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Impacts of environmental conditions on the sorption of volatile organic compounds onto tire powder

Dong I. Oh [a], Kyongphile Nam [b], Jae W. Park [c], Jee H. Khim [d],
Yong K. Kim [b], Jae Y. Kim [b],*

[a] *Division of R&D Planning and Management, Korea Institute of Environmental Science and Technology, Seoul, Republic of Korea*
[b] *School of Civil, Urban & Geosystem Engineering, College of Engineering, Seoul National University,
Gwanak-Ku, 151-742 Seoul, Republic of Korea*
[c] *Department of Civil Engineering, Hanyang University, Seoul, Republic of Korea*
[d] *Department of Civil & Environmental Engineering, Korea University, Seoul, Republic of Korea*

Abstract

A series of batch tests were performed and the impacts of environmental conditions and phase change on the sorption of volatile organic compounds (VOCs) were investigated. Benzene, trichloroethylene, tetrachloroethylene, and ethylbenzene were selected as target VOCs. Sorption of VOCs onto tire powder was well demonstrated by a linear-partitioning model. Water–tire partition coefficients of VOCs (not tested in this study) could be estimated using a logarithmic relationship between observed water–tire partition coefficients and octanol–water partition coefficients of the VOCs tested. The target VOCs did not seem to compete with other VOCs significantly when sorbed onto the tire powder for the range of concentrations tested. The influence of environmental conditions, such as pH and ionic strength also did not seem to be significant. Water–tire partition coefficients of benzene, trichloroethylene, tetrachloroethylene, and ethylbenzene decreased as the sorbent dosage increased. However, they showed stable values when the sorbent dosage was greater than 10 g/L. Air–tire partition coefficient could be extrapolated from Henry's law constants and water–tire partition coefficient of VOCs.
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Keywords: Batch test; Partition coefficients; Sorption; Tire powder; Volatile organic compounds

1. Introduction

In the Republic of Korea, it was reported that 699,214 t of volatile organic compounds (VOCs) were emitted to the atmosphere from oil stations and industries such as printing and coating facilities in 2001 [1]. Due to the problems caused by the presence of VOCs, there is an increasing interest in developing new methods to decrease the cost of VOC removal.

The disposal of scrap tires also poses a serious environmental problem in Korea. Over 23.2 million tires were discarded in 2003 [2]. Scrap tires cannot be easily disposed of due to their poor compressibility, potential combustibility, and associated toxic fumes [3]. For these reasons, application technologies to recycle and reuse large volumes of scrap tires are required. Since the main constituents of tire materials were synthetic rubber, natural rubber, and carbon black [4], scrap tires can sorb significant amounts of VOCs in the aqueous phase [5]. Tire powder may be a possible candidate for both a sorption medium in the permeable reactive barrier and a supplemental aggregate in the slurry cutoff wall for the treatment of the VOC-contaminated groundwater [6–8]. Also, scrap tires can be used for gaseous VOC removal as a filter medium [9,10].

The objectives of this study were (1) to examine the sorption behavior of VOCs onto tire powder in the aqueous and gaseous phase, and (2) to evaluate the impacts of environmental conditions (i.e., pH, ionic strength, and tire powder/solution ratio).

2. Materials and methods

2.1. Sorbates and sorbents

Benzene (BZ), ethylbenzene (EB), tetrachloroethylene (PCE), and trichloroethylene (TCE) were selected for testing

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* Corresponding author. Tel.: +82 2 880 8364; fax: +82 2 889 0032.
E-mail address: jaeykim@snu.ac.kr (J.Y. Kim).

