Multi-solute Adsorption of Organic Compounds in Soil

유기화합물들이 혼합상태에서 토양에 흡착하는 성질에 관한 연구

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적   요

혼합상태에서 유기화합물들이 토양에 흡착하는 성질에 관해서 5개의 유기화합물(페놀, 2,4 -디크로로페놀, 2,4,6-트리크로로페놀, 부루신, 따이오유리아)과 2종류의 토양을 이용하여 연구하였다. 일반적으로 따이오유리아를 제외하고는 한가지 물질이 혼합상태에 있는 다른물질에 의해 흡착에 제약을 받아서 단독으로 있을때 보다 흡착율이 낮았다. 따이오유리아는 단독인 경우보다 혼합상태일 때 더 많은 흡착을 보였는데 이는 혼합상태에서 오히려 흡착이 증가할 수도 있음을 나타낸다. 혼합이 흡착에 미치는 영향은 페놀의 혼합상태와 단독상태에서의 흡착 상태를 여러가지 형태로 비교하며 검토하였는데 산성이고 유기물질이 적은 토양에서 알카리성 이며 유기물질이 많은 토양보다 혼합으로 인한 흡착의 억제효과가 뚜렷하였다.

I. Introduction

Toxic organic compounds can be released to soil as a result of spills, improperly managed landfills and impoundments, and so-called "midnight dumping." In such cases, concentrated organic contaminants usually occur as a mixture rather than as a pure chemical. It is necessary to understand and predict the movement of mixed contaminants when evaluating the potential impact on human health and the environment or when considering a remedial action. Accurate prediction of contaminant migration requires information on the adsorption characteristics of individual compound as modified by the constituents in the mixture.[16] Therefore, multi-solute adsorption information is needed. Primary objectives of this study were: a) evaluaiton of the effect of mixture, b)evaluation of the effect of concentration change of one compound to the adsorption of the other

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compound, and c) examination of the effect of soil characteristics on the multisolute adsorption of organic compounds in soil.

This research was initiated to determine the sorption characteristics of several phenolics and other chemicals. The compounds were selected to determine whether sorption characteristics of individual pure compounds are comparable to those of the same compounds when they occur in mixtures. Phenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol are monocyclic aromatic cmpounds, while brucine(a polycyclic aromatic compound) and thiourea(an aliphatic compound) are different in structure. Phenolic compounds are prevalent in the environment and can impart objectionable taste and odor to drinking water at concentration as low as 0.005 mg/L.[9] These five chemicals were used in this research. They can be toxic and are listed on the EPA Hazardous Waste List and Appendix IX Groundwater Monitoring List.[6,7]

Most of the available data on adsorption deal with single-solute/single-solvent systems, most of these studies are related to wastewater treatment with activated carbon. Data have been presented regarding adsorption on soil from an aqueous system,[3,5,16] and this type of adsorption was of interest in this research. Rao et al.[13] and Nkedi-Kizza et al.[12] presented data for siagle-solute/ mixture solvent systems. Multi-solute/mixed solveut systems have received less attention.

Chiou et al.[3] provided evidence that sorption of nonionic organic compounds from water onto soil occurs primarily by partition into the soil organic phase, and that sorption by soil minerals is relatively unimportant in wet soils. Therefore, the more organic matter in soil, the more adsorption is expected. Soil organic matter content can help explain differences in adsorption between surface and subsurface samples of the same soil, since surface soil is expeçted to have more organic

matter.[5]

Abdul et al.[1] conducted a batch adsorption experiment with soil which was heat-treated to remove organic carbon. Results showed that no adsorption was detected after 24 hours. In addition, five soils with almost same values of organic carbon content, but with different grain size ranges showed almost the same value of partition coefficient.

In terms of soil pH, competitive adsorption did occur between compounds in an acidic soil where protonated compound species predominated in solution. In contrast, competition was minimal in a basic soil.[3,16] When the protonated and neutral species coexist, site specific sorption of the cation occurred, and when anionic and neutral species coexists neutral species sorption occurred because of the negatively charged surface area.[10,16] Maximum adsorption was attained near the point where $pH = pKa$, and competitive adsorption was more significant when the pH was near pKa.[10,12,15]

For the reasons noted above, multi-solute adsorption was studied using a basic soil with a relatively high organic carbon content and an acidic soil with a lower organic carbon content in this study.

II. Material and Methods

The five compounds were purchased from Fisher Scientific Company(phenol), Sigma Chemical Company(brucine), and Aldrich Chemical Company(2,4-dichlorophenol, 2,4,6 -trichlorophenol, and thiourea), and were used without further purification. These compounds contained 1% to 3% impurities of an unknown nature. The chemicals selected are presented in Table 1. The solvent used was distlled deionized water(DDW) obtained by passage through a Barnstead water purification cartridge #DO809. The stock solution of each organic compound obtained the maxi-

mum soluble amount of the compound in DDW at room temperature(25℃) and was stored at 4℃ until use.

