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Assessment of Degradation Pathways in an Aquifer with Mixed Chlorinated Hydrocarbon Contamination Using Stable Isotope Analysis

DANIEL HUNKELER,*,† RAMON ARAVENA,‡ KAREN BERRY-SPARK,§ AND EVAN COX§

Centre for Hydrogeology, University of Neuchâtel, Switzerland
Department of Earth Sciences, University of Waterloo, Ontario, Canada
Geosyntec Consultants, Guelph, Ontario, Canada

The demonstration of monitored natural attenuation (MNA) of chlorinated hydrocarbons in groundwater is typically conducted through the evaluation of concentration trends and parent−daughter product relationships along prevailing groundwater flow paths. Unfortunately, at sites contaminated by mixtures of chlorinated ethenes, ethanes, and methanes, the evaluation of MNA by using solely concentration data and parent−daughter relationships can result in erroneous conclusions regarding the degradation mechanisms that are truly active at the site, since many of the daughter products can be derived from multiple parent compounds. Stable carbon isotope analysis was used, in conjunction with concentration data, to clarify and confirm the active degradation pathways at a former waste solvent disposal site where at least 14 different chlorinated hydrocarbons have been detected in the groundwater. The isotope data indicate that TCE, initially believed to be present as a disposed product and/or a PCE dechlorination intermediate, is attributable to dehydrochlorination of 1,1,2,2-PCA. The isotope data further support that vinyl chloride and ethene in the site groundwater result from dichloroelimination of 1,1,2-trichlorethane and 1,2-dichloroethane, respectively, rather than from reductive dechlorination of the chlorinated ethenes PCE, TCE, or 1,2-DCE. The isotope data confirm that the chlorinated ethanes and chlorinated methanes are undergoing significant intrinsic degradation, whereas degradation of the chlorinated ethenes may be limited. In addition to the classical trend of enriched isotope values of the parent compounds with increasing distance associated to biodegradation, shifts of isotope ratios of degradation byproduct in the opposite direction due to mixing of isotopically light byproducts of biodegradation with compounds from the source are shown to be of high diagnostic value. These data underline the value of stable isotope analysis in confirming transformation processes at sites with complex mixtures of chlorinated compounds.

Introduction

Chlorinated hydrocarbons are among the most common groundwater contaminants. Monitored natural attenuation (MNA), an established site management strategy for petroleum hydrocarbon contaminated sites, is increasingly being used to manage sites contaminated with chlorinated hydrocarbons. Successful implementation of MNA requires a monitoring strategy that not only demonstrates diminishing contaminant concentrations, but also provides insight into the processes responsible for contaminant attenuation. Analysis of compound-specific isotope ratios is a potential tool to gain such process-specific information (*1*, *2*). The approach relies on the occurrence of isotope fractionation during degradation caused by slight differences in reaction rate between molecules with light (^{12}C in case of carbon) and heavy (^{13}C) isotopes, respectively. Isotope fractionation leads to a characteristic pattern of isotope ratios of reactants and transformation products. The reactant usually gets increasingly enriched in ^{13}C while the product is depleted in ^{13}C compared to the reactant and reaches the isotopic composition of the reactant as the reaction approaches completion (*1*). For chlorinated hydrocarbons, substantial carbon isotope fractionation was observed in laboratory studies for reductive dechlorination of chlorinated ethenes (*1*, *3*, *4*), dichloro-elimination of 1,2-dichloroethane (1,2-DCA) (*5*), aerobic oxidation of 1,2-dichloroethene (1,2-DCE) and vinyl chlo-ride (VC) (*6*, *7*), aerobic oxidation of 1,2-DCA (*8*), and aerobic oxidation of dichloromethane (DCM) (*9*). At the field scale, stable isotope studies have so far focused on field sites contaminated with trichloroethene (TCE) and/or tetrachlo-roethene (PCE) as primary contaminants (*1*, *10*, *11*). However, carbon isotope ratios may be particularly useful at sites with mixtures of chlorinated ethenes and chlorinated ethanes. At such sites, similar degradation products can originate from different primary compounds. For example, VC may be produced by reductive dechlorination of dichloroethenes, dichloroelimination of 1,1,2-trichloroethane (1,1,2-TCA), or dehydrochlorination of 1,2-DCA (*12*−*14*). Furthermore, some of the compounds can degrade to different products de-pending on the prevailing biogeochemical conditions. For example, 1,1,2,2-tetrachloroethane (1,1,2,2-PCA) may un-dergo dehydrochlorination to form TCE, dichloroelimination to produce a mixture of *cis*-1,2-dichloroethene (*cis*-1,2-DCE) and *trans*-1,2-dichloroethene (*trans*-1,2-DCE), or reductive dechlorination to form 1,1,2-TCA (*12*−*15*). The multiple degradation pathways and the different velocities at which different chlorinated ethanes and ethenes migrate in ground-water makes interpretation of concentration data difficult. The aim of this study was to evaluate whether carbon isotope analysis can be used to identify transformation processes at a site with a complex mixture of contaminants. The study site consisted of a former waste disposal site where 14 different chlorinated ethenes, ethanes, and methanes were detected in the underlying aquifers. Since most of the degradation intermediates were already present at the source and some of them such as VC and ethene can originate from different precursors, it was difficult to assess and quantify transformation processes based on concentration data alone. Potential transformation processes occurring at the site were previously evaluated in a microcosm study with site material (*5*).

