Fate and Origin of 1,2-Dichloropropane in an Unconfined Shallow Aquifer

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A shallow aquifer with different redox zones overlain by intensive agricultural activity was monitored for the occurrence of 1,2-dichloropropane (DCP) to assess the fate and origin of this pollutant. DCP was detected more frequently in groundwater samples collected in aerobic and nitrate-reducing zones than those collected from iron-reducing zones. Simulated DCP concentrations for groundwater entering an iron-reducing zone were calculated from a fate and transport model that included dispersion, sorption, and hydrolysis but not degradation. Simulated concentrations were well in excess of measured values, suggesting that microbial degradation occurred in the iron-reducing zone. Microcosm experiments were conducted using aquifer samples collected from iron-reducing and aerobic zones to evaluate the potential for microbial degradation of DCP and to explain field observations. Hydrogenolysis of DCP and production of monochlorinated propanes in microcosm experiments occurred only with aquifer materials collected from the iron-reducing zone, and no dechlorination was observed in microcosms established with aquifer materials collected from the aerobic zones. Careful analyses of the DCP/1,2,2-trichloropropane ratios in groundwater indicated that older fumigant formulations were responsible for the high levels of DCP present in this aquifer.

Introduction

Fumigants are frequently used during the production of crops (e.g., berries, potatoes, grapes) that are susceptible to nematodes. Because of their toxicity and mobility, fumigants pose a potentially serious risk to groundwater quality. The use of fumigants in crop production has resulted in concentrations of 1,2-dichloropropane (DCP) in groundwater exceeding health advisory levels (*1, 2*). While DCP-based fumigants are no longer used in the United States, sources of DCP still threaten groundwater quality. First, desorption of DCP derived from historical fumigant formulations may be responsible for the contamination of shallow groundwater

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(*3*). Second, while current 1,3-dichloropropene- (1,3-D) based fumigant formulations only contain trace amounts of DCP (<0.01 wt %), elevated concentrations of DCP have been observed in downgradient wells after applications of these products (*4*).

The objectives of this study were to evaluate the natural attenuation and origin of DCP found in the Abbotsford-Sumas Aquifer, which is located in the Fraser-Whatcom Lowlands of southwestern British Columbia, Canada, and northern Washington State, U.S.A. Numerous studies have been conducted on the natural attenuation of chlorinated ethenes derived from industrial spill sites; however, only a few studies examined the natural attenuation of chlorinated propanes. Studies on the natural attenuation of agronomically derived DCP contamination are complicated by the fact that pollutants derived from nonpoint sources are typically present in low concentrations as compared to the concentrations observed in groundwater plumes from industrial spill sites. Hence, methods to monitor natural attenuation that rely on the identification of transformation products in groundwater may not work for nonpoint source contaminants such as DCP. The methodology used in this study to demonstrate that natural attenuation has occurred relies on multiple lines of evidence, including (i) the frequency of detection and the concentrations of DCP in relation to the dominant terminal electron-accepting process in the entire data set as well as along groundwater flow paths, (ii) the application of a two-dimensional groundwater flow and transport model to simulate the migration of DCP along a flow path and to compare simulated DCP concentrations (assuming no degradation) to measured values, and (iii) microcosm studies with aquifer materials collected from different redox zones to evaluate the potential for microbial degradation of DCP.

Conclusions regarding the origin of the DCP contamination in this aquifer are made by relating the ratios of DCP to 1,2,2-trichloropropane (1,2,2-TCP) in groundwater to those associated with current and past fumigant formulations. DCP concentrations in fumigant formulations have decreased markedly over the last few decades while 1,2,2-TCP concentrations remained relatively stable. As a result, DCP/1,2,2-TCP ratios may be used to determine the degree to which DCP is derived from older fumigant formulations.

