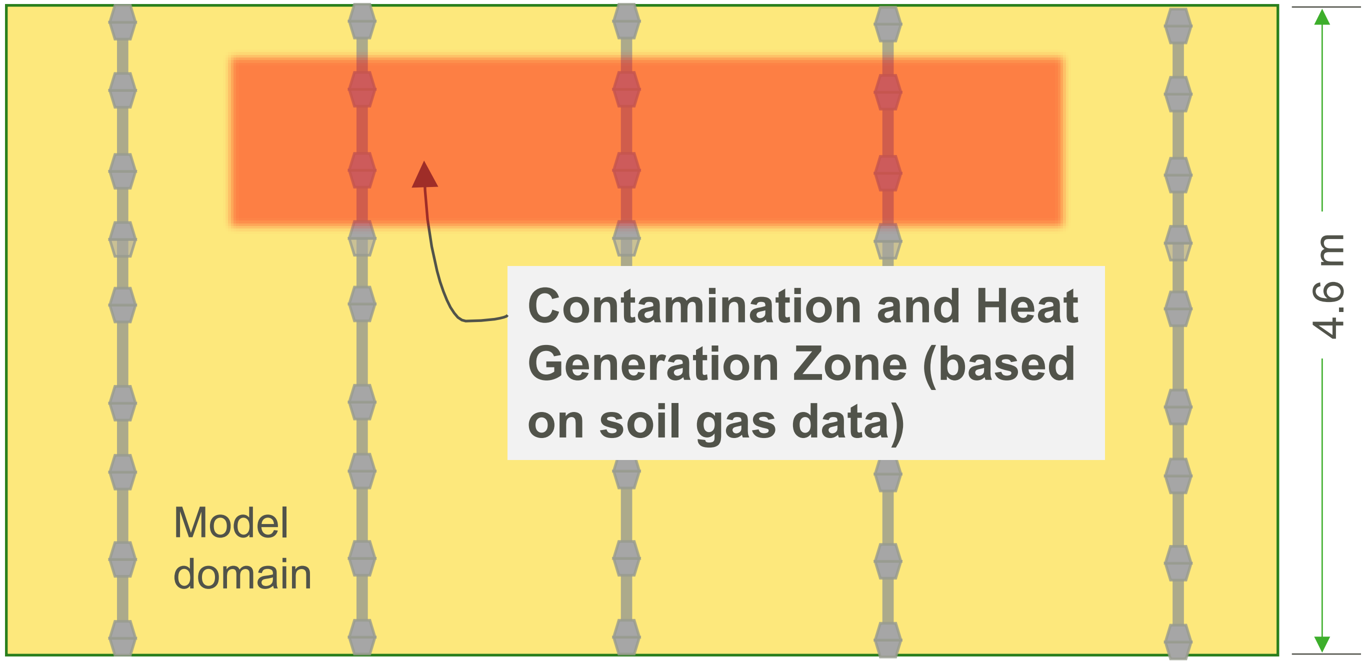
Bottom b.c. = time-varying temperature in shallow groundwater

T = temperature (K), q = heat generation (W/m^3), k = soil thermal conductivity (W/m/K), p = soil density (kg/m^3); c = soil specific heat capacity (J/kg/K), α_h = thermal diffusivity (m^2/s)), b.c. = boundary condition

TEMP/W 2D HEAT CONDUCTION EQUATION AND MODELLING PROCESS

- Heat generation zone cases:
  - Case 1: 0.2-2 m
  - Case 2: 1-1.5 m
  - Varied monthly
- Soil thermal property scenarios:
  - Scenario 1 (lab), Scenarios 2-4 (back-calculate from temp)
  - Constant in time

