

Experimental and theoretical study of combined solvent and steam stripping of 1,2,3,4,5,6-hexachlorocyclohexane (HCH) and mercury from contaminated natural soil

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Abstract

This paper reports on an experimental and theoretical study of the combined solvent and steam stripping of contaminated soil. First, feasibility experiments on the bench scale are reported concerning the stripping of soil contaminated with 1,2,3,4,5,6-hexachlorocyclohexane (HCH) and mercury. This natural soil, originating from a contaminated site, was packed and stripped in a glass column. The results of cleaning revealed removal levels to below the detection limits of the contaminants and removal efficiencies of 99.7% for HCH and 97.2% for mercury.

Subsequently, a one-dimensional nonequilibrium model is proposed which describes the unsteady mass transfer between vapors, condensate and solid phases in a column. A perturbation method is employed to obtain an approximate solution of the governing equations for small Merkel number Me (this dimensionless number constitutes the column length times the mass transfer coefficient, divided by the flushing velocity). Application of the model to the experiments performed results in values for the overall mass transfer coefficients, which can be used for future engineering computations.

Furthermore, the model enables the prediction of the initial contaminant level in the soil solely from the measured exit contaminant concentrations in the flushing fluid. A thorough comparison of this prediction with the measured soil concentration (prior to the experiment) yields excellent agreement. The presented model is applicable to any other soil flushing experiment for which $Me \ll 1$.

Keywords: Contaminated soil; Hexachlorocyclohexane; Mercury; Solvent stripping; Steam stripping

1. Introduction

In the past, the insecticide 1,2,3,4,5,6-hexachlorocyclohexane (HCH) has been produced on many different sites and in huge quantities all over the world. Fischer et al. [1] estimate a maximum world production at 200 000 tonnes per year. Nowadays, the production and use of this insecticide have been banned in most countries. Commercial and technical formulations of HCH are comprised of the α , β , γ , δ and ϵ isomers, of which the γ isomer (known as lindane) alone is insecticidal. The β isomer is a minor constituent but is dangerous to the public health, as it is persistent and accumulates through the food chain.

In the Netherlands, the production location at Hengelo (which operated from 1948 until 1952) has become well known because of the soil contamination it has caused. Besides contamination with HCH, this soil has also been contaminated with mercury. The amount of excavated soil in Hengelo amounts to approximately 200 000 tonnes. In the future, there will still be substantial amounts of contaminated soil in the Netherlands; in Hengelo a further 200 000 tonnes. Excavated and stored soil contains mainly the β isomer. High priority has been given to the cleaning of this contaminated soil.

A commercially and technically innovative remediation method is offered by combined solvent and steam stripping, for convenience named two-stage steam stripping. The University of Twente has applied for a patent covering this process [2]. In the first stage, an organic solvent is heated and passed through the soil as vapor. In the soil, which can be packed or stirred in a container, this vapor will condense. The soil is moistened and heated, whereby extraction and vaporization of HCH are promoted. Nonpolar organic solvents will be particularly effective, as HCH is also nonpolar [as is also the case for polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, mineral oil etc.]. In the second stage, steam is passed through the soil in order to remove the solvent and any remaining contaminant. Steam and solvent are separated by condensing and separation of the immiscible water and nonpolar solvent phases.

In the past, considerable attention has been paid to steam stripping of contaminated soil, starting with the patent by Maas [3]. Hilberts [4] and Vreeken and Sman [5] reported the first field experiments. Hunt et al. [6] reviewed the physical processes that trap nonaqueous phase liquids (NAPLs), and steam stripping was proposed as an efficient cleanup strategy. Hunt et al. [7] reported laboratory column experiments with artificially contaminated sand. The experiments were stopped shortly after steam breakthrough, whereby most of the volatile contaminants were already recovered. Udell and Stewart [8] reported further laboratory and field experiments on combined steam stripping and vacuum extraction. Falta et al. [9] developed a three-dimensional finite difference numerical simulator for the displacement of NAPLs, assuming equilibrium between the soil, water, free NAPL and vapor phases. In a subsequent paper, Falta et al. [10] presented one-dimensional steam displacement experiments with sand artificially contaminated with trichloroethylene. Yuan and Udell [11] developed a one-dimensional nonequilibrium model for the distillation of a free hydrocarbon and reported the results of an experiment with sand artificially contaminated with dodecane. The theory agreed with the experimental results, and it was noticed that for a long period after breakthrough a substantial amount of the contaminant was recovered, owing to the relatively

low volatility of dodecane. To the author's knowledge two-stage steam stripping has not yet been examined, either theoretically or experimentally.

In this paper, first, two-stage steam stripping experiments are reported with HCH- and mercury-contaminated natural soil in a packed column. Natural soil is used, as it is far more difficult to remove contaminants from this kind of soil than from artificially contaminated soil. The experiments show that it takes a long time and many pore volumes of flushing (typically 10^4) to remove the contaminants completely. The relatively high vapor flow presents no problem as the viscosity of vapor is low and, consequently, the pressure drop remains small. Moreover, because of the low vapor pressure of HCH, equilibrium between the soil, groundwater and vapor phases cannot be assumed. Accordingly, a simple nonequilibrium model is developed which describes the principal phenomena of the process in the column. Based on the assumption of a small Merkel number Me , an analytical approximation solution for the concentration in the soil and vapor phases is obtained. As two-stage stripping is particularly suited for the removal of NAPLs, the model is applied to the removal of HCH only. The model has been applied to the performed experiments, yielding mass transfer coefficients for the HCH removal during both the solvent stripping and the steam stripping stage.

