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# Degradation Kinetics of Aromatic Organic Solutes Introduced Into a Heterogeneous Aquifer

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Degradation rates of benzene, p-xylene, naphthalene, and o-dichlorobenzene have been measured in a heterogeneous, unconfined aquifer during a pulse injection experiment at Columbus Air Force Base, Columbus, Mississippi. Dissolved oxygen in the pulse plume maintained aerobic conditions. Degradation kinetics calculated from the complete field data set were approximately first order with the following rate constants: benzene,  $0.0070 \text{ d}^{-1}$ ; p-xylene,  $0.0107 \text{ d}^{-1}$ ; naphthalene,  $0.0064 \text{ d}^{-1}$ ; and o-dichlorobenzene,  $0.0046 \text{ d}^{-1}$ . Reaction rates were also calculated from a near-field subset of the data using a model based on the hydrologic characteristics of the aquifer. Shapes of the degradation rate curves were consistent with microbial degradation processes. Maximum degradation rates obtained are presumed to be characteristic of the microbial population metabolism. Carbon 14-labeled p-xylene was included in the injection solution to permit detection of degradation products. This technique is suggested for future field experiments, because it distinguishes solute degradation from solute losses by sorption and evaporation and allows mass balance to be demonstrated throughout the course of the reaction in the aquifer.

## INTRODUCTION

Degradation rate constants for use in fate and transport models of reactive organic compounds must be determined by experiment. Field experiments to determine degradation rates are desirable because laboratory values may not relate to conditions in an aquifer. *Madsen* [1991, p. 1665] notes that "determination of microbial activity in disturbed, displaced environmental samples incubated in the laboratory is likely to be quantitatively, even qualitatively different from the same determination in situ." Determination of a degradation rate in an aquifer should meet criteria that are applied to rate measurements in laboratory batch reactor systems. A known mass of a pure compound must be introduced to the aquifer at a particular location and time, followed by observation of changes in concentration over space and time. Since aquifers are open systems, both the reactive compound and its degradation products should be analyzed in water samples. Also, a mass balance should be maintained for both the parent compound and its degradation products. A rate constant calculated from disappearance of the contaminant may represent physical losses rather than chemical degradation. Therefore demonstration of degradation in an aquifer requires identification and quantification of reaction products. Field measurements of an organic compound degradation rate in an aquifer that meet these criteria were not found in the literature. The natural attenuation experiment con-

ducted by *Barker et al.* [1987] measured mass loss rates of aromatic compounds from a pulse plume but did not establish that observed losses were due to degradation.

The objective of this research was to measure the degradation of organic compounds in an aquifer, using a pulse injection of an aqueous solution of tritiated water, benzene, p-xylene, naphthalene, and o-dichlorobenzene at the Columbus Air Force Base, Columbus, Mississippi, macrodispersion experiment (MADE) site. Degradation rates of these compounds in the Columbus aquifer were calculated, and the rates were related to aquifer structure and hydrologic properties. The injection was made into the saturated zone of the unconfined aquifer.

This aquifer was formed by fluvial sedimentation and has a wide range of particle sizes and spatial variation in hydraulic conductivity  $K_h$  (centimeters per second) from approximately  $10^{-4}$  to 1. The magnitude of this  $K_h$  variability is even more apparent when compared to the lower and less variable ( $10^{-4}$  to  $10^{-3}$ )  $K_h$  field at the Borden Canadian Forces Base, Ontario, described by *Robin et al.* [1991]. Hydrogeologic properties of the Columbus aquifer and a description of the MADE site were given by *Boggs et al.* [1992]. *Rehfeldt et al.* [1992] measured the spatial distribution of hydraulic conductivity at the MADE site.

