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Potential for Microbial Degradation of *cis*-Dichloroethene and Vinyl Chloride in Streambed Sediment at the U.S. Department of Energy, Kansas City Plant, Missouri, 2008

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KEN SALAZAR, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Pressure		
pound per square inch (lb/in^2)	6.895	kilopascal (kPa)
Radioactivity		
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)

SI to Inch/Pound

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
micrometer (μm)	0.00003937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
meter (m)	1.094	yard (yd)
Volume		
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8×°C)+32$$

Abbreviations

ºC	degrees Celsius
cis-DCE	*cis*-dichloroethene
cm	centimeter
DOE	U.S. Department of Energy
g	gram
h	hour
L	liter
m	meter
M	molar; mole per liter
mg/L	milligram per liter
mL	milliliter
µCi/µmole	microcurie per micromole
µg/L	microgram per liter
µm	micrometer
µM	micromolar; micromole per liter
µmole	micromole
nM	nanomolar; nanomole per liter
nmole	nanomole
DCE	dichloroethene
PCE	perchloroethene; tetrachloroethene
PSI	pound per square inch
SD	standard deviation
TCE	trichloroethene
USGS	U.S. Geological Survey
VC	vinyl chloride; chloroethene

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Abstract

A series of carbon-14 (^{14}C) radiotracer-based micro-cosm experiments was conducted to assess the mechanisms and products of degradation of *cis*-dichloroethene (*cis*-DCE) and vinyl chloride (VC) in streambed sediments at the U.S. Department of Energy, Kansas City Plant in Kansas City, Missouri. The focus of the investigation was the potential for biotic and abiotic *cis*-DCE and VC degradation in surficial and underlying hyporheic sediment from the Blue River and its tributaries, Indian Creek and Boone Creek.

Substantial degradation of $[1,2\text{-}^{14}C]$ *cis*-DCE and $[1,2\text{-}^{14}C]$ VC to ^{14}C-carbon dioxide ($^{14}CO_2$) was observed in all viable surficial sediment microcosms prepared under oxic conditions. No significant accumulation of reductive dechlorination products was observed under these oxic incubation conditions. The results indicate that microbial mineralization processes involving direct oxidation or co-metabolic oxidation are the primary mechanisms of *cis*-DCE and VC biodegradation in oxic stream sediment at the Kansas City Plant.

Substantial mineralization of $[1,2\text{-}^{14}C]$ VC also was observed in all viable surficial sediment microcosms incubated in the absence of detectable oxygen (dissolved oxygen concentrations less than 25 micrograms per liter). In general, the accumulation of mineralization products ($^{14}CO_2$ and ^{14}C-methane [$^{14}CH_4$]) predominated with only trace-level detection of the reductive dechlorination product, ^{14}C-ethene. In contrast, microbial degradation of $[1,2\text{-}^{14}C]$ *cis*-DCE by reductive dechlorination or mineralization was not significant in the absence of detectable oxygen.

The potential for $[1,2\text{-}^{14}C]$ VC biodegradation also was significant in sediments from the deeper hyporheic zones under oxic conditions and in the absence of detectable oxygen. In this study, microbial degradation of $[1,2\text{-}^{14}C]$ *cis*-DCE was not significant in hyporheic sediment treatments under either oxygen condition.

Taken together, the results indicate that microbial mineralization processes in streambed sediments at the Kansas City Plant can be an important component of *cis*-DCE and VC degradation under oxic conditions and of VC degradation even in the absence of detectable oxygen. These results demonstrate that an evaluation of the efficiency of in situ *cis*-DCE and VC biodegradation in streambed sediments, based solely on observed accumulations of reduced daughter products, may underestimate substantially the total extent of contaminant biodegradation and, thus, the potential importance of the hyporheic zone and streambed sediments as barriers to the discharge of contaminated groundwater.

Introduction

Mixed chlorinated solvent plumes derived from multiple historical releases characterize the shallow groundwater system at the U.S. Department of Energy (DOE), Kansas City Plant (KCP; figs. 1 and 2). The primary contaminants in these plumes are trichloroethene (TCE) and the reductive degradation products, 1,2-dichloroethene (1,2-DCE) and vinyl chloride (VC). The general stratigraphy of the contaminated shallow aquifer is characterized by surface fill underlain by an extensive silty-clay layer and then coarse sand and gravel underlain by bedrock. The sand and gravel layer is expected to provide a zone of preferential transport for contaminants, particularly those with a density greater than water.

In the northeastern part of the study area (fig. 2), shallow groundwater flow and contaminant plume migration are generally east and northeast toward the Blue River and its tributary, Boone Creek (U.S. Department of Energy, 2006). The ongoing operation of several pumping wells in this area of the site appears to intercept effectively the primary contaminant plume and to flatten or reverse the potentiometric gradient between the pumping wells and the putative surface-water receptors, thereby preventing further contaminant transport toward the Blue River and Boone Creek (U.S. Department of Energy, 2006). Similarly, in the southern part of the study area, groundwater flow and possible contaminant migration toward Indian Creek is contained hydraulically by building footing tile drains and pumping interceptor wells (U.S. Department of Energy, 2006).

