

Effects of organic carbon content on *in situ* remediation time using steam–air injection

W. Awandu  ^{a,*} and O. Trötschler  ^b

^a Department of Civil and Structural Engineering, Masinde Muliro University of Science and Technology, P.O. BOX 190 - 50100, Kakamega – Webuye Road, Kakamega, Kenya

^b VEGAS, Universität Stuttgart, Pfaffenwaldring 61, 70569 Stuttgart, Germany

*Corresponding author. E-mail: awandu.willis@gmail.com

 WA, 0000-0003-3075-5298; OT, 0000-0002-2362-1956

ABSTRACT

Groundwater contamination by chlorinated hydrocarbons (CHC) is a common phenomenon that poses health risks to both humans and animals. These halogenated hydrocarbons infiltrate into the soil matrices and form pools at the bottoms of the aquifers thus contaminating the groundwater sources. Thermally enhanced soil vapour extraction (TSVE) using steam–air injection has gained popularity as an alternative technique to remediate the saturated and vadose source zones contaminated with CHC. This technique has been successfully applied in the remediation of contaminated sites (brownfields, industrial sites) and groundwater. However, the presence of organic carbon (OC) contents within the soil matrices has not been intensively studied. This paper, therefore, intends to contribute toward increasing the understanding of the effects of OC on the remediation time using TSVE. A 2-D flume experimental model was conducted in VEGAS laboratory using coarse sand, fine sand and silty soil with 0, 1 and 2% addition of the activated carbon as OC to investigate the desorption time of PCE and TCE as CHC during TSVE extraction using steam–air injection. 100 kg of soil mixed with the activated carbon was treated with 50 g TCE and 50 g PCE and then remediated using TSVE. The remediation times were recorded and recovered CHC was documented. It was discovered that the presence of OC enhanced the adsorption of the CHC onto the soil matrices thereby increasing the time required for the complete remediation of the contaminant from the soil. An increase of OC by 1% resulted in desorption time by a factor of 4–7.

Key words: adsorption, chlorinated hydrocarbon, desorption, organic content, TSVE

HIGHLIGHTS

- Research outcome enhances the potential application of the technology for remediation.
- Use of software to optimize the effective application of the technology.
- Increased robustness of the usability of the technology in ensuring high efficiency.
- The research outcome enhances a better understanding of the parameters and their influence on the technology.
- The outcome significantly improves subsurface water management.

INTRODUCTION

Contamination with chlorinated hydrocarbons (CHC) in the saturated and vadose zones threatens the groundwater sources. Countries such as Germany have instituted state laws that advocate for contaminated sites clean-up. The German law ([Bundes-Bodenschutzgesetz 1998](#)) (BBodSchG) has outlined an obligation required for the site owners to remediate the sites if contamination to the groundwater is detected.

The volatile halogenated hydrocarbons, the organic compounds containing atoms such as fluoride, bromide, iodide and chloride, besides carbon and hydrogen, have been extensively used as cleaning agents, solvents (e.g., PCE or TCE), refrigerants, propellants and fire-extinguishing agents ([Hiester *et al.* 2012](#)). Since they are denser than water, immiscible with water (NAPL) and with low viscosity, they mostly form pools that may sink to the bottom of the aquifer, i.e., to the aquitard by gravity. These contaminants' phase distributes dropwise along its flow path in the saturated and unsaturated zone, leading to massive remediation relevant groundwater pollution. Most of the halogenated hydrocarbons are classified as harmful to humans, since they are carcinogenic or mutant or toxic to aquatic organisms ([Gestis-Stoffdatenbank 2011](#)).

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The remediation technique to be employed entirely depends on the type of contaminants present in the soil, contaminant location, the soil's properties (physical and chemical) and the operational conditions (Albergaria *et al.* 2012). Several remediation techniques, such as adsorptive wells (Bortone *et al.* 2019), electrical resistance heating (Geng *et al.* 2021), use of nanoparticles (Idrees *et al.* 2021) and oxidation techniques using the microscale zero-valent iron (mZVI) (Tang *et al.* 2021), have been successfully employed in the remediation process of groundwater with excellent performance realized. However, with the use of some of the techniques, for example mZVI, the aging behaviour of injected mZVI particles has been reported to limit the widespread application in groundwater projects (Tang *et al.* 2021), as the corrosion precipitates greatly affects its effectiveness with time.

Similarly, the application of soil vapour extraction (SVE) has been intensively applied in the USA for the remediation process of about 23% of the projects (USEPA 2010). This technique employs creating vacuum in the soil, thereby enhancing the airflow through the soil matrix that transports the contaminants to the extraction wells and air treatment units before their release in the atmosphere (Suthersan 1999). Thermally enhanced SVE (TSVE) using steam–air injection has gained popularity as an alternative technique (Trötschler & Weber 2003) over traditional techniques such as pump and treat (Ochs *et al.* 2003) to remediate the saturated and vadose source zones contaminated with CHC. The application of thermally enhanced *in situ* remediation has been summarized in a Task Centre, UFZ Leipzig guideline (Hiester *et al.* 2012).

Thermal *in situ* remediation (TISR) has been emphasized on the dense non-aqueous phase liquid (DNAPL) source zones of the perchloroethylene (PCE) and trichloroethylene (TCE) in the last decades, which has been based on the convective heat transport (Trötschler *et al.* 2019), that is dominated by the flow and expansion of the steam as an energy source. A mixture of steam–air is injected into the subsurface to heat up the soil to a target temperature also known as co-boiling temperature ranging between 85 and 100 °C. At the contaminant and pressure-dependent co-boiling temperature, the pore-water (steam) and the contaminants are boiling simultaneously and the contaminants are vaporized and extracted by an SVE system to the surface. The injected air provides the transport agent of the gaseous contaminants toward the 'hot' SVE wells (Figure 1).

