

Permeation of Petroleum-Based Aromatic Compounds Through Polyethylene Pipes Under Simulated Field Conditions

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1. Introduction

It has long been known that organic contaminants may permeate through plastic pipes and adversely affect the quality of drinking water in a distribution system (Vonk, 1985; Thompson and Jenkins, 1987). The plastic pipe materials involved include polybutylene (PB), polyethylene (PE) and polyvinyl chloride (PVC) and the contaminants of interest include highly volatile hydrocarbons and chlorinated organic solvents (Holsen et al., 1991a).

Typically, the permeation of contaminants through a plastic pipe may involve three processes: (i) partition of the contaminant between the outer surface of pipe and the medium containing the contaminant (sorption); (ii) diffusion of the contaminant through the polymer materials of pipe; and (iii) partition between the inner surface of pipe and the water in the pipe (desorption). Under the field conditions, permeation is specifically influenced by: i) the structural characteristics of polymer materials (Vonk, 1985); the chemical activity and the molecular characteristics of the organic contaminant (Park et al., 1991); and soil characteristics, especially organic content (Holsen et al., 1991b). Other environmental factors, such as temperature, hydraulic gradient, and aging of pipe materials may also have a potential impact on permeation.

Polyethylene (PE) pipe is widely used in water service connections. PE is characterized as a semi-crystalline polymer; i.e., having both crystalline and amorphous regions. The crystalline zones act as impermeable barriers for sorption and diffusion, while the non-crystalline matrix is readily permeable since the polymeric chains in the amorphous areas are relatively “mobile” (Naylor, 1989). Generally, the diffusion of organic contaminants through PE pipe can be described by Fickian diffusion (Vonk, 1985).

In this study, the permeation of petroleum-based aromatic compounds (BTEX) through PE pipe was investigated under simulated field conditions, including subsurface gasoline spills and gasoline-contaminated groundwater with varied levels of contamination. Most of pipe permeation incidents reported were related to petroleum products, mainly gasoline spills or leaks (Holsen et al., 1991a). The effects of soil organic matter content on permeation were also examined. The main purpose of this study was to develop empirical equations which can be used to predict the permeation behavior of BTEX through PE pipe at contaminant levels typically faced in the environment.

2. Materials and Methods

2.1 Materials

One-inch HDPE pipe (SIDR-9 IPS NSF PW PE3408 ASTM-D2239-81) was obtained from a PE pipe manufacturer. Premium gasoline was purchased from the local store and the concentrations of benzene, toluene, ethylbenzene, m-xylene, and o+p-xylene were determined using gas chromatography to be 19.8 g/L, 75.9 g/L, 14.7 g/L, 33.7 g/L, and 32.5 g/L, respectively. BTEX compounds were roughly 25% by volume of the gasoline - a typical value for commercial gasoline used in the North America.

The aqueous solution saturated with gasoline was prepared by mixing 350 mL premium gasoline and 3.5 L DI water in a 4 L glass bottle for 48 h. Several preliminary experiments indicated that a mixing time of 48 h was sufficient to produce saturated gasoline solution. A freshly saturated stock solution was prepared once every week throughout this study. The concentration of the dissolved BTEX was around 150 mg/L, which was slightly higher than the 135 mg/L reported by Cline et al. (1991) for water saturated with gasolines of varied compositions. Benzene and toluene were the major aromatic compounds in the aqueous phase, accounting for nearly 90% of total BTEX. Diluted aqueous solutions of varying concentrations were obtained by diluting the saturated stock solution with DI water.

Three types of soils, including silica sand, sandy loam and organic topsoil, were used in the experiments. Granusil 4030 silica sand was purchased from UNIMIN Corporation, Portage WI. Organic topsoil, purchased from a local store, was air dried and sieved to pass a 2 mm sieve. Sandy loam soil was prepared by mixing approximately equal parts of silica sand and dried, sieved, organic topsoil with a Hobart mixer. Triplicate samples were taken randomly from each prepared soil and sent to the Soil and Plant Analysis Laboratory at Iowa State University for soil organic matter analysis. The average organic carbon content for organic top soil and sandy loam soil was 5.1% and 1.9%, respectively. The organic carbon content of the silica sand was below detection limits. Good agreement between the triplicate determinations of organic carbon content of each soil indicated that the soils were uniformly mixed.