Methods

Groundwater Sample Collection and Analysis. Fifty-nine wells were sampled in 1997 and 1998 as a part of this study (Figure 1). Well screens were usually less than 2 m in length. Water-quality sampling was conducted according to protocols established for the U.S. Geological Survey's National Water-Quality Assessment Program (*5*). Groundwater samples were analyzed for over 80 volatile organic compounds including DCP, 1,3-D, 1,2,2-TCP, and 1,2,3-trichloropropane (1,2,3-TCP) using purge-and-trap gas chromatography and mass spectrometry. For most samples, laboratory reporting levels for DCP, 1,3-D, 1,2,2-TCP, and 1,2,3-TCP were 0.07, 0.1, 0.1, and 0.16 μg/L, respectively. Values reported below these levels are considered estimates. Details of analytical and reporting methods are provided elsewhere (*6, 7*). Dissolved oxygen was measured using electrodes placed in a flow cell chamber to minimize atmospheric interactions. Water samples for the determination of iron (both ferric and ferrous) and nitrate were filtered using 0.45-μm capsule filters; samples for iron analysis were preserved with nitric acid. Iron and nitrate were analyzed using inductively coupled plasma mass spectrometry (ICP/MS) and a colorimetric method, respectively (*8*).
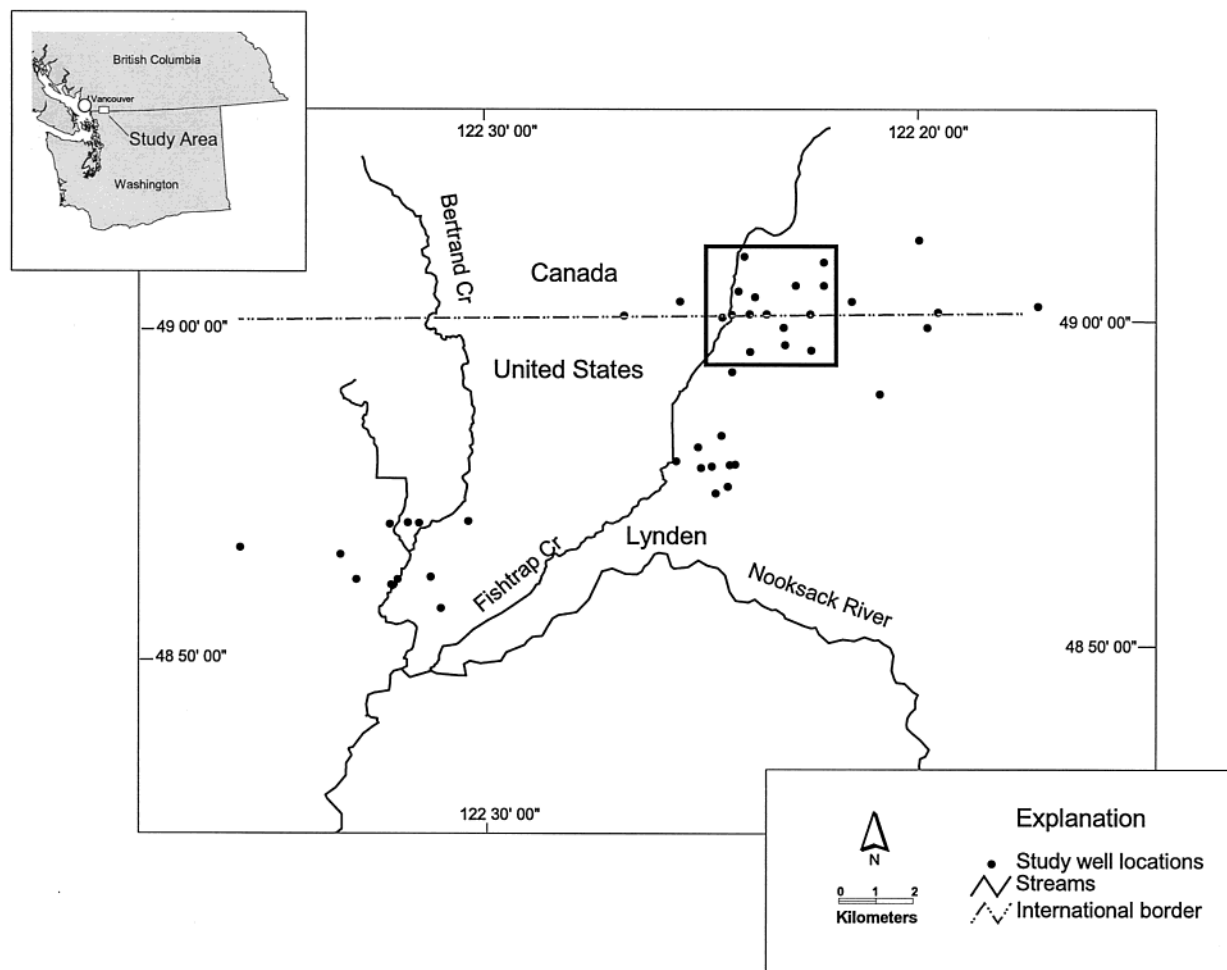
FIGURE 1. Map showing the location of the wells sampled for this investigation. Box indicates the area shown in Figure 2.