Figure 1 shows the  $K_h$  distribution over a vertical section directed along the test plume axis and indicates large-scale heterogeneity and structures that *Rehfeldt et al.* [1992] refer to as channels. Close to the injection wells  $K_h$  is relatively low, with values near  $10^{-3}$  in a region extending from the phreatic surface to the lower confining layer and to approx-

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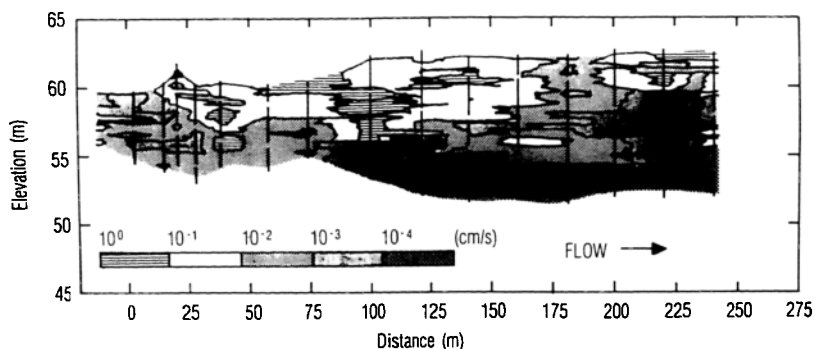


Fig. 1. Distribution of hydraulic conductivity over a vertical section along the centerline of plume motion.

imately 40 m downgradient from the injection location. Downgradient from this region,  $K_h$  in the upper 3 m of the aquifer is about  $10^{-1}$  out to 200 m, while  $K_h$  in the lower portion of the aquifer remains low. Thus a near-surface channel crosses both the intermediate and the far fields.

This experiment was similar in design to the Borden site test described by Mackay *et al.* [1986]. It differed from the earlier MADE test described by Boggs *et al.* [1992] and Adams and Gelhar [1992] in that tritiated water was used as the conservative tracer instead of bromide and that organic solutes were also injected. A pulse injection of water containing  $^3\text{H}_2\text{O}$  and organic solutes was begun on June 26, 1990. Injection wells were on a line normal to the groundwater flow direction at locations given by Boggs *et al.* [1992]. The center injection well is shown in Figure 1. Locations of injection and sampling wells are shown in plan view in Figure 2.

In order to demonstrate that organic compound losses over time in field experiments were due to degradation, a technique was developed that involved injection of a  $^{14}\text{C}$ -

labeled organic compound. In this experiment a nominal amount of  $^{14}\text{C}$ -labeled p-xylene was injected along with the unlabeled p-xylene. Then, throughout the 440-day sampling period, water samples from the aquifer were analyzed for  $^{14}\text{C}$  p-xylene and  $^{14}\text{CO}_2$  by liquid scintillation counting. The results were used to calculate the fraction of p-xylene degraded.

#### EXPERIMENTAL METHODS

Experimental parameters for the test injection included five injection wells in a line normal to the hydraulic gradient and spaced at 1-m intervals with equal, steady flow to each well. A volume of 9600 L of dilute tracer and organic compounds was injected over a period of 47.5 hours. The injection wells were screened over a 0.6-m interval at a depth of 4 m below the phreatic surface. Concentrations in the injection solution were as follows: tritium,  $55.6 \text{ nCi mL}^{-1}$ ; benzene,  $68.1 \text{ mg L}^{-1}$ ; naphthalene,  $7.23 \text{ mg L}^{-1}$ ; p-xylene,  $51.5 \text{ mg L}^{-1}$  containing ring-labeled  $^{14}\text{C}$  p-xylene,  $2.77 \text{ nCi mL}^{-1}$ ; and o-dichlorobenzene,  $32.8 \text{ mg L}^{-1}$ .

Stable organic compounds in water samples were analyzed by gas chromatography (GC). Deuterated toluene and 4-bromofluorobenzene internal standards were added to 20-mL water samples which were extracted with 2 mL of n-pentane. The extracts were analyzed for benzene, p-xylene, naphthalene, and o-dichlorobenzene by GC, using a 30 m long, 0.32-mm bore fused silica column with 1- $\mu\text{m}$ -thick DB-5 bonded phase coating and flame ionization detection. Helium carrier gas flow was  $3\text{--}5 \text{ mL min}^{-1}$ , and the split ratio was 10 to 1. Initial column temperature was held at  $50^\circ\text{C}$  for 1 min and was then increased at  $10^\circ\text{C min}^{-1}$  to  $150^\circ\text{C}$ , which was held for 5.5 min. Sensitivity of the method was  $50 \mu\text{g L}^{-1}$  for benzene and  $4 \mu\text{g L}^{-1}$  for the other compounds.