* Corresponding author tel: ++ 41 32 718 25 60; fax: ++ 41 32 718 26 03; e-mail: Daniel.Hunkeler@unine.ch.
† University of Neuchâtel.
‡ University of Waterloo.
§ Geosyntec Consultants.

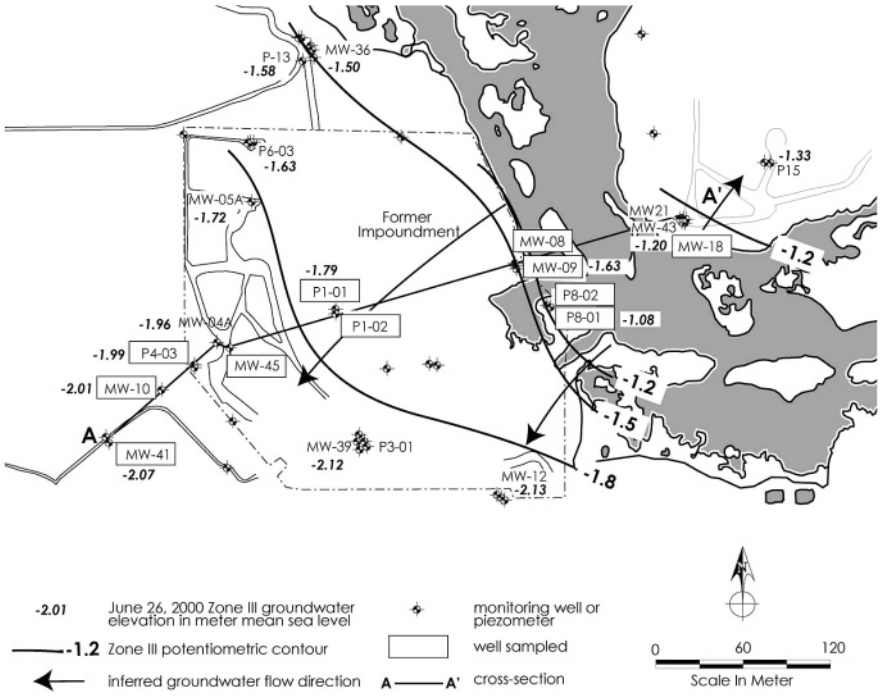

FIGURE 1. Map of field site with locations of monitoring wells and piezometric level in aquifer III.

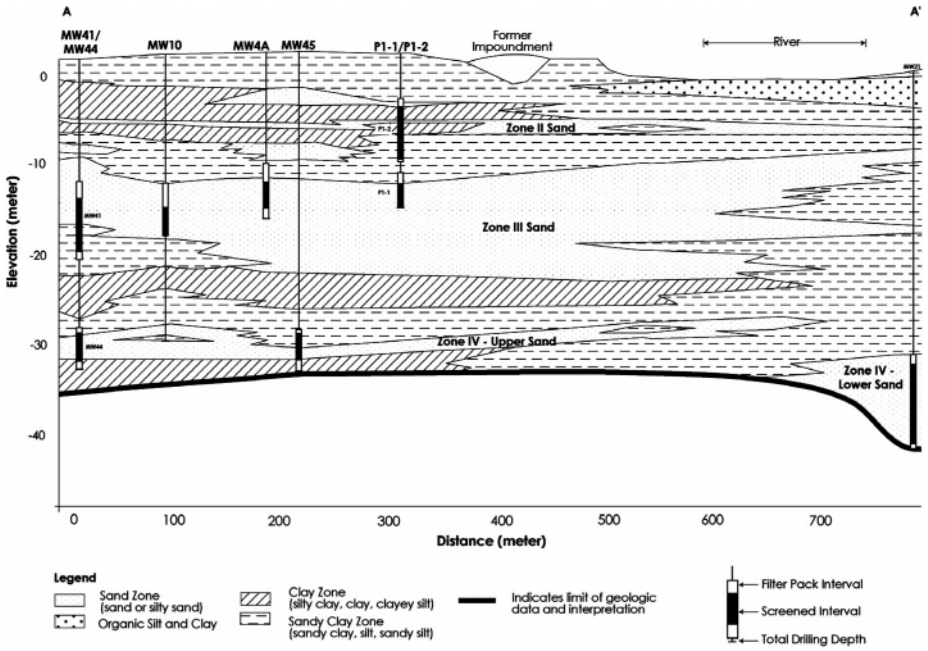

FIGURE 2. Geological cross section along A−A′ with location of the screens of the monitoring wells.