Table 1
Properties of volatile organic compounds tested at 20 °C [11]

Compound	Molecular weight (g/mol)	Specific gravity (dimensionless)	Aqueous solubility (mg/L)	log K_{ow}[a]
Benzene	78.11	0.789	1780	2.13
Trichloroethylene	131.50	1.460	1100[b]	2.42
Tetrachloroethylene	165.83	1.626	150[b]	2.60
Ethylbenzene	106.17	0.867	152	3.15

[a] The octanol–water partition coefficient.
[b] At 25 °C.

and their properties were summarized in Table 1. The liquid sorbates were obtained from Sigma–Aldrich, and the purity of these sorbates was 99% or higher. Target VOCs were analyzed using a gas chromatograph (600D; Young Lin Instrument Co., Korea) equipped with an HP-FFAP capillary column (50 m × 0.25 mm × 0.17 µm) and a flame ionization detector (FID). An aliquot of 1.0 µL liquid sample was directly injected into the column using a 10 µL gas-tight syringe. Nitrogen gas was used as a carrier with a flow rate of 2.0 mL/min. The gas flow to the FID was combined with make-up gas (N$_2$ at 26 mL/min), hydrogen (30 mL/min), and air (300 mL/min). The oven temperature was held at 65 °C. The injection port and the detector temperatures were held at 280 and 300 °C, respectively. The relative standard deviations of the sample analyses ranged from 3.8% for benzene and 12.5% for PCE.

Tire powder was obtained from the Korea Environment & Resources Corporation (Incheon, Korea). Tire powder was sieved to obtain uniform particles using two sieves with openings measuring 0.6 and 1.18 mm and was air-dried without any pretreatment. The tire powder was then stored in a desiccator. The particle size of tire powder was estimated to be 0.84 mm, obtained by taking the geometric mean of the sieve openings.

2.2. Batch test in aqueous phase

Batch tests were conducted using 40 mL screw-capped glass vials with Teflon-lined septa. VOC-containing solutions were added to the glass vial with tire powder. The volume of solution and amount of the tire powder applied were all measured by a weight scale. A VOC-containing solution was prepared by combining a few microliters of pure VOC liquid to 1 L of deionized water and stirring overnight. These tests were conducted in a constant temperature room (20 ± 1 °C) using 10–100 mg/L of the initial concentrations of the VOC solution. Sodium azide (NaN$_3$), with a concentration of 0.05% (by weight), was added in order to inhibit microbial activity in the VOC-containing solution. The vials were capped immediately after adding the VOC-containing solution and then tumbled end-to-end at 10 rpm to achieve equilibrium.

A preliminary test was conducted to determine the loss of vaporized VOCs during the batch test and to estimate the time required for the sorption equilibrium of the VOCs onto the tire powder. The overall loss of the VOCs by experimental apparatus and procedures was less than 5% after 7 days. Control vials without sorbents were used to account for any loss of VOCs and the corrected concentrations were used as initial VOC concentrations.

The change in VOC concentration in the aqueous phase was monitored to estimate the required time for VOC sorption equilibrium onto tire powder. After 24 h, there was no significant change (less than 5%) in the VOC concentration, indicating that a contact time of 24 h was sufficient enough for reaching equilibrium. In this study, a 72-h contact time was adopted to ensure sorption equilibrium. At the end of tumbling, 1 mL of supernatant was sampled and analyzed by GC/FID.

Sorption isotherms were developed with the following equation:

$$C_s = \frac{(C_i - C_e)V_l}{M_s} \tag{1}$$

where C_s is the sorbed concentration of a VOC (mg/kg); V_l the added VOC solution volume (mL); M_s the dry weight of tire powder (g); C_i the initial VOC concentration from control vials (mg/L); and C_e is the equilibrium concentration of the VOC (mg/L).

The water–tire partition coefficient, K_l, was calculated from linear regression of sorbed concentration versus aqueous equilibrium concentration:

$$C_s = K_l C_e \tag{2}$$

VOC sorption onto tire powder was also examined using Freundlich relationship:

$$C_s = K_F C_e^N \tag{3}$$

where K_F is the Freundlich adsorption coefficient and N is the Freundlich exponent.

