Modelling long-term release of chlorinated hydrocarbons from a contaminated brown coalfield, Bitterfeld, Germany

Haile A. Mengistu¹ · Molla B. Demlie² · Tamiru. A. Abiye³

© Springer Nature Switzerland AG 2019

Abstract

Three kinetic and equilibrium partitioning column experiments were performed to determine the rates and extent of desorption of five chlorinated hydrocarbons (1,2 *cis*-dichloroethylene (DCE), 1,2,2-trichloroethane (TCA), trichloroethylene (TCE), 1,2,3,4-tetrachloroethylene (PCA) and chlorobenzene) found in the contaminated sediments in a former brown coal mine. A high fraction (more than 70%) of the contaminants DCE, TCA and TCE desorbed in a single-step column test performed for a period of 50–70 days, whereas the remaining 30–40% of the initial PCA and chlorobenzene load desorbed from the contaminated sediments. When the desorption test was conducted with contaminated sediments filled columns through continuous replenishment of the deionized water, the desorbed TCE fraction increased to as high as 95% after 70 successive days of leaching and as low as 30% for PCA. It turns out that the flux rate of the desorbed contaminant fractions is strongly correlated to the organic carbon-based partition coefficient (K_{oc}) of contaminants. A coupled Ogata-Banks and the intraparticle diffusion equation analytical solution were used to predict the long-term release rates and desorption of these chlorinated hydrocarbon compounds from the contaminated sediment. The laboratory measured flux rate data were used to constrain model predictions of five effective diffusion coefficients ranging from 0.99×10^{-9} to $1.43 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The estimated effective diffusion coefficients correspond well with water partition coefficient ($\log K_{ow}$) of the five chlorinated compounds ranging from 1.86 to 2. The model, using two distinct flux rates, successfully described the long-term release and desorption of the five chlorinated hydrocarbons. The results underscore the fact that small-scale laboratory experiments and pilot-scale field trials are necessary before designing and implementing large-scale remediation of chlorinated hydrocarbon contaminated sites, which requires considerable financial commitments.

Keywords Advection · Chlorinated hydrocarbons · Desorption · Dispersion · Octanol–water partition coefficient · Rate-limited diffusion

1 Introduction

Widespread chlorinated hydrocarbon contamination is common throughout the industrialized nations because of their application as raw materials in plastic, paint, solvent and other chemical industries [1, 19, 23]. Skin cells exposure to low-level concentration of any of these compounds can disrupt the normal functioning of human organs as most of them are categorized as carcinogens

[7, 40]. Chlorinated hydrocarbon compounds have a high affinity for adsorption onto organic carbons depending on their level of hydrophobicity and subsequently are released into the groundwater slowly over decades [12, 32]. In addition, they are recalcitrant owing to their stable molecular structure [6].

Once introduced into the subsurface, prediction of contaminant transport as well as designing and implementing effective clean-up strategies becomes difficult

✉ Haile A. Mengistu, hmengistu@uwc.ac.za | ¹Department of Earth Science, University of Western Cape, Robert Sebukwe Road, Bellville, Western Cape, South Africa. ²School of Geological Sciences, University of the Kwazulu-Natal, Private Bag X54001, Durban, South Africa. ³School of Geosciences, University of the Witwatersrand, Private Bag X3, P.O. Box Wits 2050, Johannesburg, South Africa.

due to complex hydraulic properties and variations in the composition of aquifer materials, chemical and physical properties of the pollutants and poorly known aquifer–contaminant interactions [9, 11, 24, 36]. Degradation of chlorinated hydrocarbons through time is also a factor in adding further complexity in understanding the fate and transport process [15, 27]. Models that simulate the fate and transport of groundwater contaminants are important tools for understanding of transport phenomena at long-term contaminated sites and for designing remedial action plans [12, 21].

Several analytical and numerical models have been developed to describe migration and spread of chlorinated hydrocarbons in the subsurface [1, 9, 16]. Based on the body of knowledge from many years of research around the world, there is a broad consensus that most chlorinated hydrocarbons are hydrophobic and adsorption and desorption are the two processes among others that govern the contaminant migration processes in porous media [23, 30]. One of the most challenging aspects of understanding the source–pathway–recipient concept of chlorinated hydrocarbons is to have accurate estimates of parameters that are important inputs for contaminant fate and transport [21]. Site conditions (soil/rock composition, aquifer hydraulic properties) and the behaviour of the pollutants themselves have to be thoroughly characterized in complex three-dimensional field conditions [17].

One way of finding representative input parameters is to assume that contaminant spreading is one-dimensional, in which case prototypes can be set up in the laboratory with known dimension of columns filled with samples of contaminated material and on which sorption/desorption experiments could be conducted. If equilibrium sorption is assumed, use of analytical models is applicable in getting reasonable success. However, nearly all natural processes experience nonlinear sorption/desorption and therefore require considerable data, which takes into account all subsurface processes including contaminant–aquifer interactions [37]. Slow mass transfer processes between mobile and immobile regions in the sorbent layer are considered as one type of non-equilibrium model [37]. Empirical first-order mass transfer coefficients are used as fitting parameters to simulate first-order mass transfer, which is dependent on flow velocity and other column experimental conditions, especially during the earlier fast desorption process [14]. Diffusion-limited mass transfer models, on the other hand, quantify solute transport between the bulk solution to the surface and from the surface into the intra/interparticle pores of the solid sorbent material [5, 25]. Fick's law of diffusion is the basis of the diffusion-limited transport models, which could be complicated to incorporate the entire external (film) and internal (pore and/or surface) diffusion components.

Previous investigations [13, 20] indicated that slow sorption/desorption kinetics is governed by diffusive processes that may explain the extended concentration tailing of certain contaminants in a number of pump-and-treat schemes. Therefore, accurate prediction of clean-up times or potential risk of a contaminant source can only be realized through reasonable quantification of the slow mass transfer rates [18]. Reactive transport models that encompass field-scale hydraulic and physicochemical aquifer parameters heterogeneities need to be considered for a reasonable transport prediction.