The two soils were used: (a) a sandy loam from Wiggins, Mississippi, and (b) a fine sandy loam from near Austin, Texas. Surface soil samples(top 6 inches for Texas soil, and top 39 inches for Mississippi soil) were air-dried, crushed, passed through a 2mm sieve, and stored with an airtight cap at 4℃. Physical and chemical properties of these soils are presented in Table 2.

The chemicals and concentrations used in the single solute and specific mixture studies are presented in Tables 3 and 4, respectively. Adsorption at high concentrations was of interest because it was expected that any dif-

Table-1. Chemicals Selected

Compound	CAS No.*	Hzds Waste No.**	pK1, pK2***	Solubility (mg/L)
Phenol	108-95-2	U188	9.00	~45,000
2,4-DCP	120-83-2	U081	7.85	~ 5,000
2,4,6-TCP	88-06-2	U231	5.99	~ 500
Brucine	257-57-3	P018	2.50,8.16 (protonated)	~ 500
Thiourea	62-56-5	U219	2.03 (protonated)	~ 5,000

Table-2. Characteristics of Two Soils Selected

Characteristics	Texas Soil*	Mississippi Soil**
Texture	Fine Sandy Loam	Sandy Loam
pH(1:1 ratio of soil to water)	7.8	4.8
Organic Carbon(%)	3.25	0.94
CEC(Meq/100g)	10.8	6.35
Particle Size Fraction(%)		
Sand(2-0.05 mm)	61.5	68.0
Silt(0.05-0.002 mm)	31.1	23.4
Clay(<0.002 mm)	7.4	8.6

*Soil Characterization Laboratory and Soil Testing Laboratory, Texas A & M University
**Mississippi State University Soil Genesis Laboratory.

Table-3. Experiments for Single-Solute Study

Compound(soil)	*Concentrations(ppm)evaluated				
	a	b	c	d	e
Phenol(Texas)	1,000	2,000	3,000	6,000	10,000
Phenol(Miss.)	1,000	2,000	3,000	6,000	10,000
2,4-DCP(Texas)	20	30	130	700	2400
2,4-DCP(Miss.)	20	70	200	200	2500
2,4,6-TCP(Texas)	20	40	80	700	400
2,4,6-TCP(Miss.)	30	50	90	250	400
Brucine(Texas)	-	100	200	350	500
Brucine(Miss.)	30	60	100	150	300
Thiourea(Texas)	30	100	350	1,500	5,000
Thiourea(Miss.)	30	100	350	1,500	5,000

*The initial concentration before adsorption occurs, ppm=mg compound/kg soil DDW.

Table-4. Experiments for Mixture Study*

Experiment	Phenol	2,4-DCP	2,4,6-TCP	Brucine	Thiourea
Reference Isotherm	1,000	-	-	-	-
	2,000	-	-	-	-
	3,000	-	-	-	-
	6,000	-	-	-	-
	10,000	-	-	-	-
Mix.-1	1,000	100	-	-	-
	2,000	100	-	-	-
	3,000	100	-	-	-
	6,000	100	-	-	-
	10,000	100	-	-	-
Mix.-2	1,000	1,000	-	-	-
	2,000	1,000	-	-	-
	3,000	1,000	-	-	-
	6,000	1,000	-	-	-
	10,000	1,000	-	-	-
Mix.-3	1,000	-	100	-	-
	2,000	-	100	-	-
	3,000	-	100	-	-
	6,000	-	100	-	-
	10,000	-	100	-	-
Mix.-4	1,000	-	500	-	-
	2,000	-	500	-	-
	3,000	-	500	-	-
	6,000	-	500	-	-
	10,000	-	500	-	-
Mix.-5	1,000	100	100	-	-
	2,000	100	100	-	-
	3,000	100	100	-	-
	6,000	100	100	-	-
	10,000	100	100	-	-

Table-4. Experiments for Mixture Study*

Experiment	Phenol	2,4-DCP	2,4,6-TCP	Brucine	Thiourea
Mix.-6	1,000	1,000	500	–	–
	2,000	1,000	500	–	–
	3,000	1,000	500	–	–
	6,000	1,000	500	–	–
	10,000	1,000	500	–	–
Mix.-7	1,000	–	–	100	–
	2,000	–	–	100	–
	3,000	–	–	100	–
	6,000	–	–	100	–
	10,000	–	–	100	–
Mix.-8	1,000	–	–	500	–
	2,000	–	–	500	–
	3,000	–	–	500	–
	6,000	–	–	500	–
	10,000	–	–	500	–
Mix.-9	1,000	–	–	–	100
	2,000	–	–	–	100
	3,000	–	–	–	100
	6,000	–	–	–	100
	10,000	–	–	–	100
Mix.-10	1,000	–	–	–	1,000
	2,000	–	–	–	1,000
	3,000	–	–	–	1,000
	6,000	–	–	–	1,000
	10,000	–	–	–	1,000
Mix.-11	1,000	500	500	500	500
	2,000	500	500	500	500
	3,000	500	500	500	500
	6,000	500	500	500	500
	10,000	500	500	500	500

*Concentrations of specific chemicals(mg chemical/kg dry DDW.) used in the noted experiments.

ferences in sorption would be more noticeable at these concentrations. Five data points were used to develop each adsorption isotherm. Each data point was obtained using four samples, one for blank sample(only the solution) and another three for the triplicated soil samples.