Site Description

The site was used from the late 1950s to 1972 for the disposal of liquid chlorinated hydrocarbons in surface impoundments located adjacent to a river (Figure 1). In 1994−1995, the chlorinated hydrocarbons were removed from the impoundments and the impoundments were closed. The site is underlain by several sandy aquifers (referred to herein as zones II, III, and IV) at different depths, separated by sandy clay and clay layers (Figure 2). The zone II aquifer is unconfined to semi-confined and is recharged by surface water, causing a groundwater divide at the river. The zone III aquifer is confined but receives significant leakage from zone II as a result of downward vertical gradients and hydraulic interconnection. Zone III also shows the influence of recharge from the river as indicated by groundwater flow perpendicular to the river in both directions (Figure 1). Zone IV is confined and groundwater flow is generally from the northeast to south-southwest across the site. From average hydraulic conductivities, porosity, and hydraulic gradients, the groundwater flow velocity was estimated to be 0.6−3.6 m/year in zone II and 0.3−4.8 m/year in zone III.

Transformation of Chlorinated Ethenes and Chlorinated Ethanes

Chlorinated ethanes and ethenes are subject to different abiotic and biotic transformation processes as summarized in Figure 3 for the compounds present at the site. Under reductive conditions, chlorinated ethenes can be sequentially dechlorinated by microorganisms, whereby a chlorine atom is replaced by a hydrogen atom in each step. The process

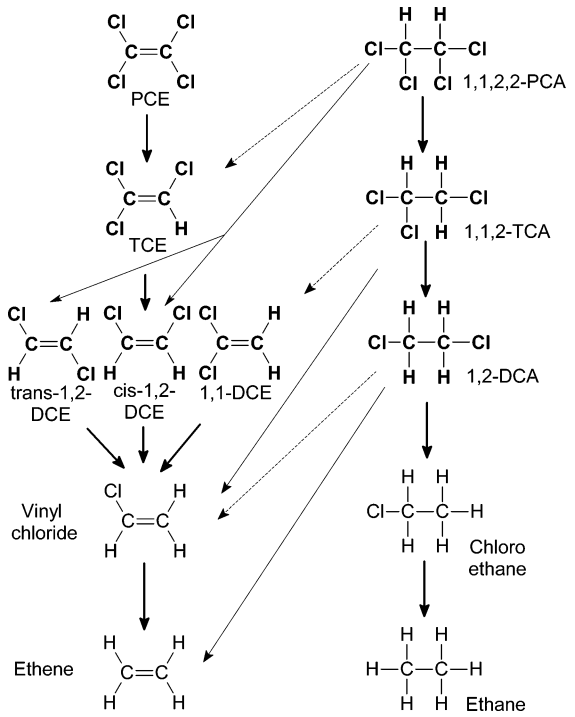

FIGURE 3. Degradation pathways of chlorinated ethenes and ethanes present at the site. Bold arrows, reductive dechlorination; fine arrows, dichloroelimination; dashed arrows, dehydrohalogenation.

can be linked to energy generation (halorespiration) or can occur as a cometabolic process, which is generally slower (*16*). Similar to chlorinated ethenes, chlorinated ethanes can also be reductively dehalogenated as demonstrated for 1,1,2-TCA by Chen et al. (*12*) and for 1,2-DCA and chloroethane by Holliger et al. (*17*). Alternatively, 1,1,2-TCA and 1,2-DCA may be transformed by dichloroelimination, generally believed to be a biotic process, to VC and ethene, respectively (*12*, *13*, *18*−*20*). In a microcosm study by Chen et al.(*12*) dichloroelimination of 1,1,2-TCA was found to be a more important process than reductive dechlorination. Dichloroelimination was also observed for 1,1,2,2-PCA under biotic (*12*, *13*) and abiotic conditions (*15*) with the formation of *cis*-1,2-DCE and *trans*-1,2-DCE at a ratio between 1.5 and 4.5. Finally, chlorinated ethanes can also be subject to abiotic transformation leading to the elimination of HCl (dehydrohalogenation) or the nucleophilic substitution of Cl by OH to form alcohols (*14*). For 1,1,2,2-PCA, base-catalyzed dehydrohalogenation to TCE was observed to be more important than neutral transformation even at neutral pH with a half-life of 0.4 years (pH = 7). Transformation of 1,1,2-TCA and 1,2-DCA was observed to be slower with half-lives between 54 and 139 years at pH = 7 (*14*, *21*). Dehydrohalogenation of 1,1,2-TCA led to the formation of 1,1-DCE (*21*). During base-catalyzed dehydrohalogenation of 1,2-DCA, vinyl chloride was detected while neutral transformation led to the formation of ethylene glycol (*14*).

In microcosm experiments with site material that was amended with DCE isomers, 1,1,2-TCA, or 1,2-DCA, reductive dechlorination of the DCE isomers to VC and ethene was observed, as was dichloroelimination of 1,1,2-TCA to VC, and dichloroelimination of 1,2-DCA to ethene (*5*). Dichloroelimination of 1,1,2-TCA to VC was very slow and incomplete. The isotopic enrichment factors associated with these and some other potentially relevant transformation processes are summarized in Table 1.

