Bull. Environ. Contam. Toxicol. (1991) 46:534–541

Bulletin of Environmental Contamination and Toxicology

Transport of a BTX Mixture in a Groundwater Aquifer Material

Christopher G. Uchrin and Jack Katz

Department of Environmental Science, Cook College, New Jersey Agricultural Experiment Station, Rutgers University, New Brunswick, New Jersey 08903, USA

Gasoline is a complex mixture of aliphatic, aromatic and alicyclic hydrocarbons. In addition, such additives as organometalic compounds, alcohols, organohalide compounds and phosphates may be present, depending on the manufacturer. The so-called "BTX" compounds (benzene, toluene, and o-, m-, and p-xylene) are, however, aromatic compounds which appear to be ubiquitous to all gasolines, regardless of maker.

The mathematical modeling of gasoline migration in the subsurface region is quite difficult as gasoline is not completely miscible in water, thus different components will partition into the water at proportions. A multiphase fluid flow problem is thus generated. The BTX compounds are among the most water soluble of the gasoline components, thus, their potential for transport in a groundwater aquifer system is great. Processes including sorption and biochemical transformation can affect the transport and fate of these compounds in a groundwater system.

This paper presents and discusses the results of a study conducted to examine the transport and fate of a BTX mixture in flow through soil column leaching studies employing material from a New Jersey aquifer.

MATERIALS AND METHODS

The aquifer material used in this study was extracted from a Cohansey aquifer outcrop near Chatsworth, NJ. This material has been used in many previous studies and properties are listed in Table 1. Organic matter content was determined by the Walkley and Black modification of the rapid dichromate oxidation technique (Nelson and Somers 1982) with organic carbon content defined as 59 % of the organic matter content.

Send reprint requests to Christopher G. Uchrin at the above address.

Table 1. Properties of Cohansey aquifer material.

Sand (%)	90.0
Silt (%)	8.0
Clay (%)	2.0
Organic Matter (%)	4.4
pH	3.8
CEC (mg/l)	5.1
Porosity	0.55
Bulk Density (g/cc)	1.78
Texture	Sand

The BTX compounds (benzene, toluene, and ortho-, meta-, and para-xylene) are common components of gasolines. All five are somewhat water soluble and quite volatile. Solubilities in water and other relevant parameters are presented in Table 2.

Table 2. BTX Characteristics (from Verschueren 1983)

Compound	Molecular Weight	Specific Gravity	Boiling Point (°C)	Solubility (mg/L)
Benzene	78.11	0.879	80.1	1780 (20°C)
Toluene	92.14	0.866	110.6	515 (20°C)
p-Xylene	106.17	0.861	138.4	156 (25°C)
m-Xylene	106.17	0.864	139.1	146 (25°C)
o-Xylene	106.17	0.880	144.4	170 (25°C)

Flow-through column studies were performed in an apparatus designed using modified techniques originally suggested by van Genuchten, et al. (1974), Rao and Davidson (1978), Enfield and Carsel (1980), Uchrin and Katz (1985), and Reduker, et al. (1988). This type of study uses a reconstituted soil column to simplify system hydraulics so that attention can be focused on the reaction mechanisms. The apparatus consisted of 5-cm (I.D.) glass columns operated in a downward, gravity mode. The systems were airtight from teflon feed bags to teflon collection bags. Inter-connecting tubing and fittings were made of either glass or teflon. Bed depth was 12-inches (30.48 cm). The apparatus is described in detail by Katz (1989). Duplicate columns were run and all experiments were performed in a constant temperature pilot room at 21°C.

