Environmental Science & Technology

Article

pubs.acs.org/est

Quantification of Degradation of Chlorinated Hydrocarbons in Saturated Low Permeability Sediments Using Compound-Specific Isotope Analysis

Philipp Wanner,*,† Beth L. Parker,‡ Steven W. Chapman,‡ Ramon Aravena,§ and Daniel Hunkeler†

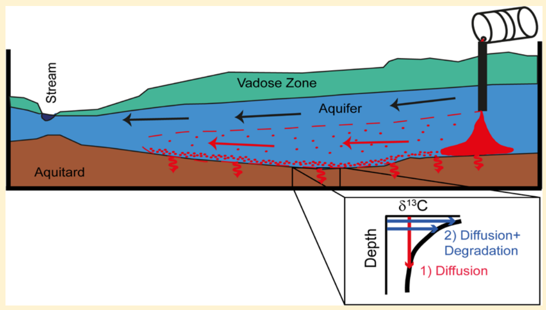
†Centre for Hydrogeology & Geothermics (CHYN), University of Neuchâtel, Rue Emil Argand 11, CH-2000 Neuchâtel, Switzerland

‡G360 Centre for Applied Groundwater Research, School of Engineering, University of Guelph, 50 Stone Road East, Guelph, Ontario, Canada N1G 2W1

§Department of Earth and Environmental Sciences, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, Canada N2L 3GI

Supporting Information

ABSTRACT: This field and modeling study aims to reveal if degradation of chlorinated hydrocarbons in low permeability sediments can be quantified using compound-specific isotope analysis (CSIA). For that purpose, the well-characterized Borden research site was selected, where an aquifer−aquitard system was artificially contaminated by a three component chlorinated solvent mixture (tetrachloroethene (PCE) 45 vol %, trichloroethene (TCE) 45 vol %, and chloroform (TCM) 10 vol %). Nearly 15 years after the contaminant release, several high-resolution concentration and CSIA profiles were determined for the chlorinated hydrocarbons that had diffused into the clayey aquitard. The CSIA profiles showed large shifts of carbon isotope ratios with depth (up to 24‰) suggesting that degradation occurs in the aquitard despite the small pore sizes. Simulated scenarios without or with uniform degradation failed to reproduce the isotope data, while a scenario with decreasing degradation with depth fit the data well. This suggests that nutrients had diffused into the aquitard favoring stronger degradation close to the aquifer−aquitard interface than with increasing depth. Moreover, the different simulation scenarios showed that CSIA profiles are more sensitive to different degradation conditions compared to concentration profiles highlighting the power of CSIA to constrain degradation activities in aquitards.



1. INTRODUCTION

Due to improper disposal and accidents, chlorinated hydrocarbons are major subsurface contaminants at many industrial sites. After releasing at the surface, chlorinated hydrocarbons migrate vertically as dense nonaqueous phase liquid (DNAPL) into aquifer systems and tend to form pools on top of low permeability sediments. With time the accumulated DNAPL phase is dissolved and transported by advection in the aquifer and by diffusion into the underlying low permeability sediments.[1,2] After reduction of the strength of the chlorinated hydrocarbon plume in the aquifer, back-diffusion occurs from low permeability sediments toward the aquifer due to the reversal of the concentration gradient, forming a long-term contamination source.[1−3,5] Most previous studies assumed that chlorinated hydrocarbons are not affected by degradation in low permeability sediments.[2−4,6] It was commonly hypothesized that microbial growth is very limited in the small pores of low permeability sediments and that degradation of chlorinated hydrocarbons is thus unlikely to occur.[7−10] In contrast, Manoli et al.[11] and Scheutz et al.[12] stimulated microbial growth in a clayey till and demonstrated that degradation can also occur in low permeability sediments despite the small pore sizes. By injecting electron donors and nutrients into fractures and sandy stringer in a low permeable clay unit, Manoli et al.[11] and Scheutz et al.[13] revealed that the electron donors and nutrients diffuse into the low permeable zones stimulating degradation activities in the surrounding clay unit. The degradation activities in the clay were strongest adjacent to the high permeability zone and decreased within a few centimeters distance. Moreover, recent studies[14,15] found evidence for degradation of chlorinated hydrocarbons in low permeability sediments without stimulating microbial growth. However, the natural occurrence of degradation activities in aquitards has not yet been well constrained. In general most degradation studies have been done at sites, where the contamination occurred accidentally[14,15] such that the initial conditions of the contamination source (composition, spill time, volume) were not well-known. This complicates the identification of

Received: December 28, 2015
Revised: April 29, 2016
Accepted: May 6, 2016
Published: May 6, 2016

DOI: 10.1021/acs.est.5b06330
Environ. Sci. Technol. 2016, 50, 5622−5630

degradation activities and hampers the quantification of degradation rates.

Compound-specific isotope analysis (CSIA) has been successfully used as a tool to assess degradation occurring in aquifer systems. This method makes use of the more rapid cleavage of bonds between light compared to heavy isotopes during degradation.[16−22] In contrast to aquifers, it is not yet clear as to what extent CSIA can also be used to quantify degradation of chlorinated hydrocarbons in saturated low permeability sediments. Recent studies[23,24] quantified for the first time isotope fractionation of organic contaminants due to aqueous phase diffusion and showed that it is associated with only a small isotope effect. Therefore, isotope fractionation associated with diffusion is not expected to impair identification of degradation in low permeability sediments using CSIA.

In this study, we investigate if CSIA can be used to identify and quantify reactive processes in saturated low permeability sediments. For this purpose, an area of the well-characterized aquifer−aquitard system at the Borden research site was selected. At this site a prior chlorinated hydrocarbon DNAPL infiltration experiment was conducted, resulting in formation of a plume in the aquifer and contamination of the underlying aquitard via diffusion below the plume. Multiple high-resolution concentration and compound-specific carbon isotope ratio profiles were determined using cores collected from the aquitard along groundwater monitoring transects at varying distances downgradient from the contamination source at about 14.5 years (5281 days) after the DNAPL release. Three different degradation scenarios were simulated for the aquitard to assess how vertically varying degradation conditions affect CSIA profiles and to identify which scenario is most consistent with measured field data. The present study provides new insight into degradation activities in a clayey aquitard from an aged controlled release experiment, which improves the understanding of the fate of chlorinated hydrocarbons in saturated low permeability sediments. Moreover, the study provides a basis for estimating the longevity of secondary contamination sources in low permeability sediments affecting adjacent aquifers.