Batch sorption studies were used to develop the data, for each adsorption study(Table 3 or 4), 50 grams of dry soil and 50ml of solution containing the chemical were added to the brown, teflon capped, 120ml capacity bot-

tles. The samples were shaken continuously at 29 rpm in a rotating tumbler for 24 hours which previously had been shown adequate to achieve apparent equilibrium conditions. The supernatant was filtered through a 0.45 μm membrane filter after centrifuging for 30 minutes at 4,000rpm, transferred to a 50ml test tube, and stored at a 4℃ until analyzed by HPLC(Waters Model 440). Biological degradation in soil samples was not considered important because the contact time was only 24 hours and the solution was stored at 4℃ after extraction to minimize microbial activity.

An aqueous solution (50 μL) of each stored extract was injected into a C-18 reversed column and eluted with two types of eluent as shown in Table 5. The UV·adsorption detector wavelength was 254μm. The flow rate of the eluted solution was 3.0mL/min, and attenuation varied from 0.005 to 2.0, depending on compound adsorption spectra. The chemicals were separated well due to different detention time or eluent as shown in Table 5.

Every analysis was duplicated to make sure the HPLC results were consistent. The amount of adsorption for the sample was determined by Equation(1):

$$q = \frac{(C_i - C_f)V}{M} \quad \cdots\cdots\cdots\cdots\cdots\cdots(1)$$

Table-5. Separation of the Chemicals using HPLC

Compound	HPLC Condition, Flow Rate=3.0mL/min.		
	Det. Time(min.)	Attenuation	Eluent Type*
Phenol	~1.5	0.2	A
2,4-DCP	~2.5	0.005	A
2,4,6-TCP	~4.2	0.005	A
Brucine	~2.5	0.2	B
Thiourea	~1.0	2.0	A

*Type A-50:50:0.1 of acetonitrile:DDW:acetic acid,

Type B-methanol+0.5% of triethylamine.

Where, q = amount adsorbed, mg/g
C_i = chemical concentration of blank sample, mg/L
C_f = chemical concentration in filtrate of soil sample, mg/L
M = mass of soil, gram
V = volume of solution, liter.

The data points of the single-solute and multisolute isotherms were transformed by taking the logarithm of the equilibrium concentrations in the liquid and soil phases. The resulting values were fit using least square linear regression methods. The t-test for paired data[8] was applied to determine whether there was any effect due to the mixtures.

The Langmuir and Freundlich equations were used to describe the equilibrium condition. The Langmuir equation may be stated as:

$$q = \frac{XbC}{1 + bC} \quad \cdots\cdots\cdots\cdots\cdots (2)$$

where, q = amount adsorbate adsorbed, mg/g
C = solution phase concentration, mg/L
X = maximum adsorption capacity, mg/g
b = Langmuir coefficient related to adsorption energy, L/mg.

The more commonly used linear from of the Langmuir equation is,

$$\frac{1}{q} + \frac{1}{X} + \frac{1}{bX}\frac{1}{C} \quad \cdots\cdots\cdots\cdots (3)$$

The terms b and X can be calculated from the intercept and slope of plots of 1/q vs 1/C. The Freundlich equation is,

$$q = K C^{\frac{1}{n}} \quad \cdots\cdots\cdots\cdots\cdots (4)$$

where, K and n are empirical Freundlich coefficients that depend on the soil-solution system. Taking logarithms of both sides of Equation (4) yields,

$$\log q = \log K + \frac{1}{n} \operatorname{lon} C \cdots\cdots\cdots\cdots (5)$$

The coefficients K and n can be obtained, respectivly, from the intercept and slope of log-log plots of q vs C. The intercept is an indicator of adsorption capacity and the slope $\frac{1}{n}$ of adsorption intensity.