2.2 Experimental apparatus

Experiments were conducted in a pipe-bottle apparatus, consisting of a 1 L glass bottle with the PE pipe mounted horizontally through holes drilled in the glass. The connections between pipe and bottle were sealed with a plastic sealant and further covered by a hydrocarbon-resistant epoxy sealant. The ends of the pipes were sealed with Teflon plugs. The Teflon plug had a small hole that was plugged with a brass plug to allow filling and draining of the water inside the pipe with a glass syringe. The bottle was capped with a Teflon-lined cap.

2.3 Experimental procedures

2.3.1 Simulated Environmental Contamination

One experiment investigated the permeation of BTEX through PE pipe exposed to pure premium gasoline. In this test, the pipe segment was first filled with DI water and the bottle filled with silica sand and premium gasoline until the bottle was nearly full and a visible liquid level of gasoline appeared above the surface of the sand. The level of gasoline liquid in the bottle was monitored visually and there was no significant drop in the level during the experimental period

of four weeks. Pipe-water samples were taken at regular intervals and analyzed for the presence of BTEX. The pipe was flushed with DI water at least three times immediately after each sampling before fresh DI water was added and the pipes sealed.

Four other experiments investigated the permeation of BTEX through PE pipe exposed to aqueous solutions at four levels of gasoline-saturation (nearly 100% saturated, 50% saturated, 10% saturated, and 1% saturated). To start the test, a PE pipe was placed and sealed in the bottle followed by silica sand into the glass bottle until the bottle was nearly filled with the sand. The bottle was loosely capped with a Teflon-lined cap through which a small hole was drilled and a Teflon tubing installed reaching the bottom of bottle. Aqueous gasoline solution was then introduced into the sand through the Teflon tubing from bottom to top, using a Masterflex pump, until the bottle was full. The Teflon tube was removed along with the cap and the bottle was then tightly capped with a Teflon-lined cap with no hole. The final water level was approximately 2 cm above the surface of the soil, with minimum headspace. Sodium azide was used to inhibit potential biodegradation of BTEX. The apparatuses were wrapped with aluminum foil to minimize photodegradation.

Each week, the silica sand and the aqueous solutions were replaced with new sand and fresh aqueous gasoline solutions to maintain relatively constant aqueous concentrations of BTEX in the bottle. BTEX concentrations in the soil pore water were periodically measured. To collect samples for this purpose, the bottles were gently rotated several times and then allowed to sit undisturbed for 10 minutes. Liquids above the soils were collected into VOC vials using a glass syringe and then centrifuged at 5,000 rpm for 10 minutes. These supernatant liquids were analyzed in the same manner as the pipe-water samples. All experiments were conducted at room temperature ($23 \pm 1.5^\circ\text{C}$).

2.3.2 Soil impact on permeation

Pipes were buried in the three types of prepared soils, which were initially saturated with water that had been saturated with gasoline. BTEX concentrations in the soil pore water and the pipe-water were collected and measured over the experimental period. The experimental procedures were same as described above, except that the soil and aqueous solution were not replenished and the BTEX concentrations in the soil pore water were periodically measured. To compensate for the liquid loss (around 4 mL) from sampling and to maintain zero headspace, additional fresh gasoline-saturated water was rapidly added to each bottle following sampling.

2.4 Analysis Method

BTEX in the water samples was determined using a gas chromatograph (Tracor 540) equipped with a packed column (6 ft \times 2 mm; 1% SP1000 on 60/80 mesh Carbopack B), a photoionization detector, and an automated purge & trap concentrator (Tekmar LSC2/ALS). The method detection limits for benzene, toluene, ethylbenzene, m-xylene and o+p-xylene were 0.36 $\mu\text{g/L}$, 0.53 $\mu\text{g/L}$, 0.44 $\mu\text{g/L}$, 0.61 $\mu\text{g/L}$, and 1.08 $\mu\text{g/L}$, respectively.

3. Results and Discussion

3.1 Simulated Environmental Contamination

3.1.1 PE pipe exposed to free gasoline

The cumulative permeation fluxes for BTEX compounds are plotted in Figure 1. The permeation of BTEX through PE pipe exposed to gasoline was extremely rapid. The breakthrough time was estimated to be one week. When breakthrough occurred, the level of benzene in the pipe-water immediately exceeded the MCL of 5 µg/L. A steady rate of permeation was reached in 26 days and the concentrations of BTEX in the pipe-water at the end of the 3-day sampling intervals were very close to those in the saturated BTEX solution.

