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Carbon and Chlorine Isotope Ratios of Chlorinated Ethenes Migrating through a Thick Unsaturated Zone of a Sandy Aquifer

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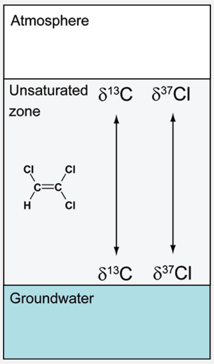
Supporting Information

ABSTRACT: Compound-specific isotope analysis (CSIA) can potentially be used to relate vapor phase contamination by volatile organic compounds (VOCs) to their subsurface sources. This field and modeling study investigated how isotope ratios evolve during migration of gaseous chlorinated ethenes across a 18 m thick unsaturated zone of a sandy coastal plain aquifer. At the site, high concentrations of tetrachloroethene (PCE up to 380 μg/L), trichloroethene (TCE up to 31,600 μg/L), and *cis*-1,2-dichloroethene (cDCE up to 680 μg/L) were detected in groundwater. Chlorinated ethene concentrations were highest at the water table and steadily decreased upward toward the land surface and downward below the water table. Although isotopologues have different diffusion coefficients, constant carbon and chlorine isotope ratios were observed throughout the unsaturated zone, which corresponded to the isotope ratios measured at the water table. In the saturated zone, TCE became increasingly depleted along a concentration gradient, possibly due to isotope fractionation associated with aqueous phase diffusion. These results indicate that carbon and chlorine isotopes can be used to link vapor phase contamination to their source even if extensive migration of the vapors occurs. However, the numerical model revealed that constant isotope ratios are only expected for systems close to steady state.



INTRODUCTION

Compounds-specific stable isotope analysis (CSIA) is increasingly used to relate contaminant plumes to their source in groundwater studies.[1,2] The method relies on differences in isotope ratios between various manufacturers of the same compound[3−5] and the conservative behavior of isotope ratios in the absence of reactive processes.[1] There is an increasing interest to apply CSIA also to relate vapor phase contamination in the unsaturated zone to subsurface nonaqueous phase (NAPL) sources or groundwater plumes. However, recent laboratory studies have suggested that in partly saturated porous media, transport and partitioning processes may lead to significant isotope fractionation. Isotope fractionation has been demonstrated for diffusion of small volatile organic molecules across a porous media, vaporization from a NAPL phase, and air−water partitioning.[6−10] At the field scale, carbon isotope fractionation was also observed during a controlled release experiment with petroleum hydrocarbons.[11] However, in that study transport and reactive processes contributed to isotope fractionation. Furthermore, the small source volume (10 L NAPL) led to highly transient conditions untypical for common subsurface NAPL contaminations.

The aim of this study was to investigate the isotope evolution of volatile organic compounds (VOCs) migrating through a thick sandy unsaturated zone based on a field study and numerical modeling. A site contaminated with trichloroethene (TCE) and tetrachloroethene (PCE) was selected as these compounds tend to be stable under oxic conditions[12] which are typically encountered in sandy unsaturated zones. Hence it is possible to evaluate the effect of transport and partitioning processes in isolation. Not only carbon isotopes but also chlorine isotopes were included because a diffusion isotope effect might especially occur for chlorine isotopes, which are two mass units apart.

The field study was carried out at a contaminated site in the coastal plain aquifer of Israel. Samples were obtained with a unique passive multilevel sampling system (MLS) using dialysis cells.[13] This system has the advantage that the saturated and unsaturated zones are sampled simultaneously at a high vertical spatial resolution. Since an identical sampling and analytical method is used for the saturated and unsaturated zones, isotope trends across the water table can be assessed with high precision. Two sampling campaigns were carried out. The first sampling campaign included carbon isotope ratios of *cis*-1,2-dichloroethene (*cis*-1,2-DCE), TCE, and PCE, while the second campaign focused on the carbon and chlorine isotope ratio of TCE which is the major contaminant at the site. In order to explore the transient evolution of isotope ratios after source emplacement, which is usually not possible at real sites where the release has occurred in the past, and to generalize the results of the field study, numerical simulations were carried out as well. Isotope trends were evaluated for different scenarios including a contaminant release to the unsaturated zone from groundwater and an unsaturated zone NAPL source. Furthermore, migration through homogeneous and layered porous media was compared. Based on the field and numerical study, conclusions were drawn about the applicability of isotope fingerprinting methods to VOC contamination under unsaturated conditions.