III. Results and Discussion

Single-soute isotherms

Typical adsorption isotherms for single-solute system are presented in Fig. 1. The Freundilich and Langmuir constants and the
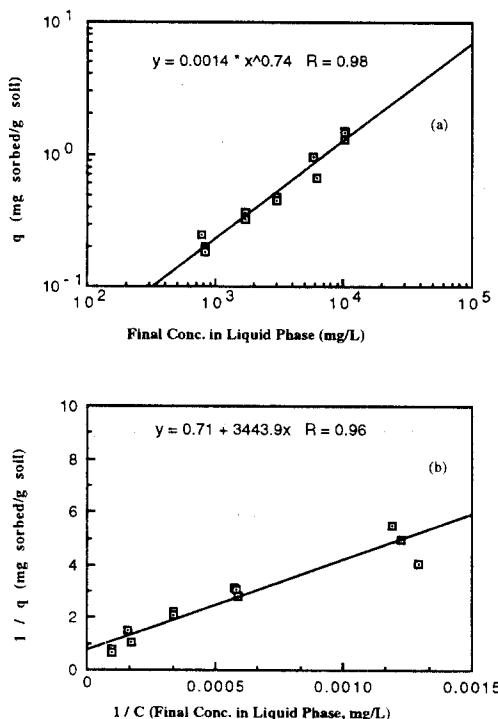

Fig. 1. **Single-solute adsorption isotherms of phenol in Texas soil: (a)Freundlich Isotherm, (b)Langmuir Isotherm**

equilibrium isotherm data for single–solute adsorption isotherms of the five compounds in both soils are presented in Table 6. Both equations fit the experimental data well. The adsorption of the five compounds are presented in Table 7 in terms of %–adsorbed to indicate the amount of sorption that occurred.

Brucine adsorbed very strongly for the whole range of concentration on both soils ; over 90% was adsorbed. Thiourea adsorbed weakly compared to the other compounds.

Phenol adsorbed more in the Texas soil than in the Mississippi soil. Phenol was undissociated (pKa=9.9) in both soils. The pH of the Texas soil was 7.8 and that of the Mississippi soil was 4.8. The organic carbon effect migtht be more significant in the adsorption of phenol than the pH effect for the same ionic form. The Texas soil had a

higher organic carbon content (3.25%) than the Mississippi soil (0.94%). The more organic carbon in soil, the more adsorption is expected. A similar result was observed with thiourea adsorption.

2.4 – dichlorophenol adsorbed more in the Texas soil than in the Mississippi soil at the higher concentrations. The pH of the Texas soil was almost the same as the pKa of 2,4-dichlorophenol (7.85). Both of the soil characteristics, pH and organic carbon content, affect positively the greater adsorption of 2,4 -dichlorophenol in the Texas soil than in the Mississippi soil.

2,4,6-trichlorophenol adsorbed more in the Mississippi soil than in the Texas soil, even though the Texas soil had a higher organic carbon content. The pKa of 2,4,6-trichlorophenol is 5.99. Therefore, it was primarily undissociated in the mississippi soil and ani-

Table-6. Freundlich and Langmuir Constants* for Single–Solute system

Soil	Chemical	Freundlich $q = K\, C(\frac{1}{n})$			Langmuir $\frac{1}{q} = \frac{1}{X} + \frac{1}{bX}\frac{1}{C}$		
		K	n	r**	X	b***	r**
Texas	Phenol	0.0014 (0.00067,0.0028)	1.35 (1.21,1.54)	0.98	1.41 (0.91, 3.16)	0.00021	0.96
	2,4–DCP	0.0051 (0.0049,0.0062)	1.31 (1.29,1.38)	1.00	0.32 (–)	0.012	0.99
	2,4,6–TCP	0.0018 (0.0015,0.0018)	1.37 (1.29,1.46)	1.00	0.11 (0.066, 0.30)	0.0091	0.99
	Brucine	0.14 (0.12,0.16)	2.98 (2.20,3.57)	0.99	0.35 (0.19, 1.65)	0.93	0.89
	Thiourea	0.00027 (0.00015,0.0048)	1.19 (1.08,1.34)	0.99	0.15 (–)	0.0011	1.00
Missi.	Phenol	0.0016 (0.00082,0.0030)	1.45 (1.30,1.64)	0.98	1.36 (0.91, 2.63)	0.00015	0.98
	2,4–DCP	0.0068 (0.0057,0.0080)	1.53 (1.47,1.62)	1.00	0.22 (0.13,0.94)	0.022	0.99
	2,4,6–TCP	0.0098 (0.0036,0.025)	1.56 (1.10,2.71)	1.00	0.17 (0.12, 0.30)	0.041	0.98
	Brucine	0.062 (0.047,0.081)	2.092 (1.63,2.92)	0.97	0.13 (0.065, 1.75)	2.00	0.90
	Thiourea	0.00081 (0.00026,0.0032)	1.77 (1.34,2.92)	0.99	0.046 (–)	0.0046	0.97

*The values in parentheses are the 95% confidence intervals. (–):Lower limtit of 95% C.I. is negative which has no physical meaning. **r=Correlation coefficient.
***No 95% C.I. for "b" value needs manipulation with X and slope.