Tritium and  $^{14}\text{C}$  in samples from the wells were analyzed by liquid scintillation counting in dual-isotope mode. A 5.0-mL aliquot of each sample was emulsified in 15 mL of Pico-Flour 40 (Packard Instrument Company) cocktail and held in darkness for at least 1 hour prior to counting. Samples were counted on a Packard model 2250A for 20 min or to a 1% error at the 95% probability level, whichever was attained first. Background levels of tritium and  $^{14}\text{C}$  in local groundwater dictated practical concentration measurement limits of approximately 2 and 3 pCi  $\text{mL}^{-1}$ , respectively. A set of tritium and  $^{14}\text{C}$  standards, including one National Institute of Standards and Technology traceable standard,

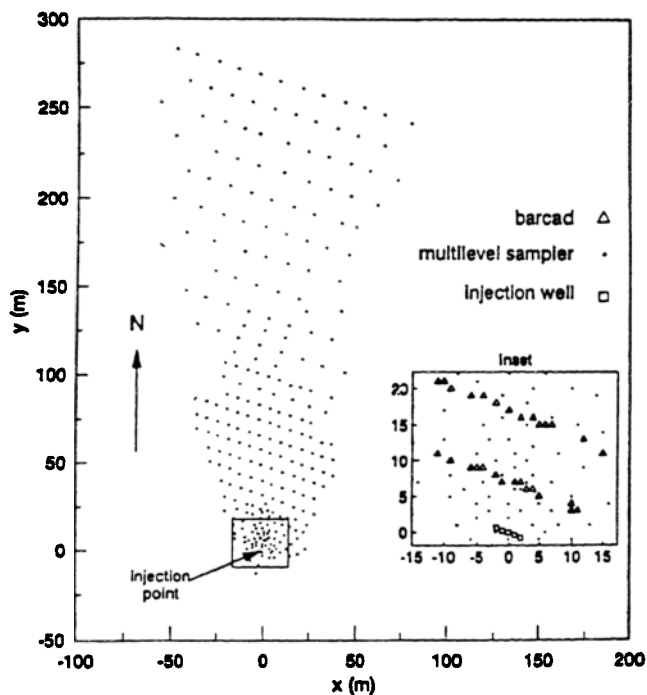


Fig. 2. Plan view of injection and sampling wells.

were counted after every set of 108 samples to check analytical accuracy and verify instrument performance. Every twenty-fifth sample was counted twice to allow estimation of measurement precision and repeatability.

Most sampling wells (328) contained multilevel samplers described by *Boggs et al.* [1992], and BarCad (Golberg-Zoino and Associates Incorporated, Newton, Massachusetts) water samplers were used in 11 wells. Water from the sampling points in the wells was analyzed to produce three-dimensional snapshots of solute concentrations at 27, 132, 224, 328, and 440 days after injection. Statistical moments for each snapshot were calculated by spatial integration over triangular right prism grid elements associated with each well sampling point. This integration was conceptually similar to the method of *Garabedian et al.* [1991], which was used in the first MADE test by *Adams and Gelhar* [1992]. Numerical implementation of the moments analysis was fully three dimensional, with the domain of integration discretized into space-filling volume elements associated with the sampling points. For each sampling point the volume element was defined by triangular grid elements of area  $A_p$  in the horizontal plane and by the vertical dimension  $z_p$ , which was the sum of one-half the distance between sampling points above and below the sampling point associated with the particular volume element. The mass of solute,  $m_p$ , of concentration  $C_p$  in a volume element with porosity  $\epsilon$  associated with a sample point  $p$  is

