

THERMAL REMEDIATION

Groundwater can be contaminated through harmful compounds being released by various human activities such as agricultural and industrial activities. Remediation of polluted groundwater includes thermal treatment that raises the subsurface temperature, leading to vaporization and removal of the contaminants. In this study, we examine the co-boiling point of several contaminants under various conditions.

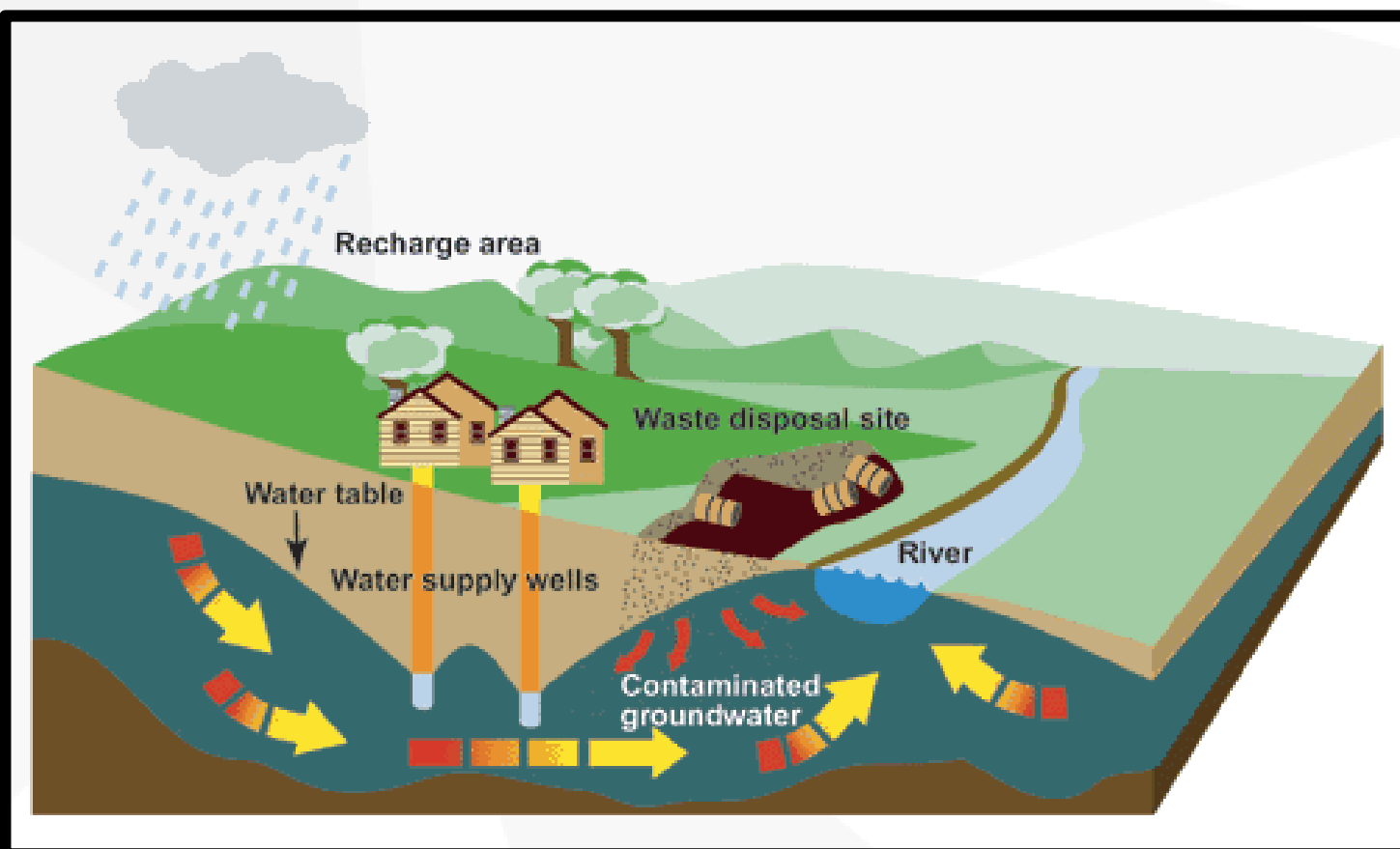


Figure 1: Groundwater contamination from waste disposal site. [1]

Research Objective

Since thermal treatment is dependant on contaminant vocalization, the boiling point is an important parameter for optimizing remediation. The objective of this study is to examine the effect of remediation depth and soil type on the co-boiling point of various compounds such as benzene, toluene and trichloroethylene.