Depending on the site characteristics, the unsaturated zones with unconsolidated soils and finely fractured bedrocks with good to moderate permeability of a k_f value range of 10^{-2} – 5×10^{-5} m/s (gravel, sand, coarse silty soils), the injected steam condenses in the cold soil matrix and releases its heat enthalpy (latent heat of vaporization) to the soil matrix (Trötschler *et al.* 2009). The steam–air mixture causes the organic contaminant to mobilize in front of the steam front by evaporation and condensation processes. Once the concentrations are too high, a liquid organic phase is mobilized and driven ahead

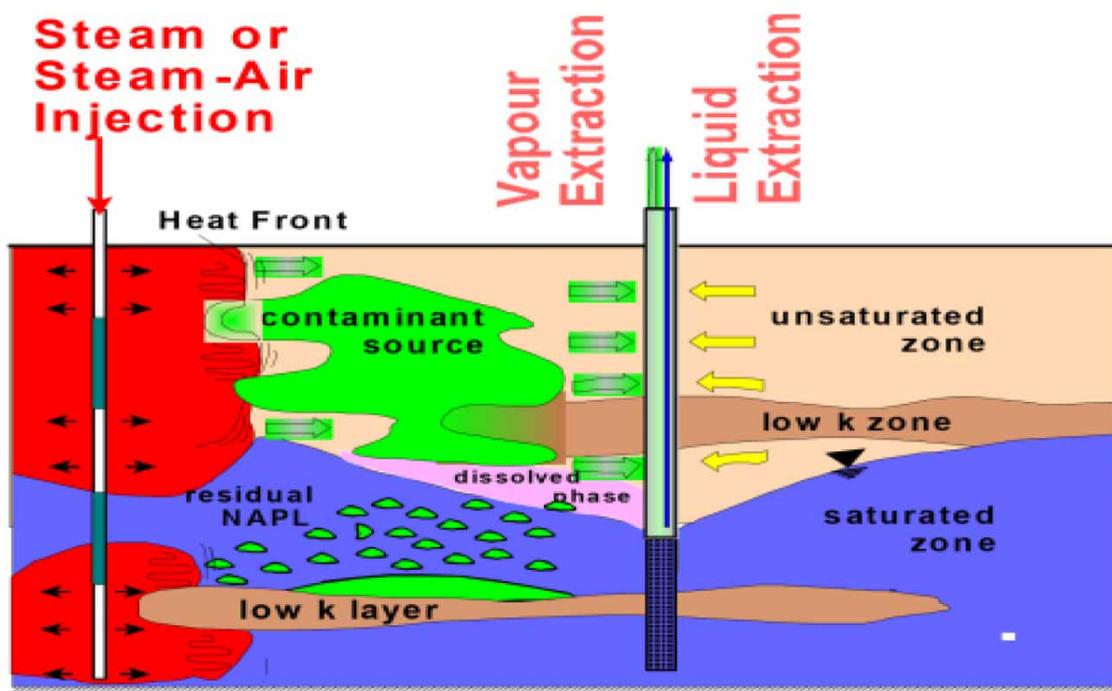


Figure 1 | Steam–air injection into the unsaturated and saturated zone (Koschitzky 2007).

of the steam front. This process requires the extraction of the water solved CHC by a groundwater pumping system, and in cases of solely using steam, a free phase extraction system (Trötschler & Weber 2003) is required. The condensation of the DNAPL phase is prevented from migrating downward, as the air is co-injected with steam. The co-injected air carries the vaporized DNAPL within the steamed zone and purges (liquid) (D)NAPL ahead of the continuously expanding steam front (Betz *et al.* 1998; Schmidt *et al.* 1998; Hiester *et al.* 2012). The hot contaminant–air mixture is transported toward the extraction wells.

Steam–air enhanced remediation improves the remediation process by increasing the vapour pressure of the volatile and the semi-volatile compounds with temperature. Heating of subsurface from 20 to 100 °C increases the vapour pressure of the contaminant by 10–30 fold (Udell 1996; Poppendieck *et al.* 1999). It is evident from field experience that utilized conventional SVE sites that compounds with vapour pressures greater than approximately 70 Pa at 25 °C are effectively removed by SVE (Goldfarb *et al.* 1994; Rathfelder *et al.* 1995). The vapour pressure saturation of straight-chain hydrocarbons up to C₂₀ can be predicted using the Antonine equation that gives the relationship between the vapour pressure and the temperature of a pure component as shown in the following equation (Equation (1)):

$$\ln(P_o) = -\frac{B}{T+C} + A \quad (1)$$

where *A*, *B* and *C* define the empirical parameters of the pure component, *T* is the temperature in °C and *P_o* is the vapour pressure. The adsorption coefficients of the organic hydrocarbons get reduced by heating and thus release the contaminants from the soil matrix (Heron *et al.* 1998b; Sleep & McClure 2001). Heating also causes a reduction in the viscosity of the NAPLs. The viscosity values of TCE and other chlorinated solvents are typically reduced by a factor of two (Heron *et al.* 1998a). Steam heating of subsurface soils enhances floating and displacement of DNAPLs by reducing the density aiding in its recovery as an LNAPL (Davis 2002). The NAPLs – water interfacial tensions for certain NAPLs – are lowered to two-folds thereby enhancing their hydraulic removal (Davis 1997; She & Sleep 1998). The elevated temperature of the subsurface also increases the solubility of the organic contaminants, and the dissolution rates are enhanced by a factor of 2–5 leading to faster NAPL dissolution and removal (Imhoff *et al.* 1997; Sleep & Ma 1997).