The permeation behavior of benzene and toluene was almost identical and accounted for nearly the entire total BTEX that permeated into the pipe-water, probably due to the higher solubility of benzene in water and the higher concentration of toluene in gasoline.

3.1.2 PE pipe exposed to aqueous solutions of gasoline

The cumulative permeation fluxes for BTEX compounds at four levels of contamination are plotted in Figure 2. The measured concentrations of BTEX in soil pore water at four levels of contamination were slightly lower than the expected values (100%, 50%, 10% and 1%), mainly due to sorption by the pipe and volatilization loss.

As shown in Figure 2, benzene and toluene permeated through PE pipe rapidly, even exposed to dilute aqueous solution. Of the five compounds of interest, benzene was the first compound to be detected in the pipe-water, probably due to the high concentration of benzene in the water surrounding the pipe and its smaller molecular diameter. The breakthrough times of benzene for four levels of contamination (nearly 100%, 50%, 10% and 1% saturation) were 13 days, 17 days, and 26 days, 43 days, respectively. The breakthrough of toluene was slightly behind that of benzene. Once breakthrough occurred, the level of benzene in the pipe-water quickly exceeded its MCL. The cumulative mass $Q(t)$ line at steady state conditions intersected the time (t) axis at the time lag, T_L . The T_L s for benzene at four levels of contamination (nearly 100%, 50%, 10% and 1% saturation) were estimated at 51 days, 53 days, 65 days and 104 days, respectively, and those for toluene were 55 days, 61 days, 72 days, and 106 days, respectively.

Based on the $Q(t)$ curve at steady state, the permeation rates for the corresponding contamination levels (nearly 100%, 50%, 10% and 1% saturation) were calculated as 1.044 µg/(cm²·day), 0.344 µg/(cm²·day), 0.057 µg/(cm²·day), 0.0046 µg/(cm²·day) for benzene and 1.011 µg/(cm²·day), 0.325 µg/(cm²·day), 0.052 µg/(cm²·day), 0.00462 µg/(cm²·day) for toluene, respectively. Obviously, the permeation rates were strongly depended on the concentrations of contaminants in the soil pore water. Higher bulk water contamination resulted in stronger permeation. The steady state permeation rates versus the external (bulk) concentrations are plotted in Figure 3. Two empirical equations were obtained to provide a correlation between the steady state permeation rate, P [µg/(cm²·day)] and the bulk concentration, C_{bulk} in soil pore water (mg/L):

$$P = 0.0079C_{bulk}^{1.1323} \quad \text{for Benzene}$$

$$P = 0.0087C_{bulk}^{1.1444} \quad \text{for Toluene}$$

The equations above can be used to predict the external concentration which would result in the exceedance of benzene or toluene MCLs in pipe-water after a period of stagnation. The concentration of contaminant in pipe-water (C_{pw}) can be estimated by:

$$C_{pw} = \frac{M}{V} = \frac{P \times \pi \times O.D. \times L \times t}{\frac{1}{4} \times \pi \times I.D.^2 \times t} = \frac{4 \times f(C_{bulk}) \times O.D. \times t}{I.D.^2}$$

The total mass of permeated contaminant (M) is estimated by:

$$M = P \times (\pi \times O.D. \times L) \times t$$

where P is the steady permeation rate of the contaminant and is a function of the bulk concentration of contaminant in the soil pore water, C_{bulk} , as above, L is the length of the exposed pipe, t is the time of exposure; and $O.D.$ is the outside diameter (cm) of the pipe. The volume of water (V) in the pipe with an inside diameter $I.D.$ is given:

$$V = \frac{1}{4} \pi \times I.D.^2 \times L$$

This expression can be used to compute the C_{bulk} required to exceed the MCL for a contaminant after a specified period of exposure. Table 1 presents the estimated bulk concentration, C_{bulk} required (at steady state permeation) to exceed the MCL for benzene (5 $\mu\text{g/L}$) and toluene (1000 $\mu\text{g/L}$) in a 1 inch SIDR-9 IPS PE pipe for stagnation periods of 1, 7, 14, and 28 days.

