Quality of Groundwater, Proceedings of an International Symposium, Noordwijkerhout, The Netherlands, 23—27 March 1981, W. van Duijvenbooden, P. Glasbergen and H. van Lelyveld (Eds.), *Studies in Environmental Science*, Volume 17

PRINCIPLES OF ORGANIC CONTAMINANT BEHAVIOR DURING ARTIFICIAL RECHARGE

PAUL V. ROBERTS
Department of Civil Engineering, Stanford University (U.S.A.)
ALBERT J. VALOCCHI
Department of Civil Engineering, University of Illinois (U.S.A.)

ABSTRACT

The behavior of a variety of organic contaminants having low molecular weight has been observed during groundwater recharge with reclaimed water. The evidence is site-specific, but is believed to have broader implications regarding the general behavior of organic contaminants in groundwater. The movement of specific contaminants such as chloroform and chlorobenzene is retarded with respect to that of a conservative tracer such as chloride. The measured retardation factors are approximately 3 and 35 for chloroform and chlorobenzene, respectively. The retardation is caused by the sorption of the solute, apparently by the organic constituents of the soil material. The magnitude of the retardation factor of an organic solute can be predicted approximately from knowledge of the organic carbon content of the aquifer material and the octanol-water partition coefficient of the solute. Sorption also contributes to attenuation (damping) of concentration fluctuations. It is shown that the degree of attenuation depends strongly on the retardation factor, the distance traveled, and the hydrogeologic characteristics of the aquifer. There is evidence of biodegradation of organic solutes in the vicinity of the recharge well.

INTRODUCTION

The principles governing organic contaminant behavior during artificial recharge are fundamentally the same as those underlying organic contaminant behavior in subsurface environments in general, apart from the singular phenomena in the vicinity of a recharge well. In seeking understanding of solute transport and transformations, artificial recharge situations offer the inherent advantage that the input of contaminants can be monitored and controlled satisfactorily, and that the subsurface system can be forced sufficiently strongly to produce substantial concentration gradients. Hence, the prospects of measuring significant spatial and temporal variation in contaminant concentrations are more favorable than in the study of groundwater contamination of coincidental or non-point origin. In this paper, the fundamental principles of organic contaminant transport are reviewed, their implications

Reprinted from *The Science of the Total Environment*, 21 (1981) 161—172

are explored, and examples drawn from field investigations are presented. The effects of sorption and dispersion in the saturated zone are emphasized.

PRINCIPLES OF SOLUTE BEHAVIOR

The phenomena that most strongly influence organic solute transport in saturated groundwater environments are: advection, dispersion, sorption and biodegradation. Advection refers to the transport of solute at a velocity equivalent to that of the groundwater movement. Dispersion is the term used to describe the spreading of a concentration front as a result of spatial variation in aquifer permeability, fluid mixing, and molecular diffusion. Sorption is the retention of solute in the soil phase by partitioning between the aqueous phase and solids. Biodegradation refers to the disappearance of organic solute from solution when the solute is utilized by microorganisms as a substrate for energy and growth.

Transport Equation

For one-dimensional horizontal flow in a saturated, homogeneous medium, the transport equation may be expressed as (ref. 1, p. 402; refs. 2,3):

$$-u \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} + \frac{\rho_b}{\epsilon} \frac{\partial S}{\partial t} + \left(\frac{\partial C}{\partial t}\right)_{rn} = \frac{\partial C}{\partial t} \qquad (1)$$

where

u = average fluid velocity [m/s]

C = solute concentration in aqueous phase [$g \cdot m^{-3}$]

x = distance in flow direction [m]

D = dispersion coefficient [$m^2 \cdot s$]

ρ_b = bulk density of soil [$g \cdot m^{-3}$]

ϵ = soil void fraction [-]

S = mass of solute sorbed per unit dry mass of soil [g/g]

t = time [s]

rn refers to biodegradation or chemical reaction

Sorption

Solutes that sorb strongly onto soil materials are retarded in their movement through an aquifer (ref. 1, pp. 402-408; ref. 3). Ignoring the second and fourth terms on the left of Eq. 1, the transport equation for a sorbing but non-reacting solute under conditions of ideal plug flow can be simplified to

$$-u \frac{\partial C}{\partial x} + \frac{\rho_b}{\epsilon} \frac{\partial S}{\partial t} = \frac{\partial C}{\partial t} \qquad (2)$$