2. Test setup and treated soil

A setup has been employed that is suited for treating both contaminated soil and water with heated air and/or steam (and other vapors). Here, the attention is restricted to the treatment of soil. Basically, the experimental apparatus consisted of

- a vertically placed thermally insulated glass column with an inner diameter of 51 mm ($A = 20.43 \text{ cm}^2$) and a height of 1 m;
- a steam generator to create solvent vapor in the first stage and steam in the second stage, the delivered pressure being variable to a maximum of 4 bar absolute;
- electrical resistance heating to avoid premature condensation in the supply channels;
- devices to measure pressure, flow and temperature;
- a condenser to condense and separate solvent, water and contaminants.

In Fig. 1 a schematic representation of the set-up is given. The soil is introduced into the test tube and tamped down. During the experiments, to prevent heat loss to the surroundings, approximately 20 mm of insulation was wrapped around the column. Prior to the experiment, the contaminated soil is stirred manually and samples are taken to determine the initial contamination (samples were also taken after the experiment). Subsequently, saturated stripping vapors are injected at the bottom, passed through the column and led away from the exit at the top to the condenser. The condensate was collected from the condenser in one liter bottles for analysis after the experiment.

The treated soil is contaminated with HCH and mercury. It originates from the depot near the town of Beckum, in the Province of Overijssel, The Netherlands. In this depot, about 200,000 tonnes of contaminated soil are stored. The tested soil originates from sector 24, parcel Heideweg, and can be considered to be representative of most of the HCH- and mercury-contaminated soil of the Province of Overijssel.

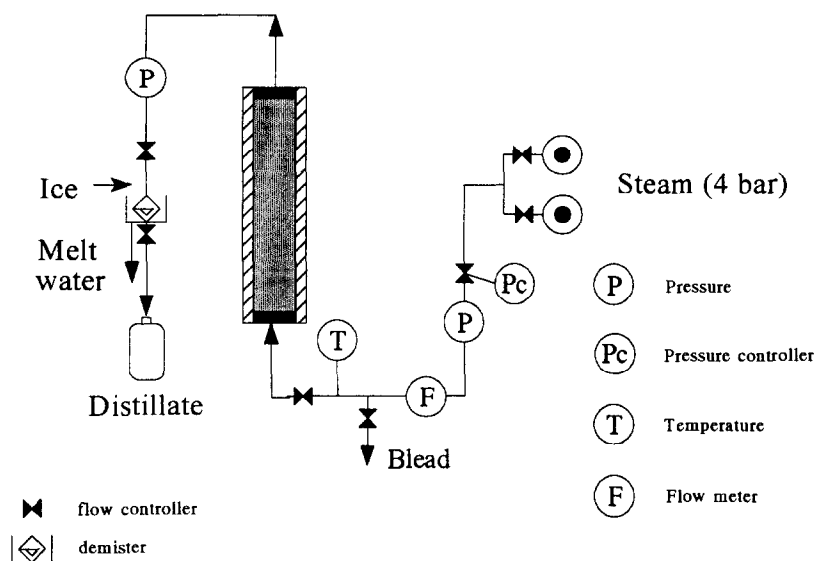


Fig. 1. Schematic representation of test set-up.

The soil was been treated without prior separation (classification) of the fine fraction. In Table 1, the composition of the contaminated soil is given. From this table, it can be seen that 12.2% of the dry weight of the soil consists of a silt and clay fraction.

Several chemical analyses revealed that the soil contains on average $5.15 (\pm 0.35)$ mg kg^{-1} of HCH on a dry weight (dw) basis (about 95% is β -HCH) and $4.1 (\pm 0.5)$ mg kg^{-1} of mercury (dw basis). The initial contamination level is determined and given separately for each experiment. This β -HCH is completely dissolved in the native moisture and sorbed onto the soil. The maximum amount of dissolved and sorbed

Table 1
Composition and particle size distribution of treated soil (sizes in mm)

Dry weight (dw)	90.0% ($C_w = 0.1$ kg water per kg dw)
Organic fraction	2.8% of dw
Particle size distribution	
$x > 1.000$	0.0% of dw
$0.500 < x < 1.000$	8.0% of dw
$0.355 < x < 0.500$	19.3% of dw
$0.250 < x < 0.355$	18.2% of dw
$0.180 < x < 0.250$	14.0% of dw
$0.125 < x < 0.180$	12.2% of dw
$0.090 < x < 0.125$	7.6% of dw
$0.063 < x < 0.090$	5.7% of dw
$0.002 < x < 0.063$	11.9% of dw
$x < 0.002$	0.3% of dw

contaminant per dry weight is presented in Appendix A and amounts to 25 mg kg⁻¹. This value indicates that no free HCH is likely to be present in the soil.