■ MATERIALS AND METHODS

Study Area. The study site (area of 43,000 m^2), a former industry facility chiefly involved in metal-working and plating, is located in the metropolitan Tel Aviv area, a topographically flat region of the central coastal plain aquifer of Israel. This aquifer is composed of Pleistocene sand and calcite-cemented sandstone interbedded with marine and continental silty clay lenses.[14] In general the aquifer is phreatic, but, in some areas, it is subdivided by clay lenses into as many as four subaquifers.[15] At the study site, where the average depth from ground surface to the saturated zone is 18 m, chlorinated hydrocarbons were used and indiscriminately disposed off on the factory grounds (between 1949 to 1998), causing severe contamination of the unsaturated and saturated zones underlying the factory premises.[16] The exact location and quantity of DNAPL release is unknown. A previous study conducted at the saturated-unsaturated interface of the same study area reported very high concentrations of VOCs (e.g., TCE 260,000 $\mu g/L_{water}$ and 124,000 $\mu g/L_{air}$). Three monitoring wells (M5, M5A, and M15; Figure S1) were sampled in the course of this study. M5 and M5A are 3 m apart, while M15 is around 25 m away from these two monitoring wells. The geological description of the boreholes is presented in the Supporting Information (Figure S1).

Sampling Method. Groundwater and vapor samples from the unsaturated zone were obtained with a Multi Layer Sampler (MLS), a passive sampling methodology based on equilibrium between water−water and water-gas phases. The MLS used in the present study has been extensively described before.[13,17] Briefly, it consists of individual sampling units assembled in a modular way. Each unit consists of a stainless steel cylinder (150 mL) closed from both sides with dialysis membranes (Versapor membrane, PALL Corporation, 0.2 mm) crimped in a PVC hoop with Viton O-ring and filled with distilled water. The dialysis cells are sandwiched between flexible Viton seals that fit into the inner diameter of the well screen, creating a 12 cm sampling interval per cell, and a physical divide between consecutive cells. The MLS units are connected to each other at desired intervals and are lowered into an observation borehole. After reaching chemical equilibrium with gas (in the unsaturated zone) or groundwater, the MLS is retrieved and the water in the dialysis cells is analyzed. A previous study showed that the time scale of equilibration of the sampler is much shorter than the time scale of concentration changes at the site (20). Hence perturbations of the equilibration process by varying concentrations that could lead to slight variations in the measured isotope ratios can be excluded.

In all sampling campaigns the MLS were located inside the monitoring wells for 2−4 weeks. The time to achieve equilibrium between compounds in the groundwater or the gas phase of the vadose zone and in the dialysis cells was found in previous studies to be less than 6 days.[18,19] Therefore, the VOC content in each dialysis cell represents the average VOC concentrations of the gaseous and/or liquid phases of the aquifer during the week before the MLS was retrieved from the monitoring well.

Two monitoring campaigns are reported. In the first one, the MLSs were retrieved from wells M5 and M5A on March 16 and June 17, 2004. In the second campaign the MLSs were retrieved from wells M5, M5A, and M15S (Figure S1) on November 23, 2009.

Analytical Methods. VOCs were determined by headspace GC/MS after a 1:5 dilution due to the high concentrations and after the addition of an internal standard,[20] using a Combi PAL Auto sampler (CTC analytics), a 6890N network GC system (Agilent Technologies), and a 5973 network Mass Selective detector (Agilent Technologies). Taking into account the dilution factor, the method detection limit was 56.5 μg/L for *cis*-DCE, 13 μg/L for TCE, and 14 μg/L for PCE. The standard uncertainty was 3.3% for *cis*-1,2-DCE, 4.1% for TCE, and 6.1% for PCE (Graber et al., 2000; Lev, 2006). VOC concentrations in the dialysis cells located in the unsaturated zone are reported as equivalent aqueous phase concentrations. Therefore, it is possible to directly evaluate concentration gradients across the water table without resorting to Henry's law calculations.