Further, assume that the mass transfer of solute to sorption sites is rapid (i.e., local equilibrium), and that the sorption equilibrium is linear

$$\frac{dS}{dC} = K_d$$

where K_d = distribution coefficient [$m^3 \cdot g^{-1}$]. For this simple case, the transport equation can be rewritten as

$$-u \frac{\partial C}{\partial x} = \left(1 + \frac{\rho_b K_d}{\varepsilon}\right) \frac{\partial C}{\partial t} \tag{3}$$

after recognizing from mass conservation considerations that the disappearance of solute from the aqueous phase due to sorption causes a corresponding increase in the sorbed concentration. The term $[1 + (\rho_b K_d/\varepsilon)]$ is known as the retardation factor. An advancing front of sorbing solute moves at a linear velocity that is smaller than the velocity of groundwater movement by a factor

$$t_r = [1 + (\rho_b K_d/\varepsilon)] = u_r^{-1}$$

where

t_r = relative residence time, or retardation factor [-]

u_r = relative velocity of movement of a concentration front of sorbing solute divided by the velocity of movement of a front of a conservative tracer.

The value of the retardation factor t_r is influenced primarily by the value of K_d; the values of ρ_b and ε differ to a much lesser extent in natural systems than does K_d. The value K_d is determined by the strength of solute-soil interactions; the greater the affinity of the solute for the soil phase, relative to its affinity for water, the more strongly the solute will sorb, and the greater the value of K_d. Hence, it is not surprising that solutes that exhibit strongly hydrophobic behavior will sorb strongly onto soil materials. In fact, Karickhoff et al. (ref. 4) have shown that sorption of organic solutes by soil materials is governed by a remarkably simple rule: the larger the organic carbon fraction of a soil or sediment, the greater the value of K_d. In experiments with 15 soil materials having organic carbon contents in the range 0.1 to 3.3%, Karickhoff et al. found that the value of K_d for a given solute was proportional to the organic carbon content of the soil. Moreover, Karickhoff et al. (ref. 4) found that the value of K_d was approximately proportional to the degree of hydrophobicity of the solute, as measured by the octanol: water partition coefficient K_{ow} (ref. 5). These observations are summarized in consistent units in Eq. 4:

$$(K_d)_i = 6.3 \times 10^{-7} f_{oc} (K_{ow})_i \tag{4}$$

where

f_{oc} = fraction of organic carbon in the soil [g organic carbon per g dry soil]

K_{ow} = octanol:water partition coefficient

i = solute index.

Equation 4 represents a best fit of experiments with ten solutes having values of K_{ow} in the range of 100 to 1,000,000 (ref. 4).

Values of the retardation coefficient calculated for ranges of values of $(K_{ow})_i$ and f_{oc} are plotted in Fig. 1. The values of ρ_b and ϵ are assumed in this example to be 2.0×10^6 g/m^3 and 0.2, respectively.

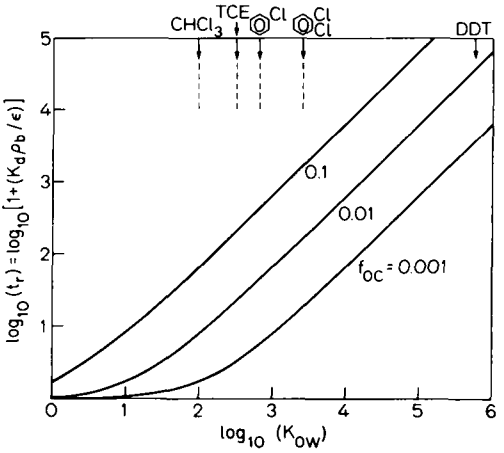

Fig. 1. Retardation factor, $t_r = (u_r)^{-1}$.