LITERATURE REVIEW

Table 1 : Various Computational Models Available [2-16]

	Thermal Remediation	Contaminant	Soil Types		Gas Modeling	
	Type of Thermal Remediation	Temperature Ranges	Type of Contaminants	Viable Soil Types	Heterogeneous vs. Homogeneous Soils	Gas Bubble Formation
TOUGH2 [2-3]	Thermal Conductive Heating, various.	Up to 800°C	VOC, NAPL, etc.	Fractured and porous media	Both	No
Cerrigan - Nitao OHM_NUFT [4]	ERH, Steam Injection, Vacuum treatment	Undefined	NAPLs(TCE), etc.	Low-Permeability Soils, CLAY	Homogeneous	No
ETM [5-6]	ERH	Undefined	Volatile Compounds	Porus media	Homogeneous	No
ET-MIP [7-8]	ERH, Subsurface Heating	Undefined	NAPLs, etc.	Porus media	Both	Yes
CompSim [9 -10]	Hot Water Flushing	22°C - 50°C, etc.	LNAPLs, Organic Compounds	Porus Media, sand.	Both	No
Chute - Vermeulen [11-12]	Electromagnetic Heating	Undefined	NAPLs, non-Organic	Oil-sands	Both	No
Keuper [13-14]	Thermal Conductive Heating.	More than 700°C	NAPLs	Porus soils/sands	Heterogeneous	Yes
MIP [15-16]	Various	Undefined	Hydro Carbons	Porus media	Homogeneous	Yes

Initially the Federal Remediation Technologies Roundtable (FRTTR) screening matrix and reference guide was used for common contaminants, remediation techniques, and soil types. [17] Various computer models have been developed to study groundwater remediation and are based on different heating methods. For example, ETM [5] is developed for electrical resistance heating (ERH), while CompSim has been used for hot water flushing.[9]. TOUGH2 is based on thermal conductive heating (TCH) but has been used in other applications [3]. Some models use a continuum approach to model gas movement while others simulate bubble clusters using a discrete model.

Table 2 : Modelling Parameters

System Properties		Units
T	Temperature	C
D	Depth of contaminant	m
Pw	Water Pressure	Pa
Sg	Gas saturation	-
Soil Properties		
Swr	Residual Water Saturation	-
Sm	Maximum Saturation	-
λ	Pore Size Index	-
Pd	Displacement pressure	Pa
Pwv	Water Vapour pressure	Pa
n	soil porosity	-
Pc	Capillary pressure	Pa
Compound Properties		
H	Henry's constant	Pa m ³ / mol
MW	Molecular weight of compound	g/mol
Mb	Total mass in system	mol/m ³
Constants		
K	Partitioning Constant	-
R	Universal Gas constant	m ³ -Pa/mol K