TABLE 1. Overview of Isotopic Enrichment Factors for Carbon Isotope Fractionation During Reductive Transformation of Chlorinated Ethenes and Ethanes

process	carbon isotopic enrichment factor ϵ (‰)	reference
PCE → TCE	−2, −2.7, −5.2, −5.5	1, 4
TCE → *cis*-1,2-DCE	−4, −2.5, −6.6, −7.1, −13.8	1−4
cis-1,2-DCE → VC	−12, −14.1, −16.1, −20.4, −19.9	1, 3−5
trans-1,2-DCE → VC	−30.3	5
1,1-DCE → VC	−7.3	5
VC → ethene	−26, −21.5, −26.6, −22.4, −31.3	1, 3−5
1,1,2-TCA → VC	−2.0	5
1,2-DCA → ethene	−32.1	5

Materials and Methods

Groundwater Sampling. Groundwater samples for chemical and isotope analysis were collected from four wells screened in zone II, six wells screened in zone III, and one well screened in zone IV in July (campaign 1) and December 1999 (campaign 2). Due to the slow groundwater flow velocity, little variation in concentrations and isotope ratios was expected between the sampling episodes, which was verified by sampling one of the wells for isotope analysis during both sampling campaigns (MW-10). In the discussion and figures, the average values for the two sampling campaigns are used. Groundwater samples were collected using Teflon bailers, following purging 3−5 well casing volumes until pH, dissolved oxygen, and oxidation−reduction potential parameters stabilized.

Chemical and Isotope Analysis. Concentrations of chlorinated hydrocarbons, ethene, and ethane were measured by gas chromatography−mass spectrometry (GC−MS) using U.S. Environmental Protection Agency (EPA) Method 8260. The extremely high concentration of chlorinated hydrocarbons in some of the samples made it necessary to dilute the samples, resulting in elevated detection limits for some samples. The anions chloride, nitrate, and sulfate were analyzed by EPA Method 300.0. Dissolved iron and manganese were analyzed by EPA Method 6010. Methane was analyzed by EPA Method 8015M. The dissolved oxygen concentration was measured directly in the field using a clark electrode.

Carbon isotope ratio analysis was performed using a gas chromatograph connected to an isotope ratio mass spectrometer via a combustion interface as described in ref *22*. Due to the high concentration of VOCs, dissolved compounds were extracted using a headspace method (*22*). Eight mL of water in 40 mL VOC vials was replaced by helium and the vials were placed on a reciprocating shaker at 120 rpm for at least 2 h. The measured isotope ratios were corrected for the small isotope fractionation for aqueous phase−headspace partitioning (*22*). Carbon isotope ratios ($^{13}C/^{12}C$) are reported in the usual delta notation ($\delta^{13}C$) relative to the VPDB (Vienna Peedee Belemnite) standard. The $\delta^{13}C$ value is defined as $\delta^{13}C = (R_s/R_r - 1) \times 1000$, where R_s and R_r are the $^{13}C/^{12}C$ ratios of the sample and the VPDB standard, respectively. The precision and accuracy of the $\delta^{13}C$ values is ±0.3 ‰.

Results and Discussion

Geochemical Conditions. Geochemical conditions in zones II and III are generally anaerobic with low dissolved oxygen and nitrate concentrations, elevated dissolved iron and manganese concentrations, and some methane (Table 2). The sulfate concentration in zones II and III is variable with concentrations as high as 741 mg/L close to the source,

TABLE 2. Concentrations and Stable Carbon Isotope Ratios of Chlorinated Hydrocarbons and Values of Geochemical Parameters[a]