Fundamental to the adoption of the current hydraulic containment strategy was the conclusion that natural attenuation in the shallow groundwater system prior to the operation
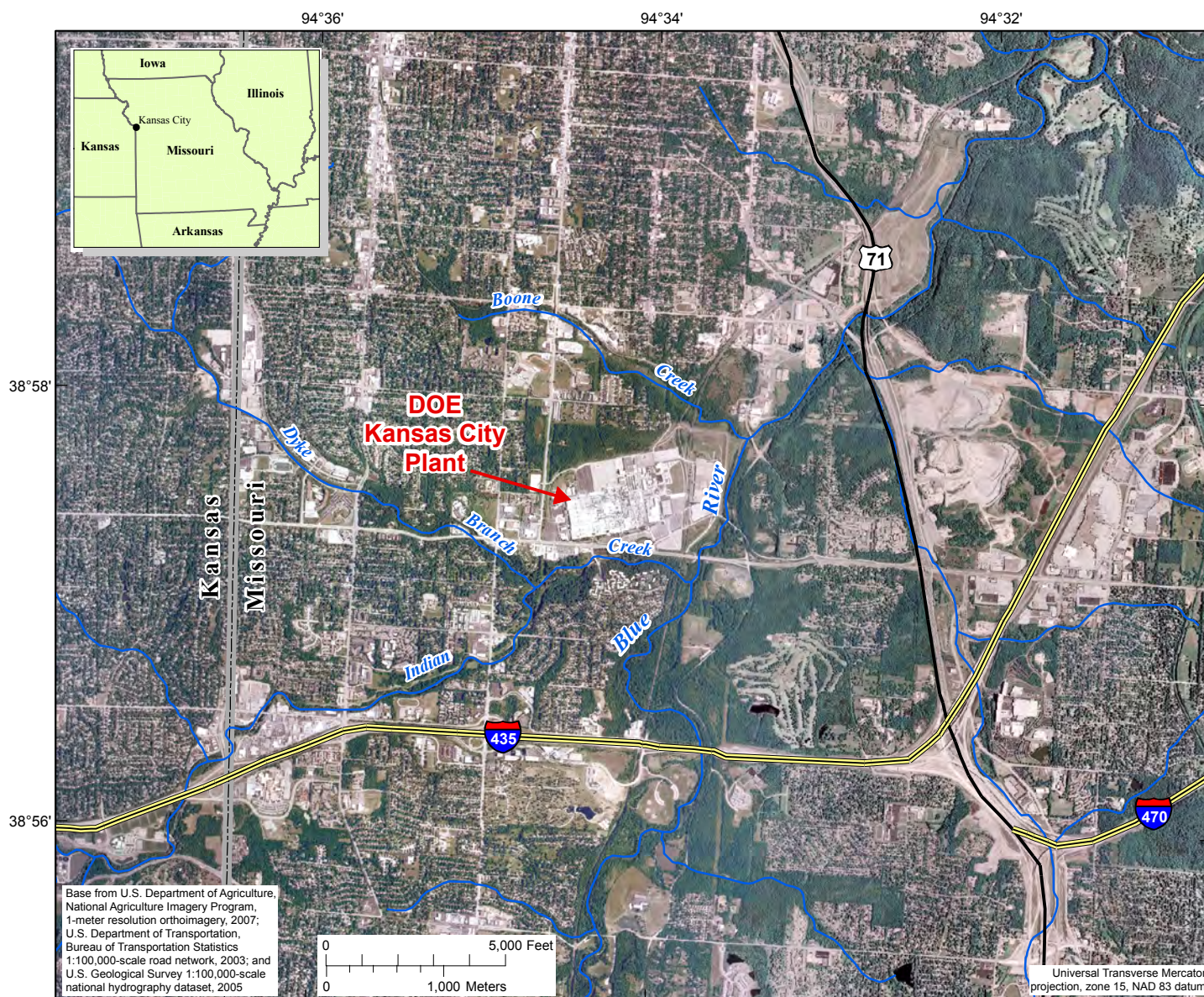
Figure 1.   Location of the U.S. Department of Energy, Kansas City Plant in Kansas City, Missouri, near the Blue River.

of contaminant-interception wells was not sufficient to prevent contaminant migration to the Blue River. In the absence of a demonstrated natural buffer that could effectively prevent contaminant discharge to the Blue River and Boone Creek, the groundwater-interception strategy was implemented. The apparently successful implementation of the current pump-and-treat strategy at the KCP has created an opportunity to investigate the feasibility of alternative remedial strategies that do not involve the long-term operation and maintenance costs associated with pump-and-treat remediation.

The results of recent U.S. Geological Survey (USGS) investigations (Bradley and Chapelle, 1997, 1998a, 1998b, 1999a, 1999b, 2000a, 2000b, 2002; Bradley, Chapelle, and Lovley, 1998; Bradley, Chapelle, and Wilson, 1998; Bradley, Landmeyer, and Dinicola, 1998; Bradley, 2003) have

demonstrated that the potential for chloroethene biodegradation is pronounced particularly in wetlands and streambed-sediment environments. Spatial and temporal variations in the hydrologic and geochemical characteristics of the sediments in these environments can lead to highly dynamic microbial communities with a wide range of metabolic capabilities and the demonstrated potential for rapid reductive and oxidative chloroethene biodegradation. Thus, because the reduced daughter products, DCE and VC, are the predominant chloroethene contaminants in the downgradient portions of the chloroethene plumes at the KCP, and because the extent and efficiency of DCE and VC biodegradation in streambed sediments has been reported to be much greater than that observed in adjacent aquifer systems (Bradley and Chapelle, 1997, 1998a, 1998b, 1999a, 1999b, 2000a, 2000b, 2002; Bradley, Chapelle, and

Figure 2.   Location of the study area, including Blue River to the east, Indian Creek to the south, and Boone Creek to the northeast (the surface-water receptors) and the distribution of volatile organic compounds (VOCs) observed in the shallow groundwater in 2008 (figure from J. Baker, Honeywell, FM&T).

Lovley, 1998; Bradley, Chapelle, and Wilson, 1998; Bradley, Landmeyer, and Dinicola, 1998; Bradley, 2003), the USGS, in cooperation with the U.S. Department of Energy, Kansas City Plant, conducted an assessment of the potential for *cis*-DCE and VC biodegradation in the streambed sediments at the KCP.

Biodegradation of chloroethene contaminants in groundwater and surface-water environments can yield two general types of degradation products—reduced daughter products associated with reductive-degradation processes or mineralization products (Bradley, 2003). The primary reductive chloroethene degradation mechanism reported in saturated environments is respiratory reductive dechlorination (chlororespiration). This process involves consecutive hydrogen-substitution reactions yielding sequentially less chlorinated daughter products (TCE, DCE, and VC) and ultimately ethene (McCarty and Semprini, 1994). The polychlorinated ethenes, tetrachloroethene (alternatively perchloroethene, PCE) and TCE, are highly oxidized compounds that readily undergo reduction reactions under anoxic conditions. Reductive dechlorination is common in anoxic groundwater and surface-water systems and appears to be the primary mechanism for in situ biotransformation of the parent compounds, PCE and TCE.

The efficiency of chloroethene reductive dechlorination appears to decrease with decreasing chlorine number. Significant reductive dechlorination of chloroethene contaminants to the non-chlorinated product, ethene, has been reported but appears to require the VC reductive dehalogenase activity of a subset of *Dehalococcoides* spp. (Furukawa, 2006; Löffler and Edwards, 2006; Cupples, 2008; Futagami and others, 2008). Moreover, reductive dechlorination to non-chlorinated products often is limited in situ because of low electron-donor supply, high electron-donor competition, the presence of alternative terminal-electron acceptors for facultative chlororespiring microorganisms, the potential absence or low activity of DCE and VC dechlorinating microorganisms, and the presence of inhibitory substances, including more oxidized chloroethene compounds (Bradley, 2003).

In contrast, the potential for chloroethene mineralization increases with decreasing chlorine number (McCarty and Semprini, 1994; Bradley and Chapelle, 1996; Bradley, 2003). Microbial mineralization to CO_2 can be an important component of in situ VC and DCE natural attenuation under oxic conditions and, in certain environments, in the the absence of detectable oxygen. The endproduct(s) of microbial chloroethene mineralization, primarily CO_2 (or CO_2 and CH_4 under methanogenic conditions), however, are not unique to chloroethene mineralization and, consequently, are not diagnostic of this process. Laboratory microcosm evaluations remain the best approach for assessing the in situ potential for microbial mineralization of chloroethene contaminants in the presence or absence of detectable oxygen (Bradley and Chapelle, 1996, 1997, 1998a, 1998b, 1999a, 1999b, 2000a, 2000b, 2002; Bradley, Chapelle, and Lovley, 1998; Bradley, Chapelle, and Wilson, 1998; Bradley, Landmeyer, and Dinicola, 1998; Bradley, 2003).