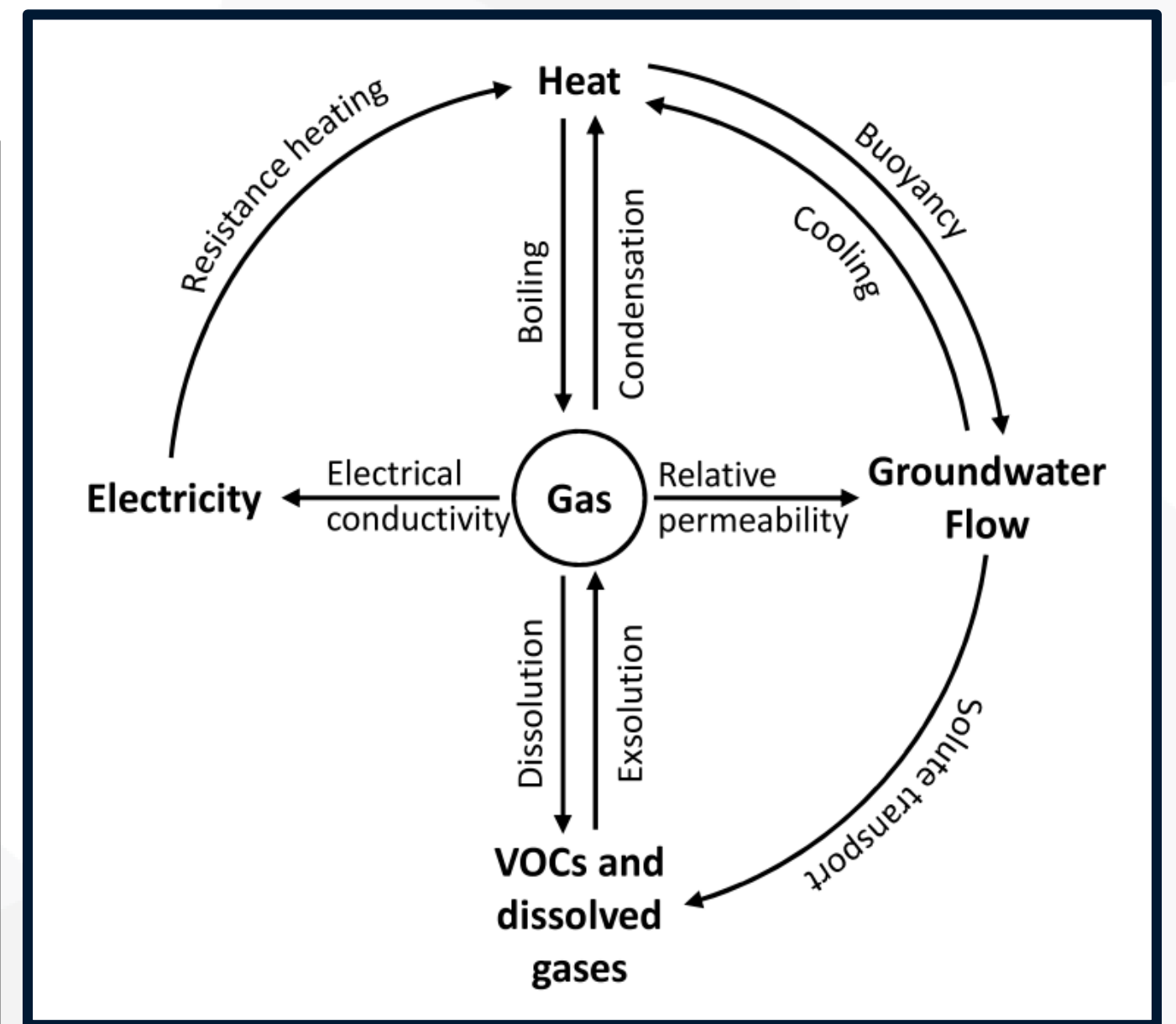


Figure 2: Conceptual model for thermal remediation

A conceptual model of the state variables (bolded text) and inter-linking processes and material processes (text above linking arrows) that govern groundwater flow, gas generation, and volatile organic carbon (VOC) removal during electrical resistance heating (ERH). [16]