For the first sampling campaign, stable carbon isotope analysis was carried out using a Thermo Trace gas chromatograph (GC) coupled to a Thermo Finnigian Delta plus XP isotope ratio mass-spectrometer (IRMS) via a GC−CIII combustion interface set at 940 °C (Thermo Scientific, Waltham, MA, USA). VOCs were extracted from water samples of 25 mL using a Tekmar Velocity Purge&Trap system (Teledyne Tekmar, Mason, OH, USA). Minimum required concentrations for PCE, TCE, and *cis*-1,2-DCE carbon isotope analysis were approximately 5, 10, and 10 μg/L, respectively. For the second sampling campaign, a Hewlett-Packard 6890 GC (Agilent, Palo Alto) coupled to a Micromass Isochrom (now Isoprime, Cheadle Hume, UK) was used as previously described.[21] Chlorine isotope analysis was performed by direct injection of the GC separated chlorinated ethenes into the ion source of a Micromass Isoprime IRMS (now Isoprime, Cheadle Hume, UK) as previously described.[22] Samples were extracted using solid phase microextraction automated with a CTC Combipal sampler (CTC, Zwingen, Switzerland). All isotope ratios are reported relative to an international standard (VPDB for carbon, SMOC for chlorine) using the delta notation $\delta = (R/R_{std}-1)*1000(‰)$ where R and R_{std} are the isotope ratio of the sample and the standard, respectively.

Numerical Modeling. Numerical modeling was used to explore in more detail how different factors influence the isotope ratios of VOCs migrating through a thick sandy unsaturated zone toward the land surface. The parameters and model domain corresponded as much as possible to the field site. However, since water and vapor transport through the unsaturated zone was not studied in detail and the exact source location and release date is not known, it was not attempted to exactly reproduce the site conditions and concentration trends. Two different source scenarios were evaluated: VOCs originating from a DNAPL source located in the unsaturated zone close to the water table, the likely scenario at the site as suggested by ref 23, and VOCs originating from a groundwater contaminant plume. Two geological configurations were also studied: a layered porous media, as present at the site, and an unsaturated zone composed of homogeneous sand (Figure S2). Only carbon isotope ratios are presented. Simulated chlorine isotope profiles have the same shape except that shifts are approximately twice the shift of carbon. The modeling approach is described in detail in the Supporting Information. Briefly, water flow and distribution was simulated based on Richard's equation and soil−water retention curves characterized by the Van Genuchten equation.[24] Transport of VOC was assumed to occur by advection, dispersion, and diffusion in the saturated zone/capillary fringe and by diffusion only in the unsaturated zone. Equilibrium partitioning between the gas and water phase was assumed. Analogously to the measured data, concentrations for the unsaturated zone are presented as equivalent aqueous phase concentrations.

■ RESULTS AND DISCUSSION

Concentration Analysis. In the first sampling campaign, TCE was present at the highest concentration among all chlorinated ethenes with concentrations reaching 31,600 μg/L in the saturated zone and 43,500 μg/L in the unsaturated zone (Figure 1c). In the zone above the water table, higher concentrations were measured in M5A than in M5 likely due to lateral concentration variations in the unsaturated zone. In M5, TCE concentrations immediately above and below the water table were comparable indicating that an air−water partitioning equilibrium had been reached. In both the unsaturated and saturated zone, TCE concentrations decreased with increasing distance from the water table (Figure 1c). In M5A that covered the entire unsaturated zone, the TCE concentration steadily decreased from 43,500 μg/L at the water table toward the land surface reaching a value of 5,180 μg/L at 2.8 m below ground surface (mbgs) indicating upward diffusion of TCE. Similar concentrations patterns were also observed for *cis*-1,2-DCE (Figure 1a) and PCE (Figure 1e), but concentrations were much lower. For TCE and PCE, the concentration gradient was steeper in the top 9 m as compared to the zone between 9 and 15 mbgs. All compounds showed steeper concentration gradients for the deepest three sampling points compared to sampling points above.