The mercury concentration in the soil (after decomposition with nitric acid and sulfuric acid) and in the condensate (after digestion with potassium permanganate and potassium peroxide sulfate) is obtained by atomic absorption spectrophotometry with a cold vapor technique. The procedure used is that prescribed by Dutch Standards NEN 5768 and NEN 6449. The inaccuracy of the analytical method is estimated to be less than 5%. The HCH concentration in the soil (after extraction with hexane) and the condensate (also after extraction with hexane) is obtained using gas chromatographic indication and mass spectrometry (GC–MS). The procedure is described in the Dutch provisional practical guideline C85-16. The inaccuracy involved in this measurement is estimated as 10%.

3. Stripping experiments

In this section the experimental results are presented. These results give insight into the feasibility of the two-stage steam stripping process. Moreover, the results will be used to validate the presented theory in a subsequent section.

First, experiment A was executed with steam stripping only. The test tube was stacked with about 1 m of contaminated soil and flushed for 8.5 h with steam at an absolute entry pressure of 1.4 bar. In all, 1.5 l of water was used. Laboratory analyses revealed that the HCH and mercury concentrations in the lower part of the contaminated soil had been substantially reduced (Table 2). “Bottom” and “top” correspond to the first centimeters of the bottom and the top soil, respectively. This observation is not surprising, as the steam is still clean here. Higher up in the test column the steam becomes contaminated with HCH and mercury, and consequently the driving force for mass transfer between soil and steam is less. Furthermore, Table 2 reveals that in the upper part of the column the HCH concentration is increased in comparison with the initial concentration. A possible explanation is that HCH is removed from the lower part, transported, and deposited in the upper part.

Next, two-stage experiments were executed. To reduce the flow resistance of the packed soil, the soil was less highly stacked. To this end, the lower three quarters of the test tube were filled with clean sand and the uppermost quarter (25 cm) with contaminated soil. The soil was flushed with an entry pressure of 1.5 bar absolute (this pressure

Table 2
Dry weight (dw) of, and HCH and mercury concentrations in, treated soil before and after treatment (Experiment A)

	dw	HCH(mg kg ⁻¹ dw)	mercury(mg kg ⁻¹ dw)
Before experiment (bottom)	86%	6.51	2.2
After experiment (bottom)	82%	1.46	0.6
Before experiment (top)	86%	4.82	2.9
After experiment (top)	83%	5.62	1.5

Table 3

Dry weight of, and HCH and mercury concentrations in, treated soil before and after treatment (Experiment B)

	dw	HCH(mg kg ⁻¹ dw)	mercury(mg kg ⁻¹ dw)
Before experiment	86%	5.18	3.6
After experiment (bottom)	95%	0.04	< 0.1
After experiment (top)	95%	0.10	1.7

was used for all the following experiments). Hexane was employed as organic solvent in the first stage. This nonpolar solvent has the advantages that it is able to dissolve HCH better than water does, it is inexpensive, relatively non-toxic and reusable, and it can be processed with standard steam equipment. Moreover, the boiling point of hexane at 1 bar is about 69°C, and therefore in the second stage it can be efficiently stripped with steam. The column adopted the saturation temperature of the flushing fluid (about 70°C during the hexane stage and about 105°C during the steam stage).

It was noticed that the hexane progressed very rapidly through sand and soil. After 10 h of hexane flushing the second stage was started. During the next 11 h the soil was flushed with steam. About 2 l of water and 5.2 l of hexane were used. The laboratory analyses after this Experiment B revealed that the HCH and mercury concentrations in the lower part of the contaminated soil had been reduced almost to the detection limit (HCH: 0.01 mg kg⁻¹ dw; mercury: 0.1 mg kg⁻¹ dw); see Table 3.

On the basis of the results obtained, a third Experiment C was performed with 0.85 kg contaminated soil and moisture (again with contaminated soil length $L = 25$ cm). About 85% of this weight consisted of dry soil and 15% of native soil moisture (Table 4). With the mass of dry soil (0.723 kg) and the total occupied volume ($AL = 511$ cm³), a soil bulk density of 1414 kg m⁻³ is obtained. Assuming a soil density ρ_s of 2625 kg m⁻³ gives a porosity ϕ of 0.46 and a pore volume of 235 cm³. During Experiment C the soil was stripped for 6.5 h with hexane and subsequently for 9.5 h with steam. In all, 8.5 l of hexane and 2.5 l of water were used. This corresponds to about 36.1 pore volumes of hexane (7957 pore volumes of hexane vapor) and 10.6 pore volumes of water (17730 pore volumes of steam). The mean mass flux amounted to 0.117 kg m⁻² s⁻¹ hexane and 0.036 kg m⁻² s⁻¹ steam.