METHODOLOGY

Co-boiling point: The temperature at which a contaminant will start to volatilize. This temperature depends on the mass of contaminant in the system (5) as well as the pressure of each component. The partial pressures are calculated using Henry's Law, Dalton's Law and the Ideal Gas Law which all depend on temperature. [7]

$$\begin{aligned} P_g^{tot} &= \sum P = P_c + P_w & (1) \quad M &= M_g + M_w \\ P_g^{tot} &= P_w + C_w H = P_c + P_w & (2) \quad M &= C_g S_g \phi + C_w (1 - S_g) \phi \\ C_w H &= P_c + P_w - P_w^{pv} & (3) \quad M &= K C_w S_g \phi + C_w (1 - S_g) \phi \\ \phi &\text{ is the porosity. Eqs.(3) and (4) are combined, resulting in:} \\ M &= K \left(\frac{P_w + P_c - P_w^{pv}}{H} \right) S_g \phi + \left(\frac{P_w + P_c - P_w^{pv}}{H} \right) (1 - S_g) \phi & (5) \\ \text{capillary pressure is a function of gas saturation as described by the Brooks-Corey relationship:} \\ P_c &= \left(\frac{1 - S_g - S_{wr}}{1 - S_{wr}} \right)^{-1} P_d & (6) \end{aligned}$$

The initial mass of contaminant/compound in the system is calculated at 20°C and depends on the molecular weight (MW), solubility limit of the compound, as well as the porosity of the soil. (M = solubility/MW * porosity). The capillary pressure also changes as the soil changes (6) and the water pressure Pw changes linearly with depth. [7] These parameters are important to analyze to understand their impact on the co-boiling point of the compounds.

Table 3 : Compounds used to compare co-boiling points. [18-19]

Compound	Molecular Formula	MW g/mol	Boiling Point C	Vapour Pressure Pa (@20C)	Solubility Limit mg/L (@20C)	Henry's Coefficient H = exp (A-B/T)	
1,1,1, TCA	C2H3Cl3	133.359	74	13300	1290	9.777	4133
TCE	C2HCl3	131.4	87.2	9197.9	1236	11.37	4780
PCE	C2Cl4	165.83	121.1	1900	200	12.45	4918
Chloroform	CHCl3	119.37	61.1	212000	8000	9.843	4612
Benzene	C6H6	78.11	80.1	10000	1800	5.5379	3216.8
Toluene	C7H8	92.14	100.6	3786.4	526	7.3502	3729.7
1,2-Dichloropropane	C3H6Cl2	112.98	96	27900	2600	6.8561	3813.7

Compounds were chosen based on the FRTTR screening matrix and reference guide,[17] as well as their unique properties and characteristics. Experimental data was obtained from the International Labour Organisation (ILO) International Chemical Safety Cards (ICSC) [18]. Henry's Coefficient (H) was modeled vs. temperature using the OSWER method (United States EPA [19]). A linear regression was done for the discrete H values to achieve an equation as described by [20].

Table 4 : Soil Types and Property. [7, 21]

Soil Type	Swr	λ	Γ = (-1/λ)	Pd	n
Sand Soils (Ottawa Sands)					
(A) SAND	0.03	4.24	-0.236	434	0.30
(B) SAND #25	0.069	3.51	-0.285	1324	0.35
(C) SAND #50	0.098	2.49	-0.402	3246	0.35
(D) SAND #70	0.189	3.30	-0.303	3435	0.35
Clay Soil (Generic Sample)					
(E) Clay Lens	0.265	0.450	-2.222	34335	0.55