The diffusion coefficients for the pipe-contaminant systems above were calculated using the time lag method. If the diffusion takes place in a hollow cylinder with outer and inner radii of a and b respectively, the expression for time lag is given by:

$$T_L = \frac{a^2 - b^2 + (a^2 + b^2) \ln(b/a)}{4D \ln(b/a)}$$

The diffusion coefficients (D) for benzene at four levels of contamination (Figure 2, nearly 100% to 1% saturation) were calculated as $3.2 \times 10^{-8} \text{ m}^2/\text{day}$, $3.1 \times 10^{-8} \text{ m}^2/\text{day}$, $2.5 \times 10^{-8} \text{ m}^2/\text{day}$, and $1.5 \times 10^{-8} \text{ m}^2/\text{day}$, respectively. The corresponding diffusion coefficients for toluene were $2.9 \times 10^{-8} \text{ m}^2/\text{day}$, $2.6 \times 10^{-8} \text{ m}^2/\text{day}$, $2.2 \times 10^{-8} \text{ m}^2/\text{day}$, and $1.5 \times 10^{-8} \text{ m}^2/\text{day}$, respectively. D versus C_{bulk} is plotted in Figure 4, and two empirical equations were obtained to give an accurate correlation with the experimental data:

$$D = \{0.626 \times \ln(C_{bulk}) + 3.172\} \times 10^{-8} \quad \text{for Benzene}$$

$$D = \{0.290 \times \ln(C_{bulk}) + 1.719\} \times 10^{-8} \quad \text{for Toluene}$$

The concentration-dependent diffusion coefficient was found to increase logarithmically with the external concentration, which agrees with previous research. This concentration effect may be attributed to increased mobility of polymer segments resulting from increases in the average free volume in the polymer caused by the presence of the diffusing contaminant. The diffusion coefficients of benzene were slightly higher than those of toluene. This is attributed to the smaller molecular diameter of benzene. Generally, the diffusion coefficient decreases with increasing average molecular diameter.

3.2 Soil Impact on Permeation

Under otherwise identical initial conditions, the BTEX concentration in soil pore water was lowest in the organic topsoil, which had the highest organic carbon content (5.1%); intermediate level in the sandy loam, which had the intermediate level of organic carbon content (1.9%); and highest in silica sand, which had an insignificant organic carbon content (Figure 5). This is attributed to different BTEX sorption capacities for different types of soil. Generally, soils behaved as a dual sorbents: the mineral matter functions as a conventional adsorbent (adsorption), and the soil organic matter as a partition medium rather than a conventional solid adsorbent (partition) (Chiou et al., 1981). Earlier studies found that water and organic chemicals compete for sorption sites on mineral surfaces and a relative high humidity may significantly inhibit the mineral adsorption of organic vapor. Since soils were saturated with water in this study, partitioning into soil organic matter is probably dominant mechanism of BTEX uptake from water. The higher organic matter in the organic topsoil resulted in greater soil uptake of BTEX and a significant decrease of BTEX concentrations in the soil pore water. Sorption of BTEX into the soil organic matter is rapid, as shown in Figure 5. BTEX in the soil pore water for the organic topsoil and sandy loam dropped dramatically within the first week (mainly due to sorption to the soil) and then decreased slowly (mainly due to sorption to the pipe and volatilization losses).

As demonstrated in the study of *Simulated Environmental Contamination* (above), the permeation strength of BTEX through PE pipes was strongly dependent on the external bulk concentration. The sorption of BTEX by soils decreased the BTEX concentration in the soil pore water and, thereby, decreased the permeation rate of BTEX through PE pipes (Figure 6). The breakthrough times of benzene for silica sand, sandy loam and organic topsoil were 13 days, 16 days, and 19 days, respectively. Since the external bulk concentration varied with exposure time, steady state permeation was not reached and, therefore, the diffusion coefficient of BTEX for the three different types of soils could not be determined. The relative permeation strengths, however, can be compared with each other. For example, after two-month exposure, the cumulative permeation flux of BTEX through the pipe buried in silica sand was nearly twice that of sandy loam, and four times that of organic topsoil. The results indicate that high soil organic matter can not be relied upon to protect pipes or gaskets from permeation because such soils will eventually reach their maximum adsorption capacities under field conditions.