Table-7. %-Sorbed* of each Compound in Single-Solute System

Soil	Compound	Five Data Points**				
		a	b	c	d	e
Texas	Phenol	20.6	16.4	13.5	12.4	12.1
	2,4-DCP	79.4	72.7	70.5	59.8	49.5
	2,4,6-TCP	48.4	44.4	36.4	29.1	28.1
	Brucine	–	99.4	98.6	95.0	91.3
	Thiourea	13.5	10.7	9.4	10.8	5.7
Mississippi	Phenol	15.0	15.2	11.5	9.2	8.4
	2,4-DCP	82.3	70.8	57.0	44.7	35.5
	2,4,6-TCP	86.1	81.9	75.6	68.2	64.5
	Brucine	99.4	96.9	96.1	94.1	95.3
	Thiourea	16.5	8.7	8.3	6.3	1.5

*Triplicated data were averaged for each data point.

**Five data points were obtained for each isotherm, moving from low (a) to high (e) which are presented in Table 3.

onic in the Texas soil. The anionic form of 2, 4,6-trichlorophenol adsorbed less in the Texas soil than the neutral form in the Mississippi soil, even though the Texas soil had a higher organic carbon content. This implies that the ionization of 2,4,6-trichlorophenol affected the sorption more than organic carbon content.

Brucine adsorbed very strongly regardless of soil characteristics. A possible reason might be structure and molecular size. Benefield[2] showed that, within a homologous series of aliphatic acids, aldehydes, or alcohols, adsorption usually increased as the size of the molecular size of the molecule became greater. The complicated structure of brucine may be captured more easily by soil particles compared to chemicals with a simpler structure. Thiourea is an aliphatic compound, relatively simple structure, and small molecule compared to the others. This can partly explain why thiourea adsorbed weakly.

Multi-solute isotherms

Among the compounds in mixtures, phenol was used to evaluate the mixture effect. The adsorption isotherms were constructed with
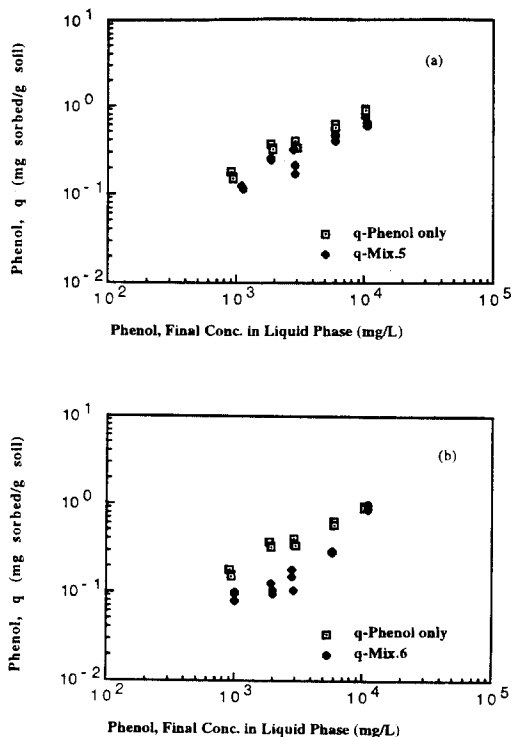

Fig. 2. Phenol adsorption isotherms in single and multisolute systems-Mississippi Soil:(a) single-solute and Mix, (b) single-solute and Mix. 6

phenol adsorption in the mixture systems, where q_{phenol} was calculated using Equation (1) with difference between the $C_{f,\ phenol}$ and the $C_{i,\ phenol}$ in the mixture. The Freundlich and Langmuir equations were applied to describe the adsorption isotherm of phenol in mixture systems, and the constants for both equations are presented in Table 8. Both equations fit the experimental data well. A typical relationship beteen a single - solute and mixture is shown in Fig. 2. The phenol adsorption isotherm in the mixture is lower than than that in the single-soulte system. The reason might be a competitive effect between the compounds in the mixture for the adsorption sites.