Top b.c. = time-varying temperature at 0.05 m depth



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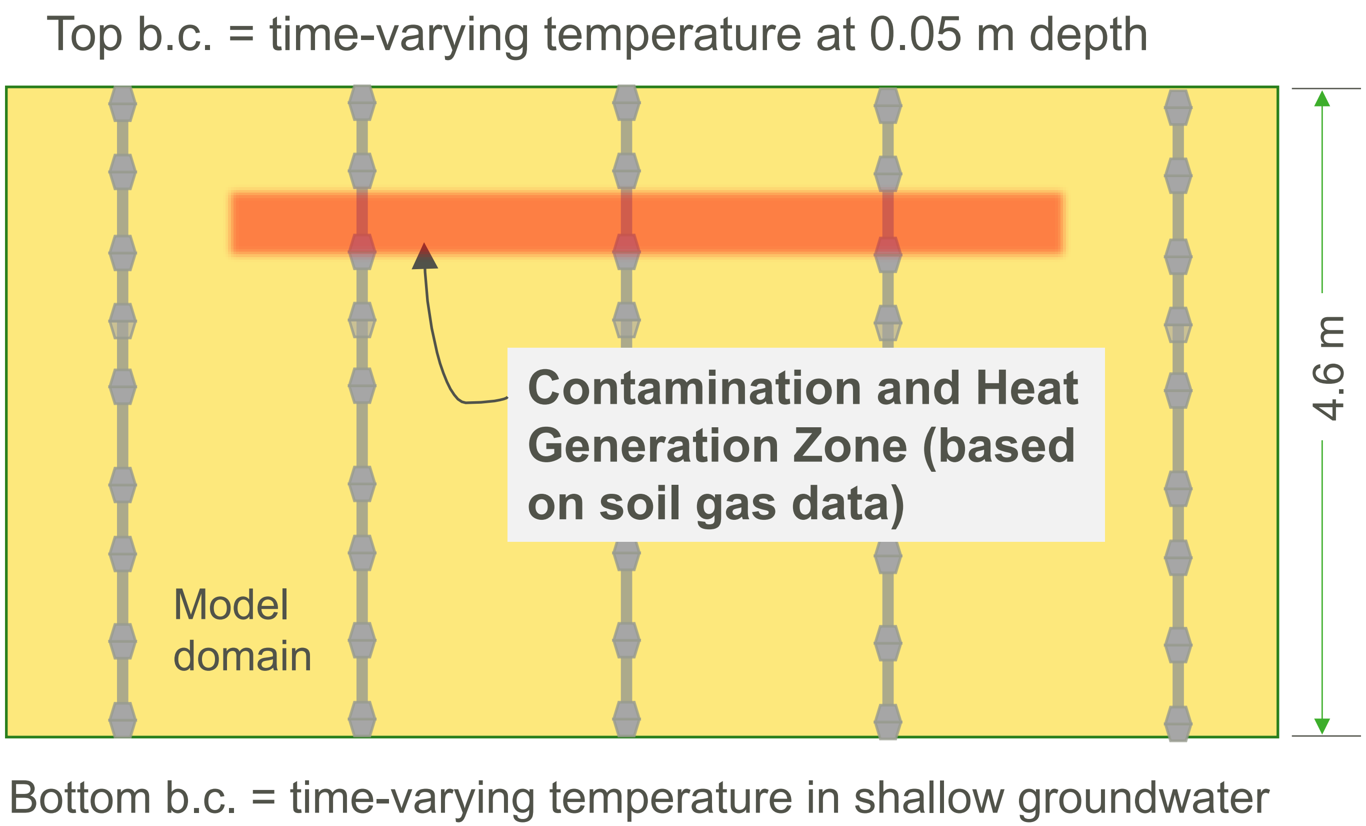