In the second sampling campaign, isotope ratios were only determined for the main contaminant, TCE, and therefore also only the concentration data for TCE are presented. In M5 and M5A, the TCE concentrations were lower than in the first sampling campaign with a maximum concentration of 13,200 μg/L in the saturated zone and 10,900 μg/L in the unsaturated zone (Figure 2a). The TCE concentration decreased nearly linearly from a value of 10,070 μg/L near the water table to a concentration of 1,330 μg/L at 1 mbgs similarly as in the first sampling campaign. In M15S, TCE concentrations were fairly stable between 8 and 17 mbgs, while they decreased toward land surface and below the water table (Figure 2d).

As considered above, unsaturated zone contamination could originate from a groundwater contaminant plume that affects the unsaturated zone by water−air partitioning and upward diffusion of VOCs. Alternatively, or simultaneously, DNAPL might be present also in the unsaturated zone. The observed concentration gradients across the water table and the results from the numerical modeling can help to distinguish between these two scenarios. For most concentration profiles (Figure 1a,c,e, Figure 2d), the concentration decreases in the top layer of the aquifer in directions away from the water table. This is consistent with the existence of a DNAPL source close to the water table creating a vapor contamination that is partitioning into the saturated part of the aquifer and migrating downward by diffusion, dispersion, and possibly convection as a result of density driven flow.[25] As shown by results of the modeling simulation, the release of contaminants from a dissolved plume would create a concentration gradient in the opposite direction (Figure 3c) due to mass transfer resistance across the top of the saturated zone and the capillary fringe.[26,27]

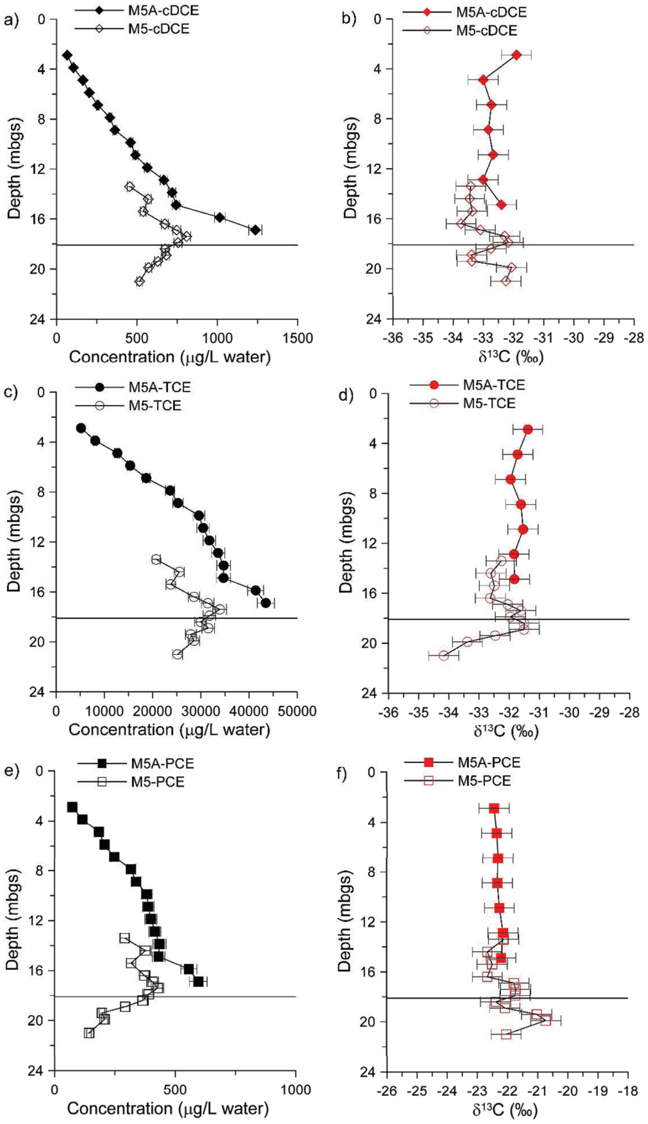


Figure 1. Concentration and stable carbon isotope ratio of *cis*-1,2-DCE (a,b), TCE (c,d), and PCE (e,f) on 17.6.2004 at monitoring wells M5A and M5. The concentrations in the unsaturated zone correspond to equivalent aqueous phase concentrations. The horizontal line indicates the location of the water table.