2. MATERIALS AND METHODS

2.1. Site Description and Controlled Release Experiment Procedure. The controlled release experiment was performed in an aquifer overlying a clayey aquitard in the forested area of the Borden research site, Ontario, Canada approximately 100 km north of the city of Toronto (Figure 1). Both the aquifer as well as the aquitard is well characterized by previous studies.[25−34] The sandy aquifer and the clayey aquitard were formed by the sedimentary deposition in the proglacial lake Algonquin 12,000 years B.P.[25] The aquifer consist of primarily horizontal, discontinuous lenses of medium grained, fine-grained, and silty fine-grained sand[26] with a mean porosity of 0.33 (n = 36; standard deviation (SD) of 0.017).[27] Despite the observed variability, the sandy aquifer is considered as relatively homogeneous.[28] At the study site the water table varies seasonally between 0.5 and 1.5 m below ground surface (bgs) and the groundwater velocity varies over the year with an average of 12 ± 8 cm/day.[29] The lateral flow direction also changes seasonally within an angle range of about 58°[30] (Figure 1). The aquifer thickness is about 3 m[29] containing a thin transition zone with occasional cobbles at the aquifer−aquitard interface. The underlying aquitard consists mainly of dioctahedral mica (likely muscovite) and chlorite with

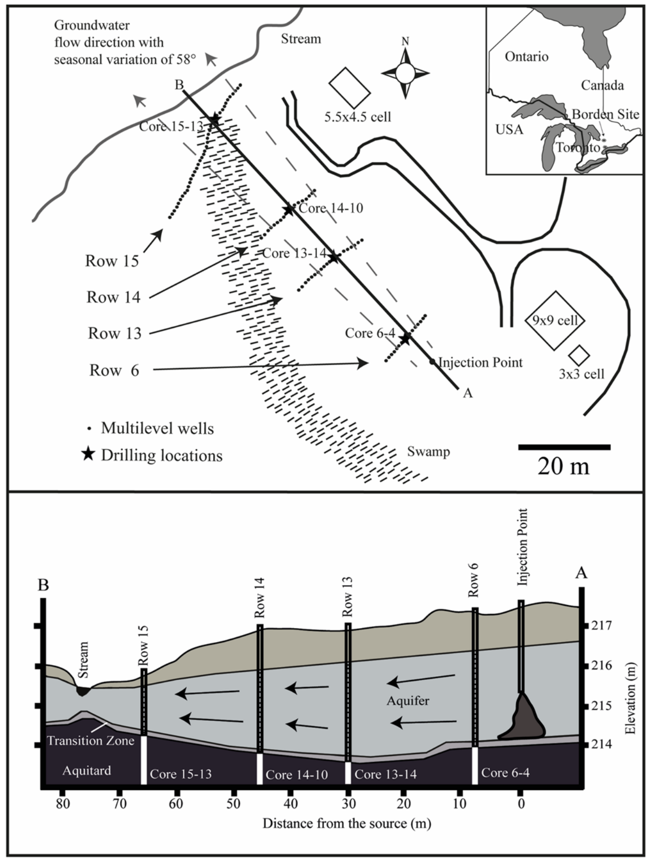


Figure 1. (A) Locations of multilevel wells along transects (only selected transects shown), drilling locations for determination of aquitard concentration and compound-specific carbon isotope ratio profiles, and injection point at the forested area at the Borden research site and (B) cross-section along the groundwater flow direction showing multilevel system depths in the aquifer and core intervals in the aquitard.

detectable amounts of kaolinite and smectite[35] with a mean porosity of 0.40 (n = 13; standard deviation (SD) of 0.09).[36] The aquitard thickness is about 8 m and is subdivided into upper and lower aquitard units.[31] The upper aquitard is about 3 m thick with a hydraulic gradient of 0.1[37] and a hydraulic conductivity ranging between 2.0×10^{-7} and 1.8×10^{-9} m/s,[31] while the lower aquitard is 5 m thick with a hydraulic gradient of 0.7[37] and a hydraulic conductivity of 1.0×10^{-8} m/s.[38]

The controlled release experiment was initiated by Laukonen[30] on April 8, 1999 by injecting 50 L of a three component DNAPL mixture containing tetrachloroethene (PCE, 45 vol %), trichloroethene (TCE, 45 vol %), and chloroform (TCM, 10 vol %) into the sandy aquifer, through an open-ended pipe 0.5 m below the groundwater table (Figure 1). After injection, the DNAPL served as a source for a natural gradient, dissolved phase plume that was monitored in detail with 16 rows of multilevel wells located perpendicular to groundwater flow direction over a distance of 95 m downgradient of the injection point by Laukonen,[30] Klein,[39] Vargas,[32] and the present study. Each multilevel row has between 8 and 30 multilevel wells containing between 7 and 16 sample points each, with a maximum 0.15 m vertical spacing, resulting in more than 3200 sampling ports total.

2.2. Groundwater Sampling, Core Retrieval, and VOC Extractions. A detailed description of groundwater sampling,

DOI: 10.1021/acs.est.5b06330
Environ. Sci. Technol. 2016, 50, 5622−5630

core retrieval, core subsampling, and VOC extraction from core subsamples can be found in section 1 of the Supporting Information (SI). In brief, groundwater from multilevel wells in the aquifer was sampled using Geopump peristaltic pumps with dedicated 0.32 cm OD diameter Teflon tubing. For the present study, multilevel well rows 6, 13, 14 and 15, located at 8, 30, 45, 65 m distance downgradient from the DNAPL injection point, were sampled in summer 2008 and 2013 (Figure 1). In contrast to the aquifer, water sampling in the aquitard was not possible as not enough water can be obtained from the aquitard. Hence, to assess chlorinated hydrocarbon concentration and compound-specific carbon isotope ratio profiles in the aquitard, continuous cores were collected adjacent to selected multilevel wells (ca. 20 cm distance) along four transects at rows 6, 13, 14, and 15 downstream of the injection point (cores referred to as 6-4, 13-14, 14-10, and 15-13, corresponding to the nearest multilevel well designation) on November 15, 2013, at about 14.5 years (5281 days) after the DNAPL release occurred (Figure 1). Continuous cores were collected from the aquitard beginning just above the interface using a Geoprobe 7720DT direct-push rig and the Envirocore dual tube sampling system described by Einarson et al.[40] To obtain high resolution chlorinated hydrocarbon concentration and CSIA profiles, retrieved cores were photographed, logged, and subsampled with a narrow spacing (~5 cm) as a function of depth, and chlorinated hydrocarbons were subsequently extracted from the subsamples in methanol as described by Parker[36] and White et al.[7]

2.3. Concentration, Compound-Specific Carbon Isotope, and Organic Carbon Content Analysis. Detail descriptions of analytical methods are available in section 1 of the SI. Briefly, chlorinated hydrocarbon concentrations in groundwater samples and in the methanol extracts of core subsamples were analyzed by a gas chromatograph coupled to a mass spectrometer (GC-MS). Compound-specific carbon isotope ratios of PCE, TCE, and *cis*-dichloroethene (cDCE) were determined by a gas chromatograph coupled to an isotope mass spectrometer (GC-IRMS). The organic carbon content in the cores was measured using a G4 Icarus combustion analyzer.