$$m_p = \epsilon C_p z_p A_p$$

and the total solute mass  $M$  in the plume is

$$M = \sum_{p=1}^n m_p$$

A mass balance for  $^3\text{H}_2\text{O}$  was confirmed by agreement between the zeroth moments for  $^3\text{H}_2\text{O}$  calculated from the snapshot data and the known mass of  $^3\text{H}_2\text{O}$  injected. Degradation of the organic solutes was confirmed by a special sampling of wells in high- and low-solute concentration regions of the plume at 421 days after injection. Selection of the wells was based on known concentration data from the last snapshot sampling. Each water sample was subsampled and processed in the field. A 10-mL subsample was placed in a glass ampoule, made basic with 1 mL of 3N NaOH and 1 mL of 3N  $\text{Ca}(\text{NO}_3)_2$ , and immediately flame sealed. A separate 2-mL subsample was mixed with scintillation cocktail and counted. A final 20-mL subsample was extracted with 2 mL of unlabeled p-xylene. One milliliter of the resulting xylene layer was transferred to scintillation cocktail and counted to determine the amount of undegraded  $^{14}\text{C}$  p-xylene which remained in the organic layer. Two milliliters of the extracted water was transferred to scintillation cocktail and counted. Upon return to the laboratory, the ampoules were centrifuged to separate a precipitate containing  $\text{Ca}^{14}\text{CO}_3$  and then broken open. The precipitate and 2 mL of the supernatant water were placed in separate scintillation vials with cocktail and counted.

Dissolved oxygen samples were taken 8 days before and 48, 111, 161, 264, and 330 days after the test injection. These samples were taken at three discrete levels from a set of 16 multilevel sampler wells located along the plume axis, including wells at 2.3 m upgradient and 3.6 m downgradient of

TABLE 1. Degradation Rate Constants for Organic Compounds Using Whole Field Data

	$k, \text{d}^{-1}$	$k_{\text{max}}, \text{d}^{-1}$
Benzene	0.0070	0.011
p-xylene	0.0107	0.020
Naphthalene	0.0064	0.011
o-dichlorobenzene	0.0046	0.010

the injection wells. Each sample was collected by a peristaltic pump and delivered into a 60-mL BOD bottle after purging about 100 mL from the multilevel sampler tube. A YSI (Yellow Springs, Ohio) model 5739 oxygen electrode was immediately inserted, and dissolved oxygen was measured on a YSI model 58 meter. The electrode response to oxygen was standardized in air saturated with water vapor after measurement of samples from each well.

## RESULTS AND DISCUSSION

Organic solutes degraded under aerobic conditions in the aquifer. Temporal average dissolved oxygen concentrations in the near field for each well sample point were above 3.8  $\text{mg L}^{-1}$ , and the minimum individual value in the near field was 2.6  $\text{mg L}^{-1}$ . There was no significant difference between dissolved oxygen concentrations in the near and far fields nor between measurements taken before and after the injection. This result was anticipated since organic solute concentrations in the aquifer were too low after mixing to significantly deplete dissolved oxygen in the near field of the aquifer. The initial measure of mixing is given by the plume pore volume of  $6 \times 10^5 \text{ L}$  at 27 days calculated from the tritium distribution. The measured dissolved oxygen concentrations were high enough so that degradation rates of the organic compounds were probably not oxygen limited. In support of this assumption, *Hänel* [1988] notes that the dissolved oxygen content in a normally operating activated sludge plant is 1–2  $\text{mg L}^{-1}$ .

Most of the undegraded solute mass remained in the low  $K_h$  region (near the injection wells) throughout the duration of the experiment. This situation allowed degradation rate constants to be determined separately from data for the entire plume and from data in the near field, low  $K_h$  region. Solute reactions were tritiated water (Tr) decay, with a  $k_d$  of  $1.548 \times 10^{-4} \text{ d}^{-1}$ , and degradation of the organic compounds with rate constants of  $k_b$ ,  $k_x$ ,  $k_n$ , and  $k_c$  for benzene (B), p-xylene (X), naphthalene (N), and o-dichlorobenzene (C), respectively.

Degradation rate constants based on data from the whole field were calculated using the zeroth moments of the plumes of tritiated water and organic solutes for each snapshot. For each organic solute, initial mass and mass remaining for each snapshot sampling time were used in a nonlinear least squares regression to fit a first-order exponential function, thus assuming a first-order degradation process. Degradation rate constants from these regressions are given in Table 1. Maximum degradation rates for all solutes occurred between 224 and 328 days after injection, as can be seen from Figure 3, and these rates are included as  $k_{\text{max}}$  in Table 1.