Werth and Hansen [35] reiterated that the slow rate of diffusion-limited desorption could further be slowed when the sorbents are organic matter with rubbery and glassy components (brown coal). Organic matter glassy and rubbery components play a dual role in maximizing hydrophobic micropores allowing preferential sorption/desorption to take place. Previous investigations underlined the importance of accurately determining the physical and chemical composition of the sorbent where the preferential sorption/desorption process takes place [20].

Batch experiments are widely used to initiate adsorption and desorption processes with measured material properties such as bulk density, organic carbon content, flow velocity as well as known attributes of pollutants, thereby estimating release rates with analytical transport equations [1, 31]. The distributed mass transfer rate model of Culver et al. [9] was used to conduct modeling of a trichloroethylene desorption experiment, while Marka et al. (1994) successfully applied first-order kinetic multi-compartment models to understand the desorption process of chlorinated benzenes from long-term contaminated sediments using column gas purge experiments [33]. On the other hand, batch desorption experiments on aged field sediments were conducted to describe the natural fate and release of chlorobenzenes, polychlorinated biphenyls and polycyclic aromatic hydrocarbons, while other studies used batch experiments for estimating rate constants by defining adsorption/desorption process as tri-phase (fast, slow and very slow fractions) (Hulscher et al. 1999) [27]. Kan et al. [17] generated tenax desorption experimental data and determined the rate constants for dichlorobenzene (both *m*- and *p*-), hexachlorobutadiene and hexachlorobenzenes with a two-compartment irreversible adsorption and radial diffusion model. Interestingly, most outcomes are valid only for specific site conditions and contaminant types and are not applicable to every condition, which merits further research and development before designing and implementing contaminated site clean-up activities.

In this study, column leaching experiments were conducted to quantify the desorption processes of five chlorinated hydrocarbons, namely *cis*-1,2-dichloroethylene

(DCE), 1,1,2-trichloroethane (TCA), trichloroethylene (TCE), 1,1,2,2-tetrachloroethylene (PCA) and chlorobenzene, and use the data to calibrate the model. Contaminated sediment samples taken from the actual site were used because estimated release rates from contaminated sediments reflect the long sediment/contaminant contact times that are not possible to mimic in laboratory experiments. The data generated are used to constrain analytical solutions that involve advection and dispersion and intraparticle diffusion processes. More importantly, the outcome of the research provides information about the dynamics of contaminant transport in the subsurface from brown fields; thereby, proper remediation schemes can be designed, implemented and monitored. The research also highlights the critical importance of conducting laboratory-based as well as pilot-scale tests and uses the outcome to design site specific, fact-based and effective industrial scale soil and water remediation technologies.

2 Site description

The research area lies in Bitterfeld district, located within the federal state of Saxony-Anhalt, Germany. The research area is located about 40 km northwest of the city of Leipzig (Fig. 1) with an area of 504 km². The main towns around the study area are Bitterfeld and Wolfen. The river Mulde, the main river in the area, divides the Bitterfeld district into two halves: the western part is characterized by flat topography and is where agriculture is dominantly practised, whereas the eastern part is characterized by a more hilly landscape covered by woodland.

The study area lies in the flood plain of the Mulde River, and the general geology is represented by the following formations: a relatively older Upper to Middle Oligocene marine silt lies below an Upper Oligocene

Fig. 1 Bitterfeld study site location map

sand of marine, littoral and fluvial origin. On top of the sand lies the lignite seam (22–28 m) of Lower Miocene age, which again is overlain by Welchesian sand and gravel and Holocene alluvium formation. There are two regional aquifers composed of gravel and sand deposits. The top unconfined sandy aquifer belongs to Quaternary age and locally known Bitterfeld Glimmer, and the lower (Tertiary age) sand aquifers are separated by the lignite seam and clay formation that has irregular thickness and acts as a hydraulic barrier between the top and bottom aquifers (Fig. 2).

A chemical plant that produced chlorine, sodium hydroxide, aluminium and magnesium was operational in Bitterfeld, for over 100 years. The plant was established at the site because of the availability of lignite in the geological sequence and clean water from the Mulde River. The whole product lines of chlorine produced (such as pesticides and dyes) encompassed a total of about 4000 different chemical compounds [38]. Highly toxic chemicals of industrial, public and domestic wastes were deposited either in several former open cast mines, excavations or in unprotected landfills. It is reported that an area of 25 km² and 200 million m³ of material is affected by the contamination. Previous studies have found out that the contaminants in the sediment comprise a complex mixture of halogenated hydrocarbons including high levels of DCE, TCE, chlorobenzene, vinyl chloride and perchloroethene [38].

Furthermore, the groundwater in the site is polluted by hexachlorocyclohexane (HCH) isomers. Moreover, approximately 4 million m³ of groundwater emanated from the landfills, where the water infiltrates and covers the entire floodplain, including the urban centre of Bitterfeld [38].

Abandoned open cast mines were favoured by chemical enterprises as cheap waste disposal sites. The old open cast mines have no effective barrier against the migration of pollutants into the groundwater within the upper unconfined sandy aquifer. Groundwater monitoring boreholes were installed in the study area of about 150 km² to continuously collect and analyse hydrochemical data of the suspect pollutants. Analysis of water samples indicated pollution by chlorinated paraffins, chlorinated benzenes and phenols as well as some unspecified pollutants from the product lines of the local industries [26] (Popp and Modder 1998).

According to Popp and Modder [26] (Popp and Modder 1998), the Upper Quaternary aquifer is polluted predominantly with chlorobenzenes, mainly monochlorobenzene (MCB), whereas chloroaliphatics are found only in traces (in the order of micrograms per litre) and un-substituted benzene is detected in relatively low concentration. The Lower Tertiary aquifer is contaminated only with small concentrations (few micrograms per litre) of dichloroethene and trichloroethenes, as well as traces of different chloroaromatics (Table 1).