Purpose and Scope

In general, established protocols (most notably, Wiedemeier and others, 1998) for evaluating the potential for natural attenuation of chlorinated solvents in groundwater systems recommend multiple lines of evidence. Because biodegradation is considered the natural-attenuation component with the greatest potential for contaminant destruction, implementation of this approach to chloroethene-contaminated groundwater sites typically involves the following: (1) field demonstration of geochemical conditions conducive to known mechanisms of contaminant biodegradation, (2) field demonstration of a distinct trend toward decreasing contaminant concentrations, (3) field demonstration of the production of daughter products indicative of contaminant biotransformation, and (4) laboratory demonstration of an indigenous mechanism for microbial contaminant degradation.

The extant regulatory emphasis on a demonstrated production of contaminant daughter products represents a major obstacle to the inclusion of oxic and anoxic mineralization mechanisms as significant components of chloroethene natural attenuation, specifically because the products of chloroethene mineralization (CO_2 and CH_4) are common microbial byproducts and not diagnostic of chloroethene biodegradation. Thus, under current (2009) U.S. Environmental Protection Agency (USEPA) guidelines, inclusion of oxic and(or) anoxic mineralization mechanisms as components of in situ chloroethene natural attenuation requires a direct demonstration of the potential significance of these processes in situ. In the absence of compelling field evidence (other than options 1 and 2 listed above), laboratory microcosm evaluations remain the best approach for assessing the in situ potential for chloroethene mineralization under oxic conditions or in the absence of detectable oxygen (dissolved oxygen [DO] concentrations less than [<] 25 micrograms per liter [$\mu g/L$]).

Thus, the potential for microbial degradation of *cis*-DCE and VC at the KCP by reductive dechlorination and mineralization mechanisms was evaluated in laboratory sediment microcosms. The results provide insight into the natural attenuation of *cis*-DCE and VC in the Blue River, Boone Creek, and Indian Creek sediments that may be expected to occur if the operation of groundwater-interception wells is decreased or ceased. This report describes the contribution of microbial reductive-dechlorination and mineralization processes to the potential natural attenuation of *cis*-DCE and VC in streambed sediments from the Blue River and its tributaries, Boone Creek and Indian Creek. This report presents the results of an investigation that

- Assessed the potential for microbial degradation of *cis*-DCE and VC in streambed sediments at the KCP using [1,2-^{14}C] *cis*-DCE and [1,2-^{14}C] VC as radiotracer substrates, and

- Assessed the effects of sediment oxygen conditions on microbial degradation of *cis*-DCE and VC in streambed sediments by evaluating degradation in oxic (ambient air) microcosms and in microcosms with no detectable oxygen (DO concentrations < 25 $\mu g/L$).

Methods

This section presents details of the study site, sediment-collection locations, and the experimental approach.

Study Site

The KCP is located within the Bannister Federal Complex in Kansas City, Missouri (fig. 1). The Federal Complex is bordered by the Blue River on the east and by its tributary, Indian Creek, on the south. Boone Creek drains to the Blue River on the northeast side of the complex (fig. 2).

A mixed chlorinated solvent plume exists in the shallow groundwater system in the northeast portion of the KCP (in the vicinity of former North and South Lagoons, not shown). This plume contains primarily TCE and the reductive-degradation products, 1,2-DCE and VC, and extends generally east and northeast toward Blue River and its tributary, Boone Creek. Currently, a series of pumping wells between the Blue River and the main body of the plume provide hydrologic control and prevent a possible discharge of groundwater contaminants to the surface-water system.

Honeywell FM&T personnel at the DOE KCP collected sediments for chloroethene-degradation microcosm studies in November 2007 from Blue River and Boone Creek (fig. 3). Blue River sediments were collected in the area where the plume is projected to discharge in the absence of hydrologic containment by pumping wells. Approximately 1 liter (L) of sediment was collected from two depths—surface 0–20 centimeters (cm) and approximately 1 meter (m) below the sediment and water interface—at three locations identified in downstream order as BLK 26.1, BLK 25.9, and BLK 25.5. In light of the theoretical possibility of discharge of contaminated shallow groundwater to the Boone Creek tributary in the absence of hydrologic containment by pumping wells, Honeywell FM&T personnel at the DOE KCP also collected sediment samples (identified as BC1) in November 2007 at two depths from a single location in Boone Creek.

Mixed chlorinated-solvent contamination also exists in the vicinity of the Main Manufacturing Building in the southern part of the KCP (fig. 2). Shallow groundwater flow and contaminant migration, which otherwise would be expected to discharge to Indian Creek, currently are controlled by building footing tile drains and pumping wells. Honeywell FM&T personnel at the DOE KCP collected Indian Creek sediments in November 2007 in the area where the contamination is projected to discharge in the absence of hydrologic containment by pumping wells. Approximately 1 L of sediment was collected from two depths—surface depth to 20 cm and approximately 1 m below the sediment and water interface—at two locations identified in downstream order as ICK 0.2 and ICK RR (fig. 3).

Radiochemicals

The potential for chloroethene biodegradation in Blue River, Boone Creek, and Indian Creek sediments was investigated by using uniformly labeled $[1,2-^{14}C]$ *cis*-DCE (4 microcuries per micromole [μCi/μmole]; Moravek Biochemicals, Brea, California) and $[1,2-^{14}C]$ VC (1.6 μCi/μmole; Perkin Elmer Life Sciences, Boston, Massachusetts). The radiochemical purity of the $[1,2-^{14}C]$ chloroethene stocks was evaluated in the South Carolina Water Science Center Microbial Studies Laboratory in Columbia, SC, by direct injection radiometric-detection gas chromatography (RD/GC) and found to be greater than 97-percent pure. Authentic $H^{14}CO_3^-$ (Sigma Biochemicals, St. Louis, Missouri) and $^{14}CH_4$ (Perkin Elmer Life Sciences, Boston, Massachusetts) were used as radiolabeled standards for calibration and methods development. Each had radiochemical purities greater than 98 percent.

Microcosm Studies

In general, sediment microcosms were composed of 10-milliliter (mL) serum vials with 10 ± 0.5 gram (g) of saturated sediment and an atmosphere of ultra high purity helium (anoxic treatments) or ambient air (oxic treatments). Triplicate experimental (viable) microcosms were prepared for each sediment treatment. Duplicate autoclaved control microcosms and a single sediment-free control microcosm were prepared for each sediment treatment and autoclaved three times for 1 hour (h) at 15 pounds per square inch (PSI) and 121 degrees Celsius (ºC) (fig. 4).

