Design and Interpretation of Microcosm Studies for Chlorinated Compounds

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Introduction

There are three lines of evidence used to support natural attenuation as a remedy for chlorinated solvent contamination in ground water. They are 1) documented loss of contaminant at field scale, 2) geochemical analytical data, and 3) direct microbiological evidence. The first line of evidence (documented loss) involves using statistically significant historical trends in contaminant concentration in conjunction with aquifer hydrogeological parameters such as seepage velocity and dilution to show that a reduction in the total mass of contaminants is occurring at the site. The second line of evidence (geochemical data) involves the use of chemical analytical data in mass balance calculations to show that decreases in contaminant concentrations can be directly correlated to increases in metabolic by-product concentrations. This evidence can be used to show that concentrations of electron donors or acceptors in ground water are sufficient to facilitate degradation of the dissolved contaminants (i.e., there is sufficient capacity). Solute fate and transport models can be used to aid the mass balance calculations, and to collate information on degradation.

Microcosm studies are often used to provide a third line of evidence. The potential for biodegradation of the contaminants of interest can be confirmed by the use of microcosms, through comparison of removals in the living treatments with removals in the controls. Microcosm studies also permit an absolute mass balance determination based on biodegradation of the contaminants of interest. Further, the appearance of daughter products in the microcosms can be used to confirm biodegradation of the parent compound.

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When to Use Microcosms.

There are two fundamentally different applications of microcosms. They are frequently used in a qualitative way to illustrate the important processes that control the fate of organic contaminants. They are also used to estimate rate constants for biotransformation of contaminants that can be used in a site-specific transport and fate model of a plume of contaminated ground water. This paper only discusses microcosms for the second application.

Microcosms should be used when there is no other way to obtain a rate constant for attenuation of contaminants, in particular, when it is impossible to estimate the rate of attenuation from data from monitoring wells in the plume of concern. There are situations where it is impossible to compare concentrations in monitoring wells along a flow path due to legal or physical impediments. In many landscapes, the direction of ground-water flow (and water table elevations in monitoring wells) can vary over short periods of time due to tidal influences or changes in barometric pressure. The direction of ground-water flow may also be affected by changes in the stage of a nearby river or pumping wells in the vicinity. These changes in ground-water flow direction do not allow simple snap-shot comparisons of concentrations in monitoring wells because of uncertainties in identifying the flow path. Rate constants from microcosms can be used with average flow conditions to estimate attenuation at some point of discharge or point of compliance.

Application of Microcosms.

The primary objective of microcosm studies is to obtain rate constants applicable to average flow conditions. These average condition can be determined by continuous monitoring of water table elevations in the aquifer being evaluated. The product of the microcosm study and the continuous monitoring of water table elevations will be a yearly or seasonal estimate of the extent of attenuation along average flow paths. Removals seen at field scale can be attributed to biological activity. If removals in the microcosms duplicate removal at field scale, the rate constant can be used for risk assessment purposes.

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Selecting Material for Study

Prior to choosing material for microcosm studies, the location of major conduits of ground-water flow should be identified and the geochemical regions along the flow path should be determined. The important geochemical regions for natural attenuation of chlorinated aliphatic hydrocarbons are regions that are actively methanogenic; regions that exhibit sulfate reduction and iron reduction concomitantly; and regions that exhibit iron reduction alone. The pattern of biodegradation of chlorinated solvents varies in different regions. Vinyl chloride tends to accumulate during reductive dechlorination of trichloroethylene (TCE) or tetrachloroethylene (PCE) in methanogenic regions (1,2); it does not accumulate to the same extent in regions exhibiting iron reduction and sulfate reduction (3). In regions showing iron reduction alone, vinyl chloride is consumed but dechlorination of PCE, TCE, or dichloroethylene (DCE) may not occur (4). Core material from each geochemical region in major flow paths represented by the plume must be acquired, and the hydraulic conductivity of each depth at which core material is acquired must be measured. If possible, the microcosms should be constructed with the most transmissive material in the flow path.

Several characteristics of ground water from the same interval used to collect the core material should be determined. These characteristics include temperature, redox potential, pH, and concentrations of oxygen, sulfate, sulfide, nitrate, ferrous iron, chloride, methane, ethane, ethene, total organic carbon, and alkalinity. The concentrations of compounds of regulatory concern and any breakdown products for each site must be determined. The ground water should be analyzed for methane to determine if methanogenic conditions exist and for ethane and ethene as daughter products. A comparison of the ground-water chemistry from the interval where the cores were acquired to that in neighboring monitoring wells will demonstrate if the collected cores are representative of that section of the contaminant plume.

Reductive dechlorination of chlorinated solvents requires an electron donor to allow the process to proceed. The electron donor could be soil organic matter, low molecular weight organic compounds (lactate, acetate, methanol, glucose, etc.), H_2, or a co-contaminant such as landfill

leachate or petroleum compounds (5,6,7). In many instances, the actual electron donor(s) may not be identified.

Several characteristics of the core material should also be evaluated. The initial concentration of the contaminated material (μg/kg) should be identified prior to construction of the microcosms. Also, it is necessary to know if the contamination is present as a nonaqueous phase liquid (NAPL) or in solution. A total petroleum hydrocarbon (TPH) analysis will determine if any hydrocarbon-based oily materials are present. The water-filled porosity is a parameter generally used to extrapolate rates to the field. It can be calculated by comparing wet and dry weights of the aquifer material.