4. Conclusions

- PE pipe was rapidly permeated when exposed to either free gasoline or aqueous gasoline solutions.
- Of the five individual BTEX compounds of interest, benzene was the first compound to be detected in the pipe-water. Once the breakthrough occurred, the level of benzene in pipe-water rapidly exceeded its MCL. Benzene and toluene accounted for nearly all the total BTEX that permeated into the pipe-water.
- The steady permeation rates of benzene and toluene were strongly dependent on the bulk concentration in soil pore water. Empirical equations were derived to give an accurate correlation with the experimental data. The equations can be used to predict the external concentration which will result in exceeding the MCL for benzene or toluene in pipe-water after a period of contamination exposure.
- The diffusion coefficients of benzene and toluene were strongly dependent on the bulk concentration in soil pore water. The concentration-dependent diffusion coefficient was found to increase logarithmically with the bulk aqueous concentration.
- Under identical initial conditions, PE pipe buried in soil of high organic matter was permeated to a lesser extent than a pipe buried in a soil of low organic matter. However, the organic content of a soil will not influence permeation rates once the soil has been saturated with the contaminant.

References

Chiou, C.T.; Peters, L.J. 1981. Soil-water equilibria for nonionic organic compounds. *Science* 213, 683-684.

Cline, P. V.; Delfino, J. J.; Rao, P. S. C. 1991. Partitioning of aromatic constituents into water from gasoline and other complex mixtures. *Environ. Sci. Technol.* 25, 914-920.

Holsen, T. M.; Park, J. K.; Jenkins, D.; Selleck, R. E. 1991 (a). Contamination of potable water by permeation of plastic pipe. *Journal AWWA* 83, 53-56.

Holsen, T.M.; Park, J. K.; Bontoux, L.; Jenkins, D.; Selleck, R.E. 1991(b). The effect of soils on the permeation of plastic pipes by organic chemicals. *Journal AWWA* 83, 85-91.

Naylor, T. deV. 1989. Permeation properties. In: Colin Booth, Colin Price (Eds.), *Comprehensive Polymer Science*, 2, Pergamon Press, Oxford, UK, pp. 643-668.

Park, J.K.; Bontoux, L.; Jenkins, D.; Selleck, R.E. 1991. Permeation of polybutylene pipe and gasket material by organic chemicals. *Journal AWWA* 83, 71-78.

Thompson C.; Jenkins, D. Review of water industry plastic pipe practices. 1987. Report to AWWA Research Foundation. Dept. of Civil Engineering, University of California, Berkeley.

Vonk M. W.1985. Permeation of organic compounds through pipe materials, Pub. No. 85, KIWA, Neuwegein, Netherlands.