The BTX feed mixture was created by mixing equal volumes of benzene, toluene, p-xylene, m-xylene, and o-xylene. This mixture served as the stock for the entire experiment and was stored in a teflon-lined crimp top bottle at 4°C. A 2.5 mL volume of this mixture was added to 4 liters of a 0.02 M calcium chloride solution in a teflon bag. The calcium chloride served as both a tracer and to stabilize the ionic balance in the column matrix. The solution was allowed to sit for 24 hours and then analyzed to determine the concentration of the five compounds. Aqueous sample concentrations were determined by flame gas chromatography (GC) after hexane extraction. In most cases, a 5.0 mL volume of sample was withdrawn and extracted with 5.0 mL of pesticide grade hexane. When concentrating a sample was necessary, a specified volume of sample and 1.0 mL of hexane were used. The extract was analyzed using a Hewlett Packard 5840A GC equiped with a flame ionization detector and fitted with a 2 mm (ID) x 6 foot glass column packed with GP 5% SP1200/1.75% bentone 34 on 100/120 Supelcoport. This packing allowed separation of the xylene isomers. Average concentrations of the five substances for each column feed are shown in Table 3.

Table 3. Column Feed Concentrations (mg/L)

Compound	Column 1	Column 2
Benzene	104.4	106.5
Toluene	67.2	68.4
o-Xylene	47.1	47.6
m-Xylene	40.1	40.7
p-Xylene	41.6	42.3

Once the concentration of each component was determined, the feed bag was attached to the column. The effluent from each column was collected in a teflon bag and analyzed periodically. After the experiment had been run in the constant feed mode for approximately 9 days (209 hours), an elution experiment was commenced by starting a feed of uncontaminated water.

RESULTS AND DISCUSSION

The resultant concentration versus time distributions for all five substances in one of the columns are displayed in Figure 1. The results for the other column were virtually identical and are shown on the subsequent figures.

The effluent chloride tracer data are displayed in Figure 2. This figure shows that the effluent chloride breakthrough data for both columns was nearly identical which could be expected since the average flow rates for the two columns were virtually identical (1.63 L/day and 1.58 L/day for columns 1 and 2, respectively). The chloride breakthrough data were

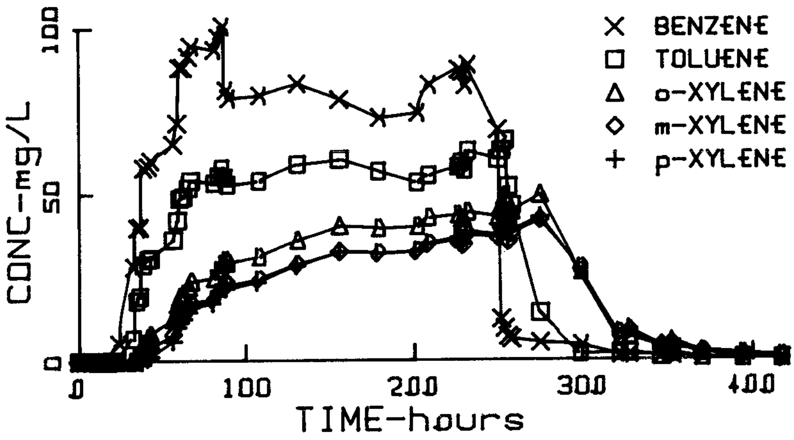

Figure 1. Effluent data for column 1.

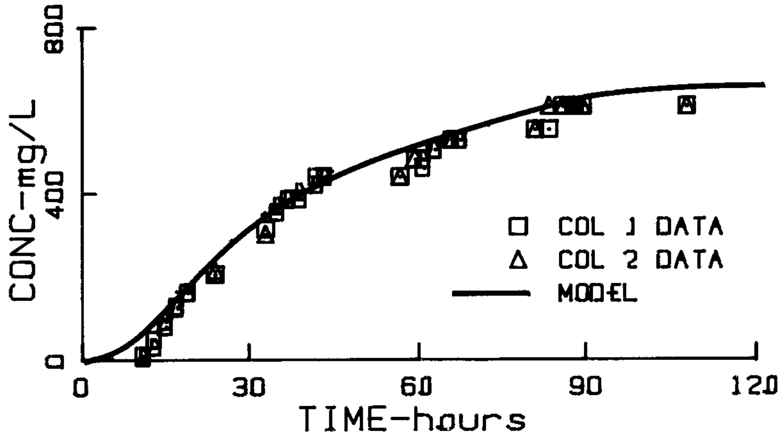

Figure 2. Chloride tracer column data and model trace.