To insure sample integrity and stability during acquisition, it is important to quickly transfer the aquifer material into a jar, exclude air by adding ground water, and seal the jar without headspace. The material should be cooled during transportation to the laboratory. Incubate the core material at the ambient ground-water temperature in the dark before the construction of microcosms.

At least one microcosm study per geochemical region should be completed. If the plume is over one kilometer in length, several microcosm studies per geochemical region may need to be constructed.

Geochemical Characterization of the Site

The geochemistry of the subsurface affects behavior of organic and inorganic contaminants, inorganic minerals, and microbial populations. Major geochemical parameters that characterize the subsurface encompasses (1) pH; (2) redox potential, Eh; (3) alkalinity; (4) physical and chemical characterization of the solids; (5) temperature; (6) dissolved constituents, including electron acceptors; and (7) microbial processes. The most important of these in relation to biological processes are redox potential, alkalinity, concentration of electron acceptor, and chemical nature of the solids.

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Alkalinity Field indications of biologically active portions of a plume may be identified by increased alkalinity, compared to background wells, from carbon dioxide due to biodegradation of the pollutants. Increases in both alkalinity and pH have been measured in portions of an aquifer contaminated by gasoline undergoing active utilization of the gasoline components (8). Alkalinity can be one of the parameters used when identifying where to collect biologically active core material.

pH Bacteria generally prefer a neutral or slightly alkaline pH level with an optimum pH range for most microorganisms between 6.0 and 8.0; however, many microorganisms can tolerate a pH range of 5.0 to 9.0. Most ground waters in uncontaminated aquifers are within these ranges. Natural pH values may be as low as 4.0 or 5.0 in aquifers with active oxidation of sulfides, and pH values as high as 9.0 may be found in carbonate-buffered systems (9). However, pH values as low as 3.0 have been measured for ground waters contaminated with municipal waste leachates which often contain elevated concentrations of organic acids (10). In ground waters contaminated with sludges from cement manufacturing, pH values as high as 11.0 have been measured (9).

Redox The oxidation/reduction (redox) potential (Eh) of ground water is a measure of electron activity that indicates the relative ability of a solution to accept or transfer electrons. Most redox reactions in the subsurface are microbially catalyzed during metabolism of native organic matter or contaminants. The only elements that are predominant participants in aquatic redox processes are carbon, nitrogen, oxygen, sulfur, iron, and manganese (11). The principal oxidizing agents in ground water are oxygen, nitrate, sulfate, manganese (IV), and iron (III). Biological reactions in the subsurface both influence and are affected by the redox potential and the available electron acceptors. The redox potential changes with the predominant electron acceptor, with reducing conditions increasing through the sequence oxygen, nitrate, iron, sulfate, and carbonate. The redox potential decreases in each sequence, with methanogenic (carbonate as the electron acceptor) conditions being most reducing. The interpretation of redox potentials in ground waters is difficult (12). The potential obtained in ground waters is a mixed potential that reflects the potential of many reactions and cannot be used for quantitative interpretation (11). The

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approximate location of the contaminant plume can be identified in the field by measurement of the redox potential of the ground water.

To overcome the limitations imposed by traditional redox measurements, recent work has focused on the measurement of molecular hydrogen to accurately describe the predominant *in situ* redox reactions (13, 14, 15). The evidence suggests that concentrations of H_2 in ground water can be correlated with specific microbial processes, and these concentrations can be used to identify zones of methanogenesis, sulfate reduction, and iron reduction in the subsurface (3).

Electron acceptors Measurement of the available electron acceptors is critical in identifying the predominant microbial and geochemical processes occurring *in situ* at the time of sample collection. Nitrate and sulfate are found naturally in most ground waters and will subsequently be used as electron acceptors once oxygen is consumed. Oxidized forms of iron and manganese can be used as electron acceptors before sulfate reduction commences. Iron and manganese minerals solubilize coincidently with sulfate reduction, and their reduced forms scavenge oxygen to the extent that strict anaerobes (some sulfate reducers and all methanogens) can develop. Sulfate is found in many depositional environments, and sulfate reduction may be very common in many contaminated ground waters. In environments where sulfate is depleted, carbonate becomes the electron acceptor with methane gas produced as an end product.

Temperature The temperature at all monitoring wells should be measured to determine when the pumped water has stabilized and is ready for collection. Below approximately 30 feet, the temperature in the subsurface is fairly consistent on an annual basis. Microcosms should be stored at the average *in situ* temperature. Biological growth can occur over a wide range of temperatures, although most microorganisms are active primarily between 10° and 35°C (50° to 95°F).

Chloride Reductive dechlorination results in the accumulation of inorganic chloride. In aquifers with a low background of inorganic chloride, the concentration of inorganic chloride should increase as the chlorinated solvents are degraded. The sum of the inorganic chloride plus the

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contaminant being degraded should remain relatively consistent along the ground-water flow path.

The following tables (Table 1, Table 2) list the geochemical parameters, contaminants, and daughter products that should be measured during site characterization for natural attenuation. The tables include the analyses that should be performed, the optimum range for natural attenuation of chlorinated solvents, and the interpretation of the value in relation to biological processes.