3. NUMERICAL MODELING

A 1D numerical reactive transport model was developed to simulate the migration of chlorinated hydrocarbons in the aquitard at the Borden site under various degradation conditions. The aim of the simulations was to assess how different degradation scenarios are reflected in concentration and CSIA profiles and to explore if degradation activities lead to unique concentration and isotope ratio patterns compared to a diffusion/back-diffusion scenario without degradation. The modeling approach is described in detail in section 2 of the SI. Briefly, it was assumed that transport is diffusion dominated in the clayey aquitard and that sorption occurs linearly and noncompetitive for the observed VOC concentration range, which is consistent with previous studies[35,36,41] Model calibration was performed against measured field data (see section 2.3. in the SI for details). The known time series of chlorinated hydrocarbon concentrations at the aquifer interface from the bottommost port on the adjacent multilevel well (ca. 20 cm distance) were used as a boundary condition (Figures S1A–D, SI). The degradation scenarios were modeled for 5281 days (~14.5 years), which corresponds to the time period between contaminant infiltration and the retrieval of the cores from the aquitard. For simulating the scenarios, initial compound-specific carbon isotope ratios ($\delta^{13}C_{VPDB}$) at the aquifer–aquitard interface in a range between −25.0‰ and −26.0‰ for PCE, between −28.0‰ and −30.0‰ for TCE, and between −33.0‰ and −37.0‰ for cDCE were used. These values correspond to groundwater CSIA measurements conducted by Vargas[32] at the aquifer–aquitard interface. Degradation activities affecting chlorinated hydrocarbons in the aquitard were taken into account in the model by considering the sequential dechlorination of PCE (Table S1, SI). Carbon isotope fractionation during the sequential dechlorination of PCE was simulated as described by Van Breukelen et al.[42] using calibrated isotope enrichment factors of ε_{PCE}= −2.0‰, ε_{TCE} = −18.2‰, and ε_{cDCE} = −24.0‰ (Table S4a). These values are within the $\pm 1\sigma$ range of the average of all published isotope enrichment factors for the sequential dechlorination of PCE (Table S2a-c, SI). Besides reactive processes, it was assumed that the diffusive transport process is also associated with an isotope effect. Isotope fractionation factors due to diffusion were defined according to Wanner et al.[23] The calibration of the model revealed that degradation is nonuniformly distributed in the aquitard (stronger close to the aquifer–aquitard interface than with increasing depth), which will be discussed in more detail in the "Results and Discussion" section. To quantify the quality of the fit between measured and modeled concentration and isotope data, the root mean squared error was used (RMSE; see eq 5 in the SI). After model calibration, two additional degradation scenarios were simulated for the aquitard, no-degradation and uniform degradation with depth, and compared with field data to investigate the sensitivity of concentration and CSIA profiles to different degradation conditions.

4. RESULTS AND DISCUSSION

4.1. Concentration Data. The groundwater concentration analysis of the present study in combination with data from previous studies[30,32,39] provides a detailed spatial and temporal data set of the long-term chlorinated hydrocarbon plume evolution in the aquifer at the Borden site (see section 3 in the SI for details). In this study, the chlorinated hydrocarbon concentration evolution is of interest in the bottom most sampling points in the aquifer at about 20 cm distance from the aquifer–aquitard interface, adjacent to the locations, where the clay cores were retrieved (Figure 1A). At these locations, the chlorinated hydrocarbon plume arrived between 100 and 700 days after DNAPL infiltration (Figures S1A–D, SI). During the migration in the aquifer, a separation of the different compounds was observed. PCE was detected later than TCE and TCM (Figures S1A–D, SI), which is attributed to different sorption behavior. PCE sorbs more strongly on the sandy aquifer material and, hence, migrates more slowly in the aquifer compared to TCE and TCM.[43] At all four coring locations, TCE shows the highest peak concentration (range: 16,000–210,000 μg/L = 0.015–0.191 Solubility$_{TCE}$) followed by PCE (range: 10,000–100,000 μg/L = 0.050–0.500 Solubility$_{PCE}$) and TCM (range: 800–50,000 μg/L = 9.76×10^{-05}–6.10×10^{-03} Solubility$_{TCM}$ (Figures S1A–D, SI). In contrast, significant cDCE concentrations (maximum of 1400 μg/L = 2.84×10^{-05} Solubility$_{cDCE}$) were detected only at the interface at the farthest downgradient core location 15-13, with the peak occurring 3300 days after injection.

Concentration analysis in the clay cores revealed that three different contaminants are present in the aquitard: PCE, TCE, and cDCE (Figures 2A–D). TCM was only detected at low

DOI: 10.1021/acs.est.5b06330
Environ. Sci. Technol. 2016, 50, 5622–5630

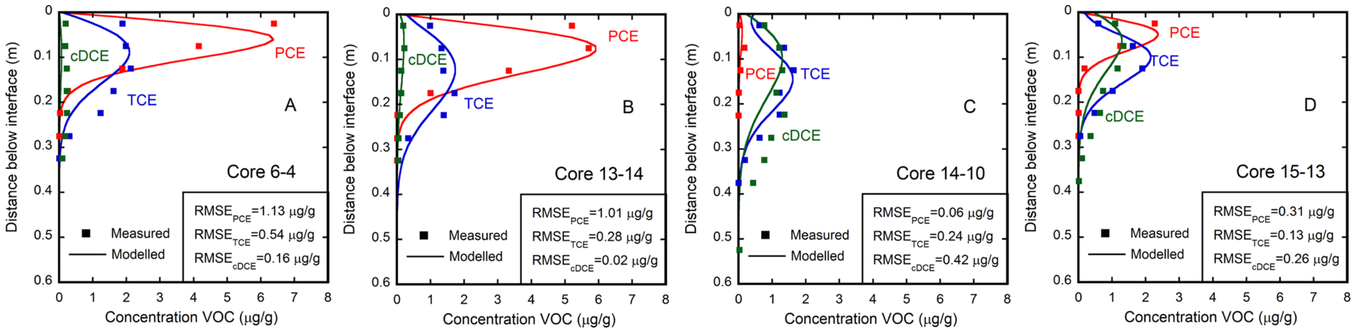


Figure 2. A–D. Measured and modeled chlorinated hydrocarbon concentrations in the retrieved clay cores 5281 days after injecting the organic contaminants into the aquifer. The continuous lines indicate the modeled concentration profiles of PCE (red), TCE (blue), and cDCE (green), while the squares represent the measuring points. The technical details of the modeling approach are provided in section 2 of the Supporting Information. The root mean squared error (RMSE) was used to quantify the quality of the fit between measured modeled concentration profiles.

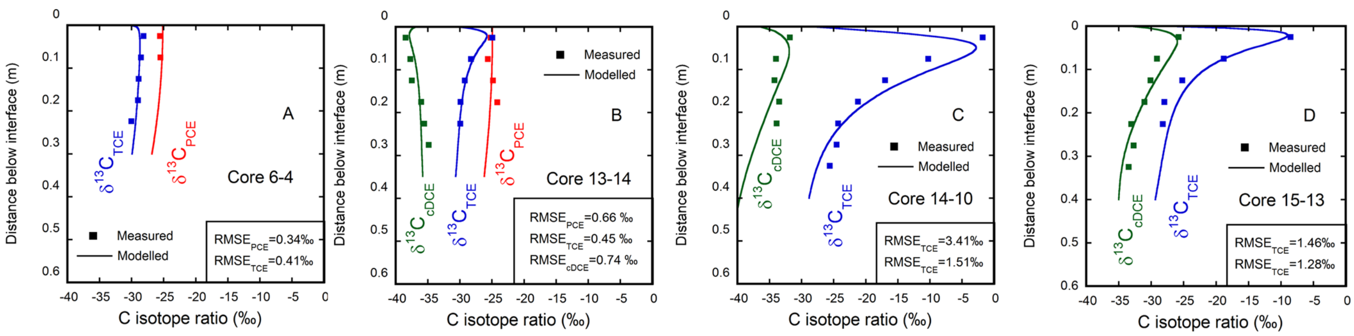


Figure 3. A–D. Measured and modeled compound-specific carbon isotope profiles in the retrieved clay cores 5281 days after injecting the organic contaminants into the aquifer. The continuous lines indicate the modeled isotope profiles of PCE (red), TCE (blue), and cDCE (green), while the squares represent the measuring points. The technical details of the modeling approach are provided in section 2 of the Supporting Information. The root mean squared error (RMSE) was used to quantify the quality of the fit between measured modeled concentration profiles.