Microcosm Experiments. Soil samples were collected at a depth of 6−7 m below ground surface at location 23 to represent iron-reducing zones and at a depth of 3.3−4.3 m at location 46 to represent aerobic zones (Figure 2). A series of experiments was conducted for each soil type to evaluate the effect of aquifer material and electron donors on the anaerobic degradation of DCP. In addition, the potential for aerobic degradation of DCP was evaluated. Microcosms were established as described before (9). Briefly, 2 g of aquifer material and 20 mM potassium phosphate buffer were placed in a 24-mL glass vial to give a total volume of 10 mL. The vials were amended with 2.5 μmol of DCP, and acetate, formate, propionate, butyrate, pyruvate, lactate, or glycerol were added individually or in combination to the vials to achieve aqueous concentrations of 2.5 mM for acetate and 2 mM for all other compounds. All electron donors were added from anoxic, filter-sterilized, aqueous stock solutions. Aerobic microcosms were established in 60-mL serum bottles and amended with DCP as the only source of carbon and energy. The culture vessels were sealed with Teflon-lined rubber stoppers, and anaerobic microcosms were incubated without shaking at 25 °C in the dark. Aerobic microcosms were shaken at 100 rpm, and oxygen consumption was monitored biweekly. Because DCP may be removed from solution by mechanisms other than degradation (e.g., sorption), the amount of degradation products measured at the end of each experiment rather than DCP loss was used to evaluate DCP degradation. After 4 months, DCP, 1-chloropropane, 2-chloropropane, propane, and propene were measured in headspace samples and analyzed by gas chromatography and flame ionization detection. Methods used here are similar to

a previous study on DCP degradation that contains more detailed information on experimental design and methods (9).

Hydrogeology. Much of the Abbotsford-Sumas Aquifer is overlain by intensive agricultural activities including dairies, poultry operations, and raspberry production. The aquifer is largely composed of glacial-fluvial coarse sands and gravels that were deposited as outwash during the Sumas Stage of the Fraser Glaciation. These deposits typically contain low amounts of organic carbon (<0.2% [w/w]).

DCP concentrations were evaluated along a transect from a recharge area near the Abbotsford Airport to a discharge area at Fishtrap Creek near the international border (Figure 2). The aquifer in this area is approximately 20 m thick and unconfined, with depths to groundwater typically ranging between 2 and 10 m. Average groundwater velocities exceeding 1 m/d have been reported (10). A six-layer transient cross-sectional model was constructed using Visual MOD-FLOW (11, 12) to represent flow from a local groundwater high to a discharge location at Fishtrap Creek (section A−A′ in Figure 2). Information on model development is provided below; however, a more detailed discussion of model development and calibration can be found elsewhere (13). No-flow boundaries were assumed for the upgradient edge of the section as well as for the bottom of the aquifer. Assuming no flow into the unit below this aquifer (i.e., the Everson Interstade) is reasonable considering the thickness (>30 m) and low hydraulic conductivity for much of this unit ($\cong 10^{-9}$ m/s, 14). The downgradient end of the section was assumed to be a constant head boundary, oscillating between 41 and 43 m based upon measured water levels in the area.
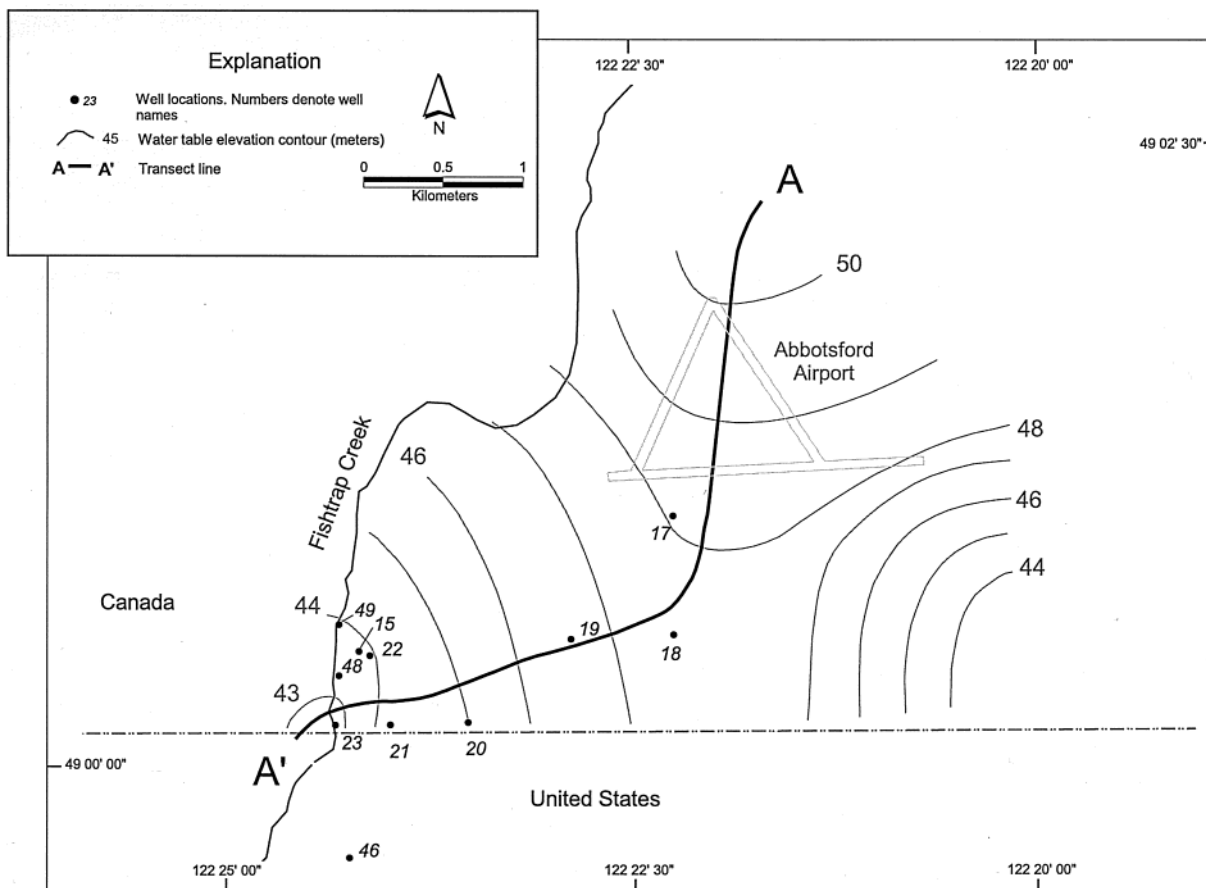
FIGURE 2. Detailed map identifying the wells used to evaluate changes in water chemistry along groundwater flow paths. Study area location is shown in Figure 1.