Microcosm Construction

During construction of the microcosms, it is best if all manipulations take place in an anaerobic glovebox. These gloveboxes exclude oxygen and provide an environment where the integrity of the core material may be maintained, since many strict anaerobic bacteria are sensitive to oxygen. Stringent aseptic precautions not necessary for microcosm construction. It is more important to maintain anaerobic conditions of the aquifer material and solutions added to the microcosm bottles.

The microcosms should have approximately the same ratio of solids to water as the *in situ* aquifer material, with a minimum or negligible headspace. Most bacteria in the subsurface are attached to the aquifer solids. If a microcosm has an excess of water, and the contaminant is primarily in the dissolved phase, the bacteria must consume or transform a great deal more contaminant to produce the same relative change in the contaminant concentration. As a result, the kinetics of removal at field scale will be underestimated in the microcosms.

A minimum of three replicate microcosms for both living and control treatments should be constructed for each sampling event. Microcosms sacrificed at each sampling interval are preferable to microcosms that are repetitively sampled. The compounds of regulatory interest should be added at concentrations representative of the higher concentrations found in the geochemical region of the plume being evaluated. The compounds should be added as a concentrated aqueous solution. If an aqueous solution is not feasible, dioxane or acetonitrile may

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be used as solvents. Avoid carriers that can be metabolized anaerobically, particularly alcohols. If possible, use ground water from the site to prepare dosing solutions and to restore water lost from the core barrel during sample collection.

For long term microcosm studies, autoclaving is the preferred method for sterilization. Nothing available to sterilize core samples works perfectly. Mercuric chloride is excellent for short term studies (weeks or months). However, mercuric chloride complexes to clays, and control may be lost as it is sorbed over time. Sodium azide is effective in repressing metabolism of bacteria that have cytochromes, but is not effective on strict anaerobes.

The microcosms should be incubated in the dark at the ambient temperature of the aquifer. It is preferable that the microcosms be incubated inverted in an anaerobic glovebox. Anaerobic jars are also available that maintain an oxygen-free environment for the microcosms. Dry redox indicator strips can be placed in the jars to assure that anoxic conditions are maintained. If no anaerobic storage is available, the inverted microcosms can be immersed in approximately two inches of water during incubation. Teflon-lined butyl rubber septa are excellent for excluding oxygen and should be used if the microcosms must be stored outside an anaerobic environment.

The studies should last from one year to eighteen months. The residence time of a plume may be several years to tens of years at field scale. Rates of transformation that are slow in terms of laboratory experimentation may have a considerable environmental significance. A microcosm study lasting only a few weeks to months may not have the resolution to detect slow changes that are of environmental significance. Additionally, microcosm studies often distinguish a pattern of sequential biodegradation of the contaminants of interest and their daughter products.

Microcosm Interpretation

As a practical matter, batch microcosms with an optimal solids/water ratio, that are sampled every two months in triplicate, for up to eighteen months, can resolve biodegradation from abiotic losses with a detection limit of 0.001 to 0.0005 per day. Rates determined from replicated batch

microcosms are found to more accurately duplicate field rates of natural attenuation than column studies. Many plumes show significant attenuation of contamination at field calibrated rates that are slower than the detection limit of microcosms constructed with that aquifer material. Although rate constants for modeling purposes are more appropriately acquired from field-scale studies, it is reassuring when the rates in the field and the rates in the laboratory agree.

The rates measured in the microcosm study may be faster than the estimated field rate. This may not be due to an error in the laboratory study, particularly if estimation of the field-scale rate of attenuation did not account for regions of preferential flow in the aquifer. The regions of preferential flow may be determined by use of a down-hole flow meter or by use of a geoprobe method for determining hydraulic conductivity in one to two feet sections of the aquifer.

Statistical comparisons can determine if removals of contaminants of concern in the living treatments are significantly different from zero or significantly different from any sorption that is occurring. Comparisons are made on the first-order rate of removal, that is, the slope of a linear regression of the natural logarithm of the concentration remaining against time of incubation for both the living and control microcosm. These slopes (removal rates) are compared to determine if they are different, and if so, extent of difference that can be detected at a given level of confidence

The Tibbetts Road Case Study

The Tibbetts Road Superfund Site in Barrington, N.H., a former private home, was used to store drums of various chemicals from 1944 to 1984. The primary ground-water contaminants in the overburden and bedrock aquifers were benzene and TCE with respective concentrations of 7,800 μg/L and 1,100 μg/L. High concentrations of arsenic, chromium, nickel, and lead were also found.

Material collected at the site was used to construct a microcosm study evaluating the removal of benzene, toluene, and TCE. This material was acquired from the most contaminated source at

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the site, the waste pile near the origin of Segment A (Figure 4). Microcosms were incubated for nine months. The aquifer material was added to 20-mL headspace vials, dosed with one mL of spiking solution, capped with a Teflon-lined, gray butyl rubber septa, and sealed with an aluminum crimp cap. Controls were prepared by autoclaving the material used to construct the microcosms overnight. Initial concentrations for benzene, toluene, and TCE were, respectively, 380 µg/L, 450 µg/L, and 330 µg/L. The microcosms were thoroughly mixed by vortexing, then stored inverted in the dark at the ambient temperature of 10°C.