The use of reducing atmospheres (hydrogen [H_2] enriched) and a variety of chemical reductants in the preparation of "anaerobic" microcosms is common practice in microbiology, but introduces a significant artifact by potentially inhibiting the contribution of a number of terminal electron accepting processes like nitrate-, manganese-, and iron-reduction, which occur in anoxic but relatively oxidizing environments (Bradley and others 2008). Consequently, in this study anoxic conditions were defined, in agreement with field evaluation protocols (DO concentrations less than 0.1–0.5 milligram per liter [mg/L]), as headspace oxygen concentrations below the analytical detection limit (corresponding to microcosm DO concentrations less than 25 μg/L). Thus, microcosms for the assessment of chloroethene biodegradation in the absence of detectable oxygen were assembled under an atmosphere of ultra high purity helium and subsequently flushed three separate times with 1,000 times the headspace volume of pure helium. All anoxic microcosm treatments were pre-incubated in the dark at room temperature (approximately 23 °C) for 7 days prior to the addition of ^{14}C-substrates in order to further ensure anoxic conditions.

Microcosms were amended with $[1,2-^{14}C]$ *cis*-DCE or $[1,2-^{14}C]$ VC to yield initial dissolved substrate concentrations
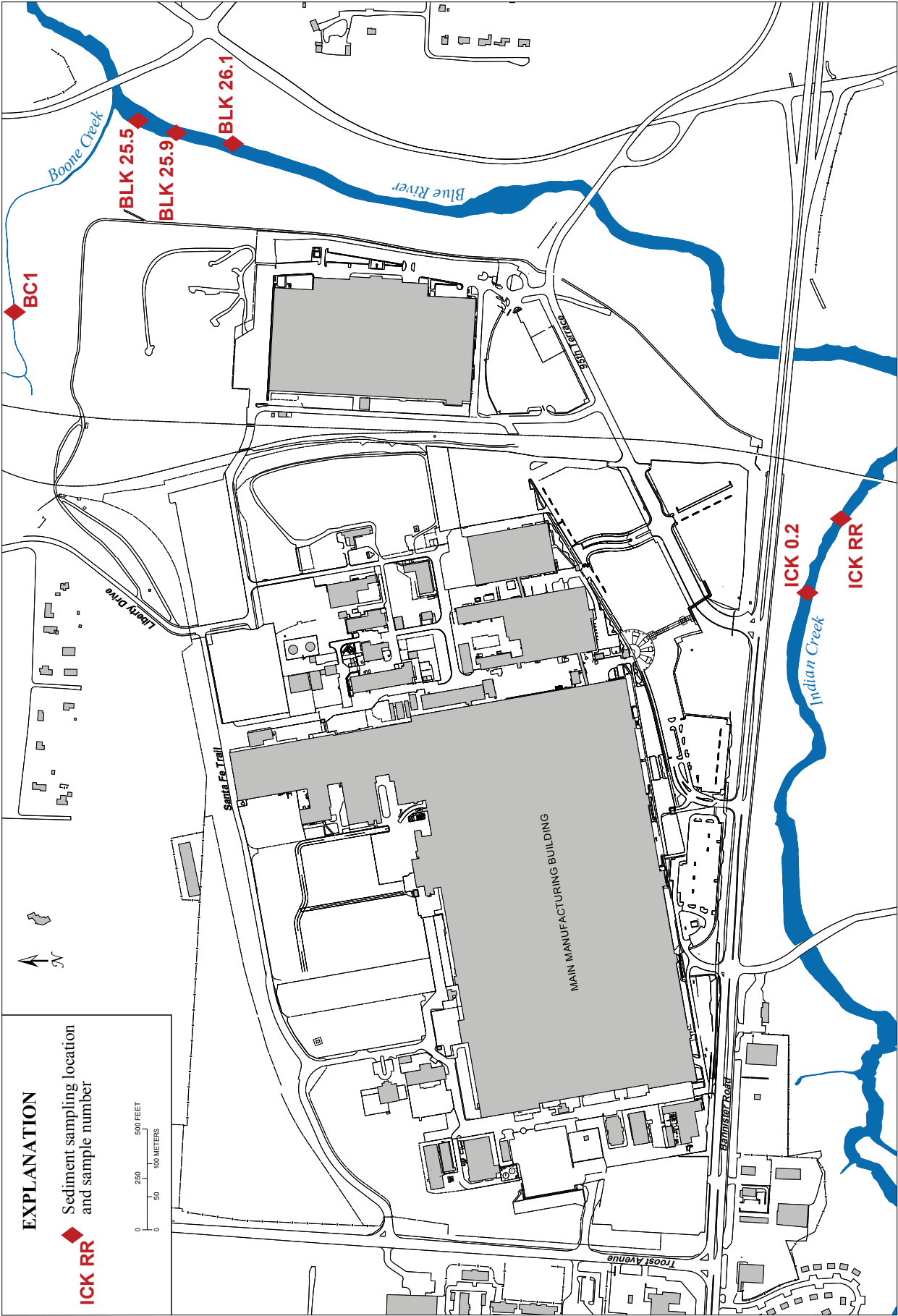
Figure 3. Locations of sediment-sampling sites in Blue River (BLK), Indian Creek (ICK) and Boone Creek (BC) near the Kansas City Plant, Kansas City, Missouri, 2008 (figure from J. Baker, Honeywell, FM&T).

detectable oxygen (microcosm DO concentrations below the minimum analytical detection limit of 25 µg/L) were confirmed in oxic and anoxic treatments, respectively, throughout the study using headspace TCD/GC, as described by Bradley and Chapelle (2000a).

Dissolved phase concentrations of ^{14}C-analytes were estimated based on experimentally determined Henry's partition coefficients (Bradley and Chapelle, 2000a). Because inorganic carbon is present as dissolved CO_2 and HCO_3^- at the circumneutral pH values observed in the collected sediments, a dimensionless partition coefficient for the distribution of inorganic carbon between the headspace and the dissolved phase was determined. $H^{14}CO_3^-$ was injected into the dissolved phase of triplicate autoclaved sediment microcosms (prepared as described for the degradation study), microcosms were allowed to equilibrate for 24 h, and the $^{14}CO_2$ radioactivity in the headspace was measured using RD/GC. The radiometric detector was calibrated by liquid scintillation counting using $H^{14}CO_3^-$.

Figure 4. Example of laboratory ^{14}C-radiotracer microcosm setup.

of 280 µg/L *cis*-DCE or 310 µg/L VC, respectively. Following the addition of ^{14}C-substrates, microcosms were incubated in the dark at room temperature (approximately 23 ºC) for up to 114 days.