The soil analyses reveal that the HCH was removed to below the detection limit (Table 4). This result implies a removal efficiency of > 99.7%. This HCH removed from the soil was all found in the water and hexane condensate. Even more HCH (about

Table 4

Dry weight of, and HCH and mercury concentrations in, treated soil before and after treatment (Experiment C)

	dw	HCH(mg kg ⁻¹ dw)	mercury(mg kg ⁻¹ dw)
Before experiment (bottom)	85%	4.79	4.3
After experiment (bottom)	86%	< 0.01	2.2
Before experiment (top)	85%	5.49	4.6
After experiment (top)	85%	< 0.01	3.4

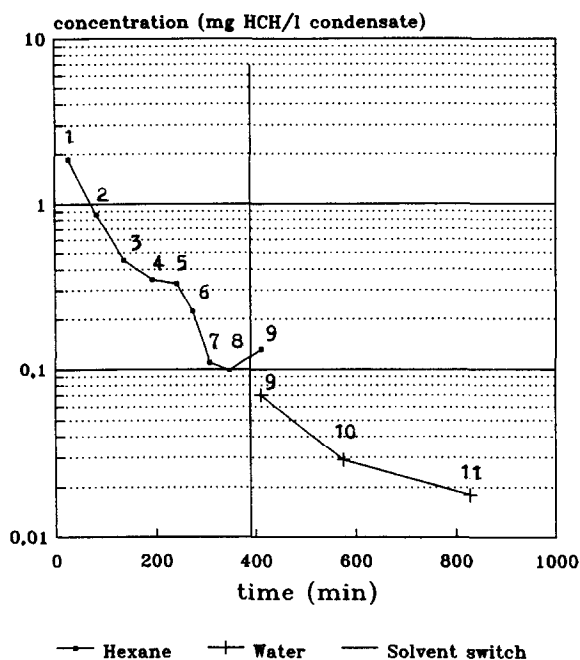


Fig. 2. HCH concentration in the condensate during Experiment C.

4.2 mg) was measured in the condensate than the amount removed from the soil, which was about 3.8 mg. This difference can be attributed to the various inaccuracies of the soil and condensate analyses. Fig. 2 illustrates that most HCH has been removed in the hexane treatment of the first stage, although the steam stage also contributes significantly to the cleaning. In this figure, the measured HCH concentrations in the filled bottles are shown versus the time. This measured concentration is the mean concentration of the flushing fluid during the filling time of a bottle. Accordingly, the measured concentration is assigned to the time at which half the bottle is filled. In the first three bottles a tiny layer of water was seen at the bottom of the bottles (about 4% by volume). This water is native moisture which has been stripped completely from the soil by the hexane (about 0.13 kg of water is recovered in total). In Appendix B it is demonstrated that the water is removed by hexane distillation. This removal of the native moisture and its replacement by hexane condensate are seen as major features of the cleaning process, as the native water forms an unwanted barrier to mass transfer of contaminant from soil to vapor.

Furthermore, in the soil practically all hexane has been removed in the second (steam) stage. The final hexane concentration amounts to only $17 \mu\text{g kg}^{-1} \text{ dw}$. One can conclude from this result that steam is efficient at stripping hexane from the soil. After the filling of bottle No. 9, no hexane was found in bottles 10 and 11. This implies that the steam is able to strip the hexane from the soil in less than 1.5 h.

Table 4 reveals, furthermore, that the mercury content during Experiment C, in contrast to Experiment B, is not greatly reduced. It is expected that mercury is

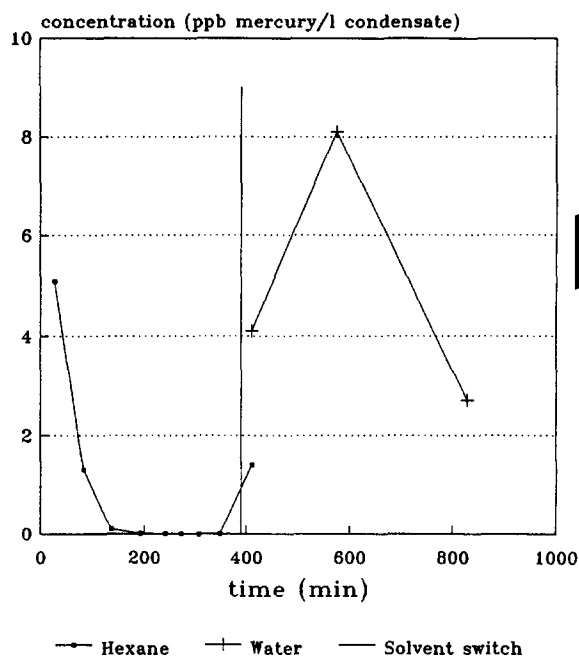


Fig. 3. Mercury concentration in the condensate during Experiment C.

particularly removed in the second stage. The amount of steam used was larger during Experiment C, but during Experiment B the steam stripping stage lasted longer. Steam has a higher saturation temperature than hexane and, hence, an enhanced evaporation of mercury will take place for the same volume of vapor. This is confirmed by Fig. 3, in which the mercury concentration in the condensate is depicted as a function of time. In the first 3 h of the process, mercury is removed by the hexane to some extent. After this start, mercury is not stripped any more by the hexane. The moment that steam is introduced, after about 400 min (6.5 h), one can see that mercury is removed again from the soil and found in the condensate. Mercury is found in the water in even greater quantities than in the preceding hexane stage. It is expected that if the steam stage were to be extended, the mercury removal would be considerably improved.