The presence of organic carbon (OC) in soils increases the adsorption of the CHC onto the soil matrices thereby decreasing the thermal desorption rates. The adsorption of the contaminant on the natural soils and sediments entirely depends on the presence of the organic matter as an adsorbent which is responsible for the sorption capacity of the volatile OC (VOC) in the soils (Grasso 1993). The soil OC water partition coefficient (*K_{oc}*) enhances the sorption of contaminants with the OC. The strong adsorption kinetics is further enhanced by the carbon concentration in the soil (*f_{oc}*) and the solid–liquid partition coefficient *K_d* (Karickhoff & Morris 1985; Brusseau *et al.* 1990). The sorption of contaminants decreases their mobility and volatility as well as extraction availability. The increasing amount of organic matter content in the soil directly influences their sorption capacity and thus leads to reduced remediation process efficiency (Maria da Conceição *et al.* 2006).

The dependency of the CHC-desorption rates during steam–air injection (DLI) in 2-D remediation experiments was defined for variable soil types (e.g., sand, gravel, and silt) and OC contents of 1 and 2%.

EXPERIMENTAL SETUP AND DESCRIPTION

The laboratory 2-D Flume (box with glass) experiments were performed at VEGAS – Institute of Subsurface Remediation at the University of Stuttgart – Germany (Figure 2).

Materials

The used PCE and TCE both obtained from Sigma-Aldrich Chemie GmbH standards were of analytical grade quality and used without further purification requirements. The chemicals (contaminants) were then dyed with Sudan IV for visibility during injection into the soil and decontamination process.

The activated carbon 8–20 mesh was obtained from Riedl. The coarse and fine sand were supplied by Dorfner GmbH, and the silty soil was obtained from the Horkheim Island field in Germany.

Apparatus

A gas chromatograph–photoionization detector (GC–PID) by meta Messtechnische Systeme, Dresden, Germany was used for the quantification of the contaminants in the extracted hot soil vapour using the external standard calibration method. The

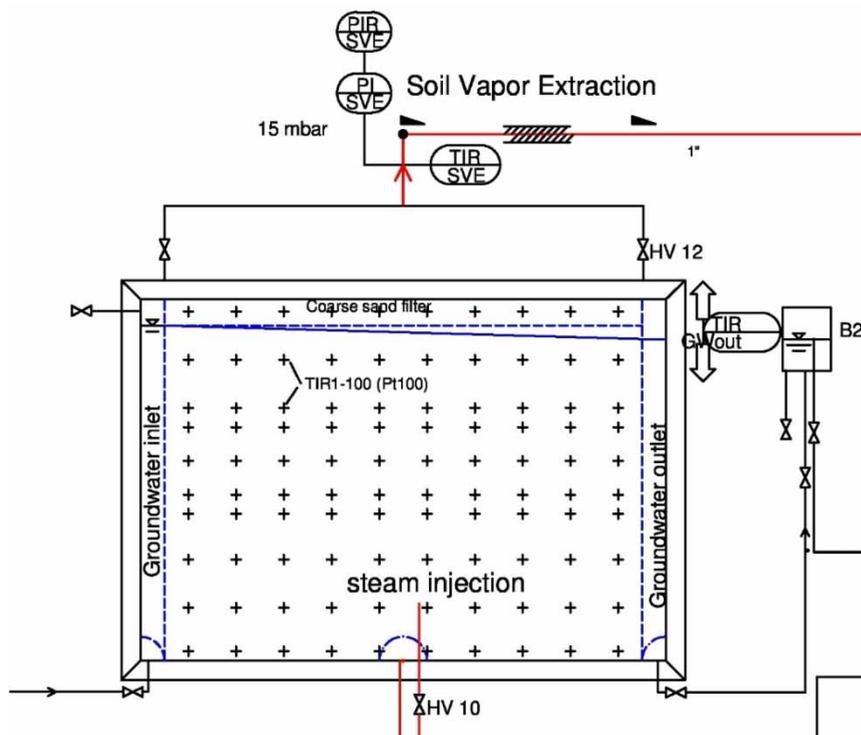


Figure 2 | Pt100 temperature sensor arrangement on the 2-D Flume Box.

device has a detection limit of 0.01 mg/m^3 . The injector and the detector were set at $200 \text{ }^\circ\text{C}$ throughout the analysis. The chromatographic data were recorded using the metaControl software that provides the raw data saving, graphical visualization and data evaluation via EXCEL – Format, etc. The set time for the detection of the contaminant was set for every 6 min.

A stainless steel 2-D flume with the dimensions of $1,100 \times 740 \times 85 \text{ mm}$ (AISI 316 Ti (1.4571)) with the front face covered with a 12 mm borofloat glass for process visualization was used. The flume was equipped with 100Nos. Pt100 temperature sensors (10 rows \times 10 columns) with an accuracy of $0.1 \text{ }^\circ\text{C}$ and a temperature range of -40 to $+125 \text{ }^\circ\text{C}$ located at the back of the flume in the target zone in a 5 cm regular spacing to monitor the heat distribution and to control the remediation process. The flume was insulated to simulate the heat losses comparable to a cylindrical setup as in nature. During brief periods, the front insulation material was taken off to enable IR spectral as well as spectral photography. The infra-red camera was also used to define and visualize the heat distribution in the flume. The IR camera (VARIOSCAN; Infratec – by Jenoptic Laser, Optik Systeme GmbH; operated at a wavelength range of $8\text{--}12 \text{ }\mu\text{m}$ and a temperature measuring range of -40 to $+1,200 \text{ }^\circ\text{C}$.