Mean annual recharge was calculated on a yearly basis from 1994 to 1996 using precipitation data and a regression equation derived for outwash-covered areas in the Puget Sound Basin (15). Annual recharge estimates vary from 660 to 890 mm during the calibration period of 1994−1996. River stage near well 23 (Figure 2) oscillated in the model between 41.9 m at base flow and 42.2 m during high flow periods based on levels measured by Environment Canada. Hydraulic conductivity values were used to calibrate the simulated head values to measured values. A hydraulic conductivity value of 3.5×10^{-3} m/s for the Abbotsford-Sumas Aquifer provided a good fit to observed data (13). This value is within the range of measured values (2.4×10^{-5} to 2.8×10^{-2} m/s) and in general agreement with the median value of 1.0×10^{-3} m/s reported for this aquifer (14).

Results and Discussion

Groundwater Quality. 1,3-D was not detected in any sample. This finding was not surprising because 1,3-D is rapidly degraded in the environment (2). Conversely, DCP was detected in groundwater from 56% of the wells sampled (33 of 59) and was the most frequently volatile organic compound detected. The median concentration of DCP was 0.07 μg/L, with a maximum concentration of 19.4 μg/L. DCP is a probable human carcinogen (16). The U.S. EPA Maximum Contaminant Level (MCL) for drinking water for DCP is 5 μg/L, while the nonenforceable Maximum Contaminant Level Goal (MCLG, the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on human health occurs) is zero (16). 1,2,2-TCP was detected in 42% of the groundwater samples that were analyzed for this constituent (20 of 48), with a maximum concentration of 0.38 μg/L. 1,2,3-TCP was detected in 17% of the ground-

water samples (10 of 59) with a maximum concentration of 0.61 μg/L; 1,2,3-TCP is considered a probable human carcinogen. An MCL or MCLG for the protection of drinking water, however, has not been established for 1,2,3-TCP or 1,2,2-TCP (16). Sample locations and data tables showing the concentrations of the contaminants are provided as Supporting Information (see paragraph at end of paper).