Analytical Methods

Headspace concentrations of O_2, CH_4, $^{14}CH_4$, CO_2, $^{14}CO_2$, ethene, ^{14}C-ethene, ethane, and ^{14}C-ethane (as well as ^{14}C-VC in [1,2-^{14}C] *cis*-DCE treatments) were assessed by analyzing 1.0 mL of the microcosm headspace using packed column GC with sequential RD and thermal conductivity detection (TCD, fig. 5). The headspace sample volume was replaced with pure oxygen (oxic treatments) or ultra high purity helium (anoxic treatments). Oxic conditions (headspace oxygen concentrations in the range of 2–21 percent v/v) and the absence of

Degradation of *cis*-DCE and VC under Oxic and Anoxic Conditions

The following sections present the results of the microcosm degradation studies conducted under oxic conditions and in the absence of detectable oxygen (anoxic conditions). The potential for *cis*-DCE and VC biodegradation was assessed first in stream sediment samples collected at the surface (top 20 cm) of the bed sediment. A time series approach was employed for up to 114 days as illustrated in figures 6 and 7 for oxic and anoxic microcosms, respectively. For simplicity, results are presented in figures 8–11 as the final accumulation of the degradation products that were detected at the end of the incubation. Microcosms prepared with sediment samples collected from the hyporheic zone (approximately 1 m below the
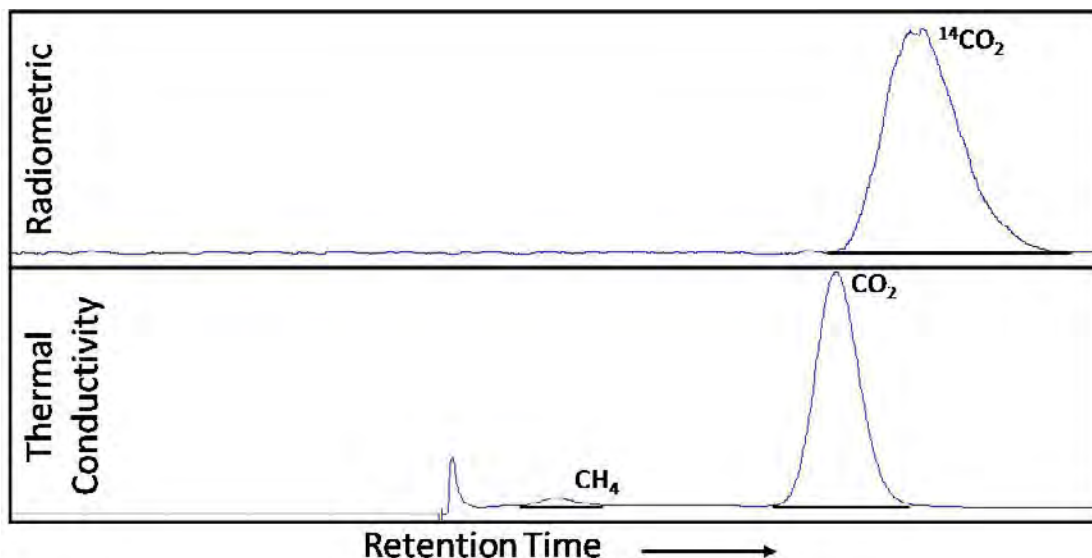

Figure 5. Illustration of gas chromatographic analysis using tandem thermal conductivity detection and radiometric detection.
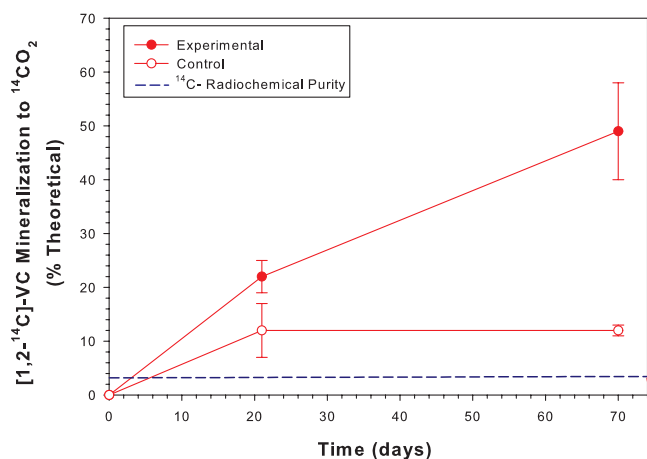
Figure 6. Mineralization of [1,2-^{14}C] VC to [14]CO_2 in sediment collected from Indian Creek (ICK RR) and incubated under oxic conditions.
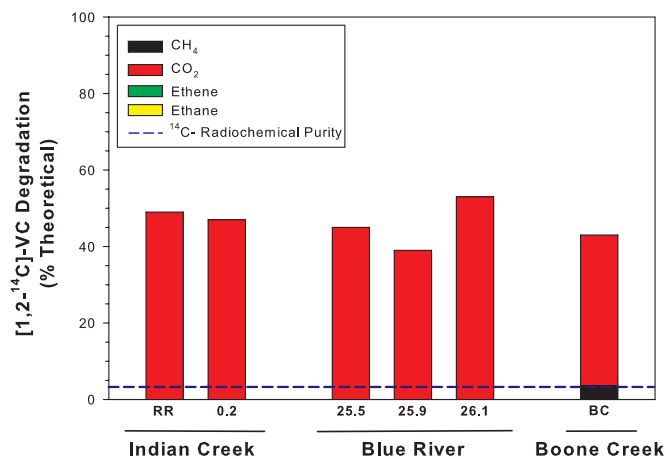

Figure 8. Final recovery of [1,2-^{14}C] VC radioactivity as ^{14}C-radiolabeled degradation products in surficial sediment microcosms incubated under oxic conditions.
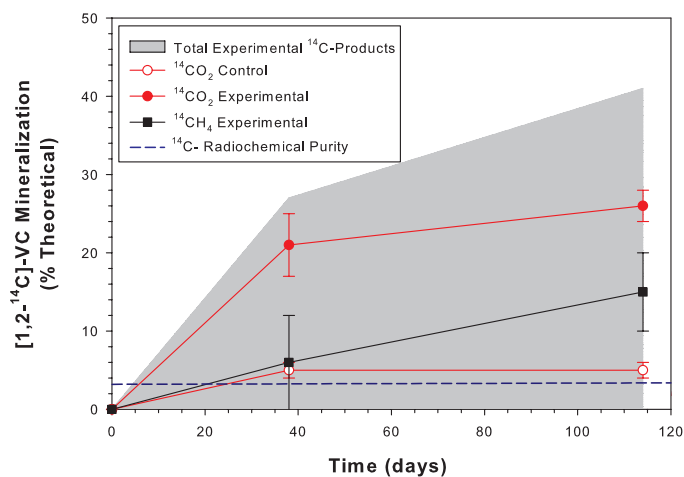