2.3. Influence of environmental conditions

In order to evaluate the effect of the presence of other VOCs on the sorption of a single VOC onto tire powder, the partition coefficients obtained from the single-solute batch tests were compared with those from the multi-solute batch tests. The values of the water–tire partition coefficient observed at three different levels of pHs (5, 7, and 9) and two levels of ionic strengths (0 and 100 mM) were compared with each other. The initial pH was adjusted with 0.1 M sulfuric acid and 0.1 M sodium hydroxide solutions. Another series of batch tests were performed to evaluate the effect of sorbent concentration on measured partition coefficients from approximately 0.5 to 60 g/L sorbent dosages.

2.4. Batch test in gaseous phase

Additional sorption tests were performed using 40 mL screw-capped Pyrex tubes with a Mininert® valve to determine the sorption constant of VOCs in the gaseous phase. The procedures used in the test include: (1) add 0.5 g of tire powder to a 40-mL Mininert® screw cap tubes, (2) spike the tire powder with a pure VOC liquid. Spiking volume was chosen so that the normalized vapor pressure (P/P_0) ranged from 0.1 to 0.9, where P is the vapor pressure and P_0 is the saturated vapor pressure of VOC, (3) tumble the tubes end-over-end at 20 °C, and (4) sample the headspace gas and analyze the gaseous VOCs by using a gas chromatograph. Control tubes, which did not contain tire powder, were also tested to account for the losses of VOCs during experiment. The gaseous concentration of VOCs exhibited no change after 12 h, indicating that a contact time of 12 h was sufficient to reach sorption equilibrium. In the gaseous phase, sorption tests were performed for 24 h to ensure sorption equilibrium. Equilibrium gaseous concentration of VOCs was low enough for gas–tire sorption to follow a linear isotherm. Dhingra and Marand [12] and Bo et al. [13] provided evidence of the linear isotherms of organic compounds at low concentrations for a rubbery polymer. Gas–tire partition coefficient can be determined as follows:

$$C_t = K_g P_e \qquad (4)$$

where K_g is the gas–tire partition coefficient of a VOC (mg/(kg atm)); P_e the equilibrium vapor pressure of the VOC in the gaseous phase (atm); and C_t is the sorbed amount of the VOC in the tire phase (mg/kg).

3. Results and discussion

3.1. Equilibrium sorption isotherm

Fig. 1 illustrates the isotherms for the sorption of BZ and TCE onto tire powder. The sorption isotherms of BZ and TCE onto tire powder were linear in the range of concentration tested. Previous studies have shown that organic chemicals are readily partitioned out of an aqueous phase and sorb onto an organic matter of soil or sediment [14–16]. Since the tire powder is mainly composed of synthetic rubber (e.g. SBR, styrene butadiene rubber), sorption of VOCs onto tire powder from aqueous phase is likely to be controlled by partitioning. The linear partition coefficients (K_l) and Freundlich parameters (K_F and N) of tested VOCs are shown in Table 2. Since the N values for target VOCs is sufficiently close to 1.0, the applicability of linear sorption was confirmed in this

Table 2
Sorption isotherm of tested compounds (single-solute)

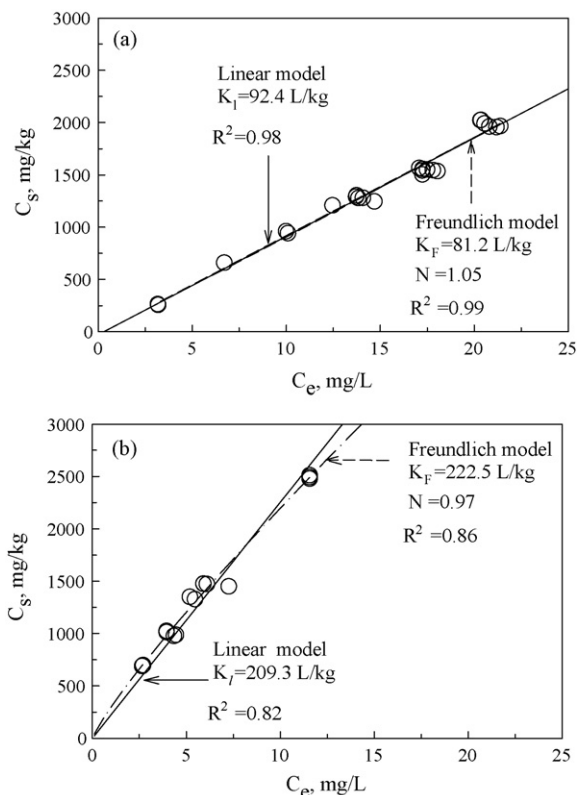| Compound	Linear model		Freundlich model		
	K_l (L/kg)	R^2	K_F (L/kg)	N	R^2
Benzene	92.4	0.98	81.2	1.05	0.99
Trichloroethylene	209.3	0.82	222.5	0.97	0.86
Tetrachloroethylene	347.8	0.81	478.2	0.87	0.89
Ethylbenzene	1157.6	0.91	1201.7	0.95	0.91