Natural Attenuation of DCP. Indirect information on the stability of DCP in the aquifer can be obtained by evaluating the frequency of detection of DCP in groundwater samples as a function of the dominant terminal electron-accepting process (TEAP). Redox zones are defined in terms of dominant TEAPs, which are determined by measuring steady-state hydrogen concentrations according to methods described elsewhere (17, 18) and by monitoring electron acceptor concentrations. Zones with groundwater containing greater than 0.5 mg/L dissolved oxygen were classified as oxygen-reducing (aerobic), while zones with groundwater with lower oxygen concentrations but greater than 0.5 mg/L nitrate were considered nitrate-reducing. Denitrification was shown to be the dominant pathway for nitrate reduction in the nitrate-reducing zones of this aquifer (13). The remaining groundwater samples had concentrations of dissolved oxygen and nitrate below 0.5 mg/L and showed increased concentrations of iron as compared to waters from the oxygen- and nitrate-reducing zones and were classified as iron-reducing.

DCP is recalcitrant under aerobic conditions, and nitrate was shown to inhibit the microbial reduction of DCP in microcosm experiments (9). Hence, no significant decrease in the DCP concentrations was expected to occur in the oxic and nitrate-reducing zones. A statistical analysis of the frequencies of DCP detection in groundwater as a function of the dominant TEAP was conducted to test the null
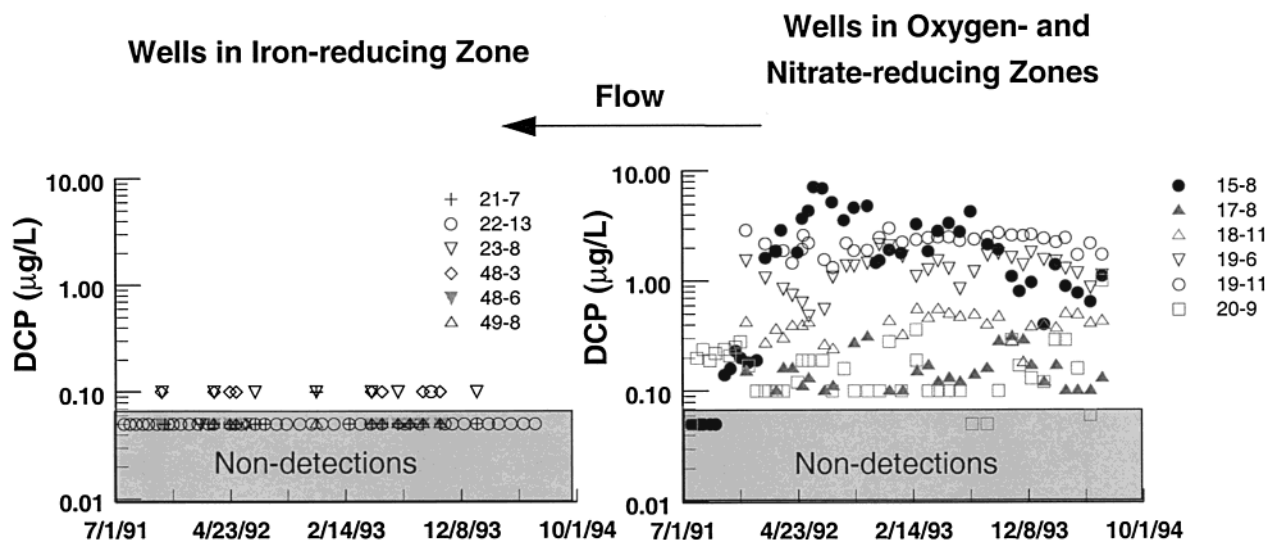
FIGURE 3. Concentrations of DCP in groundwater samples collected in iron-reducing (left) and oxygen- and nitrate-reducing (right) zones from 1991 to 1994. Well names (e.g., 21-7) refer to the location given in Figure 2 (e.g., location no. 21) and the approximate depth of the well (e.g., 7 m).
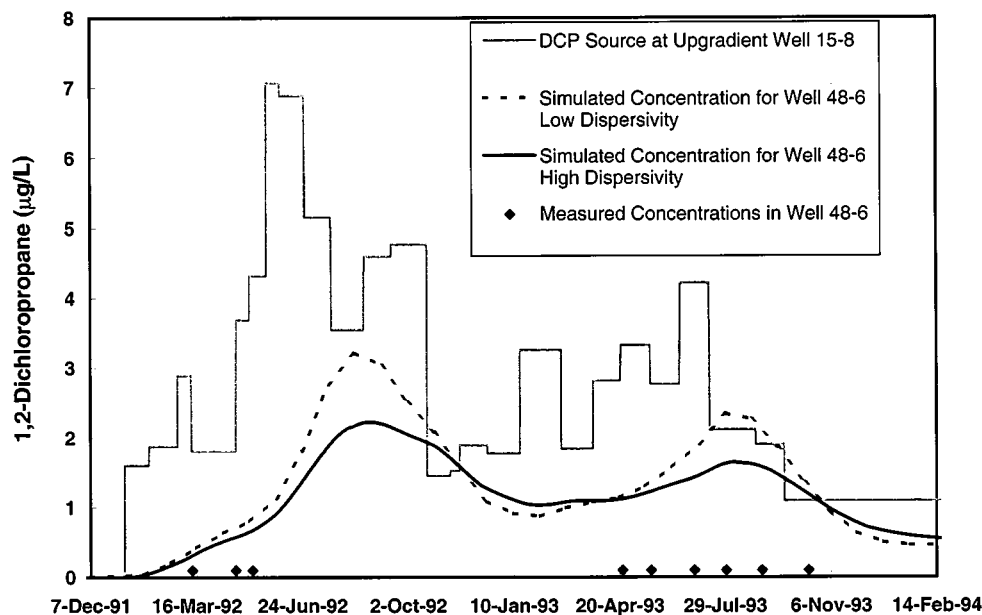