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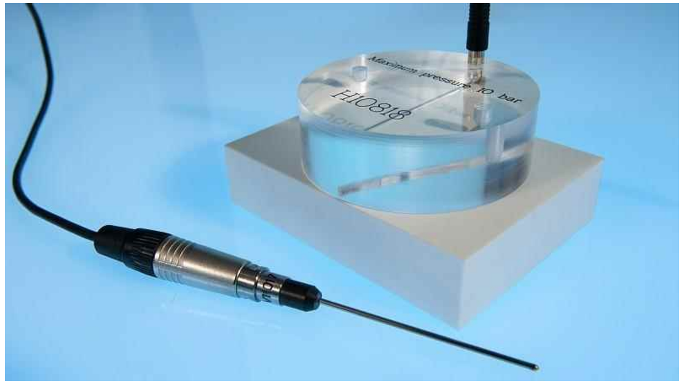
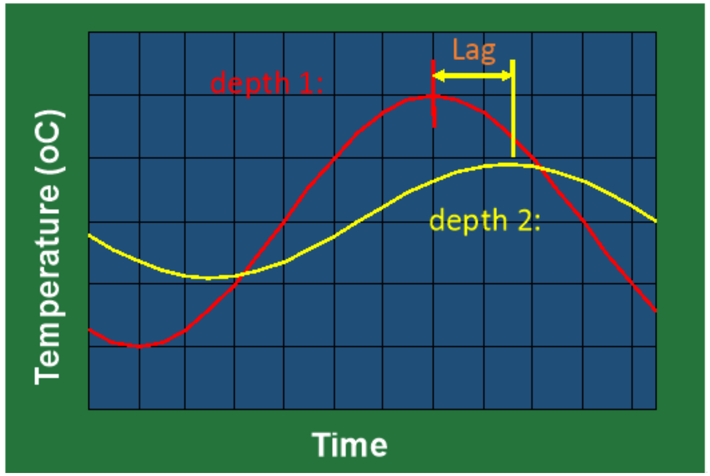
ESTIMATION OF SOIL THERMAL PROPERTIES

- **Diffusivity (m^2/s) = Conductivity ($J/s\text{-}^oC\text{-}m$) / Vol. Heat Capacity ($J/m^3\text{-}^oC$)**
  - Conductivity increases with water content, density, temperature
  - Specific heat capacity less affected by above factors