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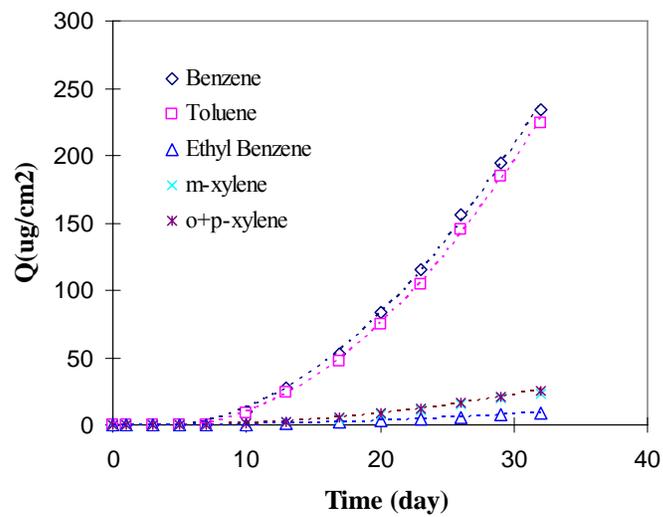
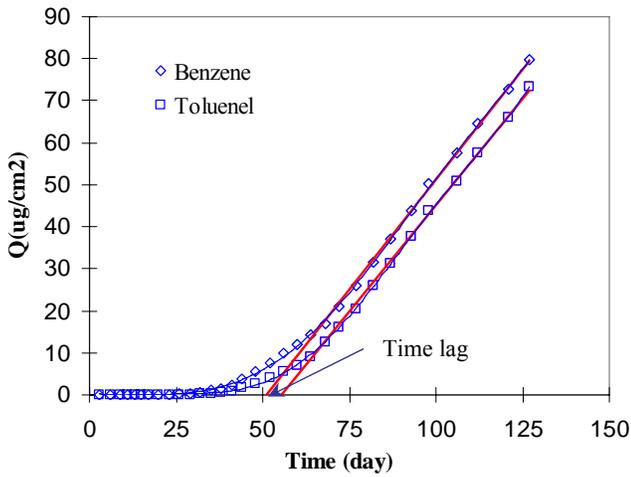
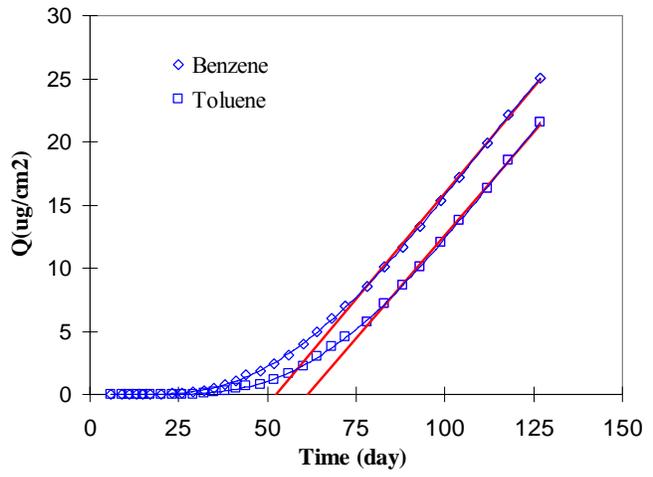


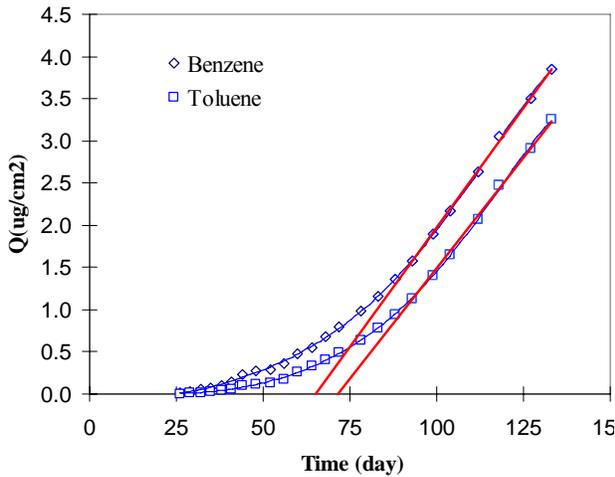
Figure 1 Cumulative permeation fluxes for BTEX compounds in PE pipe exposed to gasoline.
 Benzene, 19.8 g/L; toluene, 75.9 g/L; ethylbenzene, 14.7 g/L; m-xylene, 33.7 g/L; o+p xylene, 32.5 g/L.



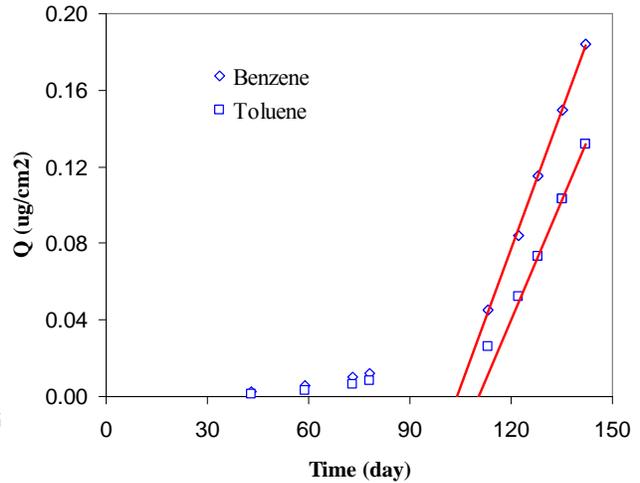
Soil pore water: total BTEX, 136.6± 13.0 mg/L;
benzene, 67.5±4.9 mg/L; toluene, 56.2 ± 4.9 mg/L;
~100% saturated with gasoline.