Fig. 2 Simplified hydrostratigraphy and contaminant flow scheme in Bitterfeld area. (Adapted from [38])

Table 1 Pollutants of groundwater in the quaternary aquifer in Bitterfeld area [26], 1998, internal UFZ reports)

Compound	Concentration ($\mu\text{g/l}$)
Monochlorobenzene	3130–33,000
1,4-Dichlorobenzene	90–1000
1,2-Dichlorobenzene	20–180
Benzene	20–180
Trichloroethene	< 10–460
1,2- <i>cis</i> -Dichloroethene	10–280
1,2- <i>Trans</i> -dichloroethene	10–60
Chloromethylphenol	43.5
Trichlorophenols	9.2
2,4-Dichlorophenol	3.3
Dimethylphenol	1.4

3 Method and materials

3.1 Column leaching experiment

Column leaching experiment is a standard laboratory procedure for generating aqueous leachate from materials using a column apparatus suitable for analysis of volatile and non-volatile organic compounds. With the column leaching experiment, the dissolution rate of residual phases in a porous media as well as contaminant concentration in the seepage water was measured. The experiment provides information on aqueous leaching of materials in a dynamic partitioning manner by allowing a continuous flux of a leaching medium (e.g. water) to move through the sample.

Three columns filled with two different grain sizes with average diameters of 0.3 mm and 0.175 mm to maintain reasonable flow rate as well as a fourth control column filled with quartz sand as a control were prepared to run the experiment. The column body used in this research is made of a glass cylinder 15 cm in length with an inside diameter of 6 cm following the column

guidelines of DEMAU [10]. The cylinder wall has sufficient thickness of approximately 6 mm to withstand operational pressure. The end inlet and the outlet of the column are sealed with a plastic screw sealed with a *Teflon* septum to reduce any chemical reaction with the leachate. Glass wool is tied at the bolts and at the junction of the glass inlets to ensure tightness. Tubing used in the set-up are all inert materials of stainless steel and *Teflon*. A peristaltic pump is connected to the column inlet via tubes with an outer diameter of 1.02 mm and 0.57 mm to initiate flow of deionized water through the brown coal-rich sediments in the columns in upward direction to ensure easy flow rate adjustment. One t-connector is used for steel tubes where as special valves are installed to sample the leachate (Fig. 3). The column effluent was sampled in 1000 ml and 200 ml (used at the beginning) glass bottles, and 50-ml vials were used for measurements of physical parameters.

Millipore water (having an electrical conductivity ranging from 0.054 to 0.066 $\mu\text{S/cm}$) is used as a leaching fluid to make sure that the initial concentration of the influent water approaches zero. Use of Millipore water is chosen for minimizing interference due to potential redox reactions and enhance desorption due to its very low concentration within a reasonable time among others. However, using water with a composition mimicking natural condition is preferable albeit the complexity it adds during data interpretation. Samples were preserved in tightly capped bottles in an 8 °C room, and the experiment is conducted in 20 °C room. The leachate samples were analysed by HP 6890 Series II gas chromatograph, HP 5972 mass spectrometer with HP 5, 60 m $\times$ 250 μm 5% phenyl methyl siloxane capillary.

A brown coal sample was taken from the core of bore-hole SAFBIT 6/97 from a depth between 27.7 and 28.0 m [22]. The brown coal consists of clay and silt size fractions with occasional inclusion of bigger than 3-mm fragments. Due to clay mixture with the brown coal, homogenisation of the samples was a prerequisite to foster passage of clean water through the column material at an average

Fig. 3 Column leaching experimental set-up used in this research

rate of about 0.6 ml/min to maintain an average pore water velocity not exceeding $1 \text{ E-}04 \text{ cm/s}$. The sample was crushed, sieved and thoroughly mixed to prevent any contaminant concentration gradient. Known average grain sizes (3 mm and 1.75 mm in diameter) and close to uniform level of contamination throughout the whole profile are likely to improve the accuracy of transport modelling. Sample preparation especially sample grinding and sieving was expeditiously conducted at 4°C temperature to minimize potential loss of highly volatile organic.

Three columns of the same dimension were prepared, with columns I and II having 183.3 and 183.5 g sample with an average grain size of 3 mm, respectively. Column III was filled with 211.8 g of crushed brown coal of finer grain size of 1.75 mm. A mass of 137.6 g of sand filter was placed at the top and bottom of the columns as a filter. To compensate for disturbance and loss of the natural water content during the crushing and sieving process and to achieve optimum packing, material filling was simultaneously accompanied by addition of Millipore water without vibration. A column filled with pure quartz sand with a leaching set-up similar to the other columns was used as a laboratory blank. All glass columns, tubes, valves and any fittings were cleaned using ultrapure double distilled water (DDI) for all analyses. In accordance with the procedure by Demau [10], pumping of Millipore water was started immediately after the whole preparation and tube connection was completed, as the conventional commencement of leaching is within 1 to 2 h.

3.1.1 Leachate sampling procedures

For the first two eluate samples, 25 μl of internal standard (fluorobenzene and naphthalene) and 10 ml of pentane were mixed in the sampling bottle. To sample for GCMS measurement, the 1 litre bottle of contaminated water is filled with Millipore water to clearly see the pentane–water interface. The pentane was then carefully pipetted and put into a 2-ml vial, which was tightly sealed to prevent any loss of volatile compounds. Vials filled with pentane were put into a -16°C refrigerator in dark brown sample bottles to avoid excessive exposure to light before measurement. Periodic water samples were taken during the leaching process for physicochemical measurements (pH, electrical conductivity, temperature, dissolved oxygen and turbidity).