In the same way, the percent sorbed of

Table-8. Frendlich and Langmuir Constants* for Multi-Solute System

Soil	Chemical	Freundlich $q = K C(\frac{1}{n})$			Langmuir $\frac{1}{q} = \frac{1}{X} + \frac{1}{bX}\frac{1}{C}$		
		K	·n	r**	X	b***	r**
Mix.1	Texas	0.00017 (0.000044, 0.00062)	1.00 (0.85, 1.21)	0.96	3.62 (−)	0.000043	0.99
	Missi.	0.0037 (0.0019, 0.0070)	1.76 (1.54, 2.04)	0.97	0.80 (0.63, 1.10)	0.00029	0.97
Mix.2	Texas	0.00083 (0.000099, 0.0070)	1.31 (0.97, 2.02)	0.86	6.71 (−)	0.000021	0.97
	Missi.	0.00097 (0.00031, 0.0030)	1.35 (1.14, 1.66)	0.96	1.54 (0.85, 8.42)	0.00011	0.95
Mix.3	Texas	0.00013 (0.000054, 0.0034)	0.98 (0.88, 1.09)	0.98	9.68 (−)	0.000018	0.96
	Missi.	0.0074 (0.0024, 0.023)	2.12 (1.50, 3.00)	0.90	0.71 (0.58, 1.06)	0.00028	0.96
Mix.4	Texas	0.00060 (0.00023, 0.0015)	1.20 (1.06, 1.40)	0.97	1.69 (1.01, 5.35)	0.00013	0.96
	Missi.	0.00095 (0.00053, 0.0017)	1.40 (1.26, 1.55)	0.98	1.16 (0.86, 1.79)	0.00012	0.99
Mix.5	Texas	0.00012 (0.00079, 0.0018)	1.35 (1.26, 1.45)	0.99	1.63 (1.23, 2.45)	0.00014	0.99
	Missi.	0.00090 (0.00027, 0.0031)	1.40 (1.16, 1.79)	0.94	1.10 (0.55, 418.94)	0.00012	0.93
Mix.6	Texas	0.00046 (0.00021, 0.0097)	1.16 (1.05, 1.30)	0.98	1.45 (0.86, 4.55)	0.00016	0.95
	Missi.	0.00091 (0.000017, 0.00050)	1.05 (0.86, 1.33)	0.94	0.47 (0.25, 3.65)	0.00021	0.87
Mix.7	Texas	0.00078 (0.00043, 0.0014)	1.27 (1.16, 1.39)	0.99	1.67 (1.06, 3.94)	0.00012	0.98
	Missi.	0.0020 (0.00069, 0.0058)	1.58 (1.32, 2.00)	0.95	1.17 (0.82, 2.06)	0.00013	0.98
Mix.8	Texas	0.00031 (0.00018, 0.00053)	1.10 (1.02, 1.19)	0.99	2.85 (1.85, 6.25)	0.000064	0.99
	Missi.	0.0027 (0.0014, 0.0053)	1.68 (1.47, 1.93)	0.97	1.11 (0.87, 1.53)	0.00015	0.99
Mix.9	Texas	0.00082 (0.00058, 0.0011)	1.26 (1.19, 1.32)	1.00	1.64 (1.11, 3.13)	0.00015	0.99
	Missi.	0.0034 (0.0019, 0.0061)	1.85 (1.63, 2.13)	0.98	0.60 (0.47, 0.81)	0.00029	0.99
Mix.10	Texas	0.00051 (0.00039, 0.0067)	1.17 (1.12, 1.21)	1.00	2.31 (1.42, 6.41)	0.000092	0.99
	Missi.	0.0036 (0.0018, 0.0070)	1.82 (1.58, 2.14)	0.97	0.56 (0.42, 0.85)	0.00041	0.90
Mix.11	Texas	0.0035 (0.00021, 0.0058)	1.72 (1.55, 1.94)	0.98	0.70 (0.55, 1.96)	0.00040	0.96
	Missi.	0.00074 (0.00025, 0.0022)	1.36 (1.15, 1.69)	0.95	0.70 (0.40, 2.82)	0.00021	0.91

*The va;ies om [aramtjeses are tje 95% confidence intervals. (−):Lower limtit of 95% C.I. is negative which has no physical meaning.
**r = Correlation coefficient.
***No 95% C.I. for "b" somce "b" value needs manipulation with X and slipe.

Table-9a. %-sorbed* of Phenol in Single and Multisolutes-Texas Soil

Experiment	Data Point(ppm)				
	1,000	2,000	3,000	6,000	10,000
Single-Solute(%sorbed) (Table Ⅶ)	20.62	16.41	13.54	12.35	12.05
Mix.1 %-sorbed	13.50	14.31	14.43	20.05	11.39
Mix.1/SS**	0.65	0.87	1.07	1.62	0.95
Mix.2 %-sorbed	11.92	11.69	15.89	15.25	5.56
Mix.2/SS**	0.58	0.71	1.17	1.23	0.46
Mix.3 %-sorbed	14.82	13.49	14.74	12.77	16.11
Mix.3/SS**	0.72	0.82	1.09	1.03	1.34
Mix.4 %-sorbed	17.68	13.12	12.27	13.90	11.80
Mix.4/SS**	0.86	0.80	0.91	1.13	0.98
Mix.5 %-sorbed	16.86	15.16	12.51	11.60	9.51
Mix.5/SS**	0.82	0.92	0.92	0.94	0.80
Mix.6 %-sorbed	17.54	12.55	11.51	12.91	11.80
Mix.6/SS**	0.85	0.76	0.85	1.05	0.98
Mix.7 %-sorbed	15.61	12.56	12.31	11.93	9.21
Mix.7/SS**	0.76	0.77	0.91	0.97	0.76
Mix.8 %-sorbed	14.87	13.39	12.93	11.06	13.15
Mix.8/SS**	0.72	0.82	0.95	0.90	1.09
Mix.9 %-sorbed	18.26	14.66	13.12	12.67	11.13
Mix.9/SS**	0.89	0.89	0.97	1.03	0.92
Mix.10 %-sorbed	16.80	14.33	13.67	12.42	11.99
Mix.10/SS**	0.81	0.87	1.01	1.01	1.00
Mix.11 %-sorbed	17.78	14.01	10.44	8.29	7.80
Mix.11/SS**	0.86	0.83	0.77	0.67	0.65