FIGURE 4. Simulated 1,2-dichloropropane (DCP) concentrations for well 48-6 assuming high (10 m) and low (0.1 m) values for dispersivity versus time. Also shown is the upgradient source profile for well 15-8 and the measured concentrations in well 48-6.

hypothesis that the detection frequency of DCP is independent of whether iron-reducing or more oxic conditions (nitrate- or oxygen-reducing conditions) are present. This type of analysis has been used extensively in the biological sciences to test for the independence of two properties (in this case, TEAP and DCP detection) and was performed by calculating expected frequencies of detection (assuming the null hypothesis is true) and comparing these to observed frequencies (*19*). The Fisher's exact test of independence was used in this study to test the validity of the null hypothesis (*19*). For the data shown in Table 1, the null hypothesis is rejected ($p < 0.005$), suggesting that groundwater from iron-reducing zones has a significantly lower frequency of detecting DCP as compared to the oxic and nitrate-reducing portions of this aquifer.

These findings suggest that DCP was degraded in the more reduced zones of the aquifer. An alternative explanation for the lower frequency of DCP detection in the iron-reducing zones is the fact that these areas are farther away from recharge areas than the oxic zones. To evaluate this possibility,

TABLE 1. Frequency of 1,2-Dichloropropane (DCP) Detections as a Function of Dominant Terminal Electron Acceptor

terminal electron acceptor	detections of DCP	nondetections of DCP	totals	% DCP detections
oxygen or nitrate	32	17	49	65
iron	1	9	10	10
totals	33	26	59	56

DCP concentrations along a flow path through different redox zones were examined in more detail. Transect A—A′ (Figure 2) includes redox zones ranging from aerobic to iron-reducing and contains upgradient sources of DCP. A detailed assessment of the redox reactions occurring along this transect concluded that iron sulfide deposits and to a lesser degree organic carbon are the dominant sources of electrons for denitrification reactions that occur before groundwater enters the iron-reducing zone near the creek (*13*). On the basis of the occurrence and orientation of alluvial deposits in the

area, it has been suggested that a relic channel or wetland may have existed to the east of Fishtrap Creek and may be responsible for the rather wide iron-reducing zone in places (*13*).