3.2 Analytical procedures

3.2.1 Hot methanol extraction

Methanol was the solvent chosen to dissolve and trap contaminants from the natural soil material. The preference

of methanol to other solvents is because it is readily miscible with water and provides an additional advantage of harvesting contaminants from the aqueous phase of the natural material. ten grams of soil samples from the columns were taken and mixed with 10 ml of methanol in a 50-ml glass crimp top vial. After sealing the vial with a Teflon-lined cap, the vial was placed in a hot sand bath (60°C) for 7 days to foster contaminant migration towards the methanol phase. After the reaction time, 2 ml pentane was added to the methanol phase to facilitate contaminants migration towards the pentane phase. Pentane is favoured in place of methanol for its high volatility during the GCMS measurement. The pentane phase was carefully pipetted and collected in a 2-ml vial. A total of six natural coal material samples were prepared from three different depths with visual evidences of the chlorinated hydrocarbons, namely from 27.7 m to 27.8 m, 27.8 m to 27.9 m and 27.9 m to 28.0 m.

3.2.2 Chemical analysis

Previous investigations by Wysick et al. [38] reported the presence of mainly the following contaminants at the study site: *cis/trans*1,2-dichloroethene (DCE), benzene, trichloroethene (TCE), 1,1,2-trichloroethane (TCA), tetrachloroethene (PCE), chlorobenzene, 1,1,2,2-tetrachloroethane (PCA), 1,4-dichlorobenzene and 1,2-dichlorobenzene). Therefore, the external standard was prepared from these compounds so that the GCMS is calibrated to measure contaminants of interest with sufficient accuracy [3].

The volume of the internal standard and pentane was varied until a better response in the GCMS was achieved with internal standard volume of 50 μl and 10 ml pentane found to be most appropriate. Moreover, after analysing

Table 2 List of compounds in the external standard, retention times and molecular masses

Name	Concentration (mg/l)	Retention time (min)	Target mass (g)
Naphthalene	1.0	13.50	128
Fluorobenzene	0.99	5.61	96
1,4DCB	1.06	11.36	146
<i>cis</i> -1,2-DCE	1.0	3.93	61
<i>Trans</i> -1,2-DCE	0.98	4.44	61
TCE	1.0	6.11	130
PCE	1.0	8.27	164
Benzene	1.0		78
Chlorobenzene	0.99	8.96	112
1,2 DCB	0.99	11.7	146
TCA	0.97	7.66	97
PCA	1.0	10.10	83

the GCMS measurements of five samples, there was a need to change the concentration of the internal standard from 937.7 mg/l to 218 mg/l to lower the response of naphthalene and increase the response of fluorobenzene. The external standard compounds used, their respective concentration, molecular mass and retention times are given in Table 2.

The calibration of the GCMS involves both qualitative and quantitative analysis [2, 16, 28]. The retention times and peak identifications were verified with pure compounds (Table 2). Other parameters such as temperature calibration for the oven, injection port, detector, length of film thickness and internal diameters of column have been set as follows:

Gas chromatograph	HP 6890 Series II
Mass spectrometer	HP 5972
Capillary	HP 5, 60 m × 250 µm 5% phenyl methyl siloxane
Nominal length	60 m
Nominal film thickness	0.25 m
Mode	Constant flow
Initial flow	1.5 ml/min
Injector temperature	250 °C
Transfer line temperature	250 °C
MS temperature	150 °C
Average velocity	31 cm/s
Carrier gas	Helium

3.2.3 One-dimensional transport modelling

A coupled analytical model that incorporates advection and intraparticle diffusion is used to predict the long-term release rates of five chemicals (DCE, TCE, TCA, PCA and chlorobenzene). Advection, dispersion, intraparticle diffusion and reaction are incorporated in the simulation. Effect of grain size and other specific properties of the material (lignite in this case) including a tortuosity factor, fraction of organic carbon, dry solid density and intraparticle porosity are taken into account. The analytical solution is organized in four sections:

1. *Column specification*: radius (cm), length (cm), volume (cm³) and flow rate (cm³/s)
2. *Soil/sediment/aquifer specification*: dry solid mass (kg), wet solid mass (kg), water content (%), grain density (g/cm³), particle density (g/cm³), bulk density (g/cm³), grain radius (cm), porosity intraparticle porosity, effective porosity (–)
3. *Desorption parameters*: organic matter fraction (–), time lag (days), sorption time (day), aqueous concentration (mg/l), K_d (–), diffusion coefficient (cm²/s), apparent diffusion (cm²/s), retardation (–), effective diffusion coefficient ((cm²/s)
4. *Hydraulic parameters*: contact time (s), flow rate (cm/s), dispersion coefficient (cm)

Measured parameters are column size, grain size, sample mass, flux and water content. The remaining parameters (compound mass, retention time, flux, water content, porosity, dispersion coefficient, distribution coefficient, pore volume) were calculated from the measured values well as from existing data from the literature. Effective diffusion was calculated from apparent diffusion, which is a fitting parameter for calculating the contaminant flux rate (mg/kg/day). The Ogata-Banks's advection–dispersion transport analytical solution, which describes process as relatively fast and an equilibrium reaction (Eq. 1) to calculate flux in the short term (< 0.1 days) (Rathwol 1997). Contaminant specific properties (such as apparent diffusion coefficient and octanol–water partition coefficient) are all calculated. Geochemical heterogeneity is not considered in the model since it is assumed that columns are packed with homogeneous materials.

$$C(x, t) = \frac{1}{2} C_0 \left[\operatorname{erfc} \left\{ \frac{X - \frac{v}{R} t}{\sqrt{4 \frac{D}{R} t}} \right\} + e^{\frac{v}{D} X} \operatorname{erfc} \left\{ \frac{X + \frac{v}{R} t}{\sqrt{4 \frac{D}{R} t}} \right\} \right] \quad (1)$$

where X is the downgradient location of interest, t is the time, C_0 is the initial concentration, v is the groundwater flow rate, D is the dispersion, R is the retardation factor, $C(x, t)$ is the concentration at a specific time, and erfc represents complementary error function.

