Adsorption of hydrocarbons by clay minerals from gasoline

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Abstract

Adsorption of six hydrocarbons (BTEXs – benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene, and *o*-xylene) from gasoline by three clay minerals (montmorillonite, illite and kaolinite) was studied using the batch equilibrium method. The clays were treated to remove organic matter before use. Four concentrations of gasoline (10, 50, 100, 150 µl/l) in water were used to get a range in concentration of the BTEXs (0.22–10.65 µl/l). Freundlich adsorption coefficient (K) for each hydrocarbon was consistently higher with montmorillonite than with illite and kaolinite. The presence of competing species resulted in a decrease of K values for toluene from 2.42 from a single solute, to 0.81 for the hydrocarbons mixture (containing benzene + toluene + xylenes) and to 0.69 for gasoline.

1. Introduction

The contamination of soil and groundwater by leaking underground storage tanks that contain gasoline is an environmental issue both for the public and researchers in the USA. Of the estimated 1.5–10 million gasoline storage tanks in US, approximately 85% are made of steel with no corrosion protection and were buried over 20 years ago [1]. Furthermore, 10–35% of those tanks are leaking into soil and aquifers [2]. Contaminants in gasoline that are major health concerns include benzene, toluene, xylenes, and ethylbenzene, and additives. Benzene is suspected as a carcinogen, and other components of gasoline may cause a variety of toxic effects [3,4].

A survey by the US EPA found that more than 60% of 12,444 releases were less than 500 gallons each [1]. Small amounts of leaking gasoline may not cause contamination of groundwater because of volatilization and/or retardation of gasoline hydrocarbons by soil. Perlinger and Eisenreich [5] pointed out that the adsorption of organic contaminants to clay minerals was the major mechanism by which the

transport of the hydrocarbons was retarded, because other natural processes (e.g. biodegradation, photolysis, volatilization) tend to occur at slower rates or not at all in the subsurface soil. Hydrocarbon adsorption using soil constituents or aquifer materials in single-component studies such as benzene [6], toluene [7], xylenes [6] and ethylbenzene [8] is well documented. Gasoline is, however, a mixture of hydrocarbons, each with unique properties, that may compete with each other for adsorption sites on clay surfaces. Information on multicomponent adsorption of gasoline hydrocarbons is not available in the literature. Most studies used soils with organic carbon content > 1% [6, 8, 9]; however, organic carbon content of the deep subsoil and aquifer material is usually lower than 0.1% [1, 5]. Banerjee et al. [10] and Schwille [11] suggested that the extent of adsorption of organic pollutants in deep soil and aquifer materials would not be controlled by soil organic matter content. Therefore, a study of the adsorption of hydrocarbons in gasoline on clay minerals without organic matter is necessary to understand the fate of hydrocarbon components from leaking storage tanks in the subsoil.

The objectives of this study were (1) to measure the adsorption of hydrocarbons in gasoline on three clay minerals and (2) to evaluate any competitive interactions between these hydrocarbons to understand better the fate of leaking hydrocarbons.

2. Theory

One of the assumption for the adsorption of gasoline hydrocarbons by a soil/clay surface is that an equilibrium is established between the gasoline components immiscible with water, aqueous hydrocarbons in solution and the hydrocarbons adsorbed on the clay surfaces:

$$C_g^i \rightleftarrows C_e^i \rightleftarrows C_s^i, \tag{1}$$

where C_g^i is the concentration of hydrocarbon i in gasoline; C_e^i is the concentration of hydrocarbon i in the solution; and C_s^i is the concentration of hydrocarbon i adsorbed by the clay. The maximum equilibrium concentration (C_m) of an individual hydrocarbon in water can be estimated, by Raoult's Law, from the water solubility of the pure compound and its fraction in gasoline when a mass of gasoline is added (assuming that both the gasoline and the hydrocarbons behave as ideal solutions and have unit activity coefficients) [12]:

$$C_m^i = S^i f_g^i, \tag{2}$$

where C_m^i is the maximum concentration of hydrocarbon i in the aqueous phase; S^i is the solubility of pure hydrocarbon i in water; and f_g^i is the fraction of the compound i in gasoline. When there is no gasoline (vapor) phase $(C_g^i = 0)$ and equilibrium concentration of individual hydrocarbons is less than the maximum C_m^i, then the hydrocarbons may only partition between the aqueous phase and the adsorbed phase:

$$C_e^i \rightleftarrows C_s^i. \tag{3}$$

The relationship between an adsorbed chemical and that in solution is usually expressed as Freundlich Isotherm [13,14] shown as an equation:

$$\log C_s = \log K + N \log C_e \tag{4}$$

where K is the adsorption coefficient, N is an exponent and an indication of whether adsorption remains constant ($N = 1$), decreases ($N < 1$) or increases ($N > 1$) with increasing adsorbate concentration.