concentrations <0.05 μg/g, likely due to its rapid depletion from the DNAPL source and rapid flushing through the aquifer; hence the results are not presented here. The penetration depth of the organic contaminations into the aquitard varied among the cores between 30 and 50 cm (Figures 2A–D). In the cores 6-4, 13-14, and 15-13 PCE shows the highest concentrations within a 10 cm distance from the aquifer–aquitard interface ranging between 2.3 and 6.4 μg/g (Figures 2A, B, and D), while in core 14-10 PCE shows the lowest concentration (<0.2 μg/g) compared to TCE and cDCE (Figure 2C). The TCE concentrations reach their maximum deeper than PCE (12–20 cm depth) ranging between 1.7 and 2.1 μg/g and declined with increasing depth (Figures 2A–D). The cDCE concentrations showed a similar distribution as for TCE. However, compared to TCE, an increase of cDCE concentrations with increasing distance from the contaminant injection point is observed reaching concentrations up to 1.4 μg/g in the farthest downgradient core 15-13 (Figures 2A–D). Fractions of organic carbon content ranging between 0.59 and 0.78% were measured in the retrieved cores (Table 4b, SI).

The low chlorinated hydrocarbon concentrations (<7.0 μg/g) in the retrieved clay cores indicate that no DNAPL phase was present at the aquifer–aquitard interface as otherwise the aquitard concentrations would be at least one order of magnitude higher.[44] The shape of the concentration profiles with the peak occurring below the interface and decreasing concentrations both with depth and toward the interface in combination with the temporal concentration evolution in the overlying aquifer is characteristic for a diffusion/back-diffusion scenario in the aquitard as observed in previous studies.[1−4,6]

The concentration profiles suggest that chlorinated hydrocarbons were initially diffusing into the clay as the plume arrived. After the peak concentrations passed through each location, concentrations at the interface diminished initiating back-diffusion toward the aquifer due to the reversal of the concentration gradient. However, the presence of cDCE in all four cores indicates that degradation is occurring in the aquifer and/or aquitard, since this compound is a degradation product of TCE and was not part of the injection mixture. The observed aerobic conditions in the aquifer between the contamination source and multilevel row 15[32] in 2004 and 2005 suggest that degradation of the chlorinated hydrocarbons is mainly occurring in the aquitard. Furthermore, the integration of the time series of chlorinated hydrocarbon concentrations at the aquifer interface and of the aquitard concentration profiles shows that cDCE represents a larger mass portion (5–75%) of the total VOC mass in the aquitard than in the aquifer (0.05–15%) (Figures 2A–D). This indicates that cDCE is mainly produced in the aquitard, which is consistent with the hypothesis that degradation is taking place primarily in the aquitard.

4.2. Compound-Specific Carbon Isotope Ratios in the Aquitard. The magnitude of the shift of compound-specific carbon isotope ratios with depth varied among the retrieved cores (Figures 3A–D). In core 6-4, located closest to the injection point (Figure 1), small shifts of PCE and TCE carbon isotope ratios in a range of $\Delta\delta^{13}C_{VPDB}$ = 2‰ were observed with increasing depth (Figure 3A). In contrast, larger shifts of carbon isotope ratios with depth were observed in cores 13-14, 14-10, and 15-13 (Figures 3B–D), which are located further

DOI: 10.1021/acs.est.5b06330
Environ. Sci. Technol. 2016, 50, 5622−5630

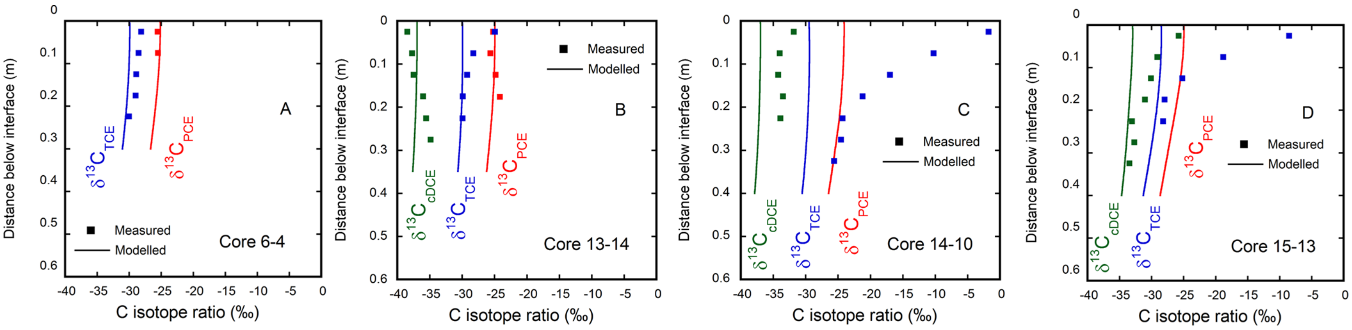


Figure 4. A–D. Comparison between measured and modeled compound-specific carbon isotope ratio profiles in the retrieved clay cores for the no-degradation scenario 5281 days after injecting the organic contaminants into the aquifer. The continuous lines indicate the modeled isotope profiles of PCE (red), TCE (blue), and cDCE (green), while the squares represent the measuring points. The technical details of the modeling approach are provided in section 2 of the Supporting Information.

downgradient from the injection point (Figure 1). In core 13-14, PCE and cDCE became enriched, while TCE was depleted in heavy isotopes with increasing depth (Figure 3B) with the magnitude of the shift of carbon isotope ratios for TCE up to $\Delta\delta^{13}C_{VPDB}$ = 4.8‰. In core 14-10, the largest shift ($\Delta\delta^{13}C_{VPDB}$ = 23.9‰) of TCE carbon isotope ratios was observed, whereas for cDCE carbon isotope ratios were only slightly shifted toward lighter signatures with depth (Figure 3C). In core 15-13 (Figure 3D) similar TCE and cDCE carbon isotope ratio profiles were observed compared to core 14-10 (Figure 3C). However, the magnitude of the shift of carbon isotope ratios of TCE in core 15-13 was smaller than in core 14-10 ($\Delta\delta^{13}C_{VPDB}$ = 19.7‰) but larger for cDCE ($\Delta\delta^{13}C_{VPDB}$ = 7.7‰).