*Triplicated data were averaged for each data point.
**SS = %-sorbed of phenol in single-solute system.

Table-9b. %-sorbed* of Phenol in Single and Multisolutes-Texas Soil

Experiment	Data Point(ppm)				
	1,000	2,000	3,000	6,000	10,000
Single-Solute(%sorbed) (Table Ⅶ)	15.02	15.19	11.49	9.15	8.40
Mix.1 %-sorbed	15.42	12.91	9.33	8.26	6.24
Mix.1/SS**	1.03	0.85	0.81	0.90	0.74
Mix.2 %-sorbed	12.99	12.97	10.80	7.02	9.04
Mix.2/SS**	0.86	0.85	0.94	0.77	1.08
Mix.3 %-sorbed	13.56	12.86	10.37	6.86	4.81
Mix.3/SS**	0.90	0.85	0.90	0.75	0.57
Mix.4 %-sorbed	11.24	9.24	10.35	7.32	6.29
Mix.4/SS**	0.75	0.61	0.90	0.80	0.75
Mix.5 %-sorbed	8.52	5.21	4.89	4.69	7.75
Mix.5/SS**	0.57	0.34	0.43	0.51	0.92
Mix.6 %-sorbed	8.52	5.21	4.89	4.69	7.75
Mix.6/SS**	0.57	0.34	0.43	0.51	0.92
Mix.7 %-sorbed	12.03	11.98	9.08	9.22	4.90
Mix.7/SS**	0.80	0.79	0.79	1.01	0.58
Mix.8 %-sorbed	12.48	11.56	9.45	7.56	4.94
Mix.8/SS**	0.83	0.76	0.82	0.83	0.59
Mix.9 %-sorbed	14.73	9.45	7.86	6.12	5.47
Mix.9/SS**	0.98	0.62	0.68	0.67	0.65
Mix.10 %-sorbed	14.73	9.45	7.86	6.12	5.47
Mix.10/SS**	0.98	0.62	0.68	0.67	0.65
Mix.11 %-sorbed	11.07	10.62	6.20	7.38	6.39
Mix.11/SS**	0.74	0.70	0.54	0.81	0.76

*Triplicated data were averaged for each data point.
**SS = %-sorbed of phenol in single-solute system.

phenol in Tables 9a & 9b were based on phenol adsorption in the mixtures. For the Mississippi soil (Table 9b), the percent sorbed in the mixture was lower than in the comparable single-solute system in all but three cases. A similar result occurred in the Texas soil (Table 9a), although in that case approximately 20% of the samples showed more phenol adsorption in the mixture than in the single-solute system. This difference might be more competitive adsorption among the compounds in the Mississippi soil than in the Texas soil. The Mississippi soil was acidic and had less avaiable sorption sites due to a lower organi content. In the acidic soil, the protonated compound species predominate and ion exchange is hypothesized to domi-

nate the sorption process. More competition is expected when protonated species adsorb via ion exchange because of electric attraction forces between the negatively charged soil particles and the protonated species, and when the sorption site are limited.

This mixture effect was evaluated using the t-test for paired data in terms of %-sorbed of phenol. The t-test table[6] gave a value of 2.132 at the 5% level of significance for the degree of freedom of 4 and a one-sided test. When the calculated t-value is greater than the tabulated t-value (2.132), the mixture effect is statistically significant ata level of 5% significance. Table 10 illustrates how the data were paired in one mixture study and how the mixture effect was

evaluated. As noted in the example, the calulated t-value for this paired data was 2.722, which is more tha the tabulated value of 2.132. Therefore, the mixture effect was significant for the Mix. 1 system in the Mississippi soil (Table 11). Such calculations were done for all the mixture systems and the calculated t-values are presented in Table 11.