The long-term (> 0.1 days) flux rate, described by diffusion-limited desorption process, is regarded as a kinetic process, limited by the diffusive transport of the solute through the tortuous pores of the matrix or particles to the sorption sites [13]. As the matrix grains/particles are assumed to be spherically symmetric, the underlying intraparticle diffusion equation (based on Fick's second law) can be written for a specific matrix grain/particle with analytical solution by Liedl and Ptak [21] as:

$$S_{\text{matrix}}(Cd) = \frac{1}{\frac{4\pi}{3} R^3 (1-\epsilon) \rho} \int_0^R 4\pi r^2 [\epsilon c + (1-\epsilon) \rho s(c)] dr,$$

where S_{matrix} is the mass of the contaminant within all grains of the matrix, R is the grain/particle radius, s is the mass of chemical desorbed from surfaces of intraparticle pores per unit mass of the grains/particles, r is the dry solid density of matrix grains/particles, c is the dissolved

Fig. 4 Initial mass loading of columns I, II and III using hot methanol extraction technique **Fig. 5** Initial concentration of the five compounds found in the columns

contaminant concentration in the intraparticle pores and ϵ is the intraparticle porosity (dimensionless).

According to Grathwohl [13], the effective diffusion coefficient (D_{eff}), accounting for the reduction in diffusion due to the tortuous pores and reduced diffusion effective area, can be empirically estimated by:

$$D_{eff} = D_{aq}^m,$$

where D_{aq} is the diffusion coefficient in aqueous solution [L^2T^{-1}], m is an empirical exponent (dimensionless) and ϵ is the intraparticle porosity (dimensionless).

4 Results and discussion

Three column experiments were conducted for about 70 days (column I and column II) and 50 days (column III), respectively. Out of ten target compounds, benzene measurements were considered unreliable because of high background levels in the laboratory blanks, whereas poor chromatographic resolution of *trans*1,2-DCE made it to be of poor quality data due to interference with the analytical technique. On the other hand, 1,2-DCB, 1,4-DCB and PCE were not found at all. The column experiment results of the remaining five compounds are presented and discussed in the following sections. These compounds are *cis*1,2-DCE (referred here forth as DCE), TCE, TCA, chlorobenzene and PCA. Initial contaminant mass loading calculated from the hot methanol extraction shows that DCE, chlorobenzene and PCA have higher masses than others (Fig. 4).

The slight difference between the two graphs can be explained by different masses of material packed in the

Table 3 Calculated distribution coefficients (K_d)

Columns	DCE	TCE	TCA	Chlorobenzene	PCA
I	39.92	49.76	122.45	540.51	191.53
II	35.34	35.97	89.25	465.33	156.56
III	116.84	36.53	84.89	730.63	267.60

columns (183 g for columns I and II and 212 g for column III) and differences in grain size (average 3 mm in the case of columns I and II and 1.75 mm in column III). It is interesting to note that after leaching is initiated, the first aqueous concentrations in the leachate water differed greatly from the trend of the initial mass loading most likely due to difficulties in maintaining the required seepage velocity inside the columns and differences in grain size (Fig. 5). It is also evident that the amount of TCE desorbed shows higher in the 0.175 mm grain size than in 3 mm grain size underscoring the influence of sediment average grain size on the desorption process.

Desorption was more effective in the larger grain size fractions packed in columns I and II than in the smaller grain size fraction of column III. Relatively low concentrations were observed for chlorobenzene and PCA in the leachate despite high initial mass loadings (Fig. 5). Slow desorption of different compounds was attributed to high distribution coefficient associated with the chemical behaviour of the compounds. Calculated distribution coefficients (K_d) based on the Octanol–water partition coefficients K_{ow} of the five chlorinated organic compounds considered in this study are presented in Table 3.

Fig. 6 **a** DCE concentration versus time plot. **b** TCE concentration versus time plot. **c** TCA Concentration versus time plot. **d** Chlorobenzene concentration versus time plot. **e** The breakthrough concentrations of PCA in the three columns

It can be noted that there is a general increase in K_d with the increase in the hydrophobicity of the compound.

For column I and column II, constant effluent concentrations were observed in the early stages of the experiment (Fig. 6a–e). Effluent concentrations decreased with time based on the detection limits reached for some compounds even before the experiment ended. Consistency of results between columns I and II, which are filled with the same grain size of lignite, highlights the fact that the

experiment is reproducible, whereas column III is filled with lignite sediments of smaller grain size. In all three columns, chlorobenzene concentrations in the effluent were constant with an average seepage velocity of 0.64 ml/min over a longer time period (about 30 days) showing very low desorption.

DCE, despite its high initial mass loadings, drops sharply below detection limit in about 22 days in columns I and II where as in column III the drop of the concentrations

below detection limit takes about 31 days (Fig. 6a). The relatively fast rate of desorption can be attributed to low K_d values and fast diffusion-limited desorption. It takes longer time for DCE to reach a value below detection in the case of column III.

TCE concentrations show a consistent decrease throughout the experimental time until the very end of the experiment. Generally, the TCE desorption process reveals the fact that it can be leached from a contaminated solid media below detection limit within a reasonable period. The influence of grain size on desorption is generally not significant enough to cause considerable tailing effects during clean-up operation using conventional systems such as pump-and-treat schemes (Fig. 6b).

TCA concentration, although not very high in its initial mass loading, drops below detection limit in about 24 days in columns I and II while it takes about 39 days in column III. Late desorption data indicate a pronounced delay in column III similar to DCE in comparison to columns I and II (Fig. 6c).

Chlorobenzene shows no appreciable reduction in concentration despite the fact that the initial mass loading is relatively high. Within the test period of approximately 70 days, chlorobenzene concentrations show a reduction in w 5% of the initial pore water concentration (Fig. 6d).

PCA is relatively consistent in its concentration reduction by roughly one order of magnitude. Early data show a more or less constant flux, whereas late data indicate a consistent diffusion-limited desorption based on the late column leaching data (Fig. 6e). Unlike the other compounds, both columns show similar data throughout the experiment indicating that any grain size does not have a significant influence on desorption of PCA.