Fig. 1. Linear and Freundlich isotherms of (a) BZ and (b) TCE onto tire powder.

study. Similar observations have been reported for naphthalene (NPT) and toluene (TOL) [17].

As shown in Table 2, the observed partition coefficient for EB was the highest among target VOCs. This phenomenon is supported by the fact that EB has the lowest solubility (S) in water and highest octanol–water partition coefficients (K_{ow}) among the tested compounds. The K_l values of target VOCs varied in the following order: EB > PCE > TCE > BZ.

3.2. Linear free energy relationship between K_{ow} and K_l

The partitioning of nonionic organic compounds between water and natural organic phases occurs due to the hydrophobicity of the compounds. This hydrophobicity can be expressed by the K_{ow}. This parameter can be used in one-parameter linear free energy relationships (LFERs) to estimate the unknown partition coefficients between two phases such as tire powder and water [18]. Fig. 2 shows the logarithmic linear relationship between the water–tire partition coefficient and the K_{ow}s of target VOCs. The regression of $\log K_l$ with $\log K_{ow}$ gives the following:

$$\log K_l = 1.01 \log K_{ow} - 0.18 \quad (R^2 = 0.94) \qquad (5)$$

Therefore, the water–tire partition coefficients of untested nonionic organic compounds onto tire powder can be estimated using Eq. (5). A number of researchers have investigated the sorption capacities of tire chips (or powder) with respect to TOL and NPT [17], BZ and o-xylene (o-XYL) [5], phenol and cresol [7]. Fig. 2 presents the sorption data of organic chemicals as reported by several authors and this study. The linear correla-
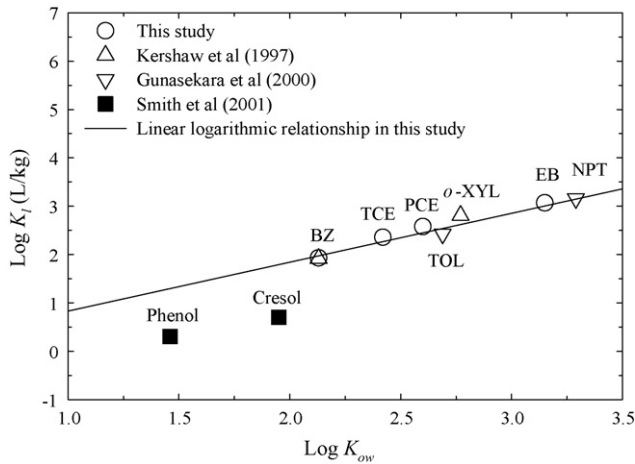
Fig. 2. Relationship between the octanol–water partition coefficient and water–tire partition coefficient of various organic compounds in the several studies.

tion between $\log K_{ow}$ and $\log K_l$ values (Eq. (5)) was applicable to the untested organic compounds (see Fig. 2). This result indicates that water–tire partition coefficients of organic compounds such as chloroform (CF), 1,1,1-trichloroethane (1,1,1-TCA), BZ, TOL, EB, and o-XYL in the aqueous phase can be estimated by Eq. (5). Only water–tire partition coefficients for phenol and cresol were overestimated. This is caused by the relatively high solubility in water of phenol and cresol because the –OH group can form hydrogen bonds with water, e.g. phenol (8700 mg/L at 25 °C) and cresol (2300 mg/L at 25 °C). In other words, the lower water–tire partition coefficients of phenol and cresol can be explained by their high hydrophilicity; sorption behavior of phenol and cresol onto tire rubber cannot be explained mainly by the hydrophobic interaction.