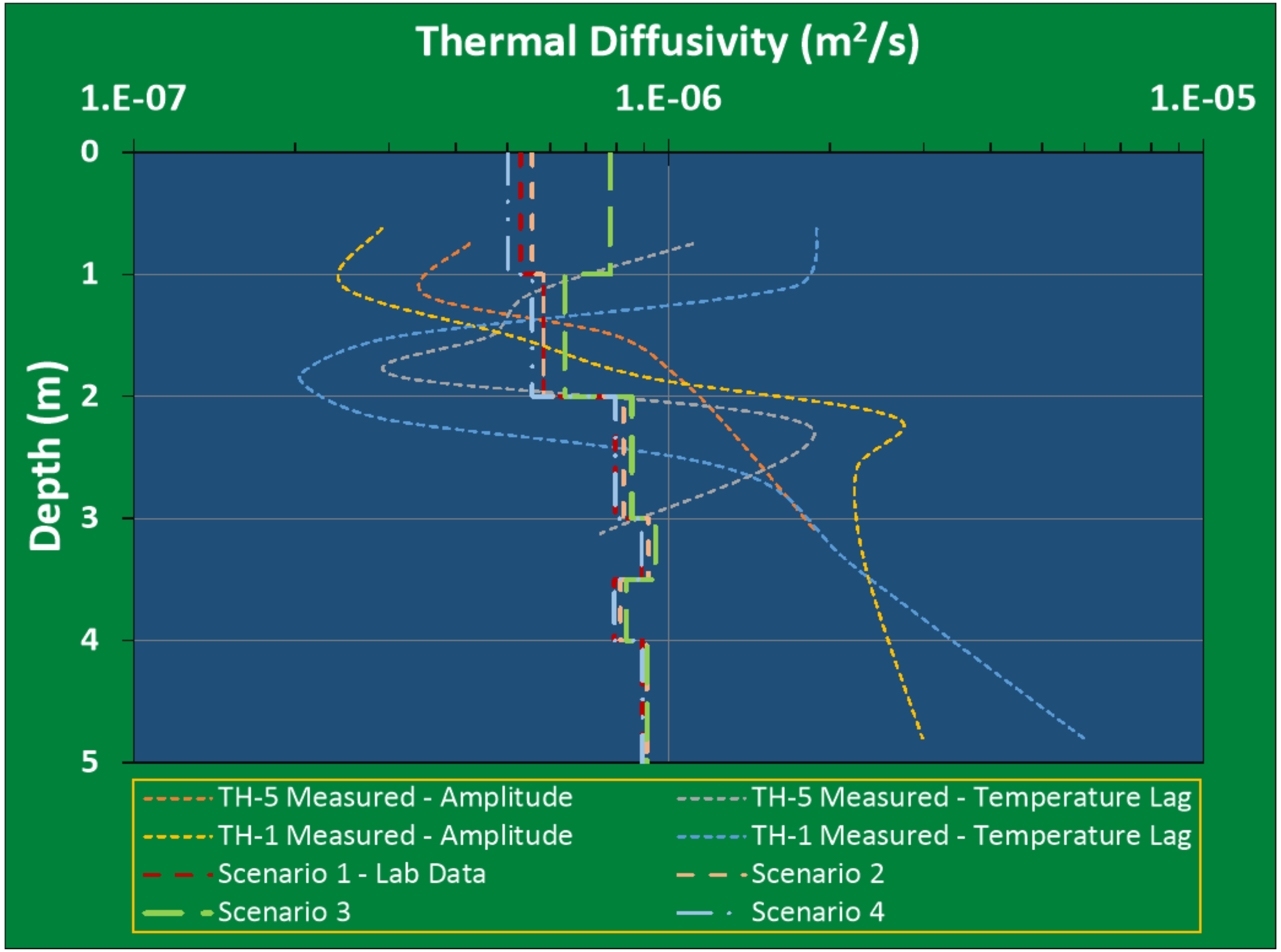


- **Laboratory Analysis** (ASTM D5334-08)
  - Needle probe method
  - Testing at varying moisture content / density
- **Fourier analysis** of background soil temperature data
  - Amplitude difference
  - Temperature lag
  - See standard soil physics text e.g. Hillel