Figure 7. Mineralization of [1,2-^{14}C] VC to [14]CO_2 in sediment collected from Boone Creek (BC) and incubated under anoxic conditions.
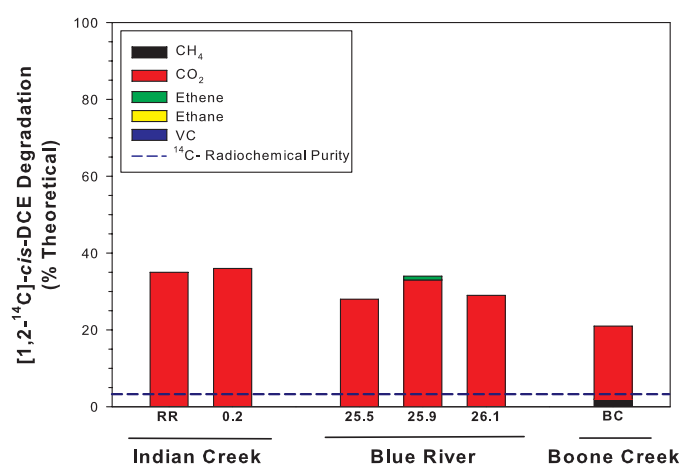

Figure 9. Final recovery of [1,2-^{14}C] *cis*-DCE radioactivity as ^{14}C-radiolabeled degradation products in surficial sediment microcosms incubated under oxic conditions.

sediment and water interface) were incubated for up to 91 days and analyzed at the end of the incubation for the presence of degradation products. Results for the deeper sediments are presented in figures 12–15.

For this study, the accumulation of ^{14}C-radiolabeled degradation products was considered significant if recovery was greater than twice the 3-percent purity level of the ^{14}C-substrates. The ^{14}C-radiochemical purity level (3 percent of theoretical) is indicated in each figure (figs. 6–15) as a dashed blue line.

Degradation of *cis*-DCE and VC in Surficial Sediments under Oxic Conditions

Degradation of [1,2-^{14}C] *cis*-DCE and [1,2-^{14}C] VC was observed in all experimental surficial sediment microcosms incubated under oxic conditions. In all cases, [14]CO_2 was the

only degradation product that was observed in significant concentration (greater than 2 times the 3-percent purity level of the ^{14}C substrates). The final recovery of [14]CO_2 from [1,2-^{14}C] VC after 70 days of incubation was comparable for all three streams (Blue River, Indian Creek, and Boone Creek) and sediment-collection locations with a mean recovery ± standard deviation (SD) for all sediments of 45 ± 6 percent of theoretical (fig. 8). Likewise, the final recovery of [14]CO_2 from [1,2-^{14}C] *cis*-DCE after 81 days of incubation was comparable for all streams and sediment-collection locations with a mean recovery for all surficial sediments of 30 ± 6 percent of theoretical (fig. 9). Because the recovery of ^{14}C-degradation products (only [14]CO_2 was observed) in heat-sterilized (autoclaved) control microcosms was less than 10 percent of theoretical in all cases, the chloroethene degradation observed in these treatments was attributed primarily to biological activity or, potentially, to sediment abiotic processes that are inhibited by autoclaving.

These results indicate that microbial mineralization, involving direct oxidation or co-metabolic oxidation, is the primary mechanism of *cis*-DCE and VC degradation in surficial stream sediments at the KCP under oxic conditions. No evidence of reductive degradation or reduced daughter products was observed under oxic incubation conditions. The generally lower mineralization efficiency of [1,2-^{14}C] *cis*-DCE compared with [1,2-^{14}C] VC was consistent with its more oxidized character and substantially diminished capacity to function as an electron donor for microbial metabolism. The demonstrated potential for mineralization of *cis*-DCE and VC to CO_2 in KCP stream sediments under oxic conditions is consistent with previous studies (Bradley and Chapelle, 1997, 1998a, 1998b, 1999a, 1999b, 2000a, 2000b, 2002; Bradley, Chapelle, and Lovley, 1998; Bradley, Chapelle, and Wilson, 1998; Bradley, Landmeyer, and Dinicola, 1998; Bradley, 2003).

Wetlands and shallow surface-water systems are characterized by considerable temporal and spatial variability in the sediment geochemistry and in the activity of associated microbial redox communities. In such settings, oxic microbial mineralization is expected to be a significant contributor to in situ DCE and VC attenuation. Thus, an evaluation of the efficiency of in situ DCE biodegradation based solely on the accumulation of reduced daughter products may underestimate substantially the actual extent of contaminant biodegradation and the overall contribution of oxic biodegradation to contaminant attenuation.

Degradation of *cis*-DCE and VC in Surficial Sediments under Anoxic Conditions

Significant degradation of [1,2-^{14}C] VC also was observed in all experimental surficial sediment microcosms incubated in the absence of detectable oxygen (DO concentrations below the analytical detection limit of 25 µg/L; fig. 10). The occurrence of substantial methanogenesis in Blue River 25.5, Blue River 26.1, and Boone Creek microcosms indicated the presence of highly reducing conditions in these sediments (data not shown). In contrast, little to no methane was detected in Indian Creek and in Blue River 25.9 microcosms, which indicates that relatively oxidized conditions persisted in these sediments even in the absence of detectable oxygen (data not shown). Nevertheless, even in the absence of detectable oxygen and, in some cases, in the presence of substantial methanogenesis, $^{14}CO_2$ remained the primary and, with the exception of Boone Creek microcosms, the only ^{14}C-radiolabeled degradation product detected. The increasing recovery percentage of ^{14}C radioactivity as $^{14}CH_4$ in Boone Creek microcosms in the absence of detectable oxygen (fig. 7) is consistent with reduction of $^{14}CO_2$ to $^{14}CH_4$ by autotrophic methanogenesis. The final recovery of ^{14}C-radiolabeled degradation products from [1,2-^{14}C] VC after 114 days of incubation ranged from 14 to 37 percent of theoretical with a mean ± SD of 26 ± 8 percent.

Because the recovery of ^{14}C-degradation products (only $^{14}CO_2$ was observed) in autoclaved control microcosms was less than 5 percent of theoretical in all cases (data not shown), the VC degradation observed in these treatments was attributed primarily to biological activity or, potentially, to sediment-abiotic processes inhibited by autoclaving.

The results of this microcosm treatment indicate that mineralization may be an important component of VC degradation in surficial sediments at the KCP even in the absence of detectable oxygen. These results further illustrate that an evaluation of in situ VC biodegradation in KCP stream sediments that is based solely on the accumulation of reduced daughter products may underestimate significantly the extent of contaminant biodegradation and the contribution of biodegradation to contaminant attenuation.