The observed direction of the shift toward lighter carbon isotope signatures with depth in the retrieved clay cores (Figures 3A–D) is consistent with what is expected for diffusive transport in saturated low permeability sediments without degradation.[23] However, the magnitude of the shifts of carbon isotope ratios is much larger (up to 23.9‰) mainly in clay cores 13-14, 14-10, and 15-13 (Figures 3B–D) than what is expected due to diffusion only (~2‰).[23] Earlier CSIA aquifer measurements performed by Vargas[32] showed that five and six years after contaminant injection isotope signatures had not changed significantly upgradient of multilevel row 15 within the zone where clay cores were retrieved. This suggests minor degradation in the aquifer upgradient of multilevel row 15 within the first six years after the contaminants were released. After the isotope measurements performed by Vargas[32] back diffusion occurred as most of the plume had passed the sampling locations (Figures S1A–D and S2A–D, SI). This indicates that the isotope ratios in the aquitard are no longer influenced by isotope signatures in the aquifer after the study performed by Vargas.[32] Hence, even if degradation had occurred in the aquifer after the isotope measurements performed by Vargas,[32] increasingly heavier carbon isotope signatures in the aquifer due to degradation followed by diffusive transport into the aquitard is not a plausible explanantion for the observed shifts of carbon isotope ratios in the aquitard. This shows consistently with the concentration data that observed shifts of isotope ratios with depth can only be explained by degradation in the aquitard. Furthermore, the observed accumulation of cDCE is also frequently detected at other contaminated sites, where degradation of chlorinated hydrocarbons occurs.[45]

However, most of the carbon isotope patterns especially in cores 13-14, 14-10, and 15-13 are opposite to what is expected when degradation occurs uniformly with depth in the aquitard (Figures 3B–D). In a uniform degradation scenario, carbon isotope ratios would be shifted toward heavier isotopes with increasing depth, which does not agree with the measured isotope ratio profiles. However, it was striking that carbon isotope ratios at the bottom of the core profiles corresponded to the ratios measured by Vargas[32] at the aquifer–aquitard interface (Figures 3A–D). This is an indication that chlorinated hydrocarbons were likely initially diffusing from the aquifer into the aquitard unaffected by degradation and only slightly fractionated due to diffusion. Afterward, degradation appears to have become more active and shifted carbon isotope ratios more strongly close to the interface than with increasing depth. Thus, the scenario of nonuniformly distributed degradation activities with depth starting with a time lag could be the reason for the opposite carbon isotope ratio profiles to what is expected when degradation is uniformly distributed with depth in the aquitard.

4.3. Simulation of Different Degradation Scenarios in the Aquitard. In order to investigate the processes that produced the observed unique carbon isotope ratio pattern and to assess how different degradation conditions are reflected in carbon isotope ratio profiles, three different scenarios were simulated: A) no-degradation, B) uniform degradation, and C) nonuniform degradation with depth in the aquitard starting with a time lag. In the no-degradation scenario, typical diffusion/back-diffusion concentration patterns were observed, and carbon isotope ratios are only slightly shifted with depth due to the diffusive transport process (Figures 4A–D and Figures S7A–D, SI). Comparing measured and modeled concentration profiles in the no-degradation scenario shows that measured PCE, TCE, and cDCE concentration profiles are in agreement (except for core 14-10) with modeled data (Figures S7A–D, SI). In contrast the large shifts of isotope ratios with depth especially in cores 13-14, 14-10, and 15-13 are clearly different than simulated profiles in the no-degradation scenario (Figures 4A–D). Thus, the comparison between measured data and the no-degradation scenario confirms the hypothesis that degradation is minimal in core 6-4 but takes place more strongly in the lower part of the aquitard downgradient of multilevel row 6 in cores 13-14, 14-10, and 15-13 (Figure 1).

In order to evaluate the dynamics of degradation with depth in the aquitard, measured concentration and carbon isotope profiles were compared with the uniform (B) and the nonuniform (C) degradation simulation scenario starting with

DOI: 10.1021/acs.est.5b06330
Environ. Sci. Technol. 2016, 50, 5622–5630

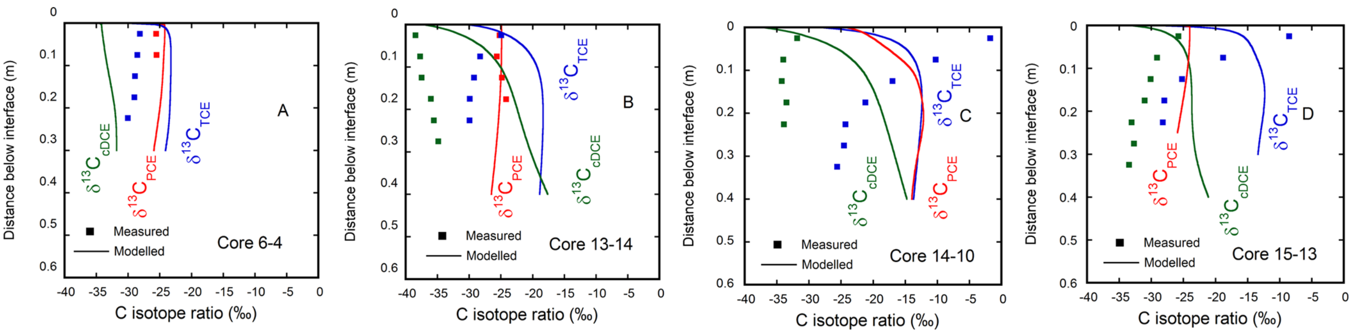


Figure 5. A−D. Comparison between measured and modeled compound-specific carbon isotope ratio profiles in the retrieved clay cores for the uniform degradation scenario 5281 days after injecting the organic contaminants into the aquifer. The continuous lines indicate the modeled isotope profiles of PCE (red), TCE (blue), and cDCE (green), while the squares represent the measuring points. The technical details of the modeling approach are provided in section 2 of the Supporting Information.

Table 1. Selected Model Parameters for Concentration and Carbon Isotope Ratio Profiles Simulations in the Retrieved Cores[c]

parameters	unit	core 6-4	core 13-14	core 14-10	core 15-13
distance from injection point	m	8	30	45	65
degradation rate PCE: k_{PCE}[b]	1/s	$3.3 \times 10^{-11} \cdot \mathrm{erfc}(0.1z)$[a]	$9.8 \times 10^{-10} \cdot \mathrm{erfc}(20z)$[a]	$9.8 \times 10^{-8} \cdot \mathrm{erfc}(0.1z)$[a]	$3.3 \times 10^{-8} \cdot \mathrm{erfc}(8z)$[a]
degradation rate TCE: k_{TCE}[b]	1/s	$9.2 \times 10^{-10} \cdot \mathrm{erfc}(0.5z)$[a]	$7.6 \times 10^{-8} \cdot \mathrm{erfc}(34z)$[a]	$8.5 \times 10^{-8} \cdot \mathrm{erfc}(11z)$[a]	$2.7 \times 10^{-7} \cdot \mathrm{erfc}(20.0z)$[a]
degradation rate cDCE: k_{cDCE}[b]	1/s	$3.3 \times 10^{-10} \cdot \mathrm{erfc}(0.1z)$[a]	$2.0 \times 10^{-9} \cdot \mathrm{erfc}(0.1z)$[a]	$4.6 \times 10^{-10} \cdot \mathrm{erfc}(0.1z)$[a]	$6.2 \times 10^{-8} \cdot \mathrm{erfc}(17.0z)$[a]
start (bio)degradation after injection[b]	days	2300	2800	2500	2600