The observed mass loss is presumed to be due to microbial catabolism (biodegradation) but is referred to simply as

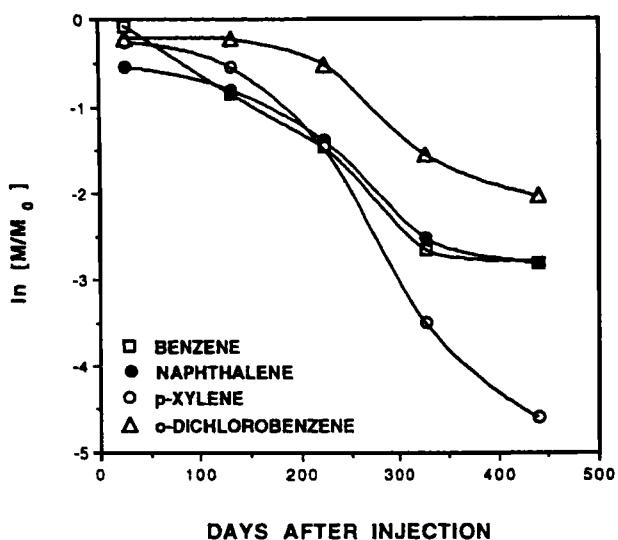


Fig. 3. Plot of organic compound masses against time, based on data from the whole field.

degradation, since biodegradation is indicated, but not proven, by this experiment. Proof of biodegradation in the Columbus aquifer would require field application of molecular biology techniques similar to those described by Fleming *et al.* [1993].

Spatial distributions of solutes are apparently related to the  $K_h$  distribution, as indicated by Figure 4a, which shows the distribution of  $^3\text{H}_2\text{O}$  concentrations at 224 days after injection. High  $^3\text{H}_2\text{O}$  concentrations remained near the injection wells, with lower concentrations in the upper portion of the aquifer from about 30–250 m downgradient. There was little  $^3\text{H}_2\text{O}$  in the lower portion of the aquifer

between 30 and 175 m downgradient. This distribution suggests that most of the  $^3\text{H}_2\text{O}$  was transported from the low  $K_h$  zone near the injection wells to the far field through an upper channel whose size, location, and  $K_h$  governed the solute loss rate from the near-field region.

The organic solutes were slightly retained and thus more confined to the near field than was the unretained  $^3\text{H}_2\text{O}$ . Accordingly, most degradation of the organic solutes occurred in the near-field zone. This zone is approximately delineated by the p-xylene distribution at 224 days after injection, shown in Figure 4b. Most of the undegraded p-xylene remained within 20 m of the injection wells. The other organic solutes were similarly distributed. The organic solutes were primarily confined to the near-field zone because they degraded rapidly relative to their transport from the near field. As a result, separate degradation rates could be calculated using only the near-field data. This technique was used because the organic solute concentrations were much higher in the near field and less subject to analytical uncertainty.

Solute mass transport from the near field to the far field is assumed to be a first-order process, with the same constant,  $k_1$ , for all solutes. Degradation and loss to the far field occurred simultaneously in the near field. The rate equations are