For several compounds, the concentration gradients change (Figure 1c and e, Figure 2d) at a depth of approximately 9 m, which might be related to a change in lithology with occurred slightly below this depth (Figure S1). For lower permeability

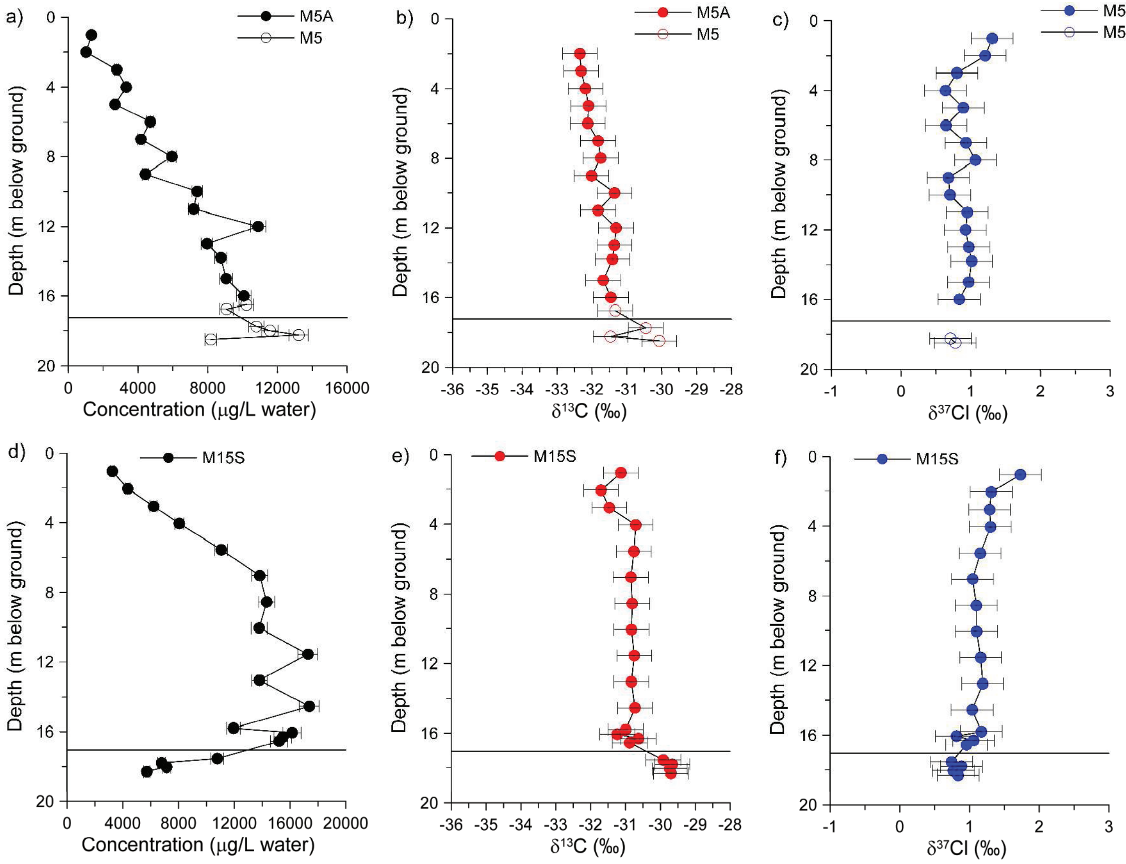


Figure 2. Concentration, stable carbon isotope ratio, and stable chlorine isotope ratio of TCE on 23.11.2009 in monitoring wells M5A and M5 (a-c), and M15S (d-f). The concentrations in the unsaturated zone correspond to equivalent aqueous phase concentrations. The horizontal line indicates the location of the water table.

zones at the top, a steeper concentration gradient is expected to maintain the same contaminant flux as in the higher permeability layers below as shown by our modeling study (Figure 3a and c).