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INITIAL RESULTS

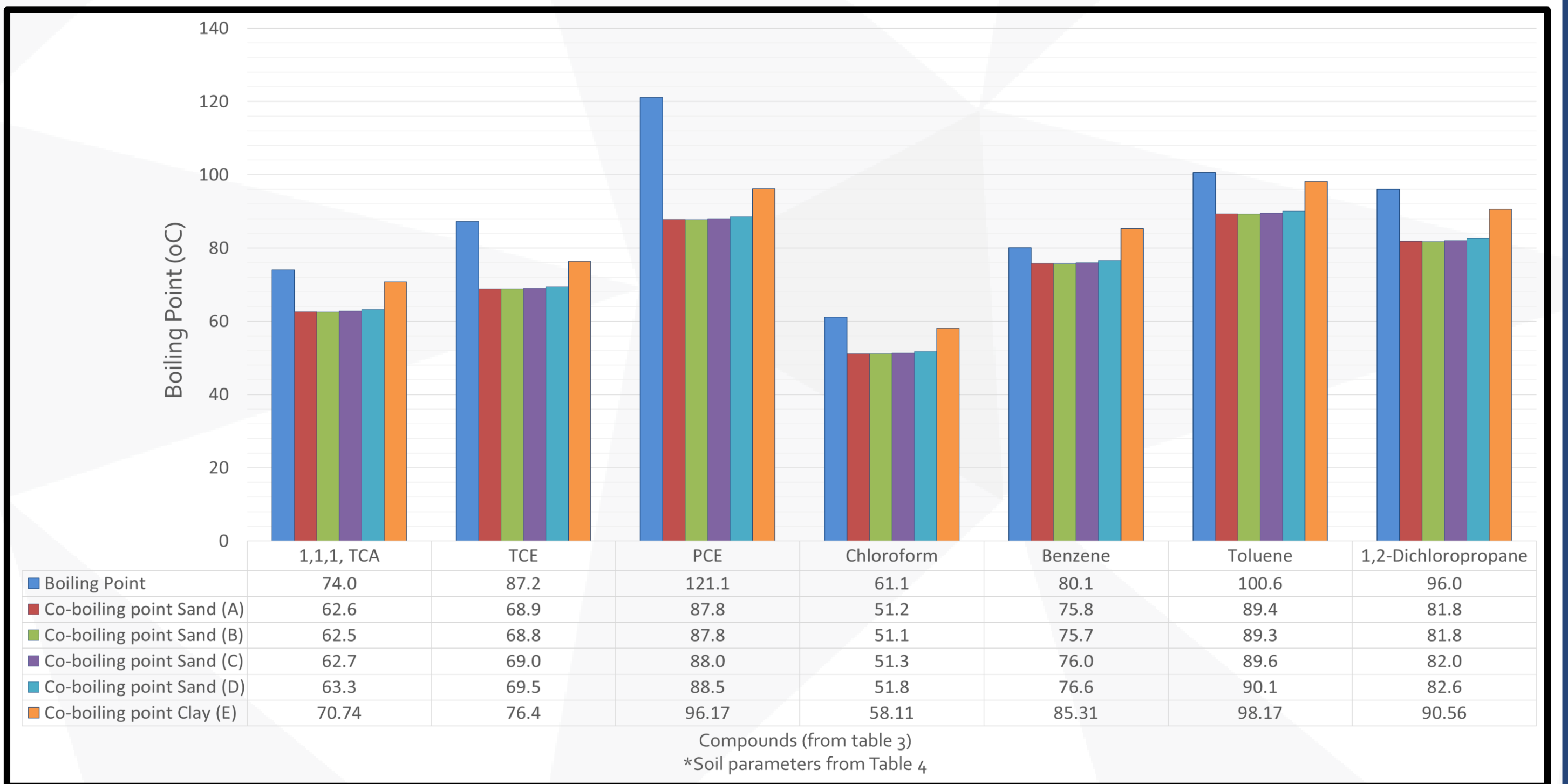


Figure 3 : Co-boiling point calculations for a each compound (Table 3) and each soil parameter (Table 4) at a depth of 10m.