		P8-02	MW8	P1-02	MW18	MW9	P8-01	P1-01	P4-03	MW10	MW10	MW41	MW45
aquifer level		II	II	II	II	III	III	III	III	III	III	III	IV
sampling campaign		2	2	2	1	1	2	1	1	1	2	2	1
distance from MW8/9 (m)		0	0	206	183	0	0	206	366	411	411	457	332
concentrations in mg/L													
carbon tetrachloride	CT	<25	<25	7.5	<0.005	72	<25	<25	<25	<25	<2.5	<0.1	<0.005
chloroform	**CF**	**120**	**1100**	**12**	**0.084**	**860**	**710**	**290**	**190**	**58**	**40**	**0.11**	**<0.005**
dichloromethane	DCM	<25	53	<0.25	<0.005	69	28	28	63	<25	4.6	<0.1	<0.005
tetrachloroethene	PCE	<25	<25	0.55	0.0083	<50	<25	<25	<50	<25	<2.5	<0.1	<0.005
trichloroethene	TCE	<25	<25	2.3	0.035	<50	<25	29	38	28	11	<0.1	0.042
***cis*-1,2-dichloroethene**	**cDCE**	**22**	**140**	**1.2**	**0.021**	**140**	**110**	**48**	**46**	**13**	**8.2**	**0.09**	**0.034**
***trans*-1,2-dichloroethene**	**tDCE**	**25**	**130**	**2**	**0.037**	**150**	**110**	**62**	**42**	**17**	**8.5**	**0.09**	**0.07**
1,1-dichloroethene	11DCE	<25	<25	0.73	0.0083	<50	<25	<25	<50	57	31	0.96	0.42
vinyl chloride	VC	62	<25	<0.25	0.11	61	89	<25	38	47	25	0.61	3.4
ethene	ET	15	0.66	0.00057	<0.0005	11	6.4	10	2.1	33	11	0.06	0.095
1,1,2,2-tetrachloroethane	1122TeCA	<25	<25	<0.25	0.0085	65	46	<25	<50	<25	<2.5	<0.1	<0.005
1,1,2-trichloroethane	**112TCA**	**220**	**690**	**15**	**0.39**	**900**	**1200**	**630**	**910**	**350**	**260**	**3.50**	**0.89**
1,2-dichloroethane	**12DCA**	**490**	**2500**	**6.8**	**0.65**	**1500**	**2800**	**1800**	**1600**	**470**	**240**	**9.05**	**3.3**
1,1-dichloroethane	**11DCA**	**<25**	**110**	**1.3**	**0.021**	**120**	**75**	**51**	**<50**	**<25**	**6.4**	**0.12**	**0.05**
chloroethane	**CA**	**<50**	**1000**	**<0.5**	**<0.01**	**330**	**72**	**<50**	**<100**	**<50**	**<5**	**<0.2**	**<0.005**
dissolved oxygen	mg/L	1.9	5.4	1	0.9	1.5	10	0.7	0.4	0.6	1.2	0.5	0.6
nitrate		2.4	<10	<0.5	<0.5	<10	<5	<0.5	<0.5	<0.5	<0.5	1.9	<0.5
manganese		21.5	53.8	0.6	7.2	22.1	32.8	3.2	3.4	-	1.9	0.7	-
iron		11.1	112	25.1	<0.1	29.4	6.25	68.9	19.3	-	6.9	1.1	-
sulfate		26.5	136	436	6.8	145	41.3	35.9	115	136	104	214	-
methane		1.13	0.42	0.0042	0.2	0.51	0.66	0.095	-	0.087	0.06	<0.0005	0.0064
stable carbon isotope ratio $\delta^{13}C$ (‰ VPDB)													
carbon tetrachloride	CT		−20.5			−23.5							
chloroform	**CF**	**−31.0**	**−29.7**	**−31.8**		**−29.1**	**−30.5**	**−29.2**	**−24.3**	**−18.6**	**−18.9**		
dichloromethane	DCM					−53.5			−57.3	−58.8			
tetrachloroethene	PCE					−28.7			−28.3	−30.5			
trichloroethene	TCE			−42.2		−36.2		−45.0	−41.9	−43.1	−42.3		
***cis*-1,2-dichloroethene**	**cDCE**	**−39.1**	**−36.7**	**−39.3**		**−38.1**	**−40.1**	**−39.5**	**−39.7**	**−39.1**	**−39.4**		
***trans*-1,2-dichloroethene**	**tDCE**	**−27.7**	**−22.9**	**−26.9**		**−23.5**	**−28.5**	**−27.7**	**−29.2**	**−28.7**	**−29.0**		
1,1-dichloroethene	11DCE							−51.6	−47.9	−55.1	−54.6	−55.8	
vinyl chloride	VC	−28.2	14.3			−18.8	−21.9	−18.5	−29.0	−37.9	−39.0	−49.4	−49.4
ethene	ET	−23.6	−26.4			−22.1	−23.8	−26.5	−31.3	−28.9	−29.3	−54.2	−43.6
1,1,2,2-tetrachloroethane	1122PCA					−39.3			−39.2	−40.1			
1,1,2-trichloroethane	**112TCA**	**−32.3**	**−33.5**	**−31.9**	**−32.3**	**−32.8**	**−33.0**	**−32.7**	**−30.9**	**−28.9**	**−28.6**	**−26.0**	**−16.0**
1,2-dichloroethane	**12DCA**	**−22.2**	**−21.1**	**−17.9**	**−20.6**	**−21.9**	**−22.7**	**−22.7**	**−23.5**	**−22.1**	**−21.2**	**−23.5**	**−20.2**
1,1-dichloroethane	**11DCA**	**−31.9**	**−31.7**			**−32.5**	**−31.9**	**−31.8**	**−31.9**	**−32.0**	**−32.6**		

[a] Bold: Compounds that are present at concentrations >100 mg/L.

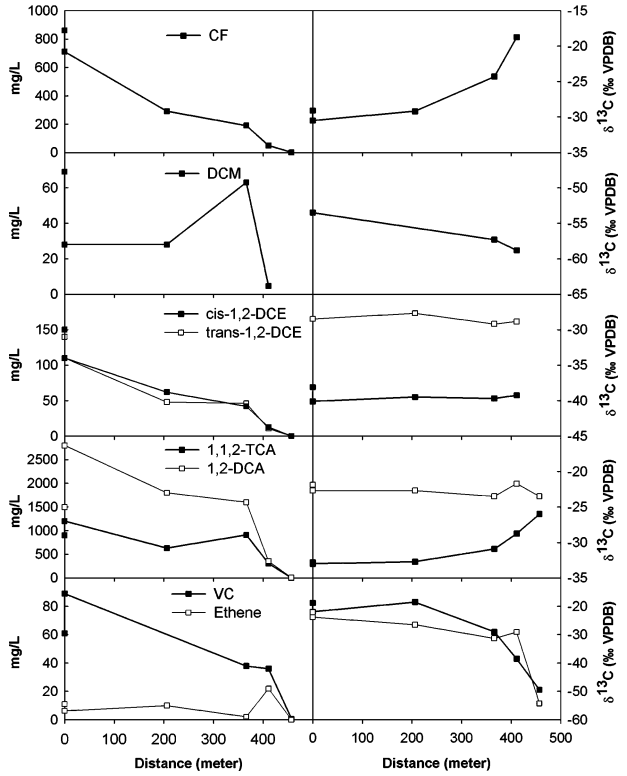

FIGURE 4. Concentration and stable carbon isotope ratios of selected compounds in aquifer III in groundwater flow direction.