Stable Isotope Analysis. In the first sampling campaign, only stable carbon isotope ratios were determined. The range of δ^{13}C values for *cis*-1,2-DCE (Figure 1b) were similar to the range of values detected for TCE (Figure 1d). This suggests that *cis*-1,2-DCE was concomitantly present in the TCE DNAPL or originated from a separate source rather than being a biodegradation product as *cis*-1,2-DCE produced by biodegradation is expected to be depleted in ^{13}C as compared to the TCE source.[28−30] This conclusion is consistent with the presence of oxygen in the saturated and unsaturated zone[20,23,31] making reductive dechlorination of PCE and TCE unlikely. In the first sampling campaign, δ^{13}C values of TCE in M5A were uniform throughout the unsaturated zone (Figure 1d). Furthermore, the δ^{13}C value of TCE in the unsaturated zone corresponded to the δ^{13}C of TCE immediately above and below the water table in M5. However, the δ^{13}C of TCE became depleted in ^{13}C in the saturated zone with increasing distance from the water table. Similarly as for TCE, *cis*-1,2-DCE (Figure 1b) and PCE (Figure 1f) showed constant δ^{13}C values throughout the unsaturated zone that corresponded to δ^{13}C values at the concentration peak in M5. Small fluctuation of δ^{13}C in *cis*-1,2-DCE and PCE occurred around the water table.

In the second sampling campaign, isotope ratios were only determined for the main contaminant, TCE, but this time chlorine isotope ratios were included as well and samples were also taken at a second location (M15S). Carbon (Figure 2b and e) and chlorine (Figure 2c and f) isotope ratios were uniform throughout the unsaturated zone. Some small variations in δ^{13}C (Figure 2e) and δ^{37}Cl (Figure 2c and f) occurred close to the land surface, which however lay within the range of uncertainty of the measurement. The average δ^{13}C value for TCE of unsaturated zone samples from M5A was similar in the first (-31.68 ± 0.20‰, $n = 7$) and second (-31.82 ± 0.36‰, $n = 16$) campaign.

When discussing the isotope data, it has to be taken into account that potential equilibrium isotope fractionation during air−water partitioning is canceled out due to the sampling method that relies on equilibrated water samples both in the saturated and unsaturated zone. Moreover, previous studies have shown that carbon isotope fractionation during equilibrium air−water partitioning is small (<0.61‰) for chlorinated ethenes.[21] In general, constant isotope ratios were observed throughout the 18 m thick unsaturated zone although diffusion coefficients vary for different isotopologues and despite of the changes in lithology within the unsaturated zone. The numerical modeling demonstrates that indeed constant unsaturated zone isotope values are expected at steady state and isotope ratios closely match those of the source although diffusion coefficients vary for different isotopologues. For a NAPL source, the simulated steady state isotope ratios are constant throughout the unsaturated zone even for a layered unsaturated zone (Figure 3b). For a groundwater