3.3. Effect of the presence of other VOCs

Competition among the target VOCs was determined by measuring the water–tire partition coefficients of each compound under various multi-solute concentrations, which are given in Table 3. According to the statistical analyses, the partition coefficients measured under two conditions were not significantly different at the 95% confidence interval with the

Table 3
Comparison of partition coefficients measured in single-solute and multi-solute sorption tests

| Compound | Water–tire partition coefficient (L/kg) | | | | | |
| | Multi-solute | | | Single-solute | | |
	x[a]	σ[b]	n[c]	x[a]	σ[b]	n[c]
Benzene	91.7	5.2	24	85.1	8.4	12
Trichloroethylene	201.9	41.3	12	226.7	25.6	12
Tetrachloroethylene	358.0	59.4	22	377.6	36.7	10
Ethylbenzene	1171.0	70.1	12	1165.1	78.5	16

[a] Average.
[b] Standard deviation.
[c] Number of observations.

Table 4
Results of statistical analysis between single-solute and multi-solute sorption tests (H_0: $K_{l,single} = K_{l,multi}$)

Compound	Degree of freedom	t (0.025, d.f.)	t value	Decision
Benzene	34	2.034	2.866	Reject H_0
Trichloroethylene	22	2.074	1.768	Do not reject H_0
Tetrachloroethylene	30	2.042	0.958	Do not reject H_0
Ethylbenzene	26	2.056	0.206	Do not reject H_0

exception of BZ (Table 4). Not including BZ, the data showed that the target VOCs do not seem to compete with each other when sorbed onto tire powder for the range of concentrations tested. This indicates that partitioning is the dominant sorption mechanism. Our results are consistent with the observation that the individual isotherms for atrazine, prometon, and TCE in the rubbery polymers such as medium-density polyethylene (MDPE), cellulose, and chitin are linear, and there is no competition between atrazine and TCE [19]. Joo et al. [20] investigated the mass transfer of 10 organic compounds such as BZ, EB, TOL, TCE, PCE, and so on into high-density polyethylene (HDPE) geomembrane. They reported that organic compounds do not significantly compete with each other during the sorption into the HDPE geomembrane in dilute solutions with individual organic chemical concentrations below 0.64 mM.

For the diverged case of BZ, sorption experiments were carried out in triplicate at a constant initial concentration of BZ (40 mg/L) varying the concentration of EB from 20 to 100 mg/L. All vials contained the identical amount of tire powder (0.5 g) and VOC solution (40 mL), and the results are presented in Fig. 3. At relatively low initial concentrations of EB (less than approximately 48 mg/L), EB reduces the activity of BZ in aqueous phase and promotes the sorption of BZ; however, as the concentration exceeds approximately 48 mg/L, the EB competes with BZ and suppresses the sorption of BZ. Further studies are required to draw any significant conclusions on the competitive sorption between BZ and EB onto tire powder.
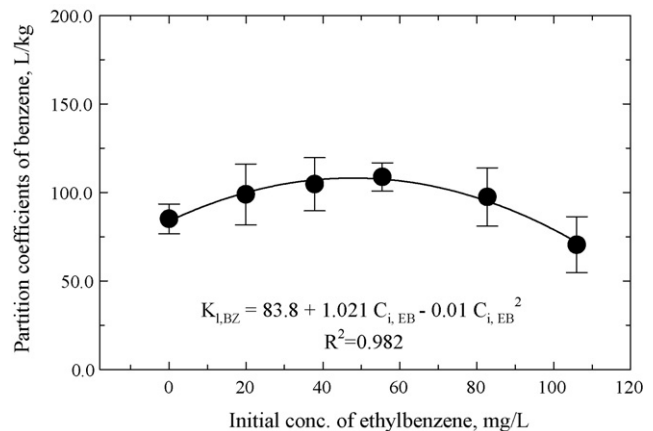

Fig. 3. Effect of ethylbenzene on sorption of benzene. Solid line is the best-fit nonlinear regression; $K_{l,BZ}$ is the water–tire partition coefficient of benzene; $C_{i,EB}$ is the initial concentration of ethylbenzene in solution.