possibly due to input of sulfate via former impoundments. The high and variable sulfate concentration makes identification of sulfate reduction difficult. However, the elevated iron concentration and the presence of methane indicate the occurrence of strongly reducing conditions that are favorable for reductive transformation processes.

Concentration of Chlorinated Hydrocarbons. Chlorinated hydrocarbons are present at concentrations of up to 2 500 mg/L in zone II and 2 800 mg/L in zone III (Table 2). Several compounds, including chloroform (CF), *cis*-1,2-DCE, *trans*-1,2-DCE, 1,1,2-TCA, and 1,2-DCA were detected at concentrations >100 mg/L. Most of the chlorinated hydrocarbons detected at the site are already present in the wells closest to the location of the former impoundments (Table 2; MW-8 and P8-02 in zone II, MW-9 and P8-01 in zone III) which are denoted as source wells. The concentration of selected chlorinated hydrocarbons for 6 monitoring wells in aquifer III located at increasing distances downgradient from the source is illustrated in Figure 4. At the source, not only typical parent compounds such as PCE, 1,1,2,2-PCA, 1,1,2-TCA, or CF were detected, but also most of their less chlorinated degradation intermediates. The presence of intermediates at the source and the fact that some of them can originate from multiple precursors makes it difficult to identify and quantify degradation processes. For example, the increasing and then decreasing concentration of TCE (Table 2) and the elevated VC concentrations at downgradient locations may be taken as evidence for sequential reductive dechlorination as typically observed at sites contaminated with chlorinated ethenes. However, VC and ethene can also originate from dihaloelimination of 1,1,2-TCA and 1,2-DCA, which show decreasing concentrations along the flow, and TCE may originate from 1,1,2,2-PCA.

Isotope Data. The variations in $\delta^{13}C$ values of different compounds cover a large range (Table 2). The largest variations are observed for VC (63.7‰) and ethene (32.1‰). Substantial variations occur also for 1,1,2-TCA (17.5‰) and CF (13.2‰). The smallest variations occurred for 1,1-DCA (0.9‰) and *cis*-1,2-DCE (3.4‰). For MW10, which was analyzed during both sampling episodes (Table 2), similar $\delta^{13}C$ values were measured confirming that the isotopic values varied little between the two sampling episodes and also demonstrating the reliability of the analytical method.

Isotope Characterization of the Contaminant Source. The evaluation of transformation processes using isotopes needs to consider potential variations in the isotopic composition of the source, particularly at waste disposal sites with a long disposal history such as the one discussed in this paper. Such variations can be evaluated by comparing the isotopic composition of different compounds at different locations and different depths (i.e., zones II and III) in the vicinity of the source. At the four source wells (MW8 and P8-02 in aquifer II; MW9 and P8-01 in aquifer III), several of the major contaminants have similar $\delta^{13}C$ values including CF (−29.1 to −31‰), 1,1,2-TCA (−32.8 to −33.5‰), and 1,2-DCA (−21.1 to −22.7‰) (Table 2). Furthermore, 1,1-DCA, frequently found to be recalcitrant, has a constant $\delta^{13}C$ value (−31.7 to −32.6‰) throughout the site. In these four source wells, the largest variations in $\delta^{13}C$ are observed for *trans*-1,2-DCE, *cis*-1,2-DCE, VC, and ethene. The substantial variation in $\delta^{13}C$ of VC and ethene is unlikely due to source variability since it is unlikely that the two gaseous compounds were disposed at the site. Instead, VC and ethene are most likely degradation intermediates that may undergo degradation themselves. The positive $\delta^{13}C$ of VC at MW8 suggests substantial degradation of VC (Table 2). It is in a range similar to that observed at another site where strong reductive dechlorination of VC occurred (*1*). The occurrence of reductive dechlorination of chlorinated ethenes in the vicinity of MW8 is consistent with the observed enrichment of ^{13}C in *cis*-1,2-DCE and *trans*-1,2-DCE compared to the other source wells. Thus, the comparison of the $\delta^{13}C$ values demonstrates that the isotopic composition of the source is likely quite homogeneous and variations in $\delta^{13}C$ for some compounds close to the source are due to degradation processes.

Isotope Variations Along the Groundwater Flow System. Comparison of the isotope ratios for contaminants in source area wells with downgradient wells screened in aquifers II and III provides evidence of various degradation processes. In aquifer II, 1,2-DCA in the downgradient well P1-02 is enriched in ^{13}C compared to the source wells, while the other compounds for which isotope ratios could be measured have a $\delta^{13}C$ value similar to that of the source. The enrichment of ^{13}C in 1,2-DCA indicates biodegradation of this compound.