Soil pore water: total BTEX, 63.9± 5.7 mg/L;
benzene, 31.2±2.9 mg/L; toluene, 26.3 ±2.4 mg/L;
~50% saturated with gasoline.



Soil pore water: total BTEX, 12.6± 1.1 mg/L;
benzene, 6.0±0.6 mg/L; toluene, 5.2 ±0.4 mg/L;
~10% saturated with gasoline



Soil pore water: total BTEX, ~1.2 mg/L;
benzene, ~0.6 mg/L; toluene, ~0.5 mg/L;
~ 1% saturated with gasoline.

Figure 2 Cumulative permeation fluxes for benzene and toluene in PE experiments simulating water-saturated field conditions

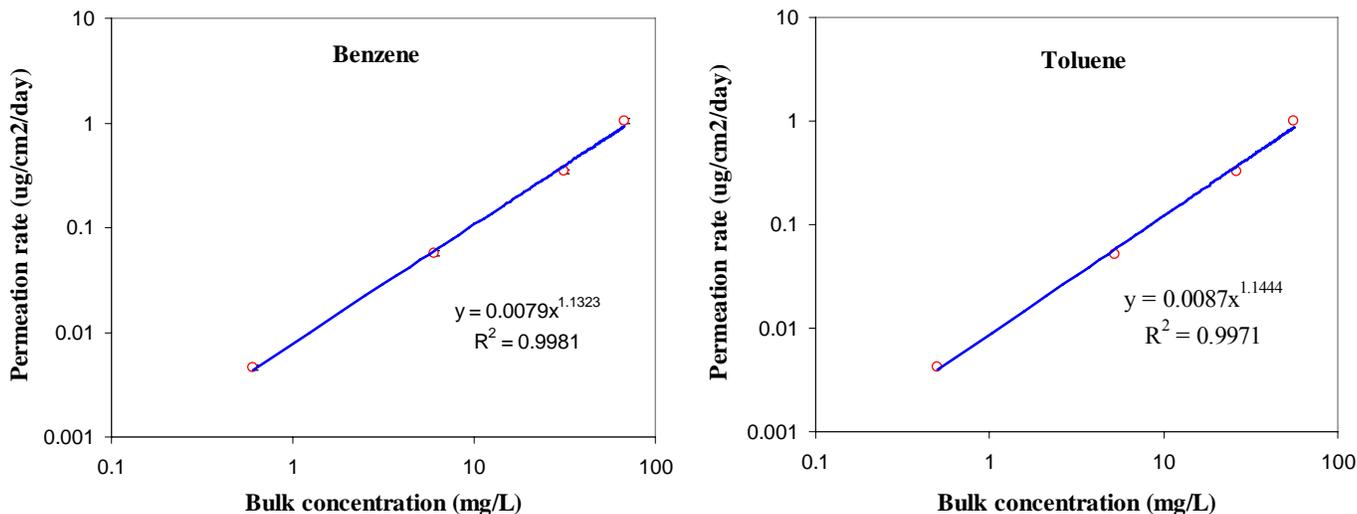


Figure 3 Correlation between the steady permeation rate and the external bulk concentration in soil pore water for benzene and toluene