4. Analysis

In this section a model is derived to explain the results presented in the previous section. From this model and the experimental results, an overall mass transfer coefficient is derived which can be used for assessing cleaning times.

Here, the common chemical engineering assumption is employed that the mass transfer between sorbed, liquid and vapor contaminant is represented by the difference

between the equilibrium and the actual concentration. The mass transfer of HCH between the condensate/vapor interface and the vapor is then

$$\dot{m} = k_v(Hc_{lv} - c_v) \quad (1)$$

In this equation k_v represents the mass transfer coefficient between liquid and vapor phase, and c_{lv} and c_v are the concentrations of the contaminant at the liquid/vapor interface and in the vapor phase, respectively. H denotes the dimensionless Henry's law coefficient

$$H = \frac{P_p(T_{\text{sat}})M_p}{RT_{\text{sat}}S} \quad (2)$$

where S denotes the solubility of HCH in the liquid condensate phase (hexane in the first stage and water in the second stage), and P_p is the saturation pressure of HCH at the saturation temperature of the stripping vapor.

In deriving Eq. (1) it has been assumed that the hexane is present in the vapor phase only. However, for heating up the soil and removal of native moisture, condensation and condensate flow are also expected to take place. Similarly, in the second stage water will condense to heat up the soil from about 70°C to 105°C and to evaporate the hexane condensate. Hence, two-phase flow of vapor and condensate will be present to some extent. If as an extreme case liquid flow only in the column is assumed and the removal of contaminant occurs solely by extraction, the form of Eq. (1) is not altered. The mass transfer coefficient k_v then constitutes the mass transfer from stagnant condensate to mobile flushing medium, c_v is the concentration in the flushing fluid, and H equals unity. In other words, Eq. (1) and Eq. (2) retain their applicability to modelling possible two-phase flow and mass transfer.

The mass transfer through the condensate film is given by

$$\dot{m} = k_l(c_{ls} - c_{lv}) \quad (3)$$

where c_{ls} constitutes the contaminant concentration at the solid/liquid interface. The mass transfer between HCH sorbed to the soil and dissolved in the condensate follows from

$$\dot{m} = k_s \left(\frac{C_s}{K_d} - c_{ls} \right) \quad (4)$$

In this equation C_s represents the mass of HCH per dry mass of soil and K_d is the distribution ratio (between hexane and soil in the first stage and between water and soil in the second stage). The sorption measurements by Wahid and Sethunathan [12] confirm the nearly linear adsorption isotherm of HCH in the concentration range considered, particularly for the β and γ isomers.

In order to express the mass transfer in terms of C_s and c_v , which can be measured, Eq. (1), Eq. (3) and Eq. (4) are combined, yielding

$$\dot{m} = k_t \left(\frac{C_s H}{K_d} - c_v \right) \quad (5)$$

with the total mass transfer coefficient

$$k_t = \left(\frac{H}{k_1} + \frac{H}{k_s} + \frac{1}{k_v} \right)^{-1} \quad (6)$$

For the vapor phase, neglecting diffusion, dispersion and accumulation, a differential mass balance of transported contaminant gives

$$u_v \frac{\partial c_v}{\partial x} = k_t \left(\frac{C_s H}{K_d} - c_v \right) \quad (7)$$

A similar approach to the contaminant vapor transport was adopted by Wilkins et al. [13] upon modelling the volatilization of nonaqueous phase liquids in nitrogen.

The decay of the contaminant sorbed in the soil by desorption to the condensate and by evaporation to the vapor phase is governed by

$$(1 - \phi) \rho_s \frac{\partial C_s}{\partial t} = -k_t \left(\frac{C_s H}{K_d} - c_v \right) \quad (8)$$

The boundary conditions pertaining to Eq. (7) and Eq. (8) read

$$c_v(x=0, t) = 0 \quad (9)$$

$$C_s(x, t=0) = C_{s0} \quad (10)$$

Eq. (9) indicates the clean vapor that enters the packed soil and Eq. (10) reflects the initial contamination level of the soil when the stripping is started. Note that the present transient model accounts for the decrease of contaminant concentration in the soil, resulting in a diminishing drive for mass transfer. This feature of the model is a result of the fact that no free HCH is present in the soil. If free HCH had been present, a simplified model could have been applied which starts from a constant contaminant concentration in the soil phase, proportional to the vapor pressure of pure HCH.