Soil preparation

100 kg of sandy (GEBA – well-sorted coarse sand and DORSILIT 2500 – a milled quartz sand) and silty soil (Loess, Horkheim Island, Germany) were used, varying the organic matter content. The soils were thoroughly mixed dry with different contents of 1–2% w/w of the activated carbon powder and well packed in layers inside the flume. For the silty soil, the lower portion of the flume was first filled with fine sand to a depth of 200 mm, since fine silt particles would block the steam injection well. The three soil types were used in their pure state without adding activated carbon; the second experimental run was done by treating the soils with 1% w/w of the activated carbon and the last run of experiment was done using 2% w/w of the activated carbon. The coarse and fine sand were used three times except for the silty soil which was utilized in its natural state and by treating it with 1% w/w of the activated carbon. This was because of the breakdown of the steam generator and the time-lapse for the thesis experiment. The soils were slightly moistened during filling into the flume. Each soil mixture was filled into the flume layer by layer and compressed using a steel plate (proctor hammer). The properties (volume/mass) of the soils were recorded. 50 g TCE and 50 g PCE as CHC were later infiltrated as contaminants of the source zone for the TISR after the flume was water-saturated.

Soil vapour extraction

The water content of the soil was not considered, since thermal enhancement of the SVE would overcome the shortcomings. After introducing the controlled amount of the contaminant into the soil, the setup was allowed to attain equilibrium. The groundwater inflow and outflow valves were then closed and the setup left for about 1 week for the contaminant to dissolve and distribute into the system. Cold SVE was run and the contaminant vaporized monitored and analysed using the metaControl software for analysis.

Steam was generated using a 40-kW steam generator and injected into the flume through the central steam port at the bottom of the flume for a typical rate of 2 kW of power, approximately 3 kg/h of steam. The steam flow was adjusted accordingly using a steam valve (pressure constant). The mass flux was measured by a variable area flowmeter for steam. The compressed air flow was measured using another area flowmeter for air and added to the steam flow prior to the injection. The steam/air mass ratio was set to 10/1.

The contaminant retention/desorption from the soil was regularly analysed by a GC-PID (meta Messtechnische Systeme, Dresden, Germany) to determine the mass removal rates in the extracted hot soil vapour. The remediation steps were determined from the measurement of the heat and mass fluxes, temperatures and pressures of the applied remediation and treatment installation. The contaminant and water vapour in the effluent air were passed through the activated carbon in the tank before being released into the atmosphere. The remediation process was deemed finished when the PCE and TCE concentrations in the gas phases were below 20 mg/m³ at temperatures of >80 °C (Tables 1 and 2).

RESULTS AND DISCUSSION

Heat propagation and distribution

The heat distribution and contaminant mobilization were observed during the various stages of the experiment using different types of soils. The temperature plots were achieved using the Tecplot RS 2018 Release 1. Infra-red camera (VARIOSCAN, Infratec) was also used at different time intervals to visualize the heat propagation and distribution during the remediation process. The steam dispersion and influence on the contaminant at different times were captured using the digital camera.

For the coarse and fine sand, the steam propagated from the injection point through convectional current, rising upward and outward thereby losing its enthalpy to the surrounding water molecules. This, in turn, heated up the soil particles and transferred the enthalpy throughout the flume heating up the contaminants. It was observed that as the heat propagation advanced, contaminants visible on the front of the flume were wiped out as seen in the Figure 3 (second row). Further steam injection after the steam breakthrough had no effect on the temperature changes in the flume. However, continued

Table 1 | Properties of different soils (Rosenstiel *et al.* 2011)

Aquifer material	Hydraulic conductivity, K (m/s)	Bulk thermal conductivity, λ (W/m/K)	Grain size, d_{50} (mm)	Porosity (n)
Coarse sand	1×10^{-3}	1.7–5	0.8	0.43
Fine sand	5×10^{-4}	1.7–5	0.14	0.40
Silt (loess)	3×10^{-5}	0.9–2.3	0.02	0.33

Table 2 | Properties of PCE and TCE (Allen & Torres 2011)

Description	TCE	PCE
Chemical formula	C ₂ HCl ₃	C ₂ Cl ₄
Density (g/cm ³)	1.465	1.6227
Solubility in water at 25 °C (mg/l)	1,100	287
Carbon adsorption coefficient (K_{oc})	86	200
Vapour pressure at 25 °C (Pa)	9,865	2,600
Henry's law constant (H^{cc})	0.397	0.928