Figure 1 can be used to estimate the retardation factor for a solute whose octanol:water partition behavior is known or can be estimated (ref. 5), in an aquifer with known organic carbon content.

For example, in an aquifer containing 1% organic carbon, chloroform (K_{ow} = 93) will be retarded by a factor of seven, whereas DDT ($K_{ow} = 5.8 \times 10^5$) will be retarded by a factor of 40,000. Clearly, chloroform is expected to migrate much more rapidly than DDT in the subsurface environment; there is little prospect that a strongly sorbing solute such as DDT will be encountered far from its source.

Dispersion

The importance of the dispersion phenomenon can be gauged by the magnitude of the dispersion coefficient D in Eq. 1. In most instances, neither laboratory experiment nor theory is of great value in predicting the value of D for a natural aquifer. The value of D is determined primarily by spatial variation of permeability, and hence must be determined by tracer measurements in the field (ref. 1).

Dispersion is reflected in a spreading of the solute concentration front as it moves through the aquifer. The dimensionless Peclet Number (Pe = ux/D) is used as a measure of the dispersion tendency; the smaller the value of Pe, the greater the extent of dispersion. Ogata and Banks (ref. 6) and Levenspiel (ref. 7) show that for Pe > 500, dispersion can be practically neglected, whereas for Pe < 5 the flow regime approaches complete mixing.

In groundwater hydrology, the dispersion coefficient is frequently found to be approximately proportional to the velocity

$$D = \alpha u \tag{5}$$

where α = dispersivity [m]. Values of α calculated from field measurements range from 1 to 100 m, or three to six orders of magnitude larger than the α values measured in homogeneous porous media in the laboratory (ref. 1). Using a representative value of $\alpha = 10$ m, the Peclet Number is then $Pe = x/\alpha = x/10$, where x is the distance traveled in meters.

An example calculation in one dimension is shown in Fig. 2; it is assumed that the dispersivity is 10 m and that observations are made at a point 50 m distant from the source of a concentration stimulus. Two cases are shown in Fig. 2: the response to a step stimulus ($\hat{F}$), and the response to a pulse stimulus ($\hat{C}$). The relative concentration C/C_o is shown as a function of the dimensionless residence time parameter, $\theta = t/\overline{t}$, where $\overline{t}$ is the average residence time. The $\hat{C}$-response is the first derivative of the $\hat{F}$-response, and the $\hat{F}$-response is the integral of the $\hat{C}$-response (ref. 7). This principle can be utilized to estimate the $\hat{C}$-response from the $\hat{F}$-response or vice versa, where field conditions permit the measurement of only one type of response.

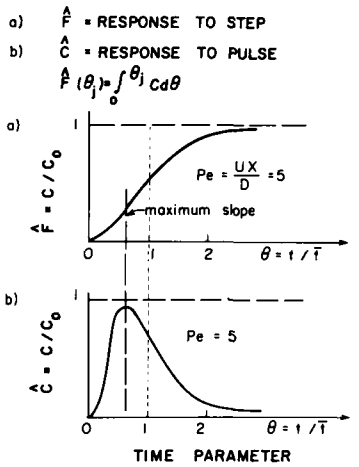

Fig. 2. Relation between $\hat{F}$- and $\hat{C}$-responses.

How does the response change with increasing distance x? Ogata and Banks (ref. 6) present a general solution of the form

$$\frac{C}{C_o} = \frac{1}{2}\left\{\operatorname{erfc}\left[\frac{1-\theta}{2(\theta/Pe)^{1/2}}\right] + \exp(Pe)\ \operatorname{erfc}\left[\frac{1+\theta}{2(\theta/Pe)^{1/2}}\right]\right\} = \hat{F} \tag{6}$$

where $\theta = ut/x$, $Pe = ux/D$. Levenspiel (ref. 7) suggests a simple approach for cases of slight or intermediate amounts of dispersion ($Pe \geq 100$). For such cases, the $\hat{C}$-response is approximately Gaussian

$$\hat{C} = \frac{C}{C_o} = \frac{1}{2\sqrt{\pi(\alpha/x)}} \exp\left[-\frac{(1-\theta)^2}{4(\alpha/x)}\right] \tag{7}$$

and its variance is given by

$$\sigma_{\hat{C}}^2 = 2\alpha/x \tag{8}$$

The breadth of the concentration front in dimensionless terms is proportional to the value of σ. Hence, the breadth of the concentration front is proportional to $x^{-1/2}$ if expressed in terms of dimensionless time or distance, but is proportional to $x^{1/2}$ if expressed in terms of absolute time or distance.