3.4. Effect of initial pH and ionic strength

Batch tests were conducted to investigate the effects of pH and ionic strength. Values of partition coefficients were observed at three different pH levels (5, 7, and 9) and two different levels of ionic strength (0 and 100 mM). Due to greater analytical errors, PCE showed more scattered K_1 values compared with other compounds.

Means [21] studied the influence of salinity upon sediment–water partitioning of aromatic hydrocarbons. He observed that sorption/desorption constants were significantly increased with increasing salinity. He suggested that increase in sorption with salinity is the results of "salting out" of hydrophobic organic chemicals. The term "salting out" refers to the decrease in aqueous solubility of neutral solute with increasing salinity [22]. Similar observations have been reported by Zhao et al. [23]. Rao and Asolekar [24] studied that the effect of ionic strength on sorption of chlorinated benzenes and phenols at the sediment–water interface. They found that ionic strength had a strong effect for ionizable chemicals such as phenol as compared to that of either polarisable chemicals such as chlorobenzene or non-polar chemicals such as benzene.

The analysis of variance (ANOVA) between the results of batch tests conducted at three different pH levels and with inorganic compounds was presented in Table 5. The hypothesis (H_0), that the average values of K_1s under different conditions were identical to each other, was not rejected for BZ, TCE, and EB. This means that the pH and ionic strength do not significantly influence organic compound sorption onto tire rubber.

3.5. Effect of tire powder/solution ratio

Batch tests were performed with various sorbent dosages to evaluate the effect of the sorbent concentration on the sorption behavior. In soil–water system, several studies reported that the partition coefficients varied when different sorbent dosages were applied [25–27]. This phenomenon in the soil–water system is known as the "solids effect". Nonsettling micro-particles (NSPs) are recognized as the primary factor related to the solids effect in soil–water systems [27]. Little information is
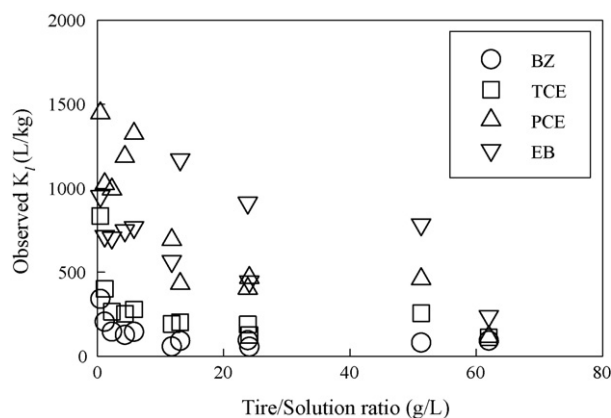

Fig. 4. Observed K_1s for BZ, TCE, PCE, and EB at varying tire powder/solution ratio.

available on the sorption of volatile organic compounds in tire powder–water system. Fig. 4 shows the dependence of measured partition coefficients on the tire powder/solution ratio for the four different VOCs. Water–tire partition coefficients of BZ, PCE, TCE, and EB decreased as the amount of tire powder increased until leveling off at relatively high sorbent dosages greater than approximately 10 g/L. The "solids effect" cannot be attributable to nonsettling micro-particles or dissolved organic carbon (DOC). Since the particle size of tire powder ranged from 0.6 to 1.18 mm, the micro-particles were not present in tire powder–water system. At the present time, the reason for solids effect observed in the present study is not clear. But according to Schwarzenbach et al. [28], the dissolved fraction of a VOC in a system can be related to both solid–water ratio and partition coefficient [28]:

$$f_w = \frac{C_e V_w}{C_e V_w + C_s M_s}$$
$$= \frac{V_w}{V_w + K_1 M_s} = \frac{1}{1 + (M_s/V_w)K_1} = \frac{1}{1 + r_s K_1} \quad (6)$$