3. Materials and methods

3.1. Preparation of clays and gasoline

Three types of clay minerals (kaolinite – Washington Co., GA, illite – Silver Hill, MO and montmorillonite – Crook Co., WY) were purchased from the Clay Minerals Society, Columbia, MO. The organic matter in the clays was removed by treatment with H_2O_2. A few samples heated to 550 °C showed no change in weight, after the H_2O_2 treatment, confirming the absence of any organic matter. The clay samples were then ground, sieved (< 0.125 mm), autoclaved at 105 °C for 30 min, and dried again at 60 °C for 48 h. Autoclaving the soil for 30 min at 105 °C, kills microorganisms, but is not expected to change the adsorption characteristics.

Benzene, toluene, and xylenes from EM Science and commercial unleaded gasoline collected from a local gasoline station were used in this study. Stock solutions (150 μl/l) were prepared by adding single hydrocarbon (toluene), mixture of hydrocarbons (benzene + toluene + xylenes) or gasoline to organic-free water produced from an ULTRApure water purification system (Barnstead D4754).

3.2. Adsorption isotherms

All glassware was cleaned, autoclaved at 105 °C for 30 min and baked in an oven at 200 °C for 24 h before use. After adding 2 g of clay, 40 ml of gasoline–water solution (10, 50, 100 or 150 μl/l) was injected with a gas/liquid-tight syringe into 40 ml glass vials with teflon septa. The clay to gasoline–water ratio was determined from preliminary experiments to find the optimum ratio and time for the adsorption equilibrium. Vials were then agitated on a mechanical (1000 rpm) shaker for 24 h at 22 ± 1 °C. The adsorbent was then separated from the mixture by centrifugation (5000 rpm) for 10 min. After centrifugation, 20 ml of the supernatant was removed through the septum with a syringe and extracted with 2 ml hexane in a 20 ml glass vial with teflon septum. A portion of the hexane containing the extracted gasoline was analyzed using a Hewlett Packard 5890A gas chromatograph with a flame ionization detector (GC/FID). A DB-1 (30 m × 0.546 mm with 1.5 μm film thickness) J and W Scientific capillary column was used with helium as the carrier gas (9.3 ml/min). The injected sample of 1.0 μl was split at a rate of 1:2. The temperature program was: initial 40 °C for 4 min, increased to 200 °C at a rate of 7 °C/min. Injector, (detector) and column temperatures were 200 °C and 250 °C, respectively. The concentration of a gasoline

hydrocarbon in hexane extract was determined by comparing the peak area against an external standard (*n*-propylbenzene). Each treatment was replicated three times. To assess any adsorption on glass and/or volatilization losses of hydrocarbons, control vials were treated similarly but with no adsorbent. The amount of hydrocarbon adsorbed on clay was calculated based on the differences of hydrocarbon concentration in control vials, and in vials with clay. Statistical analyses of the data were done using SAS.

4. Results and discussion

4.1. Hydrocarbons composition in gasoline

The chromatogram of a hexane extract of the aqueous–gasoline solution contained up to 60 peaks under the analytical conditions employed. The target peaks were identified after comparison to the pure hydrocarbon peak. Eq. (2) was modified to calculate the concentration of hydrocarbons in gasoline used for the adsorption experiments (Table 1):

$$C_o^i = f_g^i C, \tag{5}$$

where C_o^i is an initial concentration of hydrocarbon i; f_g^i is the mole fraction of hydrocarbon i in the gasoline; and C is the concentration of gasoline stock solution. The initial concentrations of individual hydrocarbons ranged from 0.22 to 10.65 µl/l.

4.2. Adsorption equilibrium

The adsorption of hydrocarbons from gasoline on clay minerals is given in Table 2. Values of K and N were obtained from the regression equation as the intercept and the slope, respectively. These Freundlich parameters and the regression coefficient (r^2)

Table 1
Aqueous-equilibrium (C_m) concentration of selected hydrocarbons and their concentrations in the stock solutions

Compound	C_m concentration (mg/l)	C1[a] (µl/l)	C2 (µl/l)	C3 (µl/l)	C4 (µl/l)
Benzene	58.38	0.33	1.64	3.28	4.92
Toluene	36.57	0.71	2.55	7.10	10.65
Ethylbenzene	3.29	0.22	1.09	2.17	3.62
p,*m*-Xylene	12.30	0.62	3.08	6.15	9.23
o-Xylene	5.20	0.26	1.32	2.63	3.95

[a] C1, C2, C3, or C4 are gasoline concentration (in water) in 10, 50, 100, or 150 µl/l, respectively, used in this study.