To illustrate this behavior, the example of Fig. 2 is extended in Fig. 3 to compare the $\hat{F}$-response at $x = 5000$ m to that at 50 m. The velocity is assumed to be 5 m/day; hence the average residence time is 10 days at $x = 50$ m and 1000 days at $x = 5000$ m. At $x = 50$ m, the concentration front passes within approximately 25 days, or 2.5 times the average residence time. At $x = 5000$ m, the concentration front passes within approximately 400 days, or 0.4 times the average residence time. Concomitantly, the ratio of the breadth of the concentration front to the average distance traveled is approximately 2.5 and 0.4, respectively, at the observation distances of 50 m and 5000 m. The basic principle is that the spread of the concentration front decreases on a relative basis as the concentration front propagates away from the origin.

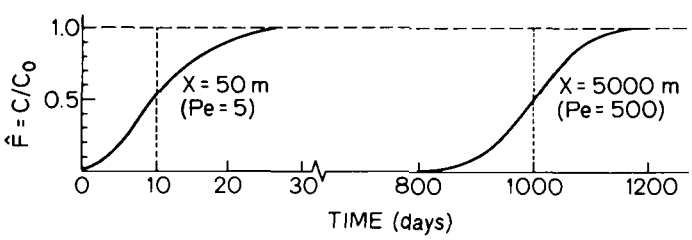

Fig. 3. Propagation of the F-response. Dispersivity $\alpha = 10$ m; average velocity $u = 5$ m/day; $u_r = 1.0$.

Sorption and Dispersion

The behavior of a solute influenced by both sorption and dispersion can be predicted by modifying the transport equation as follows:

$$-u_r u \frac{\partial C}{\partial x} + u_r D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \tag{9}$$

where all variables are defined as before.

The sorbing solute travels at an apparent velocity of $u_r \times u$, and exhibits an apparent dispersion coefficient $u_r \times D$. Because the dispersivity α is defined as $\alpha = D/u$, the apparent dispersivity of the sorbing solute

$$\alpha_{app} = \left(\frac{D_{app}}{u_{app}}\right) = \frac{u_r D}{u_r u} = \frac{D}{u} \tag{10}$$

is the same as that of a non-interacting solute (Eq. 5). The remarkable conclusion is that the concentration response of a sorbing solute with retardation factor $t_r = (u_r)^{-1}$ is exactly the same as expected for a non-sorbing solute moving at a velocity equal to u_r times the real average fluid velocity. Using the example of Fig. 3, a sorbing tracer having a retardation factor of 100 will be observed to exhibit exactly the same behavior at a distance of 50 m as the non-sorbing tracer, but at times that are multiplied by a factor of 100.

Exhaustion of the soil's sorption capacity is a general feature of sorption: the solute concentration front eventually breaks through completely at any given observation point. Thereafter the observed concentration will remain constant. However, for observation points far distant from the contaminant source, and especially for strongly sorbing solutes, the soil may continue to remove solute for many years; the time required for breakthrough can be estimated approximately as $\bar{t}_{tracer}/u_r$, where $\bar{t}_{tracer}$ is the average hydraulic or tracer residence time.

Response to Fluctuating Input

If the input concentration of a sorbing solute varies, the solute will not break through to reach a constant concentration, but rather will fluctuate around an average value equal to the average input concentration. This type of behavior is illustrated schematically in Fig. 4 for the case of a sinusoidally varying input. Characteristic features are: the amplitude of the response is diminished compared to that of the stimulus, and the maxima are shifted in phase.