Thus

$$K_1 = \frac{f_s}{f_w} \frac{1}{r_s} \quad (7)$$

Table 5
Analysis of variance (ANOVA) between the effects of pH and ionic strength on K_1s

Compound	Source of variation	Degree of freedom	Sum of squares	Mean squares	F	$F(k\text{-}1,60)$	Decision
	Between treatment	3	3557.0	1185.7	2.50	2.76	Not rejected H_0
Benzene	Within treatment	75	35538.0	473.8			
	Total	78	39095.0				
	Between treatment	3	6076.5	2025.5	1.06	2.83	Not rejected H_0
Trichloroethylene	Within treatment	47	90044.9	1915.9			
	Total	50	96121.4				
	Between treatment	3	487062.8	162354.3	14.88	2.84	Rejected H_0
Tetrachloroethylene	Within treatment	39	425401.7	10907.7			
	Total	42	912464.5				
	Between treatment	3	264689.2	88229.7	2.16	2.83	Not rejected H_0
Ethylbenzene	Within treatment	45	1837552.0	40834.5			
	Total	48	2102241.2				

where f_w is the dissolved fraction of a VOC in a system; f_s the sorbed fraction of a VOC in a system; V_w the volume of water (L); M_s the mass of solids (kg); and r_s is the solid–water ratio (kg/L).

Therefore, the solid–water ratio has a negative effect on the solid–water partition coefficients. According to the results obtained in this study, we suggest that higher tire powder dosages (greater than 10 g/L in this study) should be applied to obtain useful experimental data when the fate of VOCs in a tire powder/solution system such as a permeable reactive barrier or slurry cutoff wall is analyzed and predicted.

3.6. Sorption in the gaseous phase

Sorption of gaseous organic chemical involves a two-step thermodynamic process in polymers: (1) condensation of the gaseous organic chemical to a liquid-like density and (2) mixing of the pure compressed organic chemical with the polymer segments [29]. The first step is governed by condensability of organic chemical, and the second step depends on polymer–organic chemical interactions. For organic chemicals that interact with the polymer by means of van der Waals forces at the molecular level, their condensability plays a key role in sorption process. The critical temperature (T_c) of organic chemical can be a measure of condensability. The term "critical temperature" refers to the temperature above which unique liquid and gas phases do not exist. As the critical temperature is approached, the properties of the gas and liquid phases become identical. Above the critical temperature, there is only one phase. Shah et al. [30] reported that solubility (same as gas–particle partition coefficients) of organic chemical in polymer was correlated well with the square of reciprocal reduced temperature, $(T_c/T)^2$, where T is the actual temperature in experiment. Critical temperatures of target VOCs are BZ (562.2 K), TCE (572 K), PCE (620.2 K), and EB (617.2 K). The dependence of the gas–tire partition coefficient, K_g, on $(T_c/T)^2$ is given by the following equation:

$$\ln K_g = n\left(\frac{T_c}{T}\right)^2 + m \tag{8}$$

A plot of $(T_c/T)^2$ versus $\ln K_g$ yields a straight line with the slope n and intercept m. Fig. 5 presents the gas–tire partition coefficients of VOCs as a function of $(T_c/T)^2$. A good correlation between gas–tire partition coefficients and $(T_c/T)^2$ was
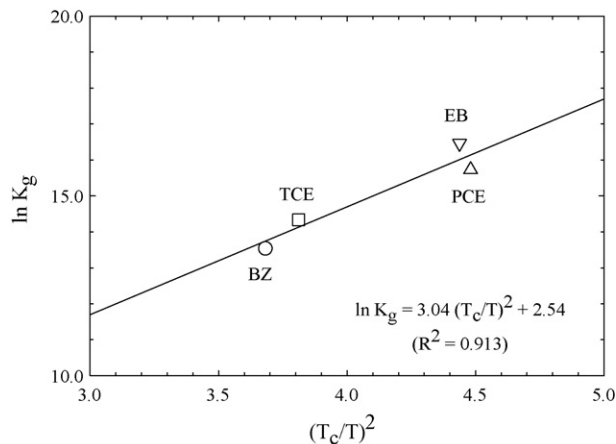