[a]z corresponds to the vertical depth in the cores. [b]Calibrated. [c]The shape of the degradation function and the start of the degradation for each clay core were determined by means of model calibration.

a time lag. In the uniform degradation scenario, carbon isotope ratios are primarily shifted toward heavier signatures with increasing depth as soon as degradation is active (Figures 5A−D). The magnitude of carbon isotope fractionation for PCE is smaller than for TCE and cDCE due to the smaller isotope fractionation factor (Table S4a, SI). Although the shape of the concentration profiles is in agreement with modeled concentration profiles for the uniform degradation scenario (Figures S8A−D, SI), modeled carbon isotope ratio profiles are clearly different than measured ratio profiles (Figures 5A−D). This demonstrates that chlorinated hydrocarbons are most likely not affected by uniform degradation in the aquitard. In contrast, in the nonuniform degradation scenario, chlorinated hydrocarbons are affected more strongly by degradation close to the aquifer−aquitard interface than with increasing depth. The nonuniformly distributed degradation activities were described by first-order degradation rates following an inverse error function dependent on the depth (Table 1) i.e. degradation activities decreased exponentially with increasing depth (Figures S6A and S6B, SI). The measured concentration and carbon isotope ratio profiles are both consistent with the nonuniform degradation scenario in all four cores (Figures 2A−D and 3A−D). This confirms the hypothesis that chlorinated hydrocarbons are influenced by nonuniform degradation in the aquitard starting with a time lag after contaminant release and arrival. The best fit between measured and modeled data (RMSE: 0.02−1.13 μg/g for concentration profiles and 0.34−3.41 ‰ for carbon isotope profiles) was achieved by setting the starting point for the degradation activities at 2300−2800 days after the contaminant release (Table 1). The simulated nonuniform degradation scenario showed that the largest enrichment of heavy isotopes occurs slightly below the aquifer−aquitard interface despite the occurrence of the strongest degradation activities at the interface. This can be explained with the slight vertical displacement of the largest enrichment of heavy isotopes due to diffusive transport as degradation and diffusion occur simultaneously in the Borden aquitard.

The successful reproduction of the measured concentrations and carbon isotope ratio profiles with the nonuniform degradation scenario by means of model calibration opened the possibility to quantify degradation rates (Table 1). Chlorinated hydrocarbons were affected most faintly by degradation close to the contamination source (core 6-4), while with increasing distance degradation activities became stronger in cores 13-14, 14-10, and 15-13 (Table 1). The variation in degradation rates might be related to spatial variations in organic carbon composition in the aquitard.

In core 13-14 determined degradation rates revealed that TCE is degraded more rapidly than cDCE and PCE (Table 1). Due to the faster degradation of TCE compared to cDCE and PCE, TCE becomes enriched in heavy carbon isotopes, while cDCE shows the opposite trend due to the accumulation of the isotopically light dechlorination product close to the aquifer−-aquitard interface. In contrast, with increasing depth TCE, PCE, and cDCE are less affected by degradation (Table 1), and carbon isotope ratios are approaching similar values as before degradation activities commenced (Figure 3B).

In contrast to core 13-14, determined degradation rates for core 14-10 showed that PCE was strongly affected by degradation (Table 1). Due to strong degradation, PCE concentrations decreased below 0.2 μg/g (Figure 2C). Furthermore, in clay core 14-10, TCE is degraded two orders of magnitude faster than cDCE (Table 1) shifting the TCE carbon isotope ratios more strongly toward heavier signatures than cDCE carbon isotope signatures with respect to the interface signatures. In core 15-13, both TCE and cDCE are degraded to a similar extent in the upper part of the core (Table 1), generating the more enriched isotope values for both compounds close to the interface compared to the interface

DOI: 10.1021/acs.est.5b06330
Environ. Sci. Technol. 2016, 50, 5622−5630

carbon isotope ratios. Furthermore, as observed for cores 13-14 and 14-10, TCE and cDCE carbon isotope ratios are approaching original values before degradation activities started due to the decrease in degradation activities with depth (Table 1).

Variable and larger porosity close to the aquitard−aquifer interface as a possible explanation for the occurrence of the nonuniform degradation scenario can be likely excluded as previous porosity measurements at different depths in the upper 15 cm of the Borden aquitard revealed that the porosity is fairly constant (n = 13; 0.40 ± 0.09).[36] A more plausible explanation for the observed gradual decrease in degradation activity with increasing distance from the aquifer−aquitard interface is the availability of nutrients diffusing from the overlying aquifer into the aquitard. Although on the larger scale this is similar to what Manoli et al.[45] and Scheutz et al.[13] observed around small fractures and stringers in low permeable units. These studies suggested that electron donors and nutrients diffuse from high into low permeability zones causing graduated degradation activities with increasing distance from the high permeability zones. Hence, analogously at the Borden site, it is likely that nutrients are transported by diffusion from the aquifer into the underlying aquitard and favor, combined with the high organic matter content in the aquitard, stronger degradation activities close the aquifer−aquitard interface than with depth. The rationale of diffusing nutrients causing the nonuniform degradation occurrence is supported by the fact that the distribution of the degradation activities with depth in the aquitard was best fitted by an inverse error function, which corresponds to the shape of diffusion profiles. Furthermore, the time lag between the degradation activities and the presence of the chlorinated hydrocarbons in the aquitard might be related with the fact that the establishment of microbial activities in the aquitard takes time and that chlorinated hydrocarbons are not compulsory immediately degraded when coming in contact with microbes.[46−49]

4.4. Advances in Understanding Degradation Processes in Saturated Low Permeability Sediments. The present study has demonstrated for the first time that compound-specific isotope analysis (CSIA), measured in depth discrete profiles, can be used for the quantification of reactive processes affecting chlorinated hydrocarbons in saturated low permeability sediments. Furthermore, the present study revealed that degradation of chlorinated hydrocarbon is possible to occur in saturated low permeability sediments despite the small pore sizes. The simulation of three different scenarios (no-degradation, uniform degradation, and nonuniform degradation) for the clayey aquitard at the Borden research site showed that in contrast to concentration profiles various degradation conditions produce characteristic carbon isotope ratio profiles. This indicates that carbon isotope ratio profiles are more sensitive to degradation activities than concentration profiles can be in aquitards. Hence, CSIA is an important complement in addition to concentration data to identify and quantify degradation activities and has the potential to become a standard tool to reveal degradation activities including spatial variability in saturated low permeability sediments. Furthermore, our study showed that the combination of aquitard isotope and concentration profiles provides more insight into the temporal dynamics of an aquifer−aquitard system and degradation processes in the aquitard. Understanding degradation processes in aquitards and low-permeability zones has important implications toward understanding long-term contaminant fate and potential magnitude and longevity of back-diffusion processes. This might have major impacts on the choice of the appropriate remediation approach for contaminated aquifer−aquitard systems. By improving the understanding of degradation processes in contaminated aquitards using CSIA, an engineered remediation might become unnecessary and can be replaced by a monitored natural attenuation approach to remediate contaminated aquifer−aquitard systems. Thus, CSIA applications in aquitards potentially help to reduce costs for the remediation of contaminated sites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b06330.