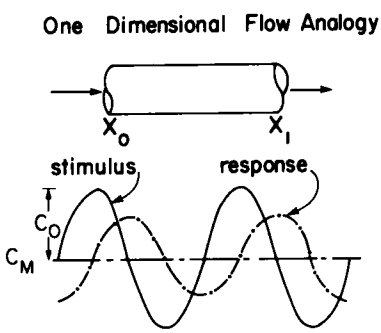

Fig. 4. Schematic illustration of damping of concentration variations in one-dimensional flow.

The steady-state response to a sinusoidal stimulus can be expressed as:

$$C(x,t) = C_M + C_o \cdot (AR) \cdot \cos(\omega t + \phi - \phi') \tag{11}$$

where

C_M = average input concentration [$g \cdot m^{-3}$]

C_o = amplitude of input fluctuation [$g \cdot m^{-3}$]

ω = frequency of input fluctuation [s^{-1}]

ϕ = phase angle of input fluctuation [-]

ϕ' = phase shift [-]

AR = amplitude ratio

$= [C_{max}(x,t) - C_M]/C_o$

The degree of attenuation of the concentration fluctuation is given by the amplitude ratio AR:

$$AR = \exp\left\{\frac{Pe}{2}\left[1 - \left(\frac{\sqrt{1 + (4A/Pe)^2} + 1}{2}\right)^{1/2}\right]\right\} \tag{12}$$

where

Pe = Peclet Number = x/α

A = Attenuation Number = $x\omega/u_r u$

and the phase shift ϕ' is

$$\phi' = \frac{Pe}{2}\left\{\frac{\left[1 + (4A/Pe)^2\right]^{1/2} - 1}{2}\right\}^{1/2} \tag{13}$$

The amplitude ratio has great practical significance, whereas the phase shift is of little consequence. The amplitude ratio decreases with both increasing distance x from the stimulus and with increasing strength of sorption (decreasing u_r). The effects of x and u_r on the amplitude ratio are illustrated in Figs. 5 and 6, which show results of example calculations for the conditions cited: fluid velocity, u = 3.3 m/day; period of fluctuation, ω^{-1} = 100 days; and dispersivity, α = 1 m. At a distance of 100 m (Fig. 5), the predicted amplitude ratio becomes vanishingly small as the retardation factor (u_r^{-1}) approaches 100. Even at a smaller value of the retardation factor, $(u_r)^{-1}$ = 10, the amplitude ratio becomes very small at a distance of 5000 m (Fig. 6).

Values of the amplitude ratio calculated from Eq. 11 are plotted versus the Attenuation Number, A, in Fig. 7, with the Peclet Number as a parameter. For each value of Pe, there is a limiting value of A beyond which the amplitude ratio becomes vanishingly small; where the value of A exceeds that limiting value (e.g., A > 10 for Pe = 10), it may be expected that transitory input concentration fluctuations will not be reflected in the observed concentration. A graphical display such as Fig. 7 may be useful in discriminating between situations where concentration fluctuations are or are not significant; such predictions may often be useful in designing groundwater-quality-monitoring systems.

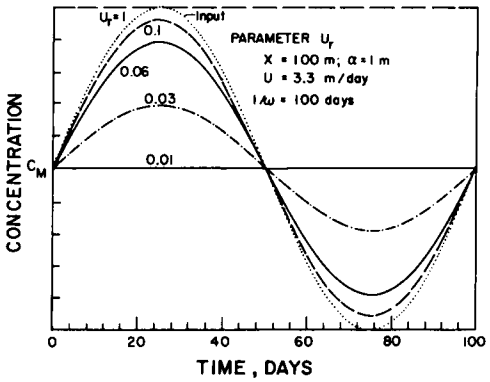

Fig. 5. Effect of retardation factor on amplitude ratio.

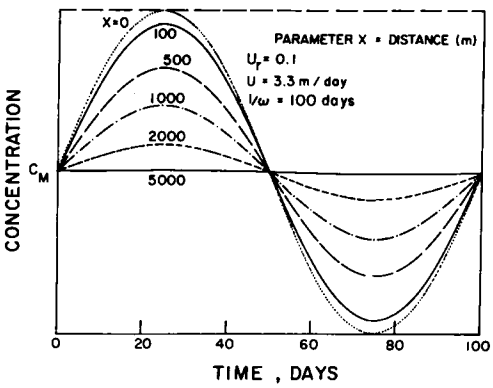

Fig. 6. Effect of distance on amplitude ratio.