modeled using the BASIC program MSTEPCOL (Uchrin and Lewis 1986) which mathematically simulates a one-dimensional, advection-dispersion, non-degrading packed bed system with linear, reversible, equilibrium partitioning between solid and liquid phases. The two sets of column data were modeled as a single system (flow rate of 1.60 L/day). A dispersion coefficient of 100 cm^2/day was calibrated to the data and the resultant model trace is also shown on Figure 2.

Figures 3-7 each display the concentration versus time traces for both columns on single plots for benzene, toluene, p-xylene, m-xylene and o-xylene, respectively. Also plotted are modeling traces. The dashed trace represents the predicted model response using partition coefficients generated by single component batch experiments for benzene and toluene (Uchrin and Mangels 1987) and the xylenes (Uchrin et al. 1987). The solid

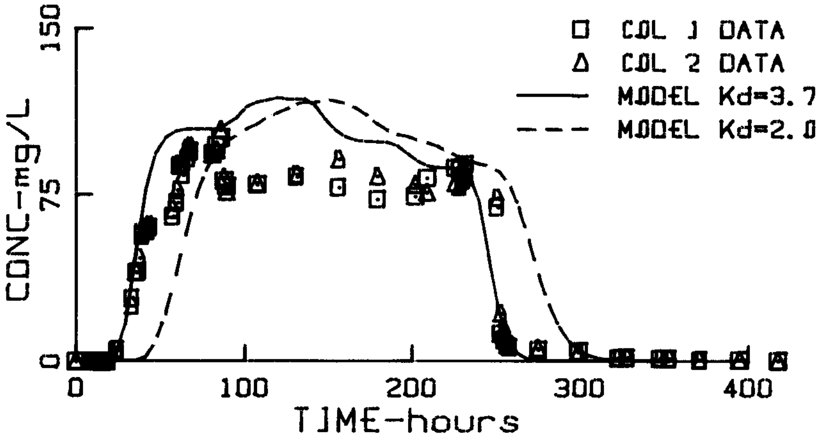

Figure 3. Benzene column data and model traces.

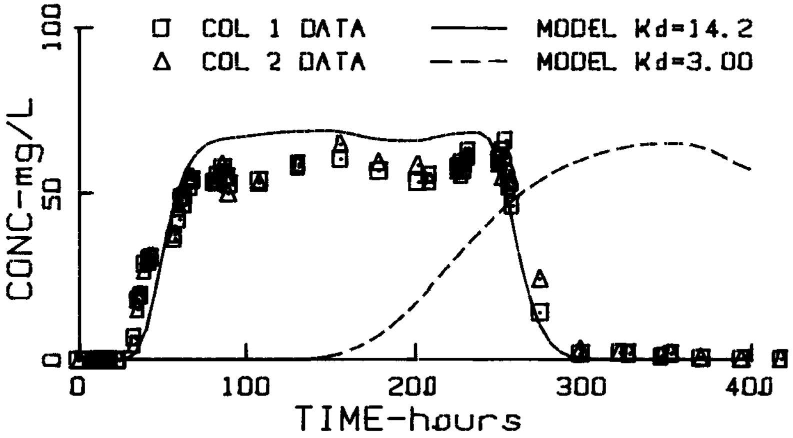

Figure 4. Toluene column data and model traces.