In contrast, the final recovery of ^{14}C-radiolabeled degradation products from [1,2-^{14}C] *cis*-DCE after 110 days of incubation in the absence of detectable oxygen was less than 10 percent of theoretical for all streams and sediment-collection locations with a mean recovery of 7 ± 3 percent of theoretical (fig. 11). Because the recovery of ^{14}C-degradation products was not systematically greater than twice the purity of ^{14}C-substrate and often did not differ substantially from that observed in autoclaved controls, microbial degradation of [1,2-^{14}C] *cis*-DCE was not considered significant over the 110-day course of this investigation.

Previous reports indicate that, with the possible exception of DCE degradation under Mn(IV)-reducing conditions, the net mineralization of *cis*-DCE involves an initial reduction to VC, which may or may not accumulate to detectable concentrations (Bradley and Chapelle, 1997, 1998b). In this study, ^{14}C-VC was detectable only at trace levels (less than 2 percent of theoretical). This observation, in turn, indicates that reductive dechlorination of *cis*-DCE is inefficient in the relatively oxidized conditions that appear significant in surficial KCP
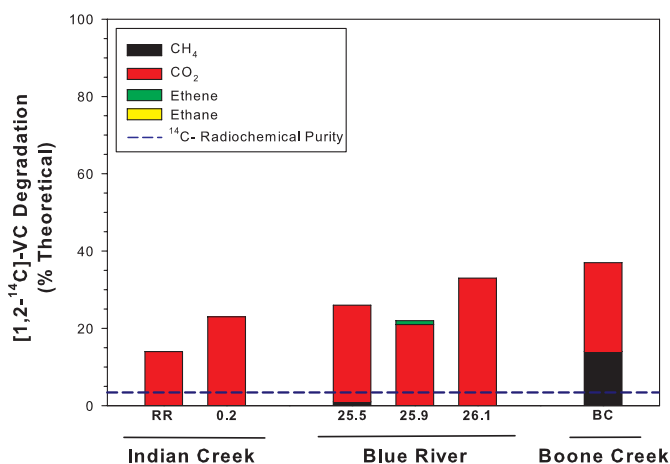

Figure 10. Final recovery of [1,2-^{14}C] VC radioactivity as ^{14}C-radiolabeled degradation products in surficial sediment microcosms incubated under anoxic conditions.
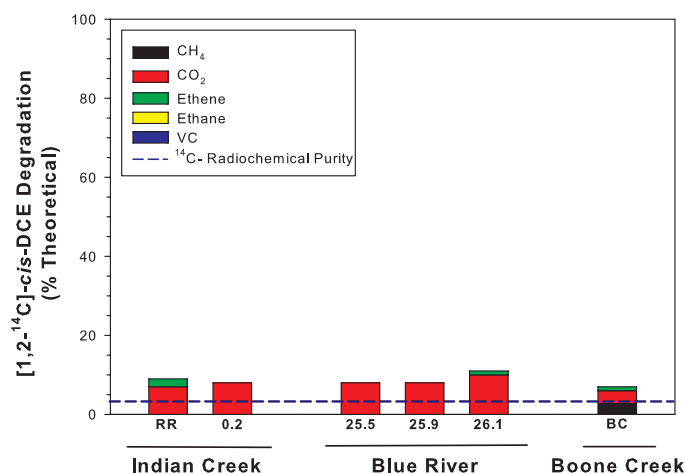
Figure 11.   Final recovery of [1,2-^{14}C] *cis*-DCE radioactivity as ^{14}C-radiolabeled degradation products in surficial sediment microcosms incubated under anoxic conditions.

Figure 12.   Final recovery of [1,2-^{14}C] VC radioactivity as ^{14}C-radiolabeled degradation products in hyporheic zone sediment microcosms incubated under oxic conditions.

Figure 13.   Final recovery of [1,2-^{14}C] VC radioactivity as ^{14}C-radiolabeled degradation products in hyporheic zone sediment microcosms incubated under anoxic conditions.

sediment even in the absence of detectable oxygen. The apparently inefficient reductive dechlorination of *cis*-DCE combined with a poor potential for DCE to serve as an electron donor and undergo oxidation contribute to the apparent inefficient biodegradation of *cis*-DCE in surficial KCP sediments in the absence of oxygen.

Degradation of VC in Sediments of the Hyporheic Zone under Oxic and Anoxic Conditions

Significant degradation of [1,2-^{14}C] VC was observed in all experimental microcosms prepared with sediment samples collected from the hyporheic zone (approximately 1 m below the sediment and water interface) at the KCP, irrespective of oxygen treatment (figs. 12, 13). Even in the absence of detectable oxygen and, in some cases, in the presence of substantial methanogenesis, $^{14}CO_2$ was the primary ^{14}C-radiolabeled degradation product detected in the sediments. The final recovery of ^{14}C-radiolabeled degradation products from [1,2-^{14}C] VC after approximately 80 days of incubation ranged from 16 to 34 percent of theoretical with a mean ± SD of 29 ± 4 percent under oxic conditions (fig. 12) and 26 ± 8 percent in the absence of detectable oxygen (fig. 13). Because the recovery of ^{14}C-degradation products (only $^{14}CO_2$ was observed) in autoclaved control microcosms was less than 7 percent of theoretical in all cases (data not shown), the VC degradation observed in these treatments was attributed primarily to biological activity or, potentially, to sediment abiotic processes inhibited by autoclaving.

These results indicate that microbial mineralization also may be an important component of VC biodegradation in
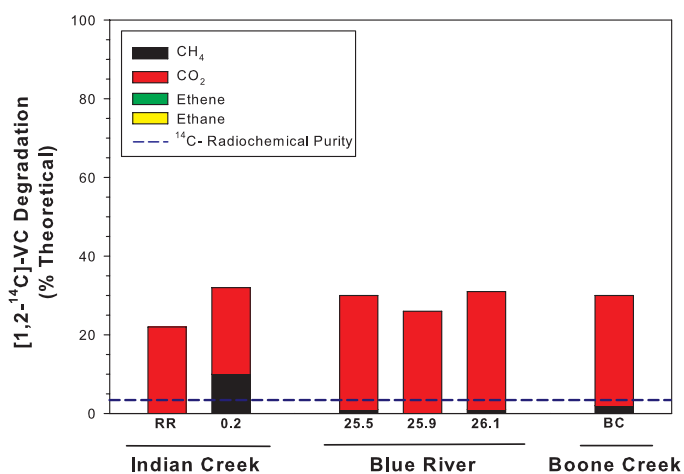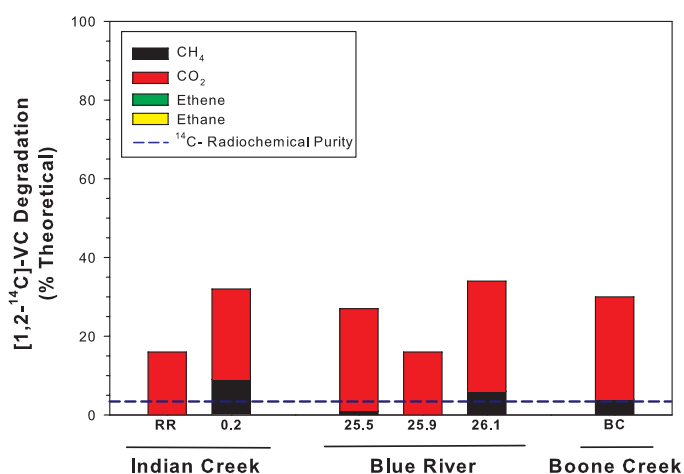
the sediments of the deeper hyporheic zone in KCP stream systems in the presence or absence of detectable oxygen. This observation, in turn, indicates that the hyporheic zone provides a significant attenuation buffer for any chloroethene contaminants that occur in groundwater discharging to the stream systems at KCP. These results reemphasize the conclusion that an evaluation of in situ VC biodegradation in KCP stream sediments that is based solely on the accumulation of reduced daughter products may underestimate significantly the extent of contaminant biodegradation and the potential importance of the hyporheic zone as a contaminant-attenuation buffer.