For aquifer III, the $\delta^{13}C$ values of selected compounds in the aquifer are plotted as a function of the distance from the source in Figure 4. For some of the compounds, little variation in $\delta^{13}C$ is observed (*cis*-1,2-DCE, *trans*-1,2-DCE, 1,2-DCA), while CF and 1,1,2-TCA show a trend of increasing $\delta^{13}C$ values with increasing distance, suggesting degradation of these compounds along the groundwater flowpath. However, there are also three compounds, DCM, VC, and ethene, that have an inverse trend, i.e., decreasing $\delta^{13}C$ values with increasing distance.

Fate of CF. CF becomes strongly enriched in ^{13}C along the flow with a shift from −29.1 to −30.5‰ at the source to −18.9‰ in MW10. This clearly indicates transformation of CF. Transformation likely takes place by a reductive process leading to the formation of DCM. Even though DCM is already present at substantial concentrations at the source (Table 2), production of DCM along the groundwater flow path is evident by the shift in $\delta^{13}C$ from −53.5‰ to −57.3/−58.8‰ and also by the relatively high DCM concentration at P4-03 (Table 2). To evaluate whether DCM is also degraded along the flow path, the $\delta^{13}C$ value for the sum of CF and DCM was calculated: values of −30.9‰ (MW9), −32.5‰ (P4-03), and −23.0‰ (MW10) were obtained. These values suggest that

transformation of CF to DCM was predominant between the source and P4-03, while further downgradient DCM was also transformed. Due to the very negative $\delta^{13}C$ of DCM, its transformation is expected to lead to an increase in $\delta^{13}C$ of the sum of CF and DCM independent of the degree of isotope fractionation associated with the process. It is noteworthy that different transport velocities of CF and DCM due to less sorption of DCM would lead to a shift for the $\delta^{13}C$ of the sum of CF and DCM in the opposite direction along the flow path.

For CF dechlorination, isotopic enrichment factors are not known yet. However, from the shift in the $\delta^{13}C$ of DCM it can be concluded that the formed DCM has a $\delta^{13}C$ of <-58.8‰. Thus the isotopic enrichment factor is expected to be <-28.3‰. This value is in a range similar to the recently reported enrichment factor for abiotic reductive dechlorination of tetrachloromethane, which amounts to -22.2 to -26.5‰ (*23*). The plausibility of the isotopic enrichment factor can be verified based on the shift in $\delta^{13}C$ of CF and DCM between the source and P4-03. In this zone, transformation of CF to DCM is expected to be the dominant process (see above). Consequently, the concentration of CF and DCM were corrected for dilution assuming that the sum of CF and DCM remains constant. The $\delta^{13}C$ of CF and DCM that is produced was calculated using the following equations (*24*):

$$\delta^{13}C_{CF} = \delta^{13}C_{CF,0} + \epsilon \cdot \ln f \quad (1)$$

$$\delta^{13}C_{DCM} = \delta^{13}C_{CF,0} + \frac{\epsilon \cdot f \cdot \ln f}{1 - f} \quad (2)$$

where $\delta^{13}C_{CF,0}$ is the average $\delta^{13}C$ of CF at the source (-29.8‰), ϵ is the estimated isotopic enrichment factor (-28.3‰), and f is the fraction of CF remaining (0.8). The generated DCM has to be combined with the DCM already present at the source to estimate the $\delta^{13}C$ at the monitoring point. The calculation yields a $\delta^{13}C$ value of -23.3‰ for CF at P4-03 which corresponds well with the measured $\delta^{13}C$ of -24.3‰. Furthermore, the observed trend of DCM toward a more negative value is reproduced quite well with a calculated $\delta^{13}C$ of -55.0‰ compared to measured value of -57.3‰. For MW10, the fraction of degradation is expected to be 34% using the estimated isotopic enrichment factor and eq 1, while the observed accumulation of DCM is smaller. This confirms the hypothesis postulated above that DCM is also consumed at downgradient locations.

Origin and Fate of 1,1,2-TCA, VC, and Ethene. 1,1,2-TCA shows a $\delta^{13}C$ enrichment trend similar to that of CF with a shift from $-32.8/-33$‰ to -16‰ indicating transformation of 1,1,2-TCA. The most likely degradation product of 1,1,2-TCA is VC. The production of VC along the flow is supported by the strong shift in $\delta^{13}C$ of VC from $-18.8/-21.9$‰ to -49.4‰. The shift can be explained by production of VC with $\delta^{13}C$ <-49.4‰ that mixes with the more positive $\delta^{13}C$ VC present in the source area. Using the same arguments as for CF, an isotopic enrichment factor for the transformation of 1,1,2-TCA to VC of <-16.4‰ would be expected. This is much larger than the enrichment factor reported in the literature (Table 1). It has to be noted that the reported isotopic enrichment factor was derived from a microcosm with slow and incomplete 1,1,2-TCA transformation. On the basis of results for dichloroelimination of 1,2-DCA (Table 1), and since dichloroelimination involves C−Cl bond breaking, a larger isotopic enrichment factor would be expected for transformation of 1,1,2-TCA to VC. Thus the field-derived value is likely more representative for dichloroelimination than the value from the microcosm. Furthermore, it is unlikely that VC originated from another compound, since the $\delta^{13}C$ values of other precursors, *cis*-1,2-DCE and *trans*-1,2-DCE are constant along the groundwater flow path. Using eq 1 and an isotopic enrichment factor of -16.4‰, a degree of degradation of 1,1,2-TCA of 66% between the source and MW41 is estimated.