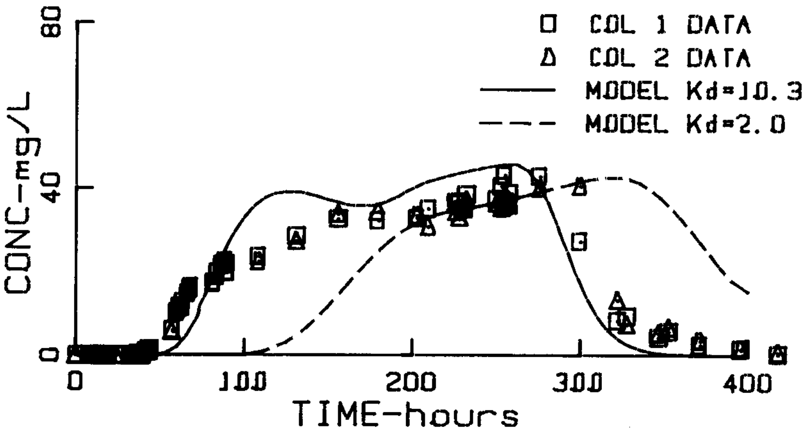

Figure 5. p-Xylene column data and model traces.

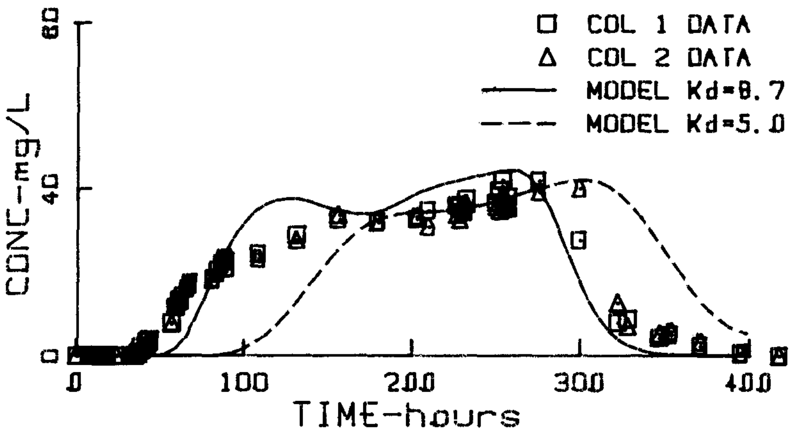

Figure 6. m-Xylene column data and model traces.

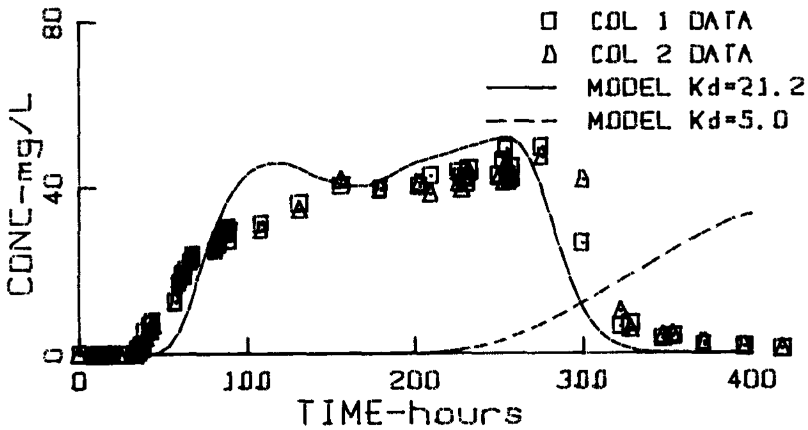

Figure 7. o-Xylene column data and model traces.

trace represents a calibrated model response. It is interesting to note that in all cases, the batch, single component partition coefficients are significantly larger than those effectively observed. This reduction in the effective partition coefficient may be a manifestation of a competitive phenomenon. A summary of partition coefficients is given in Table 4.

Head space analyses were performed on the residual soils once the columns were exhausted. Trace, non-quantifiable amounts of each component were detected.

The results from this study provide some insight into the transport dynamics of a hetergeneous mixture, such as gasoline, in a ground water system. The values reported from batch studies, which were performed in single component mode, were consistantly greater than those calibrated for the column data in this study.

Table 4. Partition Coefficients.