Fig. 5. Correlation of tire–air partition coefficients with the square of reciprocal reduced temperature $(T_c/T)^2$.

observed. This indicates that sorption process of VOCs onto tire powder in gaseous phase is governed mainly by their condensability.

It is possible to estimate the air–tire partition coefficient by extrapolating from Henry's law constants and water–tire partition coefficient:

$$K_{g,est} = \frac{C_A^{tire}}{C_A^{air}} = \frac{K_1 C_A^{water}}{K_H C_A^{water}} = \frac{K_1}{K_H} \tag{9}$$

where $K_{g,est}$ is the estimated air–tire partition coefficient of a VOC, C_A^{tire}, C_A^{air}, and C_A^{water} are the equilibrium concentration of the VOC in the tire, air, and water, respectively; and K_H is the Henry's law constant of the VOC (L atm/mg).

Both observed and estimated air–tire partition coefficients of the target organic compounds are presented in Table 6. The ratios of $K_{g,obs}$ and $K_{g,est}$ ranged from 0.6 to 2.3. This result shows that the air–tire partition coefficient of VOCs can be extrapolated from water–tire partition coefficients and the Henry's law constant using Eq. (9). Also, it is more than likely that sorption of VOCs onto tire powder in the gaseous phase is controlled mainly by partitioning. In the case of PCE, larger ratio values were obtained. It seems that the air–tire partitioning coefficient of PCE could not be accurately determined due to scattering of concentration data.

Table 6
Comparison of observed and estimated gas–tire partition coefficients

Compound	K_H[a] ($\times 10^{-5}$ L atm/mg)	$K_{g,obs}$[b] ($\times 10^5$ mg/(kg atm))	$K_{g,est}$[c] ($\times 10^5$ mg/(kg atm))	$K_{g,obs}/K_{g,est}$
Benzene	6.97	7.58 ± 1.70 (20)[d]	13.15	0.58 ± 0.13
Trichloroethylene	6.81	16.87 ± 5.82 (20)	29.64	0.57 ± 0.20
Tetrachloroethylene	12.07	67.77 ± 21.77 (16)	29.66	2.28 ± 0.73
Ethylbenzene	7.46	140.65 ± 38.82 (14)	157.01	0.90 ± 0.25

[a] Henry's law constant.
[b] Observed gas–tire partition coefficients.
[c] Estimated gas–tire partition coefficients by using Eq. (6).
[d] Values in parentheses are the number of observations.

4. Conclusions

The sorption behavior of volatile organic compounds onto tire powder and the impacts of environmental conditions and phase change on the sorption of volatile organic compounds have been studied. Based on the analyses of the experimental results, it may be concluded that:

- Sorption of volatile organic compounds onto tire powder was well demonstrated by a linear relationship, indicating that linear partitioning is a dominant mechanism. The partition coefficients of untested nonionic organic compounds can be estimated using a one-parameter linear free energy relationship, i.e., $\log K_1$–$\log K_{ow}$.
- Target volatile organic compounds did not appear to compete with each other significantly in the sorption onto tire powder for the range of concentrations tested. The influences of pH and ionic strength on the sorption of volatile organic compounds onto tire powder do not seem to be significant.
- The water–tire partition coefficient value depended on sorbent dosage (or tire:solution ratio) conditions. Thus, for practical applications tire powder dosages must be designed.
- Sorption of VOCs in the gaseous phase appears to be governed by partitioning. The air–tire partition coefficient could be extrapolated from Henry's law constants and the water–tire partition coefficient of volatile organic compounds.

Acknowledgements

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