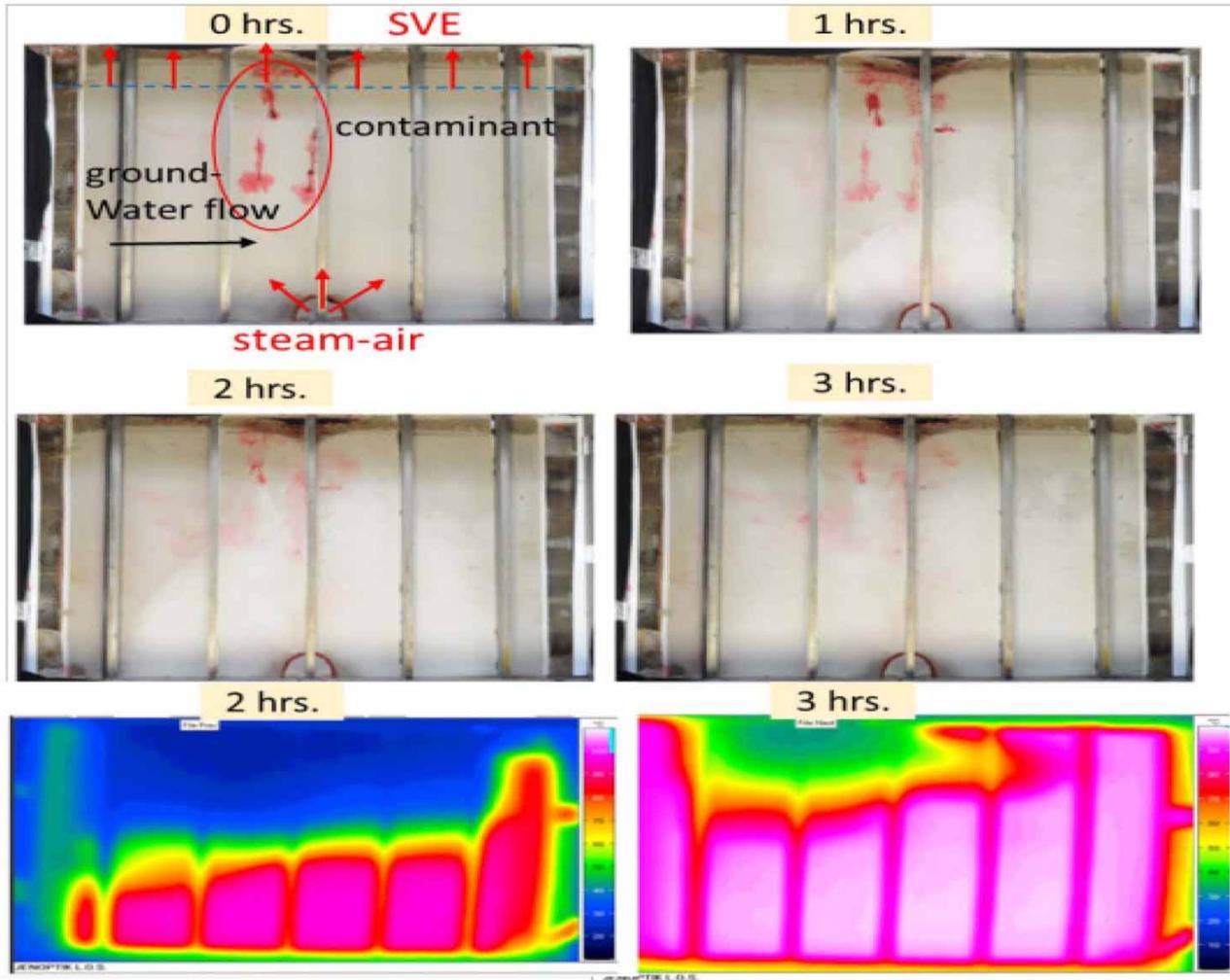


Figure 3 | 2-D remediation process in fine sand (2-D model): upper rows showing the contaminant distribution (red colored, Sudan III), lower row showing the infra-red measured heat distribution inside the flume. Please refer to the online version of this paper to see this figure in colour: <http://dx.doi.org/10.2166/aqua.2021.108>.

steam supply enhanced the removal of the contaminants. Within the zone depending on the adsorption of the contaminant and the temperature of the steam within the zone, the removal times varied accordingly.

Steam injection and heat propagation advanced perfectly in the lower fine sand layer for the silty soil remediation for around 3 h. At the silt layer sandwich, the heat conduction was low and the advective convection became pronounced to transfer heat through the silty soil. There was heat dispersion due to the mixing of the liquid thereby creating cold spots within the flume. Silty soil has low hydraulic conductivity and thus necessitates the use of thermal conductive heating for a satisfactory remediation process in soils with low hydraulic conductivity (Färber 1997).

The steam injection pressures for sandy and silty soils were maintained at 1.5 and 1.2 bars, respectively. This injection pressure depends on the effective permeability of the soil to prevent cracking of the soil thereby causing preferential flow paths in the soil (Trötschler & Weber 2003) that would have ineffective effects on the remediation process. The injection pressure is calculated based on a cylindrical expansion of the steam from the injection well for a stationary flow:

$$P_{inj} - P_o = \frac{f_{st} * \nu * \ln\left(\frac{r}{r_o}\right)}{2\pi * h * k_o * k_{r,g}} \quad (2)$$

where P_{inj} is the steam injection pressure (Pa), P_o is the atmospheric pressure (Pa), f_{st} is the steam injection rate (kg/s), ν is the kinematic viscosity of steam ($m^2 s^{-1}$), r is the radius of heated area around the steam injection well (m), r_o is the radius

of injection well, h is the thickness of heated zone (m), K_o is the permeability of the soil (m/s) and $k_{r,g}$ is the relative permeability (-) (Figure 3).

Energy balance

The energy balance of the remediation process in the flume was defined from the relevant temperature distribution measurements. From previous experiments performed, the energy components were derived from the steam injected, groundwater flows, energy losses to the surrounding, condensate energy and the SVE energy (Trötschler *et al.* 2004). The total energy input was provided by the energy released during steam condensation (Δh_v) plus the enthalpy of water at 100 °C.

$$Q_{in} = m_{si}(\Delta h_v + C_{p,w}(T_x - T_i)) \quad (3)$$

The output energy of the individual component of the SVE is defined by the following equations:

$$Q_{out} = m_{SVE}(h_w(T_{x,w}) + h_a(T_{x,a})) \quad (4)$$

where m_{SVE} is the total mass of the extracted soil vapour, h_w and h_a are the enthalpy of water and air, respectively, and $T_{x,w}$ and $T_{x,a}$ are the temperature differences of water and air, respectively. Additionally, groundwater inflow and outflow energy content and that of the condensate water in the FSL1 extracted during the soil vapour extraction are defined by the following equation:

$$Q_{out} = ((m_{GW,out} * C_{p,w} * \Delta T_{GW,out}) - (m_{GW,in} * C_{p,w} * \Delta T_{GW,in})) + (m_{c-UZ} * C_{p,w} * \Delta T_{c-UZ}) \quad (5)$$

where $C_{p,w}$ denotes the specific heat capacity of water, m_{c-UZ} mass of the condensate and the respective changes in temperature.