Technical details about the analytics, sampling methods, and the modeling approach and a detailed description of the plume evolution in the sandy aquifer at the Borden site (PDF)

AUTHOR INFORMATION

Corresponding Author

*Phone: 41 32 718 26 22. E-mail: philipp.wanner@unine.ch.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the Swiss National Science Foundation (SNFS) for financial support. Furthermore, the authors thank Robert Ingleton from the University of Waterloo who operated the Geoprobe rig and several people from the University of Guelph, Ryan Kroeker, Dan Elliot, and Keelin Scully, for their skillful help in the field and Maria Gorecka and Rashmi Jadeja for their analytical support.

REFERENCES

(1) Parker, B. L.; Chapman, S. W.; Guilbeault, M. A. Plume persistence caused by back diffusion from thin clay layers in a sand aquifer following TCE source-zone hydraulic isolation. *J. Contam. Hydrol.* **2008**, *102* (1−2), 86−104.

(2) Chapman, S. W.; Parker, B. L. Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation. *Water Resour. Res.* **2005**, *41* (12), W12411.

(3) Liu, C. X.; Ball, W. P. Back diffusion of chlorinated solvent contaminants from a natural aquitard to a remediated aquifer under well-controlled field conditions: Predictions and measurements. *Groundwater* **2002**, *40* (2), 175−184.

(4) Johnson, R. L.; Pankow, J. F. Dissolution of dense chlorinated solvents into groundwater 0.2. source functions for pools of solvent. *Environ. Sci. Technol.* **1992**, *26* (5), 896−901.

(5) Adamson, D. T.; Chapman, S. W.; Farhat, S. K.; Parker, B. L.; deBlanc, P.; Newell, C. J. Characterization and source history modeling using low-k zone profiles at two source areas. *Groundwater Monit. Rem.* **2015**, *35* (2), 52−69.

(6) Seyedabbasi, M. A.; Newell, C. J.; Adamson, D. T.; Sale, T. C. Relative contribution of DNAPL dissolution and matrix diffusion to the long-term persistence of chlorinated solvent source zones. *J. Contam. Hydrol.* **2012**, *134-135*, 69−81.

(7) White, R. A.; Rivett, M. O.; Tellam, J. H. Paleo-roothole facilitated transport of aromatic hydrocarbons through a Holocene clay bed. *Environ. Sci. Technol.* **2008**, *42* (19), 7118−7124.