ANALYSIS

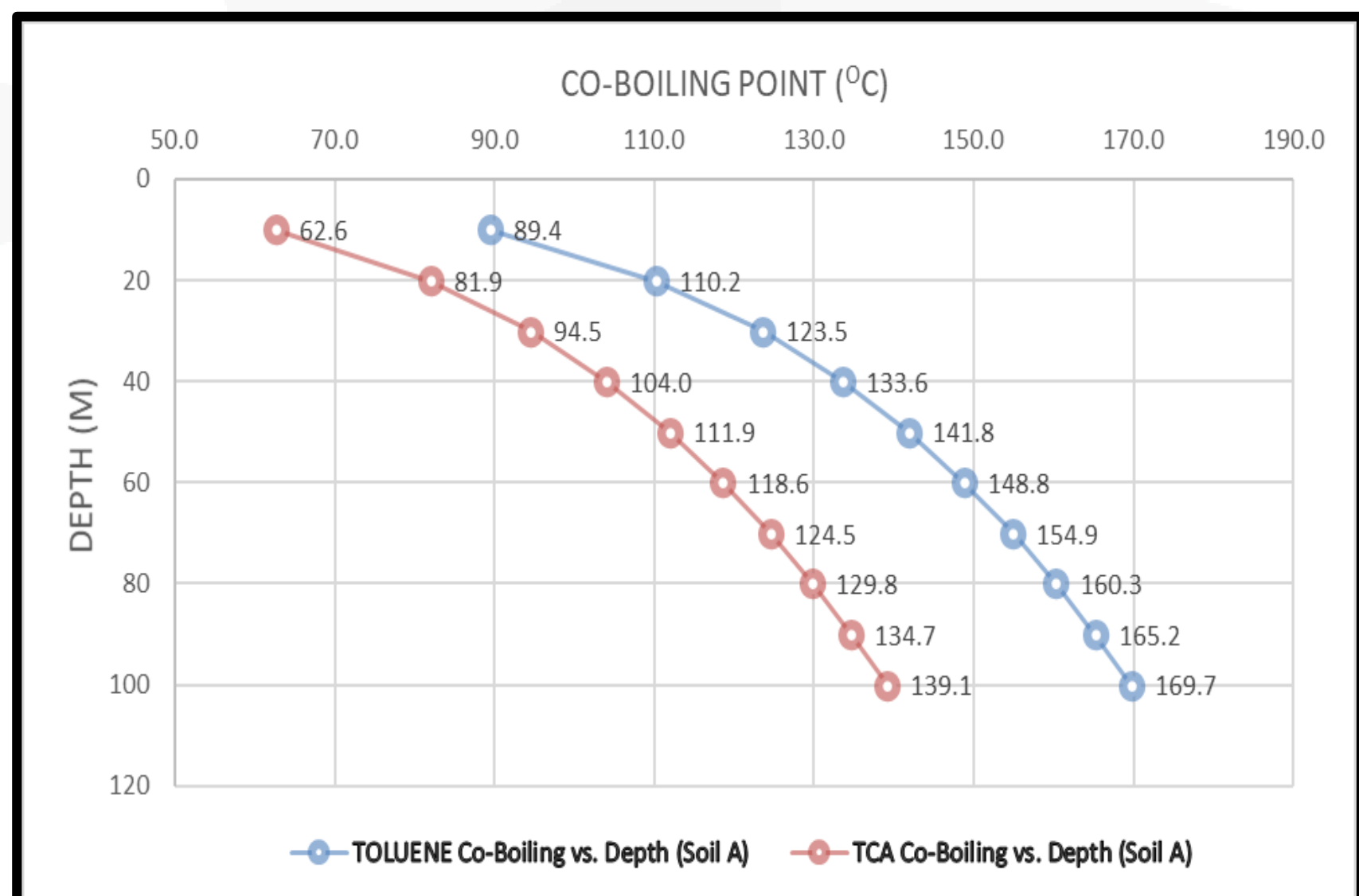


Figure 4. Co-boiling point vs. depth (Soil A), see Table

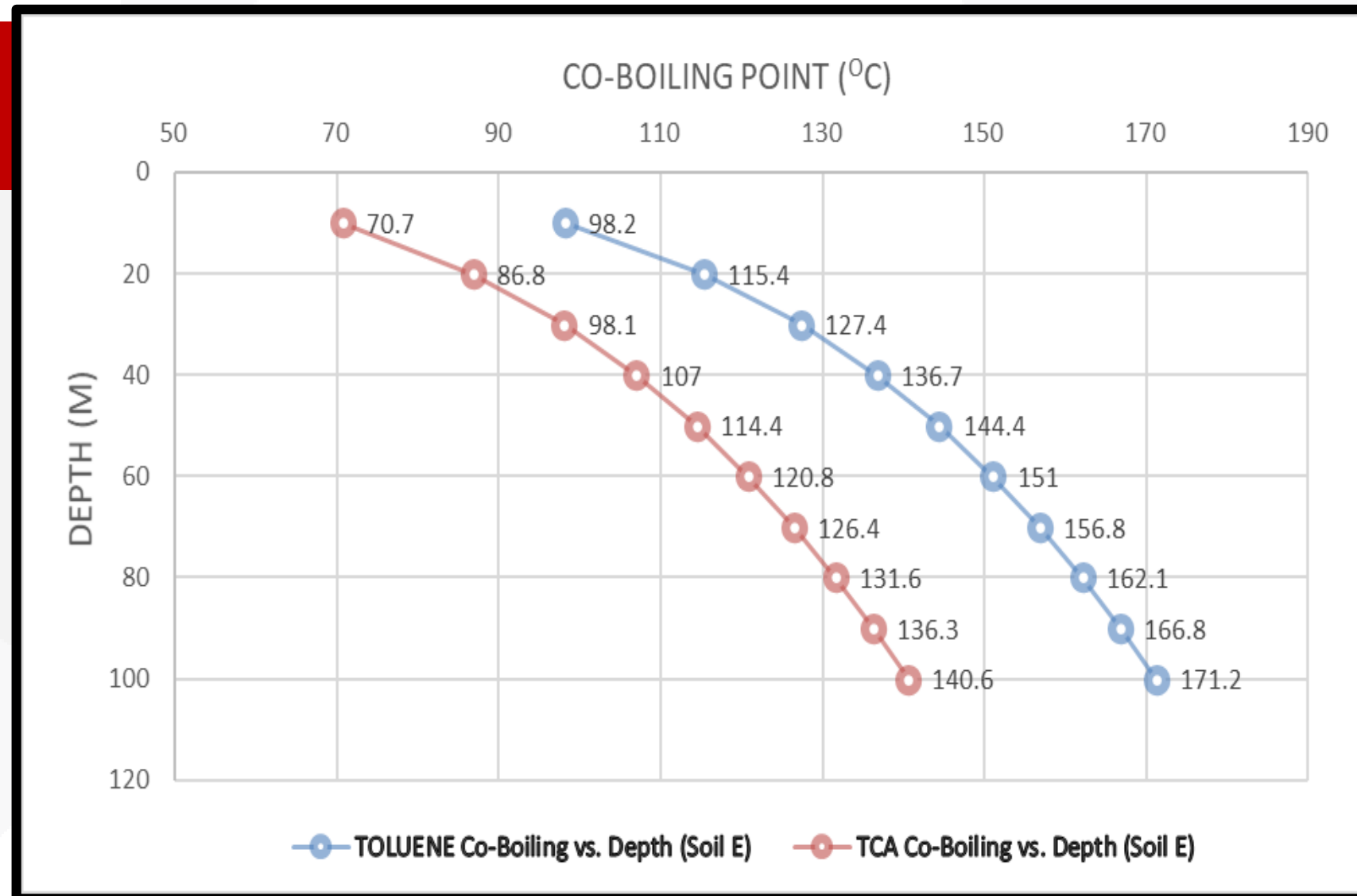


Figure 5. Co-boiling point vs. depth (Soil E), see Table

low entry pressure (e.g., clay), in which case, the co-boiling point was higher in order to overcome the entry pressure. This research shows that thermal methods requiring volatilization as a means of remediation will be less effective when contamination is located deep in the subsurface and in low permeability (i.e., clay) soils.

FUTURE WORK

Future work will include an expansion of the compounds examined as well as migrating of the solution onto a more workable platform (i.e. python). The overall goal of the project is to establish a database of compounds and soil types that would allow for the co-boiling point to be estimated using an equilibrium based approach. This would allow for practitioners to estimate their temperature required to initialize volatilization of groundwater contaminants.

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