During the experiment, part of the total input energy from the injected steam was useful in the remediation processes in the flume which is termed as stored energy in this experiment. The rest of the energy component served as the energy output which was lost in the form of soil vapour extraction, groundwater flows and losses to the environment. The energy component is graphically presented as shown in Figure 4.

Thermally enhanced SVE

The experiments were conducted with the aim of evaluating the influence of OC contents of the soil on the remediation time when thermally enhanced SVE is applied for *in situ* remediation processes. The complete remediation was defined as the time that the concentration of the contaminants in the gas phase was below 20 mg/m³ CHC.

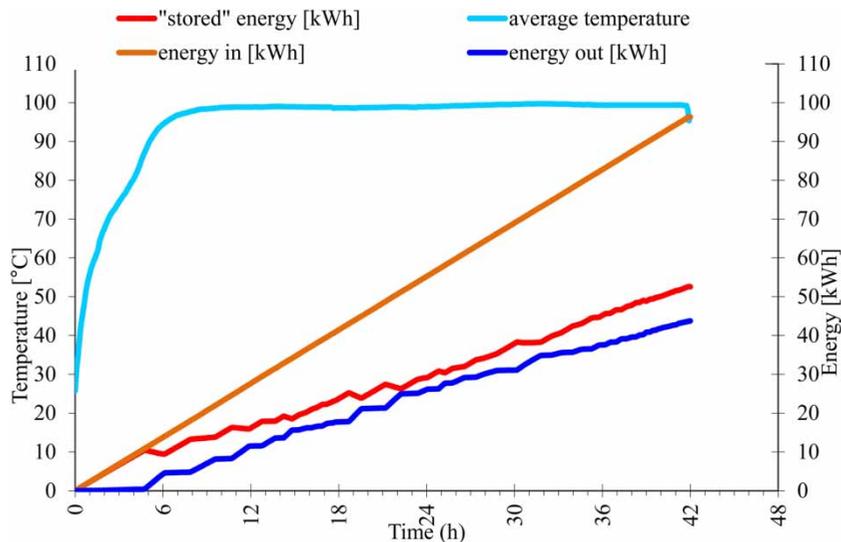


Figure 4 | Input, stored and output energy of the system.

Three sets of experiments were run for the fine and coarse sand having 0–2% activated carbon. The pure sand had initial OC content of approximately 0.001% and, therefore, was considered to be pure. Two sets of experiments were run for the silty soil with 0–1% of activated OC. The silty soil had a natural organic matter content of 8% and thus at 0% activated carbon content, and the natural organic matter played a key role in enhancing the adsorption capacity of the contaminants.

A mixture of steam–air was injected from the bottom of the flume to heat up the soil to a co-boiling temperature of 85 °C and beyond 100 °C. At 85 °C, the co-boiling of the contaminants and water begins. The temperature rises as the contaminants are removed during the ongoing heating. The steam propagates and extends, so the removal of the contaminants begins. The added air provided the transport of the gaseous contaminants toward the upper and laterally located (hot) SVE wells. Due to the air component, the desorption started shortly after starting the injection except for soils containing f_{oc} , when removal started and ended with a retardation factor (R).

The remediation was pursued in the saturated zone. During the steam front propagation, the adsorbed contaminants were desorbed from the soil and solved in the ‘hot’ aqueous phase of the condensed steam and the groundwater (K_{ow}/K_{oc} approach). The hot air sparged the hot water and transported (solves) the contaminants (Henry approach) (Reisinger & Grathwohl 1996) (Figure 5 and Table 3).

The mass of the total contaminant (TCE and PCE, combined), individual masses of PCE & TCE were calculated based on the results obtained from the contaminant concentrations as well as the SVE rate (m^3/h). These total masses were obtained by the expression:

$$\sum C_t \Delta_t Q \tag{6}$$

where C_t is the measured concentration of the contaminant at time t , Δ_t denotes the change in time and Q denotes the air flow rate at the blower. The concentration values of contaminants below 20 mg/m^3 (at temperatures of $>80 \text{ }^\circ\text{C}$) were indicative of the completion of the remediation and recovery of the contaminant. The time of complete remediation was therefore derived from that instance.

Table 3 outlines the different soils type with different content of the activated carbon as organic matter content, the measured masses of contaminants considering their concentrations in the gaseous phase after remediation, the process efficiency (η), the time to reach the remediation completion limit of the pollutant and the remediation time.