The results (Figures 1, 2, and 3; Table 3) show that significant biodegradation of both petroleum aromatic hydrocarbons and the chlorinated solvent had occurred. Significant removal in the control microcosms also occurred for all compounds. The data exhibited more variability in the living microcosms than in the control treatment, which is a pattern that has been observed in other microcosm studies. The removals observed in the controls are probably due to sorption; however, this study exhibited more sorption than typically seen.

The rate constants determined from the microcosm study for the three compounds are shown in Table 4. The appropriate rate constant to be used in a model or a risk assessment would be the first-order removal in the living treatment minus the first-order removal in the control, in other words the removal that is in excess of the removal in the controls.

The first-order removal in the living and control microcosms was estimated as the linear regression of the natural logarithm of concentration remaining in each microcosm in each treatment against time of incubation. Student's t distribution with n-2 degrees of freedom was used to estimate the 95% confidence interval. The standard error of the difference of the rates of removal in living and control microcosms was estimated as the square root of the sum of the squares of the standard errors of the living and control microcosms, with n-4 degrees of freedom (16).

Table 5 presents the concentrations of organic compounds and their metabolic products in monitoring wells used to define line segments in the aquifer for estimation of field-scale rate

constants. Wells in this aquifer showed little accumulation of *trans*-DCE; 1,1-DCE; vinyl chloride; or ethene, although removals of TCE and *cis*-DCE were extensive. This can be explained by the observation (4) that iron-reducing bacteria can rapidly oxidize vinyl chloride to carbon dioxide. Filterable iron accumulated in ground water in this aquifer.

The extent of attenuation from well to well listed in Table 5, and the travel time between wells in a segment (Figure 4) were used to calculate first-order rate constants for each segment (Table 6). Travel time between monitoring wells was calculated from site-specific estimates of hydraulic conductivity and from the hydraulic gradient. In the area sampled for the microcosm study, the estimated Darcy flow was 2.0 feet per year. With an estimated porosity in this particular glacial till of 0.1, this corresponds to a plume velocity of 20 feet per year.

SUMMARY

Table 7 compares the first-order rate constants estimated from the microcosm studies to the rate constants estimated at field scale. The agreement between the independent estimates of rate is good; indicating that the rates can appropriately be used in a risk assessment. The rates of biodegradation documented in the microcosm study could easily account for the disappearance of trichloroethylene, benzene, and toluene observed at field scale. The rates estimated from the microcosm study are several-fold higher than the rates estimated at field scale. This may reflect an underestimation of the true rate in the field. The estimates of plume velocity assumed that the aquifer was homogeneous. No attempt was made in this study to correct the estimate of plume velocity for the influence of preferential flow paths. Preferential flow paths with a higher hydraulic conductivity than average would result in a faster velocity of the plume, thus a lower residence time and faster rate of removal at field scale.

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Table 1. Geochemical Parameters

Analysis	Range	Interpretation
Redox Potential	<50 millivolt against Ag/AgCl	Reductive pathway possible
Sulfate	<20 mg/liter	Competes at higher concentrations with reductive pathway
Nitrate	<1 mg/liter	Competes at higher concentrations with reductive pathway
Oxygen	<0.5 mg/liter	Tolerated, toxic to reductive pathway at higher concentrations
Oxygen	>1 mg/liter	Vinyl chloride oxidized
Iron II	>1 mg/liter	Reductive pathway possible
Sulfide	>1 mg/liter	Reductive pathway possible
Hydrogen	>1 nMolar	Reductive pathway possible, vinyl chloride may accumulate
Hydrogen	<1 nMolar	Vinyl chloride oxidized
pH	$5 < pH < 9$	Tolerated range

Table 2. Contaminants and Daughter Products

Analysis	Interpretation
PCE	Material spilled
TCE	Material spilled or daughter product of perchloroethylene
1,1,1-Trichloroethane	Material spilled
cis-DCE	Daughter product of trichloroethylene
trans-DCE	Daughter product of trichloroethylene
Vinyl Chloride	Daughter product of dichloroethylenes
Ethene	Daughter product of vinyl chloride
Ethane	Daughter product of ethene
Methane	Ultimate reductive daughter product
Chloride	Daughter product of organic chlorine
Carbon Dioxide	Ultimate oxidative daughter product
Alkalinity	Results from interaction of carbon dioxide with aquifer minerals

Table 3. Concentrations of TCE, Benzene, and Toluene in the Tibbetts Road Microcosms

Compound	Time Zero Microcosms	Time Zero Controls	Week 23 Microcosms	Week 23 Controls	Week 42 Microcosms	Week 42 Controls
TCE	328	337	1	180	2	36.3
	261	394	12.5	116	2	54.5
	309	367	8.46	99.9	2	42.3
Mean ± Standard Deviation	299 ± 34.5	366 ± 28.5	7.32 ± 5.83	132 ± 42.4	2.0 ± 0.0	44.4 ± 9.27
Benzene	366	396	201	236	11.1	146
	280	462	276	180	20.5	105
	340	433	22.8	152	11.6	139
Mean ± Standard Deviation	329 ± 44.1	430 ± 33.1	167 ± 130	189 ± 42.8	14.4 ± 5.29	130 ± 21.9
Toluene	443	460	228	254	2	136
	342	557	304	185	2.5	92
	411	502	19.9	157	16.6	115
Mean ± Standard Deviation	399 ± 51.6	506 ± 48.6	184 ± 147	199 ± 49.9	7.03 ± 8.29	114 ± 22.0

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Table 4. First-order Rate Constants for Removal TCE, Benzene, and Toluene in the Tibbetts Road Microcosms.