In addition to VC, ethene shows a large shift in $\delta^{13}C$ from -22.1‰ to -54.2‰, indicating ethene production downgradient from the source area. A particularly large shift occurs between the two most distant sampling points. The ethene may originate from dichloroelimination of 1,2-DCA or reductive dechlorination of VC. In aquifer IV, 1,2-DCA enriched in ^{13}C in conjunction with ethene depleted in ^{13}C is detected, suggesting that dichloroelimination of 1,2-DCA occurs at the site.

Origin and Fate of TCE. The $\delta^{13}C$ values provide insight into the origin of TCE at the site. The $\delta^{13}C$ of TCE measured at downgradient locations (-41.9 to -45‰) is substantially depleted compared to the range of values known so far for pure-phase industrial TCE (-24.3 to -31.9‰ (*25*−*27*)). This indicates that TCE is most likely a degradation product rather than a primary contaminant, which is also consistent with the decrease in $\delta^{13}C$ of TCE and increase in TCE concentration between the source wells and downgradient locations. Potential sources of TCE are reductive dechlorination of PCE or dehydrohalogenation of 1,1,2,2-PCA. On the basis of published isotopic enrichment factors for the PCE−TCE dechlorination step (Table 1), it is unlikely that TCE with a $\delta^{13}C$ <-45‰ can be produced from PCE with a $\delta^{13}C$ of -28.7‰. Furthermore, the $\delta^{13}C$ of TCE at the site (-36.2 to -45.0‰) is clearly distinct from TCE observed at other sites ($\delta^{13}C$ >-30.7) where PCE with an isotopic signature comparable to this site acted as its source (*1*, *10*, *11*). Thus, TCE in the groundwater was most probably derived from 1,1,2,2-PCA, which is consistent with the depleted $\delta^{13}C$ values of -39.1‰ of 1,1,2,2-PCA in the source area. The small difference in $\delta^{13}C$ between 1,1,2,2-PCA and TCE and the absence of a shift in $\delta^{13}C$ of 1,1,2,2-PCA along the flow indicate that carbon isotope fractionation associated with the process is small. Furthermore, abiotic dehydrohalogenation of 1,1,2,2-PCA is known to occur with a half-life of 0.4 years at pH = 7 (*14*). Some production of *cis*- and *trans*-1,2-DCE from 1,1,2,2-PCA, a process that is frequently observed under anaerobic conditions (*12*, *13*), may also occur close to the source. This process may explain the shift in $\delta^{13}C$ for *cis*- and *trans*-1,2-DCE between MW9 and downgradient monitoring wells.

Thus, the major transformation processes along the groundwater flow system in aquifer III seem to be dehydrochlorination of 1,1,2,2-PCA to TCE, reductive dechlorination of CF to DCM with further transformation of part of the DCM, dichloroelimination of 1,1,2-TCA to VC, and dichloroelimination of 1,2-DCA to ethene. Reductive dechlorination of the chlorinated ethenes seems to be of minor importance. The predominance of dichloroelimination over reductive halogenation of C2 compounds may be due to the larger energy gain per mole of reduction equivalents associated with dichloroelimination. A similar argument was used by Dolfing (*28*) to explain the preferential formation of 1,2-DCE by dichloroelimination of 1,1,2,2-PCA compared to reductive dechlorination of 1,1,2,2-PCA. It is interesting to note that for 1,1,2-TCA, VC, and ethene, the shifts in $\delta^{13}C$ occur at distances >200 m from the source where CF concentrations are lower. This could be due to the inhibition of transformation processes closer to the source due to the very high CF concentrations.

In conclusion, this study demonstrates that $\delta^{13}C$ measurements, in addition to concentration data, help to confirm degradation pathways at sites with complex contaminant mixtures. The study illustrates the importance of measuring isotope ratios not only of primary compounds but also of potential degradation products. It demonstrates that at sites where degradation products are already present at the source,

the classical isotope pattern of isotopic enrichment of parent compound and parallel isotopic enrichment of degradation byproduct (*1*) does not necessarily occur. For DCM, VC, and ethene, the opposite trend toward depleted values was observed. This trend can be explained by mixing of isotopically light byproducts of biodegradation with heavier compounds from the source. Measurement of isotope ratios of primary contaminants and products made it possible to get estimates of enrichment factors and quantify the amount of transformation. The study also indicates that the isotope method can be applied to field sites with a long history of disposal of chlorinated hydrocarbons and a limited number of monitoring locations.

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