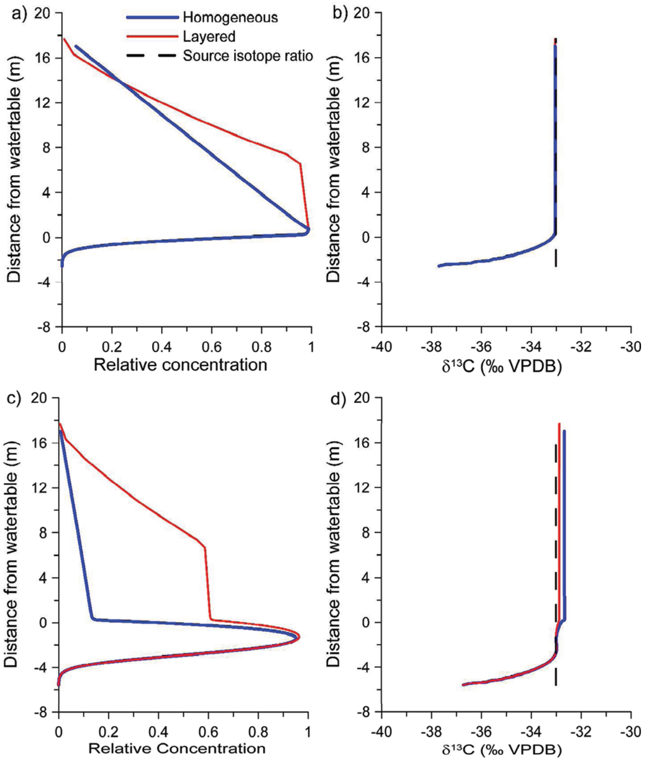


Figure 3. Simulated steady state concentration and carbon isotope ratios for TCE originating from a NAPL source above the water table (a,b) and for TCE originating from a groundwater plume (c,d) for a homogeneous sandy (red) and a layered (bold blue) unsaturated zone with a clay layer (0–2 m) and a sandy clay layer (2–9 m) overlaying a sandy layer. Dashed line: Source isotope composition.

source (Figure 3d), a small offset is expected across the water table especially for the homogeneous case. The offset is due to mass transfer limitations across the capillary fringe that leads to a slight enrichment of heavy isotopes as light isotopologues diffuse more rapidly through the unsaturated zone. For the layered case, the offset is smaller because diffusion across the lower permeability zone now also partly restricts the flux toward the atmosphere. However, in both cases, the offset is below 0.5‰ and hence in the range of uncertainty of the measurement.

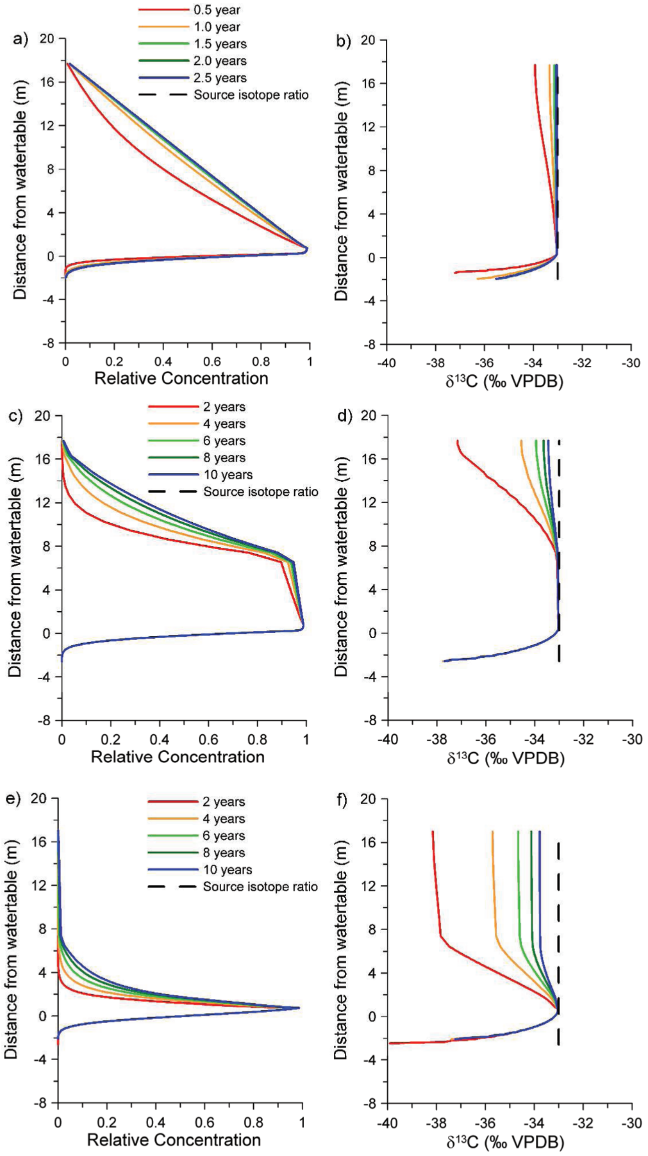


Figure 4. Simulated transient concentration and carbon isotope ratios for TCE diffusing through a homogeneous sandy unsaturated zone (a,b), a layered unsaturated zone with low permeability layers overlaying a higher permeability layer as observed at the field site (c,d) and with the inverse order (e,f) from a NAPL source. Dashed line: Source isotope composition.