Data from an intensive sampling of many of the wells along this transect (*3*) were used to see if DCP concentrations are consistently lower in the iron-reducing zone as compared to the more oxidized zones. The results of this analysis were grouped according to the dominant TEAPs, and a consistent pattern emerged. DCP was detected in nearly every sample collected in the oxygen- and nitrate-reducing zones, with concentrations remaining fairly constant throughout the sampling period (Figure 3). Conversely, DCP was rarely detected in the iron-reducing zone immediately downgradient of the nitrate- and oxygen-reducing zones (Figure 3). To evaluate whether dispersion was responsible for the decline in DCP concentrations as groundwater enters the iron-reducing zone, a groundwater flow model was applied to predict the concentrations of DCP that would be expected at well 48-6. An upgradient source term described by measured concentrations at well 15-8 was incorporated into the model (Figure 4). Sorption was considered by using an organic carbon-normalized solid−water partition coefficient (K_{oc}) value of 47 L/kg (*20*) and a fraction of organic carbon (f_{oc}) value of 0.002, which is the maximum value found in this portion of the aquifer. A hydrolysis half-life of 16.6 yr was used; however, an even longer half-life is likely at ambient groundwater temperatures (*21*). While included in the simulations, DCP loss by hydrolysis is negligible for this time period. Dispersivity values are scale dependent. For the approximately 200 m distance between wells 15-8 and 48-6, longitudinal dispersivity values for this aquifer are likely to range between 0.1 and 10 m, and a ratio of longitudinal to vertical dispersivity of 100 is assumed (*22*). (Transverse dispersion could not be considered in this cross-sectional model; however, given the nonpoint source nature of the contaminant, the reduction of DCP concentrations by this process is expected to be negligible over this distance.) Even assuming high dispersivity, simulated concentrations of DCP for well 48-6 were well above measured concentrations (<0.1 μg/L) (Figure 4); other wells in this area also showed very low concentrations of DCP (Figure 3). The disparity between simulated and measured concentrations in well 48-6 (Figure 4) supports the argument that degradation of DCP occurs as groundwater passes from a nitrate-reducing zone in the vicinity of well 15-8 to an iron-reducing zone at well 48-6.

Microcosm Experiments. Microcosm experiments were conducted using aquifer materials from both the oxic and iron-reducing zones to determine whether and by what mechanisms DCP degradation occurs in these environments. No degradation products were detected in microcosms that were established with aquifer materials collected in the aerobic zone. In contrast, both 1-chloropropane and 2-chloropropane were detected in a constant ratio of about 8:1 in most anaerobic treatments conducted with aquifer materials collected from the iron-reducing zone and indicated that hydrogenolysis of DCP occurred (Figure 5). The formation of propene however was never observed, suggesting that vicinal reduction of DCP or the dehydrochlorination of monochlorinated propanes did not occur during the 4-month time period. Similarly, hydrogenolysis of monochlorinated propanes did not occur since propane was also not detected.

The incomplete dechlorination of DCP at slow rates and the positive correlation between the production of monochlorinated propanes and methane (Figure 6) suggest that the observed dechlorination reactions in the microcosm experiments were most likely due to anaerobic cometabolism (*18*). In contrast, the complete reductive dechlorination of DCP to propene in enrichment cultures derived from streambed sediments (from a different study area) occurred via vicinal
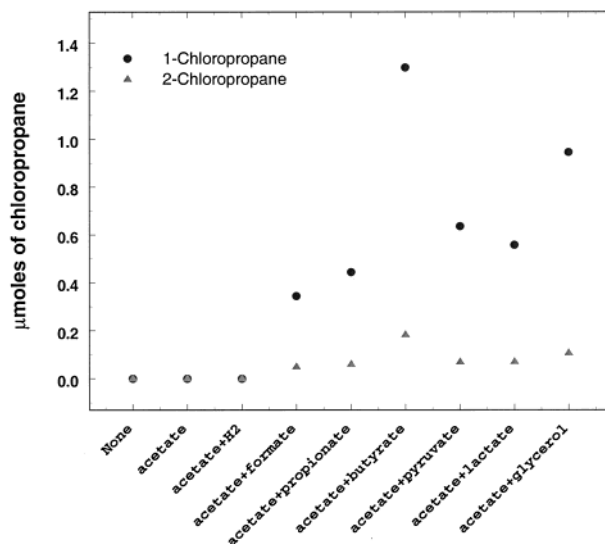

FIGURE 5. Monochloropropanes produced in microcosm experiments using aquifer materials from the iron-reducing zone under different electron donor conditions.
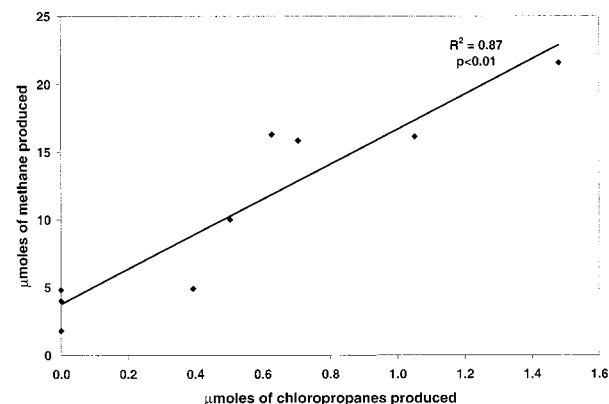

FIGURE 6. Plot of micromoles of methane produced versus micromoles of monochloropropanes produced during microcosm experiments shown in Figure 5.

reduction without the intermediate formation of monochlorinated propanes and was catalyzed by populations that derived energy from the reductive dechlorination reaction (*9*, *18*). Interestingly, this study also reported the formation of 1-chloropropane and 2-chloropropane in ratios of 8:1 in methanogenic microcosm (*9*).