Parameter	Living Microcosms	Autoclaved Controls	Removal Above Controls
	First-order Rate of Removal (per year)		
TCE	6.31	2.62	3.69
95% Confidence Interval	± 2.50	± 0.50	± 2.31
Minimum Rate Significant at 95% Confidence			1.38
Benzene	3.87	1.51	2.36
95% Confidence Interval	± 1.96	± 0.44	± 1.83
Minimum Rate Significant at 95% Confidence			0.53
Toluene	5.49	1.86	3.63
95% Confidence Interval	± 2.87	± 0.45	± 2.64
Minimum Rate Significant at 95% Confidence			0.99

Table 5. Concentration of Contaminants and Metabolic By-products in Monitoring Wells along Segments in the Plume used to Estimate Field-scale Rate Constants.

Parameter	Segment A		Segment B		Segment C	
Monitoring well	80S	79S	70S	52S	70S	53S
	Up Gradient	Down Gradient	Up Gradient	Down Gradient	Up Gradient	Down Gradient
	--------------------------(ug/liter)--------------------------					
TCE	200	13.7	710	67	710	3.1
cis-DCE	740	10.9	220	270	220	2.9
trans-DCE	0.41	<1	0.8	0.3	0.8	<1
1,1-DCE	0.99	<1	<1	1.6	<1	<1
Vinyl Chloride	<1	<1	<1	<1	<1	<1
Ethene	<4	<4	7	<4	7	<4
Benzene	510	2.5	493	420	493	<1
Toluene	10000	<1	3850	900	3850	<1
o-Xylene	1400	8.4	240	71	240	<1
m-Xylene	2500	<1	360	59	360	<1
p-Xylene	1400	22	1100	320	1100	<1
Ethylbenzene	1300	0.7	760	310	760	<1
Methane	353	77	8	3	8	<2
Iron						27000

Table 6. First-order Rate Constants in Segments of the Tibbetts Road Plume.

	Flow Path Segments in Length and Time of Ground-water Travel		
	Segment A 130 feet = 6.5 years	Segment B 80 feet = 4.0 years	Segment C 200 feet = 10 years
Compound	First-order Rate Constants in Segments (per year)		
TCE	0.41	0.59	0.54
cis-DCE	0.65	produced	0.43
Benzene	0.82	0.04	>0.62
Toluene	>1.42	0.36	>0.83
o-Xylene	0.79	0.30	>0.55
m-Xylene	>1.20	0.45	>0.59
p-Xylene	0.64	0.31	>0.70
Ethylbenzene	1.16	0.22	>0.66

Table 7. Comparison of First-order Rate Constants in a Microcosm Study, and in the Field at the Tibbetts Road NPL Site.

Parameter	Microcosms Corrected for Controls		Field Scale		
	Average Rate	Minimum Rate Significant at 95% Confidence	Segment A	Segment B	Segment C
	---------------(First-order Rate per year)--------------				
Trichloroethylene	3.69	1.38	0.41	0.59	0.54
Benzene	2.36	0.53	0.82	0.04	>0.62
Toluene	3.63	0.99	>1.42	0.36	>0.83

Figure Titles

Figure 1. TCE Concentrations in the Tibbetts Road Microcosm Study.

Figure 2. Benzene Concentrations in the Tibbetts Road Microcosm Study.

Figure 3. Toluene Concentrations in the Tibbetts Road Microcosm Study.

Figure 4. Location of Waste Piles and Flow Path Segments at the Tibbetts Road Superfund Site.