Desorbed masses from the flow-through column experiments were compared with the total initial mass loadings and the data were plotted as the ratio of desorbed mass at the end of the sampling time compared to the initial mass (Table 4). The initial masses were deduced from the hot methanol extractions of the lignite samples. The near

straight-line plot after 10 days indicates that the PCA mass removed from the columns is constant over time (Fig. 6e). In general, the higher the K_d , the longer the time it takes to cause mass removal.

While per cent desorbed mass ranges from 40% to roughly 85%, values slightly above 100% were calculated for TCE, possibly due to gas chromatography and mass spectrometer (GCMS) measurement uncertainty. However, there is trend showing that for the compounds with the higher K_d , i.e. CB and PCA, the fraction of desorbed mass is lower compared to DCE and TCA.

4.1 Modelling results and discussion

With all input parameters (measured and calculated, Table 5) entered into the analytical model, apparent diffusion coefficient was used as a fitting parameter between the model calculated and the measured mass flux data (mg/kg/day). Model input parameter values for columns I and II are similar, whereas column III has different input parameter values for the average grain size (0.175 cm) and dry and bulk solid mass (kg) of 0.112 and 0.212, respectively (Table 7).

4.1.1 DCE

The early data plot (up to 3 days), which is dominated by fast release via advective process (flushing), indicates relatively poor fit due to problems of maintaining a constant flow velocity and associated experimental errors. Similar to earlier studies by Liedl and Ptak [21], a short-term mass transfer data sensitivity to change in the flow velocity is observed. Late measured data after around 40 days deviate from model prediction (Fig. 7a) due to inability of the GCMS to measure very low concentrations, which simply assigns zero to values below its lowest measurement range. After about 50 days, it is evident from the laboratory data that slow process (intraparticle diffusion) dominates the process.

Table 4 Total mass desorbed and mass desorbed versus initial loading

	DCE	TCE	TCA	Chlorobenzene	PCA
M_{des} (mg)					
Col. I	1.49	0.67	0.06	0.46	0.3
Col. II	1.4	0.66	0.07	0.43	0.27
Col. III	1.32	0.82	0.15	0.37	0.31
M_{des}/M_s (%)					
Col. I	86.11	> 100	66.53	58.98	64.84
Col. II	80.55	> 100	77.84	54.37	58.72
Col. III	65.89	> 100	> 100	40.56	57.42

Table 5 Model input parameters

Radius (cm)	3
Length (cm)	16
Dry solid mass (kg)	0.096
Wet solid mass (kg)	0.183
Grain density (kg cm^{-3})	0.7
Particle density (kg cm^{-3})	1.48
Bulk density (kg cm^{-3})	0.404
Grain diameter (cm)	0.3
Intraparticle porosity (–)	0.0112

Fig. 7 **a** DCE desorption modelling result versus measured data. **b** TCE desorption modelling result versus measured data. **c** TCA desorption modelling result versus measured data. **d** PCA desorption

modelling against measured data. **e** Chlorobenzene desorption modelling result versus measured data

4.1.2 TCE

Model prediction and measured TCE desorption data show very good fit (Fig. 7b) demonstrating that the processes responsible for mass transfer are properly accounted for. In this case, late data are reasonably described by the model indicating that complete desorption was achieved during the experiment within a reasonable time period. It is interesting to observe that the fast release time spans only one tenth of a day, even shorter than that for DCE. This model fit indicates a better correlation than that is reported by Werth and Hansen [35].

4.1.3 TCA

The TCA measured desorption data reasonably fit the model prediction albeit slight earlier data scatter likely due to inability to maintain constant flow rate during flushing (Fig. 7c). Poor short-term desorption rate fit is also tied to the chemical attribute of TCA as other aspects of the experiment are similar to DCE and TCE.

4.1.4 PCA

The results in Fig. 7d indicate a considerable long-term tailing effect of PCA desorption with the flux rate considerably slower than DCE, TCE and TCA likely because of its high hydrophobicity. The model fit is reasonably acceptable in the long-term mass flux data except that the prediction is slightly faster than the measured data (Fig. 7d). Early measured and predicted desorption data misfit is possibly due to difficulty maintaining constant flow rate. The model flux prediction in the long-term clearly demonstrates that the dominant mass transfer process is diffusion-limited desorption.

4.1.5 Chlorobenzene

Model prediction and measured flux data show discrepancies in the short-term flux rate (Fig. 7e), indicating limitation to control flow rate fluctuation. Significant measured flux rate data scatter in the long-term period which underscores that high K_d of CB delays the diffusion-limited desorption process within the experimental

timescale. High CB K_d causes the measured concentration values to be approaching the lowest detection limit of the GCMS. Poor fitting of desorption release rate between predicted and modelled data is also attributed to hysteretic diffusion of compounds within sediment particles including intra-organic matter diffusion and intraparticle micropore diffusion [39].

The column experiment and the modelling of these five chlorinated hydrocarbons show that desorption is a two-step diffusion process with a fast early release rate and slow extended diffusion-limited desorption process, consistent with findings of Cornelissen et al. [8].

4.2 Determination of effective diffusion coefficient

The effective diffusion coefficients of the five chlorinated hydrocarbons were calculated from the apparent diffusion coefficient, which was used as a fitting parameter between the coupled analytical approximation and the measured daily flux. In conformity with the K_{ow} and K_d values, the effective diffusion rate of PCA is less than the effective diffusions of all the other four compounds, with the DCE having the highest effective diffusion coefficient (Table 6).