In an attempt to verify the microbial reduction of DCP to monochloropropanes in the field, selected groundwater samples were collected from the iron-reducing zone in 1997 and 1998 (wells 21-7, 22-13, and 23-7) and analyzed for 1-chloropropane and 2-chloropropane. Neither compound was detected (<0.1 μg/L). The fact that these compounds were not detected may be due to the further degradation of monochloropropanes to other compounds (e.g., propene) and/or the existence of multiple pathways that may have caused monochloropropane concentrations to decrease to nondetectable levels (especially given the lower DCP concentrations observed in the late 1990s when this sampling occurred). To establish whether the reaction pathways observed in the microcosm experiments are indeed those occurring in this aquifer, a more intensive sampling grid at the interface between the nitrate- and iron-reducing zone is needed.

Origin of DCP in Groundwater. Because fumigant formulations have markedly changed in composition over the past decades, it is possible to use the ratios of different
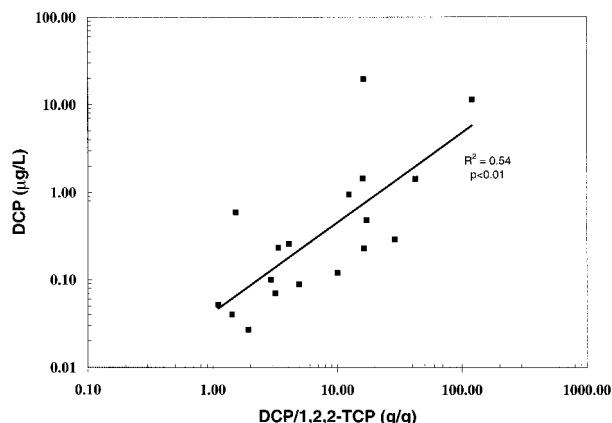
FIGURE 7. DCP concentrations versus DCP/1,2,2-TCP ratios for groundwater samples with detectable concentrations of each compound. DCP/1,2,2-TCP ratios of 88 and 0.55 have been observed for leachate from applications of Telone I and II, respectively (*25*).

chlorinated propanes in groundwater as indicators of the origin of these compounds. Using the DCP/1,2,2-TCP ratios as an indicator of the fumigant source requires that differential degradation does not appreciably alter these ratios. Loss or retardation of DCP and 1,2,2-TCP from the groundwater system is not likely to significantly alter these ratios because both compounds are unlikely to degrade under aerobic conditions (*9*), have similar physicochemical properties, and have long hydrolysis half-lives at ambient groundwater temperatures (*21, 23*).

The following weight percent values were determined for formulations of Telone I (from the 1960s) and Telone II (1990s), respectively: DCP, 15.6, 0.06; 1,2,2-TCP, 0.32, 0.19; 1,2,3-TCP, 0.17, ≪0.1 (*24*). Telone I and II are used as examples to demonstrate the trend in chlorinated propane concentrations in fumigants. It is noted that other historical fumigant formulations have high DCP concentrations, such as Shell D−D, which may also have been used at the site. A recent study demonstrated that leachate from aquifer columns had DCP/1,2,2-TCP ratios of 88 and 0.55 for Telone I and II, respectively (*25*).

The DCP/1,2,2-TCP ratios of groundwater samples collected in this study are roughly bounded by the ratios reported for Telone I and II and suggest that chlorinated propanes may be derived from both formulations (Figure 7). DCP concentrations tend to increase as DCP/1,2,2-TCP ratios increase (Figure 7). This relation suggests that samples having high concentrations of DCP are primarily the result of earlier fumigant formulations. Further evidence that high DCP/1,2,2-TCP ratios indicate earlier formulations is provided by the fact that 1,2,3-TCP, present in Telone I but not in Telone II, was only detected in the seven samples with the highest DCP/1,2,2-TCP ratios. In conclusion, the most likely explanation for the data observed is that high concentrations of DCP detected in the aquifer are largely derived from applications of older fumigant formulations (prior to 1990) that contained high concentrations of both DCP and 1,2,3-TCP.

Acknowledgments

Supporting Information Available

One table showing well depth and water quality information and one figure showing the location of the wells (5 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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