Eq. (7) and Eq. (8) are written as

$$\frac{\partial c_v}{\partial X} = \text{Me}(c_s - c_v) \quad (11)$$

$$\frac{\partial c_s}{\partial \tau} = -(c_s - c_v) \quad (12)$$

with, as dimensionless coordinate

$$X = \frac{x}{L} \quad (13)$$

as dimensionless time

$$\tau = \frac{k_t H t}{K_d (1 - \phi) \rho_s} \quad (14)$$

as soil concentration

$$c_s = \frac{C_s H}{K_d} \quad (15)$$

and as Merkel number

$$\text{Me} = \frac{k_t L}{u_v} \quad (16)$$

The boundary conditions of Eq. (11) and Eq. (12) now follow from Eq. (9), Eq. (10), Eq. (13), Eq. (14) and Eq. (15) as

$$c_v(X=0, \tau) = 0 \quad (17)$$

$$c_s(X, \tau=0) = \frac{C_{s0} H}{K_d} \quad (18)$$

Eq. (11) and Eq. (12) with boundary conditions Eq. (17) and Eq. (18) are also encountered in modelling crossflow heat exchangers [14]. The solution of this system has been obtained in closed form, represented by series expansions (Baclic and Heggs [15]). In order to obtain compact and practically useful expressions, an asymptotic analysis is executed here, following Van Dyke [16].

The Merkel number may be thought of as the ratio of mass transfer rate to vapor velocity. For the experiments performed (and most practical situations) this number is much smaller than unity. Substituting the following perturbation expansions

$$c_s = c_s^0 + \epsilon c_s^1 + O(\epsilon^2) \quad (19)$$

$$c_v = c_v^0 + \epsilon c_v^1 + O(\epsilon^2) \quad (20)$$

with

$$\epsilon = \text{Me} \quad (21)$$

into Eq. (11) and Eq. (12), equating the coefficients of equal power of ϵ and solving the resulting equations for the zero-order term yield

$$c_s^0 = \frac{C_{s0} H}{K_d} e^{-\tau} \quad (22)$$

$$c_v^0 = 0 \quad (23)$$

The solution of first order term equations yields

$$c_s^1 = \frac{C_{s0} H}{K_d} X \tau e^{-\tau} \quad (24)$$

$$c_v^1 = \frac{C_{s0} H}{K_d} X e^{-\tau} \quad (25)$$

Combining Eq. (16), Eq. (20), Eq. (21), Eq. (23) and Eq. (25) yields as the first order approximation of the contamination concentration of the vapor at the exit of the column ($X = 1$)

$$c_v(x = L, t) = \frac{k_t HC_{s0} L}{K_d u_v} e^{-\lambda t} \quad (26)$$

with the time constant

$$\lambda = \frac{k_t H}{K_d (1 - \phi) \rho_s} \quad (27)$$

From Eq. (26) it can be concluded that the contaminant concentration in the vapor phase decreases exponentially with time. This trend is supported by the measured HCH concentrations of the first three bottles, which are situated on a straight line in Fig. 2. In the next section the theoretical results are applied to the experimentally obtained results.

5. Application of theoretical model

On the basis of the derived model and the experimental results the overall mass transfer coefficient is estimated. Furthermore, it will be shown that, with the help of the model and the measured exit HCH concentration in the hexane condensate, it is possible to determine the initial contaminant level in the soil. As this contaminant level has been determined explicitly before each experiment, the model can be verified on the basis of its prediction of the initial contaminant level.

The measured concentration in the collected condensate is related to the exit concentration in the vapor phase via

$$c_c(x = L, t) = \frac{\rho_c}{\rho_v} c_v(x = L, t) \quad (28)$$

The superficial vapor velocity u_v is related to the condensate flow via

$$u_v = \frac{\rho_c}{\rho_v} u_c \quad (29)$$

where the superficial hexane condensate velocity u_c , and likewise u_v , is based on the cross-sectional area of the tube. u_c follows directly from the time needed to fill a one liter bottle (about 55 min for each of the first three bottles). Combining Eq. (26), Eq. (28) and Eq. (29) yields

$$c_c(x = L, t) = c_{c0} e^{-\lambda t} \quad (30)$$

with c_{c0} the exit contaminant concentration in the condensate at $t = 0$

$$c_{c0} = \frac{k_t HC_{s0} L}{K_d u_c} \quad (31)$$

From Eq. (30) and Eq. (31) it follows that the velocity and density of the vapor in the packed bed have cancelled out. To apply the model it is irrelevant which parts of the

Table 5
HCH concentration in hexane condensate (Experiment C)

Bottle No.	t (min)	c_c (mg l ⁻¹)
1	27	1.856
2	82	0.860
3	136	0.453

flushing fluid were in the vapor and which in the liquid phase. The model is written completely in terms of the condensate density and velocity, which are easy to measure during filling of the bottles (likewise the contaminant concentration of the condensate in the bottles).

In Table 5 the measured HCH concentration of the first three bottles are listed. The tabulated HCH concentrations and the corresponding time are for the points marked by 1, 2 and 3 in Fig. 2. From the time and concentration pertaining to bottles 1 and 3, c_{c0} and λ are computed with the help of Eq. (30), yielding $\lambda = 2.156 \times 10^{-4} \text{ s}^{-1}$ and $c_{c0} = 2.63 \text{ mg l}^{-1}$. This concentration is the value at the intersection of the line through points 1 and 3 with the vertical axis of Fig. 2.