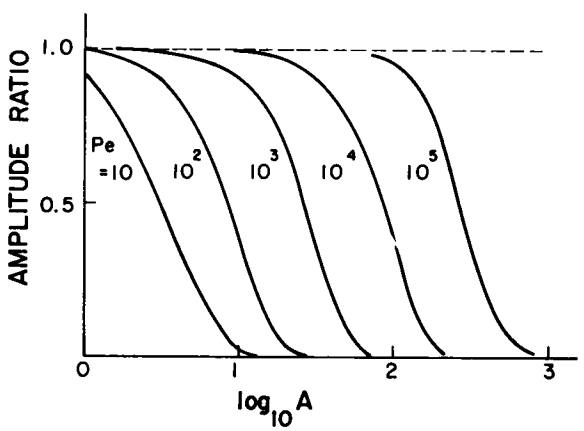

Fig. 7. Dependence of amplitude ratio on Peclet and Attenuation Numbers.

RESULTS OF FIELD STUDY

Numerous examples that illustrate the behavior described above have been observed in the course of a field study of artificial recharge in the Palo Alto Baylands. Field studies have been in progress since 1977; the conditions and results have been reported elsewhere (refs. 3,8-10).

Retardation of Sorbing Solutes

Retardation factors have been estimated for a number of solutes based on field measurements of concentrations. The necessary condition for such an interpretation is that the stimulus approximates a step change, usually at the outset of recharge operations; the measured response is then an $\hat{F}$-response in the nomenclature of Levenspiel (ref. 7). Roberts et al. (ref. 3) described a simple procedure for analyzing the response data using an approach based on mass balances for aquifer elements of arbitrary shape.

Values of the retardation factor obtained from the Palo Alto Baylands study are summarized in Table 1. The observations were made at sampling wells 8 to 40 m distant from the recharge well. The values of t_r were independent of the direction and distance of the observation well, within 50% (ref. 9). McCarty et al. (ref. 10) showed that the experimental values of the retardation factor t_r inferred from field measurements were in accordance with predictions based on Karickhoff's model (Eq. 4), assuming an average organic carbon content of 1% in the aquifer material.

TABLE 1

Retardation factors estimated from field study results

Compound	Estimated retardation factor, t_r	Reference
$CHCl_3$	2.5 to 4.5	8, 9
$CHBr_3$	6	9
$CHClBr_2$	6	9
Cl_3CCH_3	12	9
C_6H_5Cl	33 to 36	3, 9
$1,2\text{-}C_6H_4Cl_2$	> 200	3

Comparison of Step and Pulse Responses

We observed responses in both step- and pulse-stimulus experiments in the field. The $\hat{F}$-responses from the step experiment agree well with the residence distribution obtained by integration of the $\hat{C}$-responses from the pulse experiment, as demonstrated in Fig. 8 for chloroform.

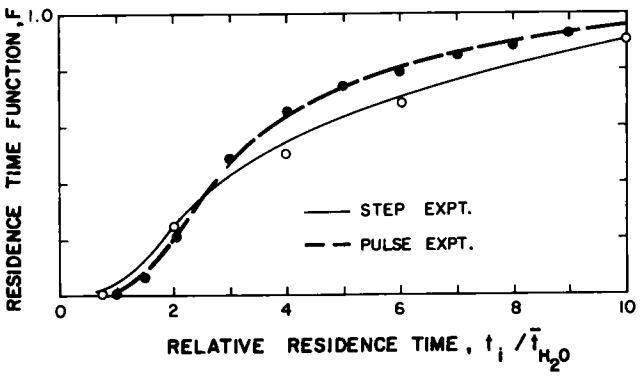

Fig. 8. Comparison of residence time distributions estimated for chloroform from responses to step and pulse experiments in the field.