Table 7 Summary of mass loaded, desorbed and retained

	DCE	TCE	TCA	CB	PCA
Mass retained (mg)					
Col. I	0.0076	0	0	0.16	0.02
Col. II	0.0053	0	0	0.1	0.014
Col. III	0.0048	0	0	0.13	0.02
Mass Des. (mg)					
Col. I	1.50	0.67	0.06	0.23	0.30
Col. II	1.40	1.42	0.07	0.43	0.27
Col. III	1.32	0.82	0.15	0.37	0.30
Mass loading (mg)					
Col. I	1.73	0.18	0.10	0.79	0.46
Col. II	1.74	0.18	0.10	1.79	0.46
Col. III	2.00	0.21	0.11	0.91	0.53

Table 6 Effective diffusion coefficient of the five chlorinated hydrocarbons generated by the coupled model with associated octanol–water partitioning coefficient from previous studies [2]

Parameters	Chlorobenzene	PCA	TCA	TCE	DCE
Effective diffusion coefficient	1.09×10^{-9}	9.91×10^{-10}	1.10×10^{-9}	1.14×10^{-9}	1.42×10^{-9}
Octanol–water partition coefficient	2.64	2.93	2.01	2.47	1.86

4.2.1 Results of mass balance calculation

The mass balance method compares the amount of mass loaded, desorbed and retained in the columns. The measured masses retained for all other compounds except TCE shows a lower value than the calculated value (Table 7). This provides an evidence to the fact that methanol does not completely extract the contaminants. It is also evident for chlorobenzene, the experimental result demonstrates that experimental artefacts, the most common of which is nonattainment of sorption/desorption equilibrium since the true equilibrium can require very long times (longer than 3 months [34]. The outcome of this study is in agreement to that of Bouwers [4], who reported modelling of column flush on natural soils and concluded that desorption of DCE is a nonlinear process during the entire 60-day experimental period.

4.3 Model limitations

It has to be taken into account that the field situation is modified while crushing, sieving and homogenizing the sample partially accounting for the model versus measured data discrepancy. Moreover, as a rule of thumb, it is easy to judge that the release rate was over exaggerated due to an assumed infinite bath (concentration of pumped water is nearly zero) and big flow rate. Assumption of one-dimensional flow to a complex and rather heterogeneous field condition may contribute to the model prediction uncertainty especially in high K_d species (CB and PCA). Future modelling and laboratory studies incorporating aqueous speciation and three-dimensional flow estimation would likely improve the model prediction in comparison to field situations [29]. Moreover, hot methanol extraction may have contributed to the disparities in the estimation of mass retained and mass adsorbed.

5 Conclusions

From the elution profiles, it was found that the more volatile compounds (DCE, TCE and TCA) showed a fast desorption behaviour with concentrations dropped below the detection limit (DCE and TCA), whereas concentration versus time plots of chlorobenzene and PCA proved delayed decrease in concentration. Release rates of all the five chlorinated hydrocarbons diminish with time indicating a nonlinear process.

Chlorobenzene showed a relatively high initial mass loading while the concentration in the leachate remained comparatively low. Therefore, high contamination in the aquifer material does not necessarily lead to high contaminant concentration in the aqueous phase.

However, concentrations for chlorobenzene stayed more or less constant in the leachate over the entire experimental time of 70 days. It is to be remarked that the compounds with higher K_d tend to desorb very slowly (chlorobenzene and PCA). Short-term fluxes poor fit the measured data in the early desorption process but slow desorption kinetics become important in the long-term.

Grain size has a significant influence on the more volatile compounds. In DCE and TCA, late values show a slow diffusion-limited desorption in finer grain size (column III), whereas in TCE grain size has a rather opposite effect in that late values become faster for finer sizes (column III). In chlorobenzene and PCA, the effect of grain size is less pronounced on desorption. However, generally, the finer the grain size, the faster is the diffusion rate constant.

Within the experimental time of 70 days, almost a complete desorption was achieved for DCE, TCE and TCA. However, a substantial fraction of chlorobenzene and PCA still remained in the lignite fraction at the end of the experiment. This provides evidence that chlorobenzene and PCA will continue to desorb in a very small amount for much longer time. Effective diffusion coefficients and octanol–water partition coefficients of PCA and chlorobenzene explain the reason why some contaminants show profound tailing,

The one-dimensional coupled analytical model reasonably describes the laboratory column leaching data through a two-step desorption process and help generate improved effective diffusion coefficients for the five chlorinated hydrocarbons.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest in regard to any financial or personal relationship with a third party whose interests could be positively or negatively influenced by the article's content.

References

1. Booij K, Achterberg PE, Sundby B (1992) Release rates of chlorinated hydrocarbons from contaminated sediments. *Neth J Sea Res* 29(4):297–310
2. Bold S, Kraft S, Grathwohl P, Liedl R (2003) Sorption/desorption kinetics of contaminants on mobile particles: modelling and experimental evidence. *Water Resour Res* 39(12):1329. <https://doi.org/10.1029/2002WR001798>
3. Bruner F (1993) Gas chromatographic environmental analysis; principles, techniques, instrumentation. Wiley, Hoboken, p 233
4. Bouwers HJH (1999) Transport models for desorption from natural soils packed in flushed columns. *Water Resour Res* 35(6):1771–1780