From the derived value of λ , now the overall mass transfer coefficient Hk_l/K_d can be obtained with Eq. (27) as the bulk density $(1 - \phi)\rho_s$ is known. In the Section 3 (Stripping experiments) this product has been derived from the dry mass of contaminated soil in the column divided by the volume occupied in the column, yielding $(1 - \phi)\rho_s = 1414 \text{ kg m}^{-3}$. From this value, $\lambda = 2.156 \times 10^{-4} \text{ s}^{-1}$ and Eq. (27), it follows that $Hk_l/K_d = 0.304 \text{ kg m}^{-3} \text{ s}^{-1}$. This value gives an indication of the mass transfer coefficient encountered with solvent stripping and can be used for engineering end purposes.

The reliability of the derived model can be investigated with the help of the measured and/or computed values c_{c0} , Hk_l/K_d , u_c and L and Eq. (31). With these data, one is in a position to assess the initial HCH mass fraction C_{s0} , which can be compared with the measured C_{s0} before the experiment. Substituting all relevant values into Eq. (31) gives $C_{s0} = 5.13 \text{ mg kg}^{-1} \text{ dw}$. This initial HCH fraction is in excellent agreement with the values obtained from analysis of the soil, see Table 4. This agreement is an indication of the accuracy of the model derived and applied. Furthermore, it is demonstrated that, with the aid of the model presented, it is possible to assess the initial soil contamination level from the measured exit properties of the flushing fluid alone.

Finally, with the measured HCH concentrations in bottles 10 and 11, see Fig. 2, which were filled with water during the steam stage, the overall mass transfer coefficient during the steam stripping stage was determined. In Table 6 the measured HCH concentrations are tabulated. With these values and Eq. (31), c_{c0} and λ are computed as

Table 6
HCH concentration in water condensate (Experiment C)

Bottle No.	t (min)	c_c (mg l ⁻¹)
10	575	0.029
11	827	0.018

$0.861 \times 10^{-1} \text{ mg l}^{-1}$ and $0.316 \times 10^{-4} \text{ s}^{-1}$, respectively. Analogously to the procedure followed with hexane, an overall mass transfer coefficient can be derived, $Hk_t/K_d = 0.445 \times 10^{-1} \text{ kg m}^{-3} \text{ s}^{-1}$.

This coefficient is about a factor of 7 smaller than the value found with solvent stripping. For a better understanding of this difference, attention is first given to k_t . From Eq. (6) it follows that k_t is built up from k_s , k_l and k_v . As the mass transfer coefficient to the vapor phase k_v is much larger than the transfer coefficient from solid to liquid and through the liquid phase (the diffusion coefficient in the gas phase is larger by a factor of $> 10^4$ than in the liquid phase), k_t is dominated by k_l and k_s ; hence

$$k_t \cong \frac{1}{H} \left(\frac{1}{k_l} + \frac{1}{k_s} \right)^{-1} \quad (32)$$

implying that

$$\frac{Hk_t}{K_d} \cong \frac{1}{K_d} \left(\frac{1}{k_l} + \frac{1}{k_s} \right)^{-1} \quad (33)$$

The distribution ratio K_d is expected to be larger for water–soil systems than for hexane–soil systems, as the nonpolar HCH has a higher affinity for hexane than for water. This smaller K_d of hexane should explain the observed larger value of Hk_t/K_d for hexane stripping than for steam stripping.

This effect apparently exceeds the effect of the higher saturation temperature of steam (about 100°C) in comparison with hexane (69°C). Schwarzenbach et al. [17] state that K_d decreases with increasing temperature. Moreover, the diffusion coefficient in the condensate increases approximately linearly with the absolute temperature (Reid et al. [18]). The measured values of Hk_t/K_d indicate that these positive thermal effects on k_s , k_l and K_d for steam are minor in comparison with the previously discussed lower affinity of water. This reasoning is confirmed by adsorption experiments with γ -HCH, soil materials, hexane and water carried out by Mills and Biggar [19]. Experiments at various temperatures revealed that K_d decreases with increasing temperature, but that this effect is minor in comparison with the higher affinity for hexane.

6. Conclusions

In this paper the first results of the two-stage stripping experiments are reported for soil contaminated with mercury and (predominantly β -) HCH. During the first stage the packed soil is stripped with a solvent (here hexane) and in the second stage with steam.

The results reveal the possibility of reducing the HCH and mercury levels below the detection limit. A removal efficiency $> 99.7\%$ appears to be achievable for HCH and $> 97.2\%$ for mercury. It is expected that similar results could be obtained with other nonpolar contaminants such as mineral oil, PAHs, other pesticides and so on. The experimental results suggest further investigation of

- the removal of mercury, in particular in the second (steam) stage;

- the optimization of the process, that is to say, treatment of larger amounts of soil and minimization of the flushing time and the amounts of flushing fluids.

For a better understanding of the process, a model has been derived for describing the HCH transport during the first and the second stage. This model starts from mass transfer between solid, condensate and vapor phases (it is demonstrated that no free HCH is present in the soil). With the help of this model and the measured HCH concentration in the flushing fluid, overall mass transfer coefficients Hk_i/K_d are obtained for the solvent stage ($0.304 \text{ kg m}^{-3} \text{ s}^{-1}$) and the steam stage ($0.455 \times 10^{-1} \text{ kg m}^{-3} \text{ s}^{-1}$). These results should facilitate future engineering computations. Furthermore, with the help of the model presented and the measured exit quantities of the flushing fluid, the initial soil contamination level can be computed a posteriori. Here, this predicted soil contamination level has been compared with the actual value measured prior to the experiment. This comparison yields excellent agreement, i.e. confirming the usefulness and reliability of the presented model.