DISCLAIMER

The U.S. Environmental Protection Agency through it's
Office of Research and Development partially funded and
collaborated in the research described here. It has been
subjected to the Agency's peer review and has been approved for
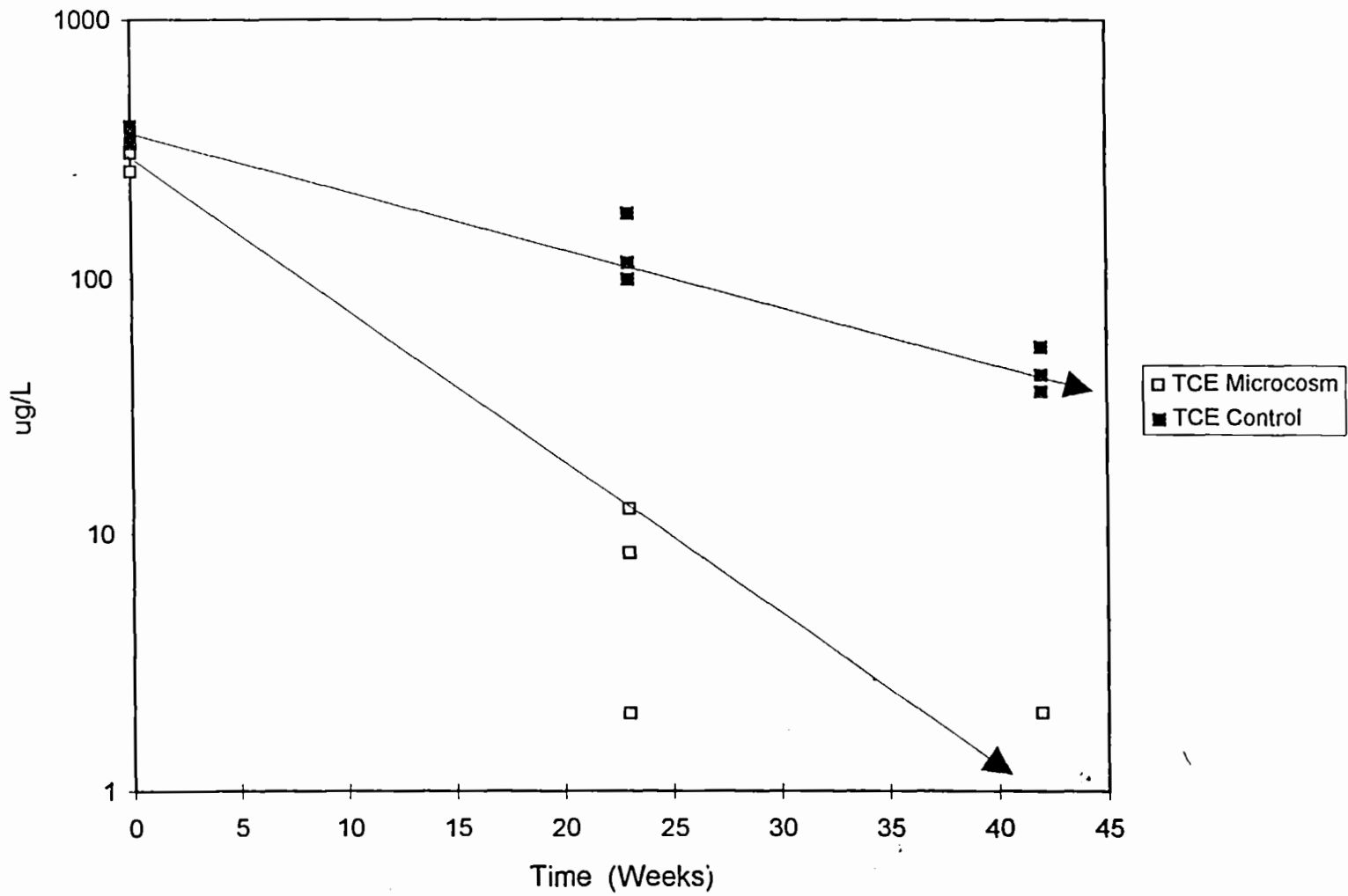publication in an EPA document.

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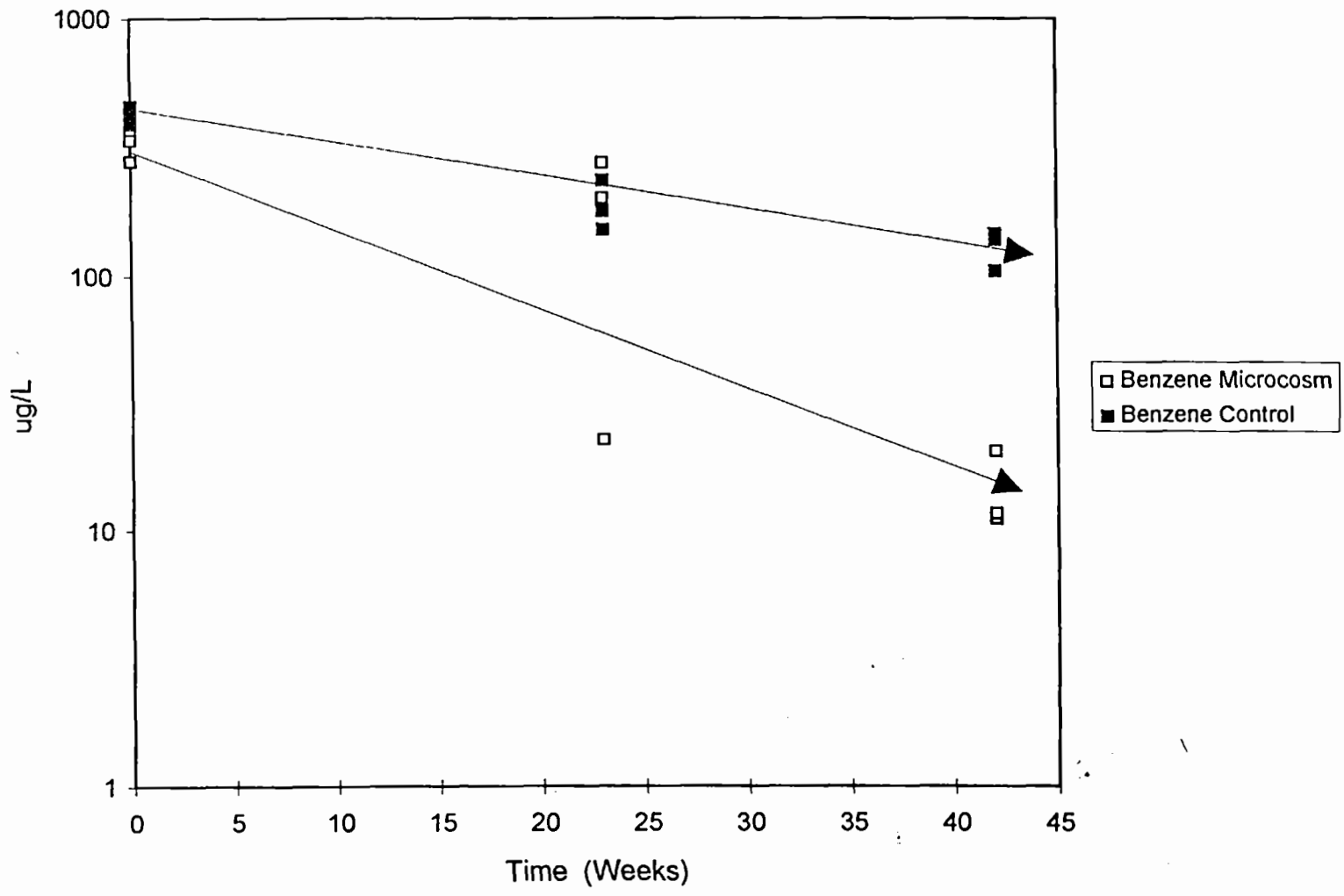Figure 1. TCE Concentrations in the Tibbetts Road Microcosm Study.