Table 2
Adsorption of hydrocarbons from gasoline on three clay minerals

Stock solution (μl l^{-1})	Benzene	Toluene (ng g^{-1})	Ethylbenzene (ng g^{-1})	p,m-Xylene (ng g^{-1})	o-Xylene (ng g^{-1})	clay-mean
Montmorillonite						1298.0[m]
10	12.4[c]	52.1[b]	10.3[c]	38.5[c]	8.7[c]	
50	26.2[bc]	63.7[b]	—	74.2[b]	20.2[c]	
100	66.0[b]	221.5[a]	35.4[b]	108.1[b]	107.3[a]	
150	84.8[a]	224.6[a]	74.2[a]	222.4[a]	171.6[a]	
Illite						948.5[mn]
10	7.7[c]	23.9[d]	10.5[d]	14.8[d]	2.7[c]	
50	25.9[c]	48.0[c]	40.0[c]	62.4[c]	73.5[a]	
100	51.9[b]	73.5[b]	124.8[b]	290.1[b]	80.1[a]	
150	109.7[a]	125.5[a]	188.2[a]	543.4[a]	81.17[a]	
Kaolinite						836.8[n]
10	—	32.1[c]	—	13.1[b]	—	
50	—	54.6[b]	—	73.3[a]	—	
100	—	89.3[a]	—	—	—	
150	—	98.4[a]	—	83.7[a]	—	
Hydrocarbon-mean	1286.6[x]	1709.9[x]	365.4[y]	1431.5[x]	482.3[y]	

Values are means of three replications and values followed by different letters are significantly different from each other at $P < 0.05$ (Waller–Duncan K-ratio tests).

are shown in Table 3; regression coefficients (r^2) were 0.89–0.99, indicating an excellent fit of the data to the Freundlich equation. The analyses of variance indicated that the type of clay, type of hydrocarbons, and concentration of hydrocarbons had a significant ($P \leq 0.05$) effect on adsorption (Table 4). The amounts of hydrocarbons adsorbed on montmorillonite were consistently higher than those adsorbed on illite and kaolinite. The K values for the three clays followed the order: montmorillonite > illite > kaolinite. Similar results on the adsorption of hydrophobic compounds by clays have been reported [15]. One explanation is that montmorillonite is a 2:1 expandable lattice clay with a large surface area (about 800,000 m^2/kg) whereas illite is non-expandable 2:1 clay and kaolinite is non-expandable 1:1 clay; surface areas of illite and kaolinite are about 100,000 and 30,000 m^2/kg, respectively [16]. Many different adsorption mechanisms between clay/soil and hydrocarbons have been reported. Pore size and structure are known to have little effect on the adsorption processes under these conditions. Hunt et al. [17] and Samiullah [14] assumed the non-aqueous phase liquid was chemisorbed to the soil surface. Studying clays and aromatic hydrocarbons, Eltantwy and Arnold [18] presented evidence of interlayer sorption of n-hexane and n-dodecane by Ca-Wyoming montmorillonite. Similar results were confirmed using Fourier transform infrared (FTIR), differential scanning

Table 3
Freundlich parameters: K, N, and regression coefficient (r^2) for adsorption of gasoline hydrocarbons on various clays

Hydrocarbon	K	N	r^2
Montmorillonite			
Benzene	0.15	0.74	0.97
Toluene	0.69	0.63	0.89
Ethylbenzene	0.31	0.65	0.96
p,m-Xylene	1.00	0.92	0.97
o-Xylene	0.02	1.09	0.94
Illite			
Benzene	0.03	0.99	0.94
Toluene	0.52	0.77	0.97
Ethylbenzene	0.06	0.96	0.99
p,m-Xylene	0.40	0.99	0.94
o-Xylene	0.01	1.09	0.97
Kaolinite			
Toluene	0.17	0.72	0.99
p,m-Xylene	0.02	1.02	0.99

Table 4
Analyses of variance for adsorption of hydrocarbons on clay minerals from gasoline

Source	DF	SS	F-value
Model	10	6.6×10^5	11.42[a]
Clay type	2	5.9×10^4	5.13[b]
Hydrocarbon type	4	2.0×10^5	8.80[a]
Hydrocarbon concentration	3	4.2×10^5	24.55[a]
Replicate	1	220	0.04
Error	94	5.4×10^5	

[a],[b] Significant at 1 and 5% probability levels, respectively.

calorimetry (DSC), gas chromatography-mass spectroscopy (GC/MS), and thermo-gravimetric analyses (TGA) for phenol and nitrobenzene [19].

Freundlich adsorption coefficient (K value) for toluene were 2.42 from a single solute and 0.81 from the mixture of benzene + toluene + xylenes. The K value for the adsorption of toluene was only 0.69 from gasoline. The decrease in K values can be the result of the competitive adsorption of other hydrocarbons in gasoline, especially the polar organic solvents (e.g. methanol, ethanol, t-butyl alcohol) which are added as additives [20]. Similar competitive effects have also been reported by MacIntyre and defur [21] and Zachara et al. [22].

5. Conclusions

The adsorption of hydrocarbons from gasoline was described by the Freundlich equation for the ranges of aqueous concentrations studied. The values for the Freundlich adsorption coefficient (K) were relatively lower than the K values reported, on soils with high organic content, in the literature. Adsorption coefficients for the hydrocarbons studied were consistently higher with montmorillonite than with illite and kaolinite. The adsorption of toluene on clays decreased in the presence of other competing hydrocarbons.

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