$$-d[\text{Tr}]/dt = k_d[\text{Tr}] + k_1[\text{Tr}] \quad (1)$$

$$-d[\text{B}]/dt = k_b[\text{B}] + k_1[\text{B}] \quad (2)$$

$$-d[\text{X}]/dt = k_x[\text{X}] + k_1[\text{X}] \quad (3)$$

$$-d[\text{N}]/dt = k_n[\text{N}] + k_1[\text{N}] \quad (4)$$

$$-d[\text{C}]/dt = k_c[\text{C}] + k_1[\text{C}] \quad (5)$$

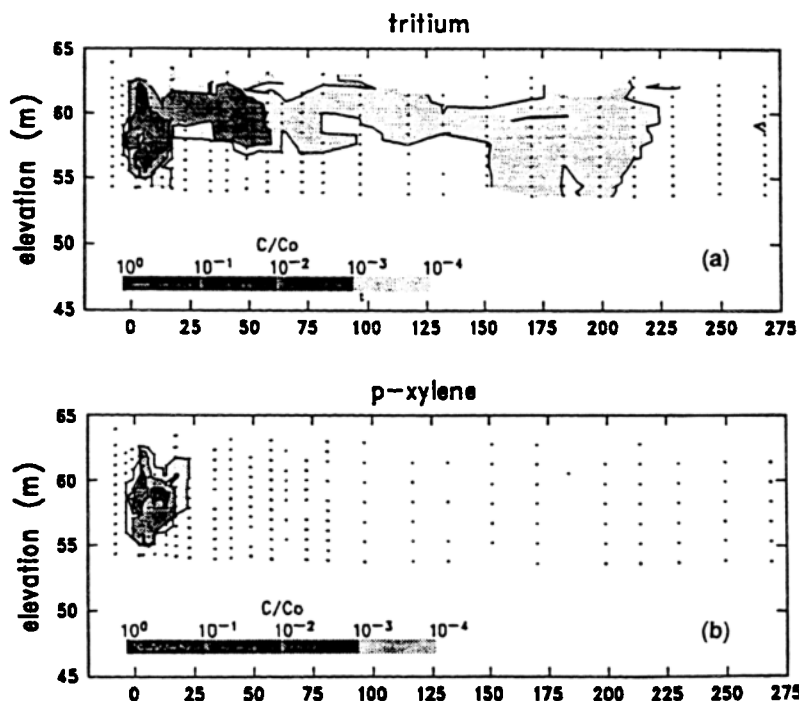


Fig. 4. Distribution of (a) normalized tritium concentration and (b) normalized p-xylene concentration over a vertical section along the centerline of plume motion at 224 days.

with initial conditions  $t_0 = 0$ ,  $[Tr]_0 = 0.539$  Ci,  $[B]_0 = 660$  g,  $[X]_0 = 402$  g,  $[N]_0 = 70$  g, and  $[C]_0 = 318$  g.

Integration of rate equations (1)–(5) with these conditions gives solute masses in the near field as a function of time. The transport rate constant,  $k_1$ , is calculated from the integrated form of (1), using the known  $k_d$  of tritium. Degradation constants for the organic solutes are then determined by substitution of  $k_1$  and solving the integrated forms of equations (2)–(5) for  $k_b$ ,  $k_x$ ,  $k_n$ , and  $k_c$ , respectively.

Sorption of organic solutes was not included in rate calculations using the near-field data. Aromatic solutes were weakly sorbed on Columbus aquifer material [MacIntyre et al., 1991; Lion et al., 1990]. Batch sorption coefficients measured on subsamples of a 20,000-kg composite sample of Columbus aquifer material for naphthalene, o-dichlorobenzene, p-xylene, and benzene were 0.085, 0.065, 0.048, and 0.059 L kg<sup>-1</sup>, respectively. Retardation effects on organic solute distributions in the near field were not detected due to the predominant influence of degradation. Sorption-desorption processes at aquifer material surfaces are assumed to be fast relative to the chemical degradation processes considered here, as indicated by Spiro [1989], and they are assumed to be rate limited by physical transport of organic solute molecules to and from the solid-solution interface. The aromatic compounds may have been microbially degraded from solution, sorbent surfaces, or both. Sorption processes probably did not limit microbial degradation of organic solutes in this experiment since sorption kinetics has been shown to be rapid for organic compounds on this aquifer material [MacIntyre et al., 1991].

Loss of organic solutes by transport from the near to the far field was assumed to be proportional to the loss of tritium from the near field, defined as the portion of the plume volume within 10 m downgradient from the injection wells. The amount of tritium in the near field at a given time was calculated by the spatial integration method described above. Total tritium in this zone decreased exponentially with time, as shown in Figure 5. The tritium values used were corrected for tritium decay. This plot indicates that solute leakage from the reactor was apparently first order,

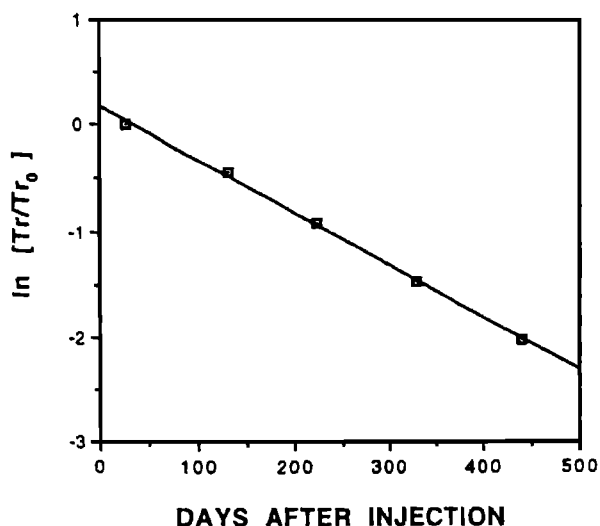


Fig. 5. Plot of normalized tritium concentration in the near-field region against time.