Attenuation of Concentration Fluctuations

Significant attenuation of concentration fluctuations has been observed to result from flow through 10 to 40 m of aquifer material (ref. 9). The variance of the concentration distribution of chloroform was only 1/5 as great at 40m as at 10 m, and only 60% as great at the 10 m observation well as at the recharge well. Moreover, fluctuations in the chlorobenzene concentration were attenuated more strongly than those of chloroform (ref. 9), as expected based on chlorobenzene's stronger sorption affinity.

Biodegradation

There is evidence of biodegradation of specific organic solutes in the vicinity of the recharge well (refs. 2,3). Specifically, naphthalene demonstrated a characteristic partial breakthrough, followed by a decline to a low, steady-state concentration level of less than 100 ng/l. This behavior suggests that biodegradation of naphthalene ensued as a population of microorganisms, capable of utilizing naphthalene as a substrate, developed after the onset of recharge (ref. 2).

Moreover, the concentration of organic matter, measured collectively as total organic carbon (TOC), decreased during flow through the aquifer, principally in the vicinity of the recharge well (ref. 9). The average TOC concentration decreased from 2.8 to 1.3 mg/l during flow through 40 m of aquifer; half of the observed decrease occurred in the first 10 m. The portion of TOC that was not degraded appeared to be transported essentially as rapidly as a non-sorbing tracer (refs. 3,9,11).

CONCLUSIONS

There is ample evidence that organic trace contaminants interact with soil solids and microorganisms during artificial recharge. Sorption serves to retard solute transport, whereas both sorption and dispersion attenuate concentration fluctuations. The long solute residence time, owing to sorption coupled with low hydraulic velocities, affords unusual opportunities for microbial growth and biodegradation.

Stimulus-response experiments provide useful information regarding the behavior of organic solutes in the subsurface environment. Such information is valuable in predicting the rate of transport, and in identifying solutes that are likely to be transformed, under the conditions of the particular environment. Moreover, such knowledge of solute transport rate and dynamic behavior greatly facilitates the rational design of groundwater-quality-monitoring systems .

REFERENCES

1 R.A. Freeze and J.A. Cherry, Groundwater, Prentice-Hall, Inc., Englewood Cliffs, NJ (USA), 1979.
2 B.E. Rittmann, P.L. McCarty and P.V. Roberts, Ground Water, 18:3(1980)236-243.
3 P.V. Roberts, P.L. McCarty and M. Reinhard, J. Water Poll. Control Fed., 52:1(1980)161-172.
4 S.W. Karickhoff, D.S. Brown and T.A. Scott, Water Research, 13(1979)241-248.
5 A. Leo, C. Hansch and D. Elkins, Chem. Rev., 71(1971)575-616.
6 A. Ogata and R.B. Banks, A Solution of the Differential Equation of Longitudinal Dispersion in Porous Media, U.S. Geological Survey Prof. Paper 411-A, Washington, D.C., 1961, p. A-4.
7 O. Levenspiel, Chemical Reaction Engineering, John Wiley & Sons, Inc., New York, 2nd ed., 1972.
8 P.V. Roberts, in W. Kühn and H. Sontheimer, Oxidation Techniques in Drinking Water Treatment, U.S. Environmental Protection Agency, EPA-570/9-79-020, 1979, pp. 647-672.
9 P.V. Roberts, J. Schreiner and G.D. Hopkins, Organic Water Quality Observations During a Field Study of Groundwater Recharge, Water Research, accepted for publication.
10 P.L. McCarty, B.E. Rittmann and M. Reinhard, Trace Organics in Groundwater, Env. Sci. Tech, 15:1(1981),40-51.
11 P.V. Roberts, P.L. McCarty and W.M. Roman, Jour. Env. Eng. Div., ASCE, 104:EE5(1978)933-949.

ACKNOWLEDGMENT

This paper is based on work supported in part by the Robert S. Kerr Environmental Research Laboratory of the U.S. Environmental Protection Agency (Grant No. R-804431) and the Office of Water Research and Technology (Grant No. 14-35-0001-8824). R. Scott Summers carried out some of the computations.