7. Notation

A	cross-sectional area of the test tube [m^2]
C_s	mass of contaminant per dry mass of soil
c	contaminant concentration [kg m^{-3}]
H	dimensionless Henry's law coefficient, Eq. (2)
K_d	distribution ratio [$\text{m}^3 \text{ kg}^{-1}$]
k	mass transfer coefficient [s^{-1}]
L	length of column packed with contaminated soil [m]
M	mass of one kmol of substance [kg]
Me	Merkel number, Eq. (16)
\dot{m}	mass flux [$\text{kg m}^{-3} \text{ s}^{-1}$]
P	pressure [Pa]
R	gas constant [$\text{J K}^{-1} \text{ kmol}^{-1}$]
S	solubility [kg m^{-3}]
T	temperature [K]
t	time [s]
u	superficial velocity [m s^{-1}]
X	dimensionless coordinate, Eq. (13)
x	coordinate [m]
Y	liquid volume fraction

7.1. Greek symbols

ϵ	perturbation quantity, Eq. (21)
λ	time constant, Eq. (27) [s^{-1}]
ρ	density [kg m^{-3}]
τ	dimensionless time, Eq. (14)
ϕ	porosity

7.2. Subscripts

c	condensate in bottle
h	hexane
l	condensate in column
m	maximum
p	contaminant
s	solid
t	total
v	vapor
w	water
0	initial condition

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Appendix A. Distribution of β -HCH

In this appendix, the maximum β -HCH concentration that can sorbed onto the soil and dissolved in native moisture is assessed. This quantity follows from

$$C_{sm} = \frac{C_w S}{\rho_{lw}} + K_d S \quad (\text{A-1})$$

With the values for solubility of β -HCH in water $S = 5 \text{ mg l}^{-1}$ [20], density of water $\rho_{lw} = 1 \text{ kg l}^{-1}$, β -HCH distribution ratio of soil and water $K_d > 5.13 \text{ l kg}^{-1}$ [12] and water content C_w 0.1 kg of water per kg dw (Table 1), $C_{sm} > 25 \text{ mg kg}^{-1}$ dw is obtained. This computation reveals that the major part of the contaminant is sorbed onto the soil and that no free β -HCH is likely to be found in the treated soil.

Appendix B. Distillation of water by hexane

During the hexane stage in the soil both native water and hexane condensate are present. The two liquid phases are immiscible, implying that the total vapor pressure consists of the sum of the partial pressures of both pure substances. The relevant distillation temperature that prevails in the soil is such that the sum of these pressures equals the imposed pressure in the column.

Table 7

Vapor pressures of water and hexane ($\ln(P_w/\text{bar}) = 11.6835 - 3816.44/(227.02 + T_s/[\text{°C}])$, $\ln(P_h/[\text{bar}]) = 9.2165 - 2697.55/(224.37 + T_s/[\text{°C}])$ [18], the total pressure P_t , the water vapor mole fraction, and the liquid water volume fraction after condensing (Eq. (B-1))

T_s (°C)	$P_w(T_s)$ (bar)	$P_h(T_s)$ (bar)	$P_t(T_s)$ (bar)	P_w/P_t	Y_w
61	0.2086	0.7895	0.9982	0.210	3.5%
62	0.2184	0.8160	1.0345	0.211	3.6%
63	0.2286	0.8432	1.0718	0.213	3.6%
64	0.2392	0.8711	1.1103	0.215	3.7%

In Table 7 the partial pressures of pure hexane and water at various temperature are listed. Furthermore, the total pressure P_t ($P_h + P_w$), the water vapor mole fraction (P_w/P_t) and the volume fraction of water in the condensed mixture are also tabulated. The volume fraction of water follows from

$$Y_w = \frac{\frac{P_w M_w}{\rho_{lw}}}{\frac{P_w M_w}{\rho_{lw}} + \frac{P_h M_h}{\rho_{lh}}} \quad (\text{B-1})$$

with $M_w = 18.02 \text{ g mol}^{-1}$, $M_h = 86.18 \text{ g mol}^{-1}$, $\rho_{lw} = 1 \text{ kg l}^{-1}$ and $\rho_{lh} = 0.66 \text{ kg l}^{-1}$. In deriving Eq. (B-1) the amounts of hexane and water that remain in the vapor phase are neglected, i.e. complete condensation is assumed. This is allowed, as the condenser is cooled with ice and consequently the pressures of both substances are negligibly small; furthermore, the vapor mass is small in comparison with the mass of condensate.

It can be readily seen that, for the total pressure encountered in the column, P_t drops from about 1.1 to ambient pressure across the contaminated soil, the equilibrium water volume fraction amounts to 3.5%. Indeed, this volume fraction is observed in the first bottles with condensate. This experimental observation confirms the assumed distillation of water from the soil in the hexane stage.

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