From the data presented in Table 3, it can be observed that an increase in the organic content increased the remediation time. For instance, at 1% organic content in fine and coarse sand, the remediation time almost doubled. Since the silt soil had its natural organic content of 8%, the initial remediation time tripled that of fine and coarse sand without additional activated

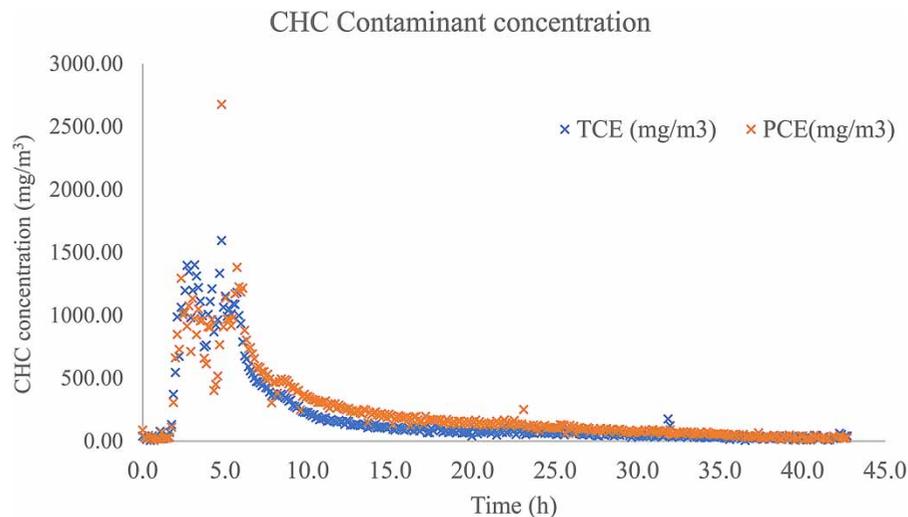


Figure 5 | CHC concentration in gaseous phase for coarse sand with 2% activated carbon.

Table 3 | SVE experiments' results for the various components: organic content, contaminant mass in gaseous phase, remediation efficiency and the remediation time

Soil type	Activated carbon content (%)	Mass of CHC removed in gaseous phase (g)	Remediation efficiency, η (%)	Remediation time, t_{rem} (h) CHC	t_{rem} (h) TCE	t_{rem} (h) PCE
Coarse sand	0	84	93.3	3.15	2.92	3.15
	1	84	93.3	10.5	7.5	10.5
	2	83	92.2	21.5	16	21.5
Fine sand	0	88	97.7	3	2.68	3.03
	1	88.5	98.3	7	5.1	7
	2	87	96.6	20	11	20
Silt	0	46	51.1	9	–	–
	1	88	97.7	38	–	–
	2	–	–	–	–	–

carbon content. This can be attributed to the fact that an increase in organic content increases the sorption capacity of the contaminant thereby increasing the time for remediation (Maria da Conceição *et al.* 2006).

A mathematical fitting was observed between the remediation time and the presence of organic content for the fine and coarse sand (see Figure 6(a) and 6(b)). A good correlation coefficient ($R^2 = 0.987$) perfectly fitted the experiment giving a linear equation to preview the remediation time of the soils with contents of organic matter (OC) in the coarse sandy soil:

$$t_{rem} = 2.5417 + 9.175 * (OC) \quad (7)$$

Similarly, a good correlation coefficient ($R^2 = 0.9978$) perfectly fitted the experiment of fine sand giving an exponential equation to preview the remediation time of the fine sand with organic contents:

$$t_{rem} = 2.9004e^{0.9486(OC)} \quad (8)$$

The mathematical model for silt soil was not performed since there existed a pair of data that would not depict the real situation.

The remediation efficiency for natural silt without activated carbon was low (51%). This can be attributed to the breakdown of the steam generator which lasted for 2 weeks to be repaired. The efficiency was achieved via cold SVE which remained in operations, and the rest of the contaminant was lost via the groundwater outflow. For the second experiment with silt soil having an additional 1% of the activated carbon, the remediation time increased from 9 h for 0% activated carbon to 38 h (close to 2 days) of continuous steam injection. Since silt soil is less permeable, it slowed down the flow of the gaseous media. Additionally, the higher percentage of naturally occurring organic matter has a higher surface area for adsorption of the contaminant hence requiring longer heating for the desorption kinetics to set in.

The removal rates of the PCE and TCE were observed to occur differently. The removal rate of TCE occurred faster as compared to the complete removal of PCE. Based on previous laboratory experiments on desorption rates, it was observed that desorption rates decreased with increasing sorptivity (increasing K_{ow} – decreasing water solubility) of the contaminants (Karickhoff & Morris 1985; Brusseau *et al.* 1990). TCE has an octanol/water partition coefficient (K_{ow}) of 2.42, while PCE has a coefficient of 2.88. It has been shown from the laboratory experiments that the desorption rates decreased with the increasing sorptivity (increasing K_{ow} – decreasing water solubility) of the contaminants (Karickhoff & Morris 1985; Brusseau *et al.* 1990). So, PCE is stronger and greatly adsorbed on the OC. The Henry coefficient H_{cc} of TCE is 0.392 (25 °C) and that of PCE is 0.723 (25 °C) but the aqueous solubility of TCE (1,100 mg/L, 25 °C) is approximately 7× higher than that of PCE (151 mg/L, 25 °C). So, PCE will remain longer in the aqueous phase compared to TCE. The slower removal of the contaminant mixture resulted from PCE having a higher hydrophobic sorption of the chemical onto the organic phase of the porous media. Generally, the retardation of TCE is 20–40% lower than that of PCE; similar factors were found during the full-scale remediation.