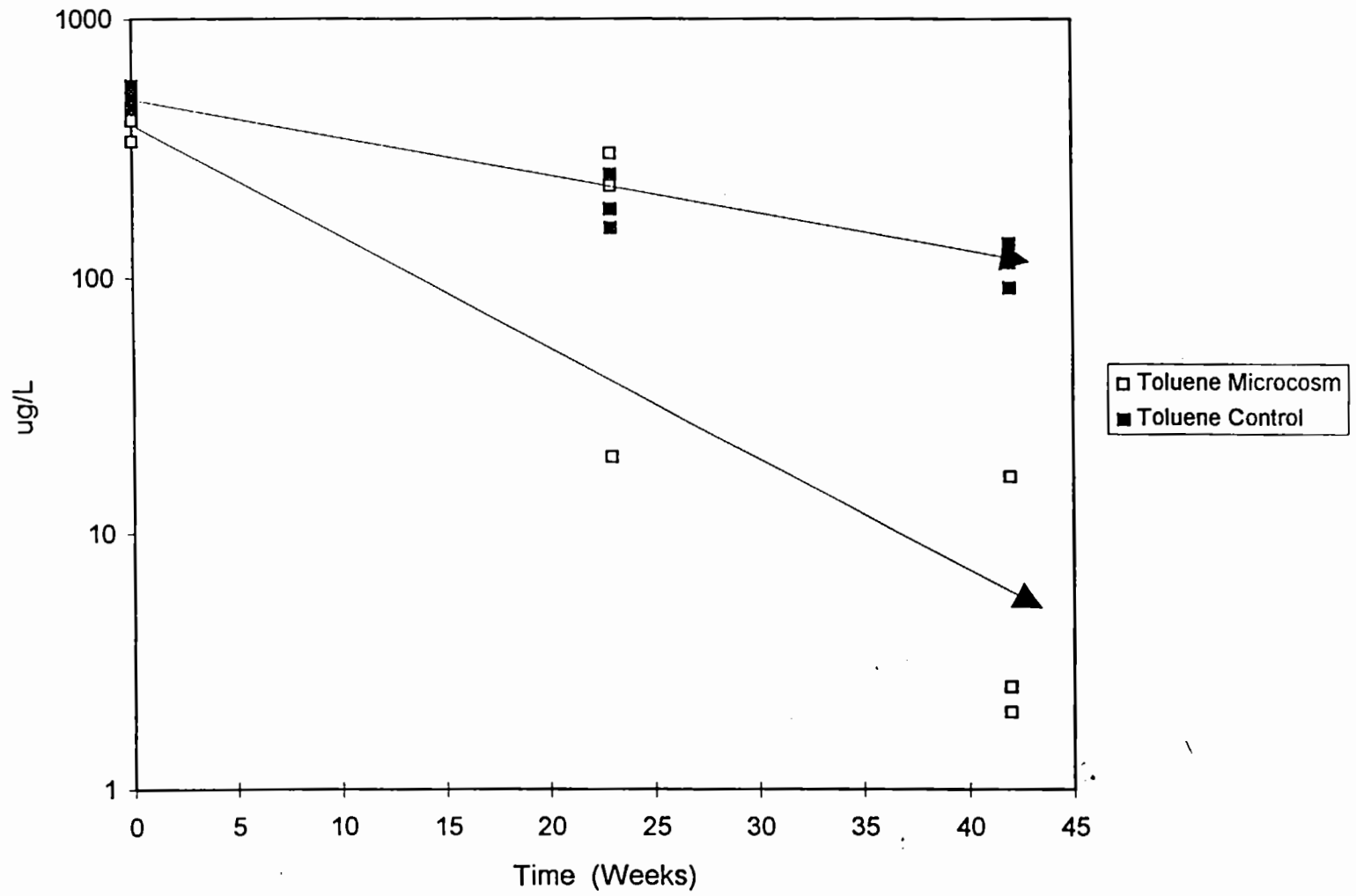Figure 2. Benzene Concentrations in the Tibbetts Road Microcosm Study.