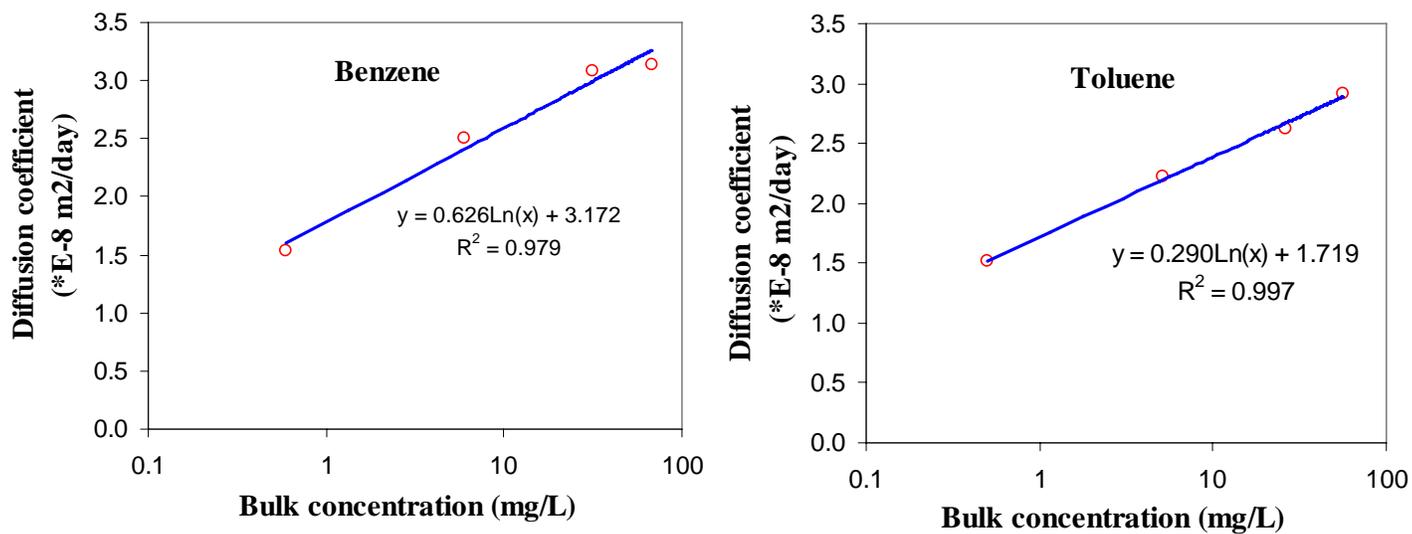


Figure 4 Correlation between the diffusion coefficient and the external bulk concentration in soil pore water for benzene and toluene

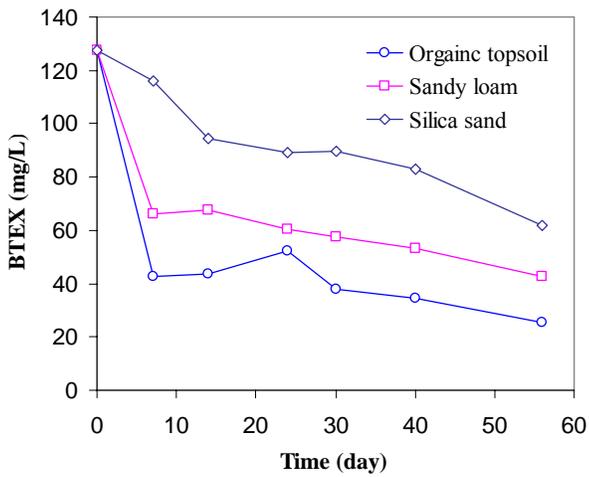


Figure 5 Change of concentration of total BTEX in soil pore water with exposure time

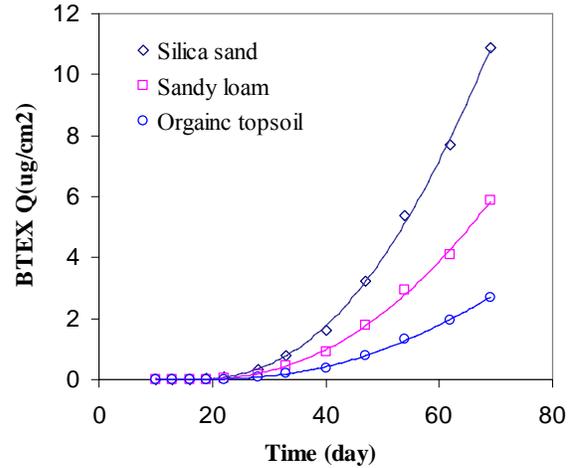


Figure 6 Cumulative permeation flux of total BTEX in pipes

Table 1 Estimated external bulk concentration which would result in exceeding the MCL for benzene or toluene in pipe-water after a period of water stagnation

Benzene			Toluene		
MCL (µg/L)	Exposure time (days)	External bulk concentration (µg/L)	MCL (µg/L)	Exposure time (days)	External bulk concentration (mg/L)
5	1	387.7	1000	1	36.9
5	7	69.5	1000	7	6.7
5	14	37.7	1000	14	3.7
5	28	20.4	1000	28	2.0