Insignificant Degradation of *cis*-DCE in Sediments of the Hyporheic Zone under Oxic and Anoxic Conditions

The final recovery of ^{14}C-radiolabeled degradation products from [1,2-^{14}C] *cis*-DCE after approximately 90 days of incubation under oxic conditions or in the absence of detectable oxygen was less than 10 percent of theoretical for all streams and sediment-collection locations with a mean recovery of 6 ± 3 percent of theoretical (figs. 14, 15). Because
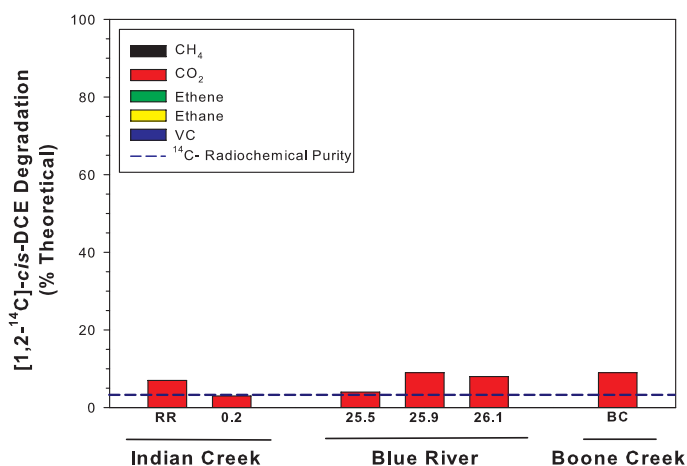

Figure 14. Final recovery of [1,2-^{14}C] *cis*-DCE radioactivity as ^{14}C-radiolabeled degradation products in hyporheic zone sediment microcosms incubated under oxic conditions.

Figure 15. Final recovery of [1,2-^{14}C] *cis*-DCE radioactivity as ^{14}C-radiolabeled degradation products in hyporheic zone sediment microcosms incubated under anoxic conditions.
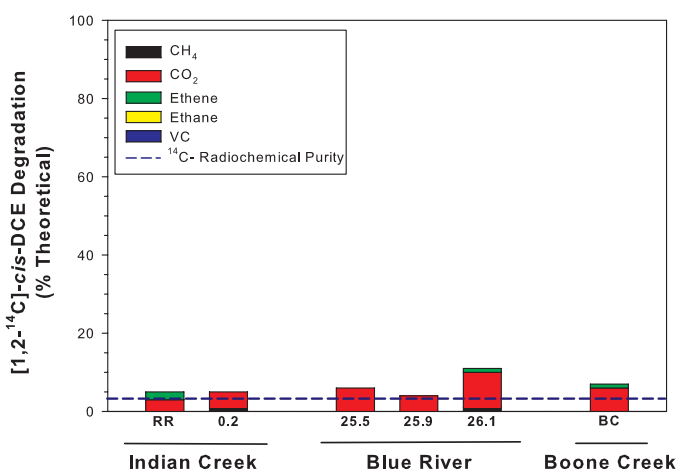
the recovery of ^{14}C-degradation products in these treatments did not exceed systematically the criteria for significant recovery (twice the radiochemical purity level of the ^{14}C substrate) and typically did not differ substantially from that observed in autoclaved controls, microbial degradation of [1,2-^{14}C] *cis*-DCE was not considered significant in hyporheic-zone microcosms over the 90-day course of this investigation.

As noted above, the results of previous studies indicate that the net mineralization of *cis*-DCE involves an initial reduction to VC, which may or may not accumulate to detectable concentrations (Bradley and Chapelle, 1997, 1998b). In these treatments, ^{14}C-VC was detectable only at trace levels (less than 2 percent of theoretical). Thus, reductive dechlorination of *cis*-DCE appears to be inefficient in hyporheic-zone sediment at the KCP even in the absence of detectable oxygen. This inefficiency combined with a poor potential for DCE to serve as an electron donor and undergo oxidation contribute to an apparent poor potential for *cis*-DCE biodegradation in the hyporheic zone in KCP streams. The substantial mineralization of [1,2-^{14}C] *cis*-DCE observed in surficial KCP sediments under oxic conditions indicates the existence of a significant attenuation buffer for any chloroethene contaminants that occur in groundwater discharging to the stream systems at KCP. The lack of evidence for efficient biodegradation of [1,2-^{14}C] *cis*-DCE in the deeper streambed sediment samples collected from KCP indicates that this natural buffer against *cis*-DCE discharge depends on the presence of oxygen and may be restricted to the surface sediment.

Summary

A series of ^{14}C-radiotracer-based microcosm experiments was conducted by the USGS South Carolina Water Science Center in 2008 to assess the mechanisms and products of degradation of *cis*-dichloroethene (*cis*-DCE) and vinyl chloride (VC) in streambed sediments at the U.S. Department of Energy (DOE), Kansas City Plant (KCP) site in Kansas City, Missouri. The potential for biotic and abiotic *cis*-DCE and VC degradation in surficial and underlying hyporheic sediment from the Blue River and its tributaries, Indian Creek and Boone Creek, were investigated. The results indicate that microbial mineralization processes in the streambed sediments at the KCP can be an important component of *cis*-DCE and VC degradation under oxic conditions and of VC degradation even in the absence of detectable oxygen. These results demonstrate that an evaluation of the efficiency of in situ *cis*-DCE and VC biodegradation in KCP streambed sediments that is based solely on the observed accumulation of reduced daughter products may underestimate substantially the total extent of contaminant biodegradation and, thus, the potential importance of the hyporheic zone and the streambed sediments as buffers against the discharge of contaminated groundwater.

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