5. Çamur MZ, Yazıcıg H (2005) Laboratory determination of multi-component effective diffusion coefficients for heavy metals in a compacted clay. *Turk J Earth Sci* 14:91–103
6. Chen W (1997) Sorption and desorption of hydrocarbons to and from historically contaminated Lake Charles sediments. Masters Thesis, Rice University
7. Chien F (1972) Adsorption and desorption of chlorinated hydrocarbon pesticides by organic humic sludge. Masters Thesis, University of Missouri, Rolla. http://scholarsmine.mst.edu/masters_theses/5052
8. Cornelissen G, Van Noort CMP, Govers AJH (1997) Desorption kinetics of chlorobenzenes, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls: sediment extraction with tenax and effects of contact time and solute hydrophobicity. *Environ Toxicol Chem* 16(7):1351–1357
9. Culver BT, Hallisey PS, Sahoo D, Deitsch JJ, Smith AJ (1997) Modeling the desorption of organic contaminants from long-term contaminated soil using distributed mass transfer rates. *Environ Sci Technol* 31(6):1581–1588
10. Demau (2013) Guideline protocol for soil-column experiments assessing fate and transport of trace organics, the European Union Seventh Framework Program (FP7/2007–2013) under Grant Agreement No. 308339, www.demeau-fp7.eu
11. Deutsch J (1997) Groundwater geochemistry, fundamentals and applications to contamination. CRC Press, Boca Raton, p 232
12. Fetter W (1993) Contaminant hydrogeology, 2nd edn. Maxwell Macmillan Publishing Company, New York, p 500
13. Grathwohl P (1997) Diffusion in natural porous media—contaminant transport, sorption/desorption and dissolution kinetics. Springer, New York, p 207
14. Grathwohl P, Reinhard M (1993) Desorption of trichloroethylene in aquifer material: rate limitations at the grain scale. *Environ Sci Technol* 27(12):2360–2366
15. Grathwohl P, Pyka W, Merkel P (1994) Desorption and release of polycyclic aromatic hydrocarbons (PAHs) from contaminated aquifer material. In: Dracos TH, Stauffer F (eds) Transport and reactive processes in aquifers. Balkma, Rotterdam, pp 469–474
16. Jaiswal KD, Kumar A, Yadav RR (2011) Analytical solution to the one-dimensional advection–diffusion equation with temporally dependent coefficients. *J. Water Resour Prot* 3:76–84
17. Kan AT, Chen W, Tomson MB (2000) Desorption kinetics of neutral hydrophobic organic compounds from field-contaminated sediment. *Environ Pollut* 108:81–89
18. Kile DE, Chiou CT (1995) Partition of nonpolar organic pollutants from water to soil and sediment organic matters. *Environ Sci Technol* 29:1401–1406
19. Kim J, Corapcioglu M (2003) Modeling dissolution and volatilization of LNAPL sources migrating on the groundwater table. *J Contam Hydrol* 65:137–158
20. Kleinedam S, Rugner H, Grathwohl P (1999) Impact of grain scale heterogeneity on slow sorption kinetics. *Environ Toxicol Chem* 18(8):1673–1678
21. Liedl R, Ptak T (2003) Modeling of diffusion-limited retardation of contaminants in hydraulically uniform media. *J Contam Hydrol* 66:239–259
22. Meryl K (1987) Manual of sampling and analytical methods for petroleum hydrocarbons in groundwater and soil. American Petroleum Institute, Issue 4449
23. Patil SB, Chore HS (2014) Contaminant transport through porous media: an overview of experimental and numerical studies. *Adv Environ Res* 3(1):45–69
24. Persson Y (2007) Chlorinated organic pollutants in soil and groundwater at chlorophenol contaminated sawmill sites. Doctoral dissertation, UMEÅ University, Finland
25. Pignatello JJ, Xing B (1996) Mechanisms of slow sorption of organic chemicals to natural particles. *Environ Sci Technol* 30(1):1–11
26. Popp P, Möder M (1997) Sanierungsforschung in regional kontaminierten Aquiferen (SAFIRA): Bericht zur Machbarkeitsstudie für den Modellstandort Bitterfeld. In: Weiß H, Teutsch G, Daus B (eds) Organische Analytik. UFZ Leipzig-Halle GmbH, Leipzig, pp 73–75
27. Riley RG, Szecsody JE, Sklarew DS, Mitroshkov AV, Brown CF, Thompson CJ, Gent PM (2005) Carbon tetrachloride and chloroform partition coefficients derived from aqueous desorption of contaminated Hanford sediments. Pacific Northwest National Laboratory, PNNL-15239
28. Rödel W (1987) A guide to gas chromatography. Verlagsguppe Huthig Jehle Rehm GmbH
29. Rodríguez JF, Valverde JL, De Lucas A, Carmona M, González M (2005) Model for the determination of diffusion coefficients of heterovalent ions in macro-porous ion exchange resins by the zero-length column method. *Chem Eng Sci* 60:5836–5844
30. Schrap SM, Sleijpen LGG, Seinen W, Opperhuizen A (1994) Sorption kinetics of chlorinated hydrophobic organic chemicals. *Environ Sci Polut Res* 1(2):82–92
31. Schuth C, Grathwohl P (1994) Non-equilibrium transport of PAHs: a comparison of column and batch experiments. In: Dracos TH, Stauffer F (eds) Transport and reactive processes in aquifers. Balkma, Rotterdam, pp 143–148
32. Schwarzenbach RP, Gschwend PM, Imboden DM (1981) Environmental organic chemistry, 3rd edn. Wiley, Hoboken
33. Tenhulscher TEM, Vrind BA, Vandenheuvel H, Andervelde LE, Van Noort PCM, Beurskens JEM, Govers HAJ (1992) Triphasic desorption of highly resistant chlorobenzenes, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in field contaminated sediment. *Environ Sci Technol* 33:126–132
34. Wang G (2008) Sorption/desorption reversibility of polycyclic aromatic hydrocarbons (PAHs) in soils and carbonaceous materials. Doctoral Dissertation
35. Werth C, Hansen K (2002) Modeling the effects of concentration history on the slow desorption of trichloroethene from a soil humidity. *J Contam Hydrol* 54:307–327
36. Wisconsin Department of Natural Resources (WDNR) (2014) Understanding chlorinated hydrocarbon behavior in groundwater: guidance on the investigation, assessment and limitations of monitored natural attenuation. <http://dnr.wi.gov/files/PDF/pubs/rr/RR699.pdf>. Accessed in March 2017
37. Worch E (2004) Modeling the solute transport under non-equilibrium conditions on the basis of mass transfer equations. *J Contam Hydrol* 68:97–120
38. Wysick P, Weiss H, Kaschl A, Heidrich A, Sommerwark S (2002) Groundwater pollution and remediation options for multisource contaminated aquifers (Bitterfeld/Wolfen, Germany). *Toxicol Lett* 140:343–351
39. You J, Pehkonen S, Landrum PF, Lydy MJ (2007) Desorption of hydrophobic compounds from laboratory-spiked sediments measured by Tenax absorbent and matrix solid-phase micro-extraction. *Environ Sci Technol* 41:5672–5678
40. Zabiegała B (2006) Organic compounds in indoor environments. *Polish J Environ Stud* 15(3):383–393

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.