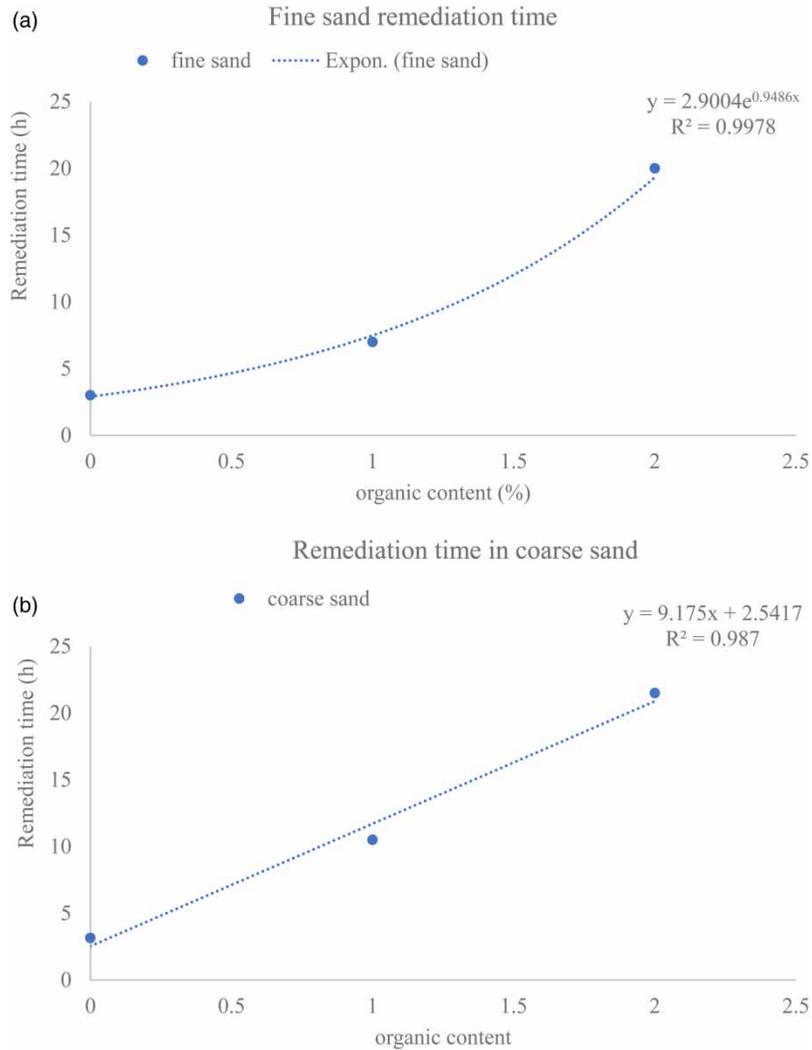


Figure 6 | (a) Comparison of the remediation times of fine sand through the mathematical fitting of experimental results. (b) Comparison of the remediation times of coarse sand through the mathematical fitting of experimental results.

The retardation factor of 1.0 indicates the absence of OC in the soils. A factor that is larger than 1.0 indicates the reduction of the contaminant desorption process. The retardation factor was determined using (Schwarzenbach & Westall 1981) formula after the determination of (K_{oc}), which relates the variation in removal rates of contaminants to their sorptive nature in soils. The retardation factor can be achieved by employing the following equations:

$$\log K_{oc} = 0.72(\log K_{ow}) + 0.5 \tag{9}$$

$$K_{oc} * f_{oc} = K_d \tag{10}$$

$$R = 1 + K_d * \frac{\rho_d}{n} \tag{11}$$

where K_d denotes the sorption distribution coefficient (L/kg), $\log K_{ow}$ denotes the octanol/water partition coefficient (-), $\log K_{oc}$ denotes the OC/water partition coefficient (L/kg) and f_{oc} denotes fraction OC (-). The retardation factor for PCE and TCE for coarse sand with 0–2% of the activated carbon, as shown in Tables 4 and 5, gives a clear indication of the variation in desorption that implies increased remediation time as the organic content increases.

After each set of experiments, new soil material was utilized, and the already remediated soil was safely stored in metallic waste bins that were effectively lined with plastic bags for safe disposal. It was, therefore, not established if the remaining

Table 4 | Retardation factor for coarse sand with 1% activated carbonCoarse sand with $n = 0.43$, $f_{oc} = 1\%$, $\rho_d = 2.65 \text{ g cm}^{-3}$

Desorption CHC	Log K_{ow}	K_{oc}	K_d (L/kg)	R
TCE	2.42	174.7	1.747	1.28
PCE	2.88	374.6	3.746	1.61

Table 5 | Retardation factor for coarse sand with 2% activated carbonCoarse sand with $n = 0.43$, $f_{oc} = 2\%$, $\rho_d = 2.65 \text{ g cm}^{-3}$

Desorption CHC	Log K_{ow}	K_{oc}	K_d (L/kg)	R
CE	2.42	174.7	3.494	22.53
PCE	2.88	374.6	7.492	47.17

amount of contaminant in the already remediated soils had an effect on the sorption capacity of the soils to affect the remediation efficiency.

CONCLUSIONS

The experimental results presented herein show the effectiveness of steam–air injection in the remediation of sites contaminated with volatile and semi-volatile CHC compounds. The TSVE remediation process compared to cold soil vapour extraction methods is more efficient in terms of the remediation time requirement thereby reducing the cost of remediation. The presence of organic contents in the soils enhanced the adsorptive properties of the CHC onto the soil matrices thereby causing longer desorption time. For instance, the use of silt indicated that an additional 1% of the activated carbon required close to 2 days for complete clean-up. Considering a larger volume, the time requirement could have been longer. Whereas complete clean-up time was considered for the overall CHC concentration limit of 20 mg/m^3 , PCE having a higher octanol/water partition coefficient was better adsorbed on the OC thereby remaining longer in the aqueous phase and thus requires longer steam–air injection time to be completely extracted from the soil matrix via hot soil vapour extraction. The laboratory experiment based the investigation on the influence of organic matter (OC content) on the remediation time. However, further investigations on the soil water content could also be considered. Furthermore, the contaminant distribution in the soil and influence of the vapour pressure of the contaminant could be considered in future investigations.

DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

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