$$T = T_a + A_o\left[\frac{t}{\tau} + \varphi\right]; z = 0$$

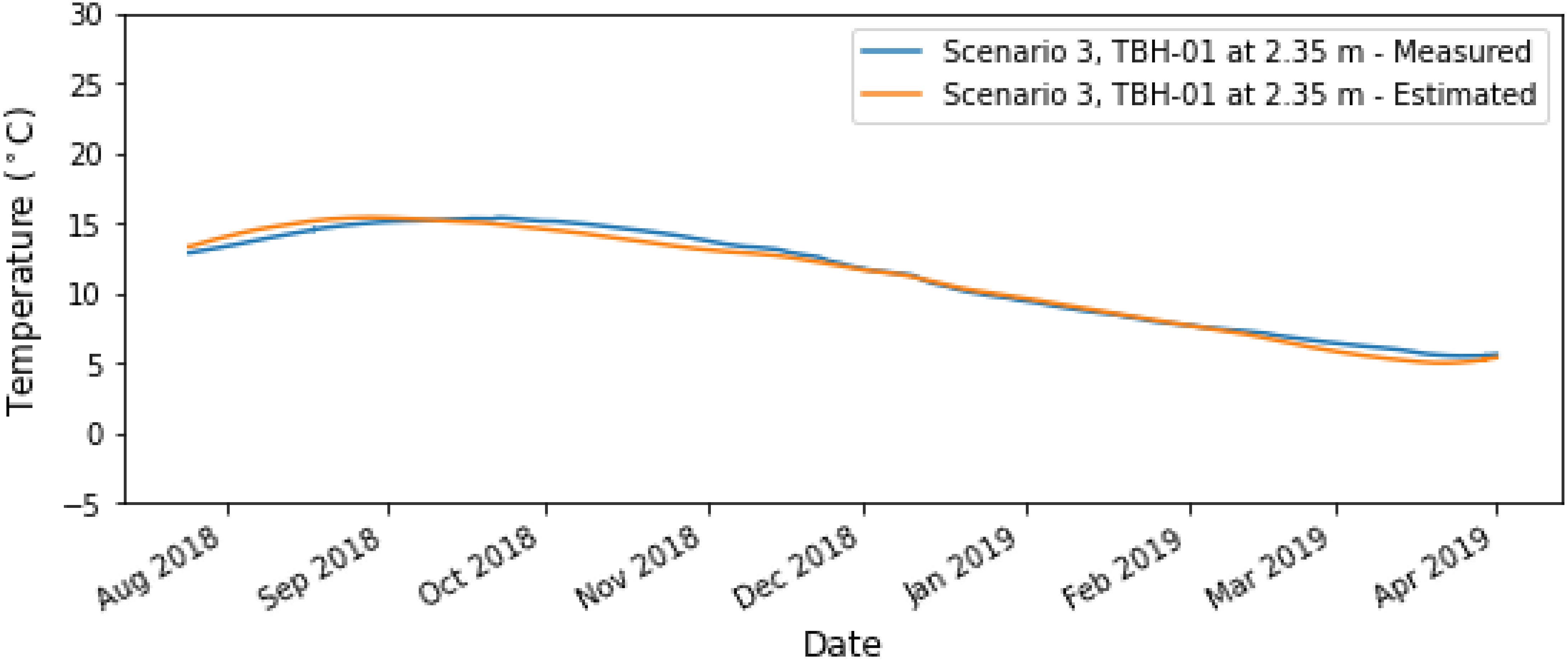


SOIL THERMAL DIFFUSIVITY RESULTS

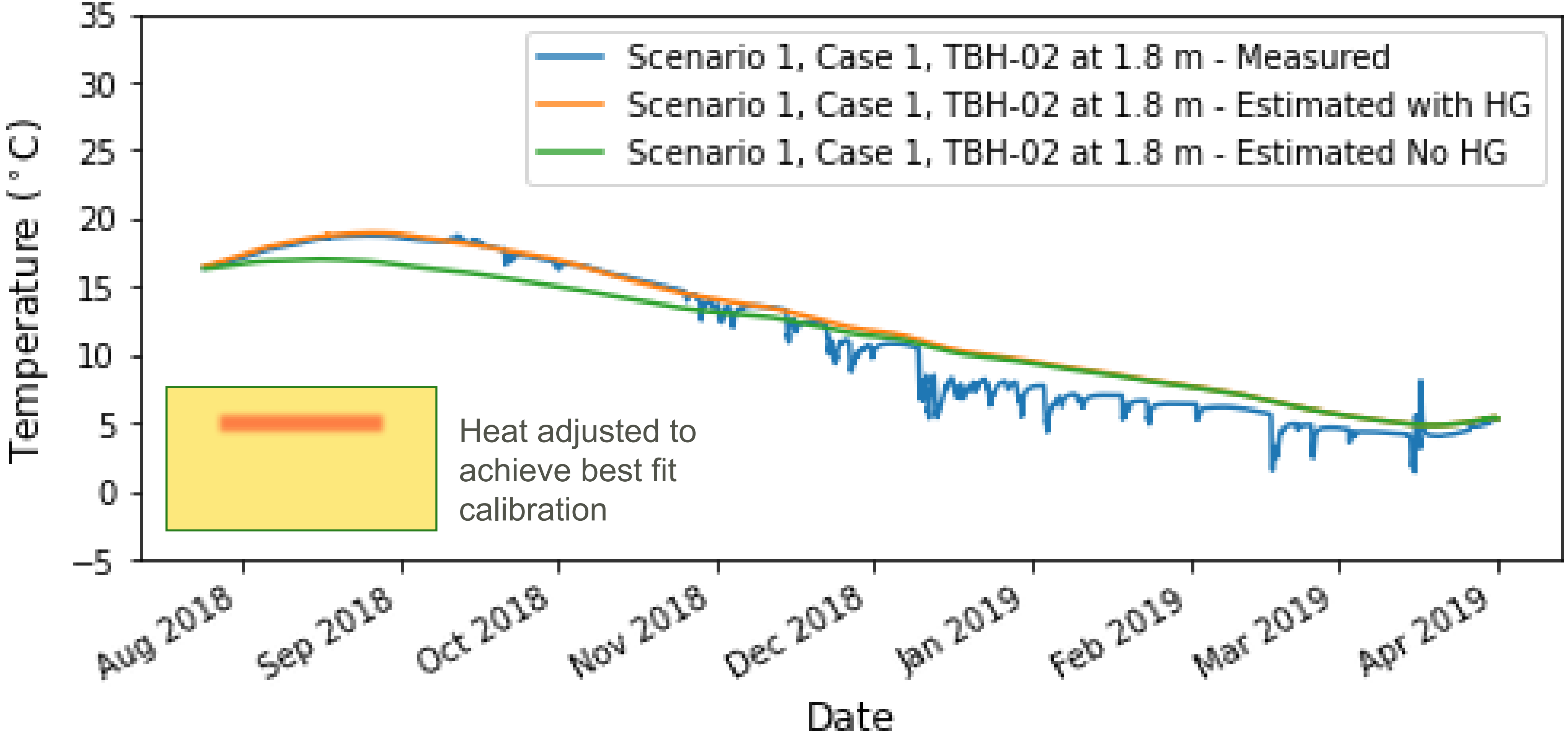


- Back-calculated values from Fourier analysis highly variable and inaccurate at depth (possibly because varying groundwater temperature)
- Additionally used Temp/W model at background locations and evaluated fit between measured and predicted temperature
- Selected Scenarios 1 and 3 for modeling