DOI: 10.1021/acs.est.5b06330
Environ. Sci. Technol. 2016, 50, 5622−5630

(8) Lima, G. d. P.; Sleep, B. E. The spatial distribution of eubacteria and archaea in sand−clay columns degrading carbon tetrachloride and methanol. *J. Contam. Hydrol.* **2007**, *94* (1), 34−48.
(9) Stotzky, G. *10 Influence of Soil Mineral Colloids on Metabolic Processes, Growth, Adhesion, and Ecology of Microbes and Viruses*. 1986.
(10) Fredrickson, J.; Garland, T.; Hicks, R.; Thomas, J.; Li, S.; McFadden, K. Lithotrophic and heterotrophic bacteria in deep subsurface sediments and their relation to sediment properties. *Geomicrobiol. J.* **1989**, *7* (1−2), 53−66.
(11) Manoli, G.; Chambon, J. C.; Bjerg, P. L.; Scheutz, C.; Binning, P. J.; Broholm, M. M. A remediation performance model for enhanced metabolic reductive dechlorination of chloroethenes in fractured clay till. *J. Contam. Hydrol.* **2012**, *131* (1−4), 64−78.
(12) Scheutz, C.; Broholm, M. M.; Durant, N. D.; Weeth, E. B.; Jorgensen, T. H.; Dennis, P.; Jacobsen, C. S.; Cox, E. E.; Chambon, J. C.; Bjerg, P. L. Field evaluation of biological enhanced reductive dechlorination of chloroethenes in clayey till. *Environ. Sci. Technol.* **2010**, *44* (13), 5134−5141.
(13) Scheutz, C.; Broholm, M. M.; Durant, N. D.; Weeth, E. B.; Jørgensen, T. H.; Dennis, P.; Jacobsen, C. S.; Cox, E. E.; Chambon, J. C.; Bjerg, P. L. Field evaluation of biological enhanced reductive dechlorination of chloroethenes in clayey till. *Environ. Sci. Technol.* **2010**, *44* (13), 5134−5141.
(14) Takeuchi, M.; Kawabe, Y.; Watanabe, E.; Oiwa, T.; Takahashi, M.; Nanba, K.; Kamagata, Y.; Hanada, S.; Ohko, Y.; Komai, T. Comparative study of microbial dechlorination of chlorinated ethenes in an aquifer and a clayey aquitard. *J. Contam. Hydrol.* **2011**, *124* (1−4), 14−24.
(15) Damgaard, I.; Bjerg, P. L.; Baelum, J.; Scheutz, C.; Hunkeler, D.; Jacobsen, C. S.; Tuxen, N.; Broholm, M. M. Identification of chlorinated solvents degradation zones in clay till by high resolution chemical, microbial and compound specific isotope analysis. *J. Contam. Hydrol.* **2013**, *146*, 37−50.
(16) Elsner, M.; Zwank, L.; Hunkeler, D.; Schwarzenbach, R. P. A new concept linking observable stable isotope fractionation to transformation pathways of organic pollutants. *Environ. Sci. Technol.* **2005**, *39* (18), 6896−6916.
(17) Hunkeler, D.; Abe, Y.; Broholm, M. M.; Jeannottat, S.; Westergaard, C.; Jacobsen, C. S.; Aravena, R.; Bjerg, P. L. Assessing chlorinated ethene degradation in a large scale contaminant plume by dual carbon-chlorine isotope analysis and quantitative PCR. *J. Contam. Hydrol.* **2011**, *119* (1−4), 69−79.
(18) Hunkeler, D.; Aravena, R.; Berry-Spark, K.; Cox, E. Assessment of degradation pathways in an aquifer with mixed chlorinated hydrocarbon contamination using stable isotope analysis. *Environ. Sci. Technol.* **2005**, *39* (16), 5975−5981.
(19) Hunkeler, D.; Aravena, R.; Butler, B. J. Monitoring microbial dechlorination of tetrachloroethene (PCE) in groundwater using compound-specific stable carbon isotope ratios: Microcosm and field studies. *Environ. Sci. Technol.* **1999**, *33* (16), 2733−2738.
(20) Sherwood Lollar, B.; Slater, G. F.; Sleep, B.; Witt, M.; Klecka, G. M.; Harkness, M.; Spivack, J. Stable carbon isotope evidence for intrinsic bioremediation of tetrachloroethene and trichloroethene at area 6, Dover Air Force Base. *Environ. Sci. Technol.* **2001**, *35* (2), 261−269.
(21) Meckenstock, R. U.; Morasch, B.; Griebler, C.; Richnow, H. H. Stable isotope fractionation analysis as a tool to monitor biodegradation in contaminated acquifers. *J. Contam. Hydrol.* **2004**, *75* (3−4), 215−255.
(22) Kuder, T.; Wilson, J. T.; Kaiser, P.; Kolhatkar, R.; Philp, P.; Allen, J. Enrichment of stable carbon and hydrogen isotopes during anaerobic biodegradation of MTBE: microcosm and field evidence. *Environ. Sci. Technol.* **2005**, *39* (1), 213−220.
(23) Wanner, P.; Hunkeler, D. Carbon and chlorine isotopologue fractionation of chlorinated hydrocarbons during diffusion in water and low permeability sediments. *Geochim. Cosmochim. Acta* **2015**, *157*, 198−212.
(24) Jin, B.; Rolle, M.; Li, T.; Haderlein, S. B. Diffusive fractionation of BTEX and chlorinated ethenes in aqueous solution: Quantification of spatial isotope gradients. *Environ. Sci. Technol.* **2014**, *48* (11), 6141−6150.
(25) Brewster, M. L.; Annan, A. P.; Greenhouse, J. P.; Kueper, B. H.; Olhoeft, G. R.; Redman, J. D.; Sander, K. A. Observed migration of a controlled DNAPL release by geophysical methods. *Groundwater* **1995**, *33* (6), 977−987.
(26) Sudicky, E. A. A natural gradient experiment on solute transport in a sand aquifer - spatial variability of hydraulic conductivity and its role in the dispersion process. *Water Resour. Res.* **1986**, *22* (13), 2069−2082.
(27) Mackay, D. M.; Freyberg, D. L.; Roberts, P. V. A natural gradient experiment on solute transport in a sand aquifer 1. approach and overview of plume movement. *Water Resour. Res.* **1986**, *22* (13), 2017−2029.
(28) Freyberg, D. L. A natural gradient experiment on solute transport in a sand aquifer 2. spatial moments and the advection and dispersion of nonreactive tracers. *Water Resour. Res.* **1986**, *22* (13), 2031−2046.
(29) Hartog, N.; Cho, J.; Parker, B. L.; Annable, M. D. Characterization of a heterogeneous DNAPL source zone in the Borden aquifer using partitioning and interfacial tracers: Residual morphologies and background sorption. *J. Contam. Hydrol.* **2010**, *115* (1−4), 79−89.
(30) Laukonen, K. A. Long-term natural gradient experiments in the Borden sand aquifer: A bromide slug and a chloroform plume from a three-component DNAPL source. MSc Thesis, University of Waterloo, 2001.
(31) Morrison, W. E. Hydrogeological controls on flow and fate of PCE DNAPL in a fractured and layered clayey aquitard: A Borden experiment. MSc Thesis, Universitiy of Waterloo, 1998.
(32) Vargas, I. Assessment of the fate of a tetrachloroethene (PCE) and trichloroethene (TCE) plume at the Borden aquifer. MSc Thesis, University of Waterloo, 2005.
(33) Hwang, Y. K.; Endres, A. L.; Piggott, S. D.; Parker, B. L. Long-term ground penetrating radar monitoring of a small volume DNAPL release in a natural groundwater flow field. *J. Contam. Hydrol.* **2008**, *97* (1), 1−12.
(34) Sudicky, E. A.; Illman, W. Lessons learned from a suite of CFB Borden experiments. *Groundwater* **2011**, *49* (5), 630−648.
(35) Allen-King, R. M.; Groenevelt, H.; Warren, C. J.; Mackay, D. M. Non-linear chlorinated-solvent sorption in four aquitards. *J. Contam. Hydrol.* **1996**, *22* (3-4), 203−221.
(36) Parker, B. L. Effect of molecular diffusion on the persistence of Dense Immiscible Phase Organic Liquids in fractured porous geologic media. PhD Thesis, University of Waterloo, 1996.
(37) Meldrum, C. I. Use of a new multi-level monitoring system for determining hydraulic head distribution in the Borden aquitard. BSc Thesis, University of Waterloo, 1999.
(38) Foley, S. Influcence of sand microbeds on hydraulic response of an unconfined clay aquitard. MSc Thesis, University of Waterloo, Waterloo, 1992.
(39) Klein, J. J. P. Comparison of groundwater VOC concentration profiles from different sampling scales and techniques in the Borden sand aquifer. BSc Thesis, University of Waterloo, 2002.
(40) Einarson, M. D.; Casey, M. B.; Winglewich, D. L.; Morkin, M. I. *Enviro-core - A dual-tube direct push system for rapid site characterization*; Environmental & Engineering Geophysical Society: Wheat Ridge, 1998; pp 1−10.
(41) Allen-King, R. M.; Groenevelt, H.; Mackay, D. M. Analytical method for the sorption of hydrophobic organic pollutants in clay-rich materials. *Environ. Sci. Technol.* **1995**, *29* (1), 148−153.
(42) Van Breukelen, B. M.; Hunkeler, D.; Volkering, F. Quantification of sequential chlorinated ethene degradation by use of a reactive transport model incorporating isotope fractionation. *Environ. Sci. Technol.* **2005**, *39* (11), 4189−4197.
(43) Rivett, M. O.; Feenstra, S.; Cherry, J. A. A controlled field experiment on groundwater contamination by a multicomponent DNAPL: creation of the emplaced-source and overview of dissolved plume development. *J. Contam. Hydrol.* **2001**, *49* (1), 111−149.

DOI: 10.1021/acs.est.5b06330
Environ. Sci. Technol. 2016, 50, 5622−5630

(44) Parker, B. L.; Cherry, J. A.; Chapman, S. W. Field study of TCE diffusion profiles below DNAPL to assess aquitard integrity. *J. Contam. Hydrol.* **2004**, *74* (1−4), 197−230.

(45) Manoli, G.; Chambon, J. C.; Bjerg, P. L.; Scheutz, C.; Binning, P. J.; Broholm, M. M. A remediation performance model for enhanced metabolic reductive dechlorination of chloroethenes in fractured clay till. *J. Contam. Hydrol.* **2012**, *131* (1), 64−78.

(46) Ellis, D. E.; Lutz, E. J.; Odom, J. M.; Buchanan, R. J.; Bartlett, C. L.; Lee, M. D.; Harkness, M. R.; DeWeerd, K. A. Bioaugmentation for accelerated in situ anaerobic bioremediation. *Environ. Sci. Technol.* **2000**, *34* (11), 2254−2260.

(47) Kao, C.; Lei, S. Using a peat biobarrier to remediate PCE/TCE contaminated aquifers. *Water Res.* **2000**, *34* (3), 835−845.

(48) Lendvay, J.; Löffler, F. E.; Dollhopf, M.; Aiello, M.; Daniels, G.; Fathepure, B.; Gebhard, M.; Heine, R.; Helton, R.; Shi, J. Bioreactive barriers: a comparison of bioaugmentation and biostimulation for chlorinated solvent remediation. *Environ. Sci. Technol.* **2003**, *37* (7), 1422−1431.

(49) Scheutz, C.; Durant, N. d.; Dennis, P.; Hansen, M. H.; Jørgensen, T.; Jakobsen, R.; Cox, E. e.; Bjerg, P. L. Concurrent ethene generation and growth of Dehalococcoides containing vinyl chloride reductive dehalogenase genes during an enhanced reductive dechlorination field demonstration. *Environ. Sci. Technol.* **2008**, *42* (24), 9302−9309.

DOI: 10.1021/acs.est.5b06330
Environ. Sci. Technol. 2016, 50, 5622−5630