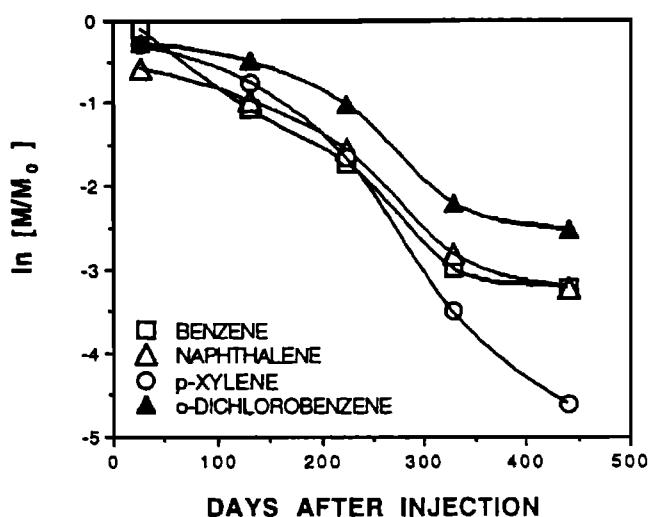


Fig. 6. Plot of organic compound masses against time, based on data from the near field.

with leakage rate constant  $k_1 = 5.45 \times 10^{-3} \text{ d}^{-1}$ . A mass balance for tritium that was calculated using spatial integration over the entire plume showed that the injected tritium mass was accounted for at the times given in Figures 3 and 6. This result implies that the tritium mass loss in the near field was primarily due to leakage.

Degradation rates of organic solutes in the near field are shown in Figure 6. The curves shown in Figures 3 and 6 suggest that degradation in the Columbus aquifer may be first order, with an initial lag period. The departure of the curves in Figures 3 and 6 from linearity is attributed to microbial adaptation, cell growth, and substrate limitation. Spain [1990] has described lag period dependence on microbial growth and adaptation to the substrate. The observed lag period is followed by degradation at a maximum rate, which is also a characteristic of microbial metabolism. Simkins and Alexander [1984] have indicated that degradation in a laboratory microcosm can be expected to follow Monod kinetics for a microbial population not limited by nutrients and with a sufficient substrate concentration, but first-order kinetics are observed at low substrate concentrations. Organic solute concentrations in this experiment were quite low, so this conclusion is consistent with previous experimental results. Larson [1979] notes that the rate of decrease in concentration as a function of substrate concentration can often be expressed as a first-order equation and that first-order kinetics are generally expected for biodegradation at low organic substrate concentrations.

Finally, the rate decreases, and this change is concurrent with reduced solute (substrates) concentrations due to degradation and dilution. Rubin et al. [1982] have demonstrated in laboratory experiments that microbial degradation rates of aromatic compounds can be reduced at low substrate concentrations. Similar substrate limitations are thus a possible explanation for the rate decrease shown in Figures 3 and 6.

Table 2 shows degradation rate constants calculated from the near-field data. Initial mass and mass remaining for each sampling time were used in a nonlinear least squares regression to fit a first-order exponential function to determine the first-order rate constant  $k$  ( $\text{d}^{-1}$ ) for each compound. The maximum rate constants  $k_{\text{max}}$  were calculated from the

TABLE 2. Rate Constants for Organic Solute Degradation in the Near Field

	$k$ , $d^{-1}$	$k_{max}$ , $d^{-1}$	$k_{max}(c)$ , $d^{-1}$
Benzene	0.0079	0.0120	0.0066
p-xylene	0.0106	0.0196	0.0141
Naphthalene	0.0072	0.0118	0.0063
o-dichlorobenzene	0.0060	0.0114	0.0059

maximum slopes of the curves shown in Figure 6. Rate constants corrected for organic solute leakage from the near field,  $k_{max}(c)$ , were obtained by subtracting the leak rate constant  $k_1$  from  $k_{max}$  values. The relative values of the degradation rates given in Tables 1 and 2 appear reasonable. The most slowly degraded of the four compounds was o-dichlorobenzene, which is in agreement with the results of Callahan et al. [1979].