TEMP/W COMPARISON AT BACKGROUND LOCATIONS

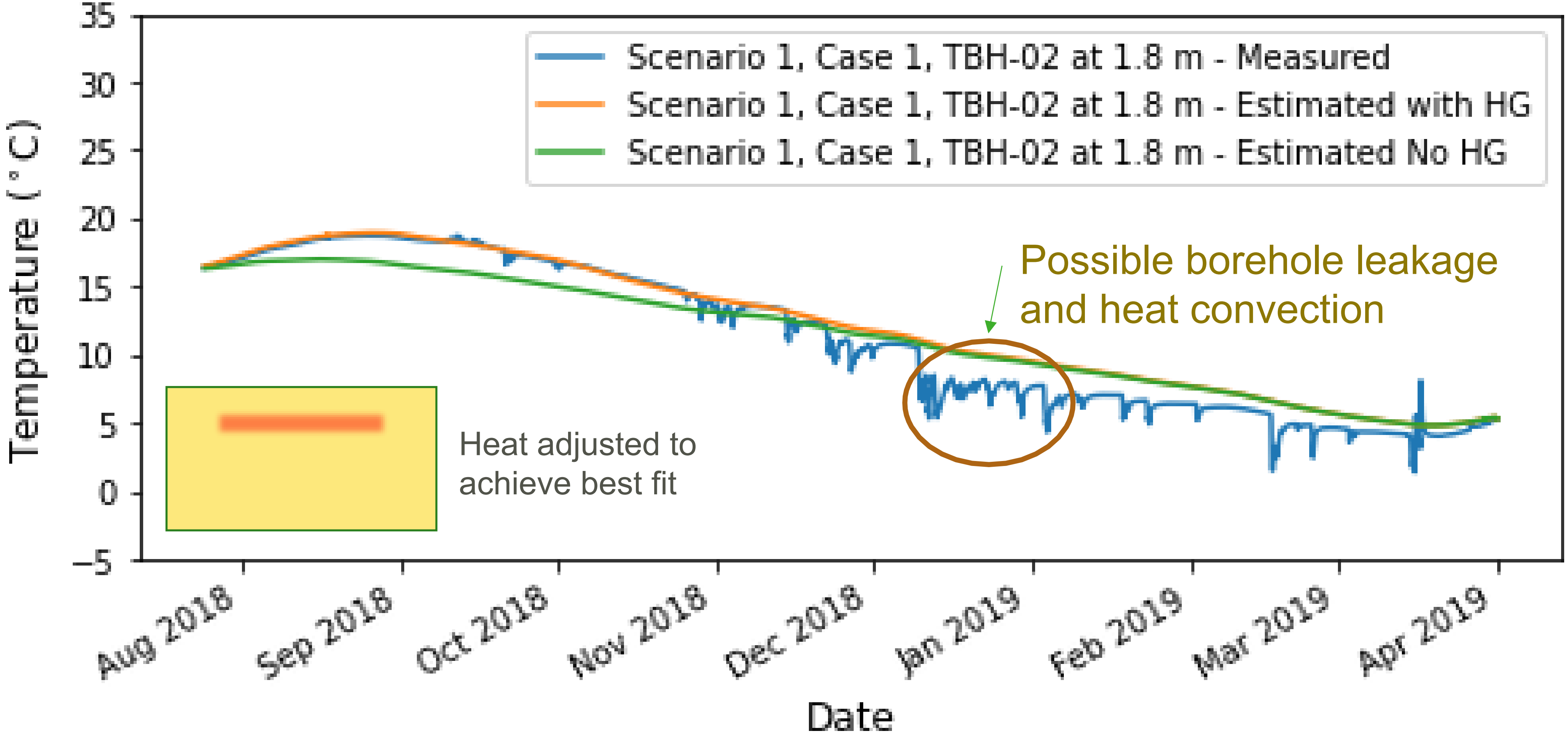


TEMP/W FITTING IN CONTAMINATION AREA WITH HEAT GENERATION



Heat Generation was adjusted on monthly basis, absolute [measured-estimated] temp summed for all thermistors/depths, with objective to minimize total difference as “best” fit

TEMP/W FITTING IN CONTAMINATION AREA WITH HEAT GENERATION



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COMPARISON OF NSZD RESULTS

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Methods	Estimated NSZD Rates (USGal/acre/yr)	
	Jul / Aug 2018	Sept / Oct 2018
Temperature Method		
Temp/W Model	3,600	2,100
***Single Stick* Model**	1,700	980
Background Corrected Analytical Sol'n *	1,860	1,020
CO_2 Efflux Method Continuous Data *	1,200	340
Soil Gas Gradient Method Discrete Data *	1,600**	N/A

Note: * Reported in Wozney et al. (2022); ** Monitoring event in July.

TEMP/W RESULT SENSITIVITY IN ESTIMATED RATES

Mean difference between:	Relative Percent Difference (%)	Comment
Scenarios 1 and 3 Soil Properties	38	Soil thermal properties "moderately" sensitive
Scenario 3 vertically-variable & uniform[1] profile	17	"Low" sensitivity to uniform or vertically increasing diffusivity
Cases 1 and 2	21	"Low" sensitivity to position of heat (bio) source, for cases evaluated

[1] $D_T = L_T / \Sigma (L_i/D_i)$

More research is needed, but detailed measurement of soil thermal properties may not be warranted (and is also challenging) given overall uncertainty in method, and instead use of literature values, e.g., 1-2.7 J/s/m/^{o}C (Hillel 1998; Campbell & Norman 1998; Becker et al. 1992; Mahdavi et al. 2016) for thermal conductivity may be reasonable

COMPARISON OF THERMAL ANALYSIS METHODS

Model	Advantages	Disadvantages	Sources of Uncertainty
Background-corrected analytical solution	Relatively simple method	Requires background correction	Varying background solar radiation & soil properties
Single Stick semi-analytical model	No need for background correction; automated simulation of position of subsurface heat source	Computationally complex	Varying thermal properties and external subsurface heat sources
Numerical Temp/W	No need for background correction; can model variable soil thermal properties, heat sources and boundary conditions; model available	Complex fitting procedure to back-calculate transient rates	Boundary conditions, initial conditions, position heat source, data fitting procedure

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General Site Sources of Uncertainty: Variable contamination; variable soil; shallow contamination (makes distinguishing heating from PHC biodegradation, natural organics and solar surface heating challenging) and variable lower boundary condition.

SUMMARY AND KEY LEARNINGS

- Temperature is an effective proxy for petroleum hydrocarbon biodegradation
- NSZD rates were highly seasonally dependent, with relatively higher rates during dry, warm summers and lower rates in cool, wet winters
- Rates from single-stick and background-corrected analytical sol’n were within ~ factor of 1.5X of CO_2 efflux and soil gas gradient methods, TEMP/W model ~ 2X higher than single-stick/background methods
- Site factors including shallow, variable contamination and variation in surface/base boundary conditions contributed to uncertainty (particularly for TEMP/W method)
- Longer-term temperature monitoring data can improve analysis
- More research needed on temperature analysis methods, conditions when background method is sufficiently accurate, use of weather measurement data and surface energy balance in analysis, case studies

HERS Environmental Consulting, Inc.

Thank You!

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