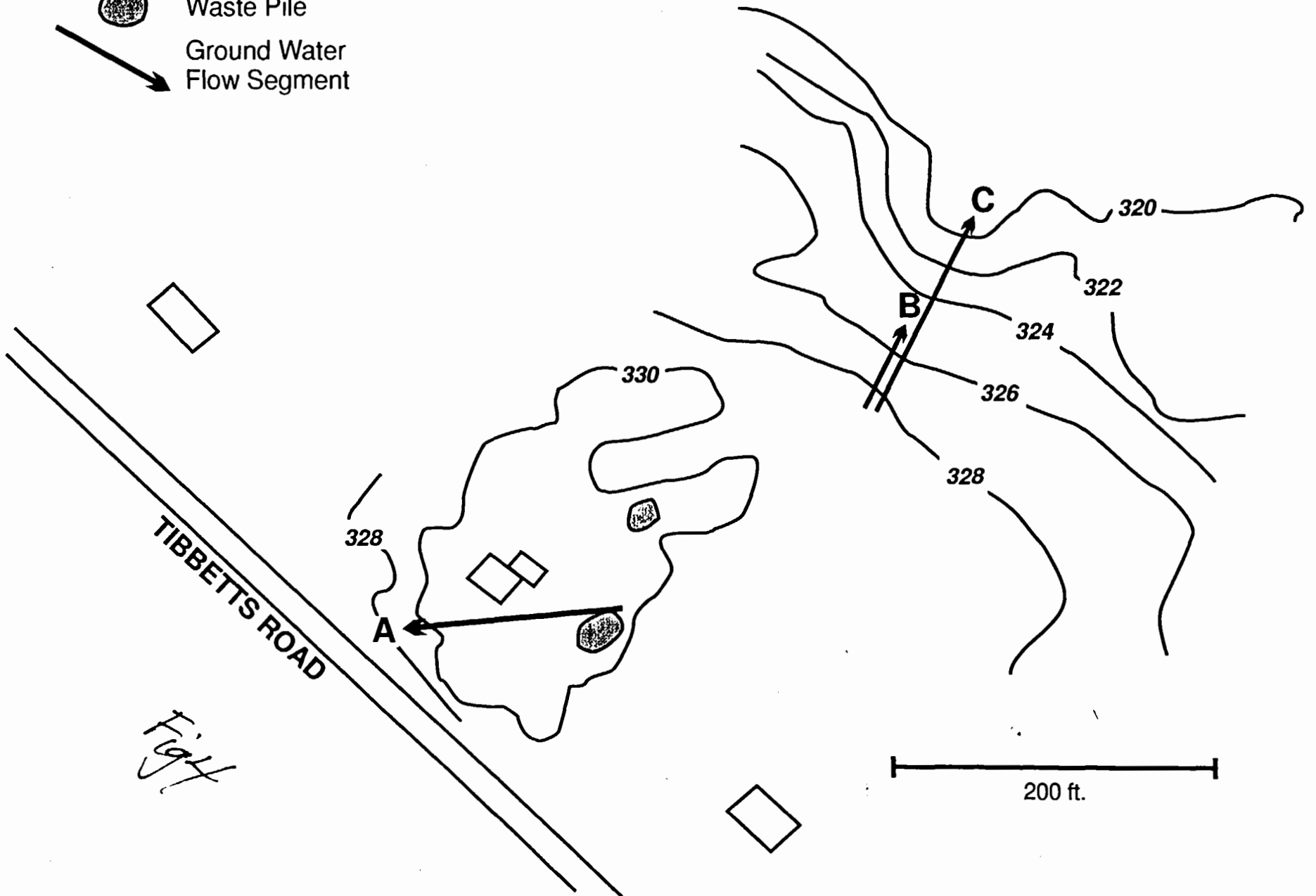Figure 3. Toluene Concentrations in the Tibbetts Road Microcosm Study.

Waste Pile

Ground Water
Flow Segment

C

B

A

320

322

324

326

328

330

328

TIBBETTS ROAD

Fig. H

200 ft.

1. REPORT NO. EPA/600/A-96/093	2.	3.

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16. ABSTRACT

Table 7 compares the first-order rate constants estimated from the microcosm studies to the rate constants estimated at field scale. The agreement between the independent estimates of rate is good; indicating that the rates can appropriately be used in a risk assessment. The rates of biodegradation documented in the microcosm study could easily account for the disappearance of trichloroethylene, benzene, and toluene observed at field scale. The rates estimated from the microcosm study are several-fold higher than the rates estimated at field scale. This may reflect an underestimation of the true rate in the field. The estimates of plume velocity assumed that the aquifer was homogeneous. No attempt was made in this study to correct the estimate of plume velocity for the influence of preferential flow paths. Preferential flow paths with a higher hydraulic conductivity than average would result in a faster velocity of the plume, thus a lower residence time and faster rate of removal at field scale.

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