In the transient simulations, a uniform isotope profile is reached within a year for a homogeneous sandy unsaturated zone (Figure 4b). However, in the layered case, a trend toward depleted isotope ratios in the direction of the land surface persists for several years in the low permeability cover layer, while isotope ratios stabilize rapidly in the deeper sandy zone (Figure 4d). For an inverse lithology, isotope gradients again persist for several years in the deeper zone, while isotope ratios in the sandy shallower zone follow the trend of the deeper zone with little spatial variation for a given time (Figure 4f). Hence the simulations demonstrate that transient isotope ratio gradients can especially be expected in zones where the effective diffusion coefficient is low. The transient isotope gradients are due to a faster advancement of light isotopologues compared to heavy isotopologues as the vapor plume expands by diffusion.[11] As the isotopologue concentrations evolve toward steady state, the trend toward a depleted isotope composition vanishes. At steady state, the relative concentration profiles of isotopologues only depend on the porosity and water content distribution and hence are identical for all isotopologues (see Supporting Information). As a result, uniform isotopologue ratio and isotope ratio profiles are expected although concentration profiles are nonlinear. Advective transport (e.g., due to barometric pumping) might further accelerate the trend toward uniform isotope profile as advective transport is not associated with isotope fractionation.

The comparison of measured and modeled data in this study suggests that close to steady state conditions prevailed at the field site despite the occurrence of recharge events during winter. Close to the water table the steady state conditions might have been perturbed by fluctuations of the water table, which might have led to the small variations in isotope ratios observed for some compounds. The evolution toward constant isotope profiles despite differences in diffusion coefficients is consistent with a previous laboratory study with petroleum hydrocarbons.[6]

However, the time scale required to reach constant isotope profiles is very different in the previous laboratory study compared to the current simulations. The simulations suggest that for extended transport distances and especially lower permeability porous media it might take years to reach constant isotope profiles, while for a thick sandy unsaturated zone, uniform isotope profiles are reached within a year (Figure 4). In fully water saturated systems with low diffusion rates, isotope ratio gradients were observed to persist over several 1000s of years.[32]

When considering the top layer of the saturated zone, the most pronounced isotope trend was observed for the main contaminant, TCE, in the first sampling campaign with a depletion of ^{13}C away from the water table (Figure 1d). This trend could be due to isotope fractionation associated with diffusion and dispersion,[33] with the light isotopes migrating more rapidly away from the water table. Interestingly, this isotope trend is expected to persist under steady state conditions and does not level out as expected for the isotope profile in the unsaturated zone (Figure 3b, d and f). A similar isotope profile was not observed in the second sampling campaign possibly due to perturbation by water table fluctuations or microscale convection caused by slight density variations of the groundwater.[25]

Implications for Isotope Forensics. There is an increasing interest to use isotope ratio analysis to relate vapors detected in the unsaturated zone and in buildings to groundwater contamination. This work provides the first field and scenario modeling study on isotope trends of chlorinated hydrocarbons diffusing through an unsaturated zone. The study demonstrates that the isotope signature of chlorinated ethenes is conserved during migration across the unsaturated zone despite variations in the concentrations of more than one order or magnitude and nonlinear diffusion profiles likely related to changes in lithology. Furthermore, the isotope ratio agreed well between the high concentration zone in groundwater and the unsaturated zone, and isotope ratios did not change between the two sampling campaigns 5 years apart. These observations clearly demonstrate that stable isotope analysis can be used to link soil gas contamination to groundwater contamination even if soil gas samples are taken at a large distance from the water table. However, the modeling study demonstrates that variations in isotope ratios can occur under transient conditions. Furthermore, variability above the analytical precision of the measurement can be introduced by the disturbance of steady state profiles by rainfall events or pressure fluctuations and during sampling. These variations have to be taken into account when applying the method in isotope forensic studies.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Lithology of sampling locations. Additional information about modeling approach. This material is available free of charge via the Internet at http://pubs.acs.org.

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