Compound	Batch	Calibrated
Benzene	3.71	2.00
Toluene	14.2	3.00
o-Xylene	10.3	4.50
m-Xylene	8.74	5.00
p-Xylene	10.3	5.00

The successful use of a chloride tracer rules out the possibility of "short-circuiting" as an explanation. A possible explanation is that competition is occurring which would tend to reduce the effective partition coefficient.

A comparison can also be made to single component partition coefficients determined using published correlations to soil organic carbon fraction, f_{oc}, and the octanol/water partition coefficient, K_{ow}. Table 5 presents soil/water partition coefficients, K_p, calculated from Karickhoff, et al. (1979):

$$\log K_{oc} = \log K_{ow} - 0.21$$

where K_{oc} is the organic carbon normalized partition coefficient:

$$K_{oc} = K_p/f_{oc}$$

Table 6. Partition Coefficients from Literature Correlations (from Miller, et al. 1985).

Compound	$\log K_{ow}$	K_p
Benzene	2.13	2.16
Toluene	2.65	7.17
o-Xylene	3.13	21.6
m-Xylene	3.20	25.4
p-Xylene	3.18	24.3

Comparing Tables 4 and 5, one notices that all the calculated partition coefficients except for the smallest, benzene, greatly exceed the observed values although the relative positions are similar. Care must thus be exercized when using literature values.

Acknowledgements. This work was supported in part by the N.J. Dept. Environ. Protection (R.T. Mueller, Project Director) and the N.J. Agricultural Experiment Station, publication No. D-07525-1-90.

REFERENCES

Enfield CG, Carsel RF (1980) Mathematical prediction of toxicant transport through soil. In: Test protocols for environmental fate and movement of toxicants. Assoc Offic Anal Chem. Wash. D.C. p 233-250

Karickhoff SW, Brown DS, Scott TA (1979) Sorption of hydrophobic pollutants on natural sediments. Water Research 13:241-248

Katz, J (1989) Examination of competitive adsorption and ion additions on the elution characteristics of organic compounds from aquifer solids. Ph.D. Thesis. Rutgers University. New Brunswick. New Jersey

Miller MM, Wasik SP, Huang GL, Shiu WY, Mackay D (1985) Relationships between octanol-water partition coefficient and aqueous solubility. Environ Sci Technol 19:522-529

Nelson DW, Somers LE (1982) Total carbon, organic carbon, and organic matter. In: Page AL, Miller RH, Keeney DR (eds.) Methods of soil analysis, Part 2: Chemical and microbiological properties, 2nd ed. Am Soc Agron Inc and Soil Sci Soc Amer Inc. Madison. Wis. p 565-571

Rao PSC, Davidson JM (1979) Adsorption and movement of selected pesticides at high concentrations in soils. Water Research 13:375-380

Reduker S, Uchrin CG, Winnett G (1988) Characteristics of the sorption of chlorothalonil and azinphosmethyl to a soil from a commercial cranberry bog. Bull Environ Contam Toxicol 41:633-641

Uchrin CG, Hunter JV, Chan P (1987) A characterization of the binding of toxic and hazardous substances to soil particulates. Report Center for Research in Hazardous and Toxic Substances. NJIT. Newark. N.J.

Uchrin CG, Katz J (1985) Modeling aromatic compound transport in groundwater. O'Shaughnessy JC (ed.) Proc. ASCE Nat. Conf. on Environ. Engrg., Boston

Uchrin CG, Lewis TE (1986) A BASIC encoded model for flow-through fixed-bed adsorber and one-dimensional ground water systems. J Environ Sci Health A21:267-279.

Uchrin CG, Mangels G (1987) Sorption equilibria of benzene and toluene on two New Jersey coastal plain ground water aquifer solids. J Environ Sci Health A22:743-758

van Genuchten MT, Davidson JM, Wierenga PJ (1974) An evaluation of kinetic and equilibrium equations for the prediction of movement through porous media. Soil Sci Soc Amer Proc 38:29-35.

Verschueren K (1983) Handbook of environmental data on organic chemicals, 2nd ed. Van Nostrand Reinhold Co. New York. NY

Received June 11, 1990; accepted September 19, 1990