Rate constants were based on the analysis of stable compounds by gas chromatography. Ring labeled  $^{14}C$  p-xylene was used to show that p-xylene was degraded rather than lost in the aquifer. Carbon 14 p-xylene was oxidized to  $^{14}C$ -labeled intermediates and carbon dioxide, which exists as both  $H_2^{14}CO_3$  and  $H^{14}CO_3^-$  at the groundwater pH of approximately 5. The special sampling and analysis described above permitted measurement of  $^{14}C$  p-xylene degradation products. Degradation values calculated from data obtained on these samples are given in Table 3. The  $^{14}C$  activity in the carbonate precipitate was divided by the total  $^{14}C$  activity in the basic sample (supernatant plus precipitate) to obtain the fraction of p-xylene converted to  $CO_2$ . The amount of  $^{14}C$  in the water after extraction was divided by the amount  $^{14}C$  in the unextracted water sample to obtain the fraction of p-xylene converted to polar intermediates and  $CO_2$ .

The  $^{14}C$  p-xylene conversion values compare well with mass losses calculated from the moments analysis of p-xylene remaining in the plume. Mass loss at day 421 was obtained by interpolation from mass losses at the given snapshot times. It is assumed that all of the organics injected, because of their structural similarity, were degraded rather than lost to other processes.

Conversion values in Table 3 imply that most of the p-xylene went to energy production and was not incorporated into new biomass. Differences between degradation in the high- and low-concentration regions of the aquifer was not significant. Some of this difference may have been due to analytical errors (e.g., loss of  $Ca^{14}CO_3$  during precipitate transfer prior to counting or  $CO_2$  dissolution in xylene). Conversions were calculated separately for high- (>1 ppm) and low- (<1 ppm) concentration regions of the plume. The

TABLE 3. Degradation of  $^{14}C$  p-Xylene in Water Samples Taken at 421 Days After Injection, Expressed as Weight Percent

	Converted to $CO_2$ Precipitation Method	Converted to $CO_2$ Extraction Method	Mass Loss From Moments Analysis
[X] >1 ppm ( $n = 8$ )	72.7 ( $\pm 11.5$ )	85.1 ( $\pm 6.3$ )	98
[X] <1 ppm ( $n = 10$ )	75.7 ( $\pm 6.9$ )	82.6 ( $\pm 6.1$ )	98

similarity of these results implies nonlocalized, concentration independent degradation. Toxic effects and nutrient or oxygen limitations on the microbiota are not indicated.

Groundwater at this site is undersaturated with respect to calcite. The absence of carbonate minerals was confirmed by the similarity of total carbon and organic carbon contents (at the 0.005% level) determined using a Leco Corporation (St Joseph, Michigan) model WR112 carbon analyzer. Carbonate minerals in the saturated zone of an aquifer would preclude the use of this  $^{14}C$  method for determining degradation of organic compounds.

## CONCLUSIONS

Degradation rates have been determined in situ for four aromatic compounds in the Columbus aquifer. These rates will be used in the design and modeling stages of a new field test at the same site, which is now in preparation. It is proposed that similar experiments using aqueous solutions of organic compounds would provide accurate estimates of aerobic degradation rates. Results from these experiments could then be used to further develop and refine models for predicting the fate and transport of organic contaminants in aquifers.

The organic solutes used in this study degraded quickly, suggesting that for similar solutes in an aquifer with approximately steady flow the plume of organic solutes leaching from a liquid hydrocarbon mixture source region might reach a steady state spatial limit. The boundary of such an area would be determined primarily by the hydrology of the site, solute sorption, redox capacity, nutrient supply, and degradation by indigenous microbes.

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