For the mixture study in the Texas soil, Table 11, the adsorption of phenol was signif-

Table-10. The t-test fpr paired data with % -sorbed of phenol, Mix.1, Mississippi Soil

X1(Single-sol.)	X2(Mix.1)	Y=X1-X2	(Y-Yavg.)²
15.02	15.42	-0.40	3.305
15.19	12.91	2.28	0.743
11.49	9.33	2.16	0.551
9.15	8.26	0.89	0.279
8.40	6.24	2.16	0.551
Sum 0f =		7.09	5.429
Avg. of =		1.418	

$$t = \frac{Yavg.}{\sqrt{\dfrac{\sum (Y-Yavg.)^2}{n(n-1)}}} = 2.722$$

Table-11. Calculated t-values for comparison of phenol adsorption in mixtures and single-solute system.

Paired Data*	Texas	Mississippi
Single-Solute-Mix.1	0.107	2.722**
Single-Solute-Mix.2	1.244	2.309**
Single-Solute-Mix.3	0.356	6.288**
Single-Solute-Mix.4	1.393	5.871**
Single-Solute-Mix.5	3.308**	6.099**
Single-Solute-Mix.6	2.079	3.686**
Single-Solute-Mix.7	3.188**	5.538**
Single-Solute-Mix.8	1.644	7.471**
Single-Solute-Mix.9	2.164**	5.079**
Single-Solute-Mix.10	1.468	3.586**
Single-Solute-Mix.11	7.278**	8.131**

*Paired Data: %-sorbed values of phenol in single-solute and mixture are paired for each data point.

**Mixture results were statistically different.

icantly less in the mixtures than phenol adsorption alone when concentration of the added compound was low (Mix. 5,7, and 9). However, the adsorption of phenol in the mixture was not significantly different when the concentration of the additional compound was high (Mix. 6,8, and 10.) This results seem counterintuitive to the general sorption behavior.

For the Mississippi soil, all the calculated t-values were greater than the tabulated t-value, while more than half of such t-values wre less than the tabulated t-value in the Texas soil. This implies that the mixture effect was more significant in phenol adsorption for all the soil-compound combinations in the Mississippi soil, but was not significant for more than half of the soil-compound combinations in the Texas soil. This result agrees with the results of other researchers [3,16], in dicating that the competitive effect was severe in acidic soil but minimal in basic soil.

The effect of sorption of two chlorinated phenols in a mixture was evaluated. Table 12 shows %-sorbed of 2,4-dichlorophenol and 2, 4,6-trichlorophenol in mixtures which contained both chemicals (Mix. 5,6,11-Table 4). 2,4-dichlorophenol consistently adsorbed more in the Texas soil than in the Mississippi soil. However, 2,4,6-trichlorophenol adsorbed more in the Mississippi soil than in the Texas soil. This result agrees with the results that occurred in a single-solute system, the ionization of 2,4,6-trichlorophenol affected the sorption of it more than the organic carbon content. The %-sorbed of 2,4,6-trichlorophenol in Texas soil was 30-50% in Mix.5 (Table 12). However, very little adsorption was observed in Mix. 6 and Mix.11. The difference in sorption might be due to strong competition with the high concentration of 2, 4-dichlorophenol. 2,4-dichlorophenol concentrations in Mix. 5, Mix. 6 and Mix. 11 were 100 ppm, 1,000 ppm, and 500 ppm, respecti-

Table-12. %-sorbed* of 2,4-DCP and 2,4,6-TCP in Mix.5, 6, and 11

Data Point	Chem.	Mix.5		Mix.6		Mix.11	
		Texas	Missi.	Texas	Missi.	Texas	Missi.
1,000	24DCP	70.48	54.89	60.33	40.50	60.90	46.10
	246TCP	26.91	71.61	0.92	55.31	0.00	46.27
2,000	24DCP	68.00	54.68	49.34	33.72	61.81	51.40
	246TCP	51.91	71.72	4.91	54.17	0.00	51.01
3,000	24DCP	64.17	3.77	56.30	36.31	56.65	33.24
	246TCP	45.90	71.64	8.12	58.29	0.00	39.34
6,000	24DCP	64.58	51.58	54.55	33.63	62.33	38.04
	246TCP	35.88	72.29	0.00	47.24	4.19	45.26
10,000	24DCP	61.86	43.10	55.22	33.39	62.51	47.44
	246TCP	45.77	67.17	0.00	49.66	15.22	63.08

*Triplicated data were averaged for each data point.

vely. When the concentration was not high (Mix. 5), the sorption site might not be limited, and competition might be less. However, in highter concentrations (Mix. 6 and Mix. 11), 2,4-dichlorophenol and 2,4,6-trichlorophenol could have competed such that very little of 2,4,6-trichlorophenol, which had a lower affinity to the Texas soil due to ionization, was adsorbed. This is important, especially when a specific pollutant competes severely with a higher affinity of another compound in a mixture with high concentrations. In this situation, the pollutant of concern may migrate faster than expected with the sorption data evaluated in a single-solute system. Therefore, multisolute adsorption behavior of the chemicals in the mixture should be considered for the prediction of pollutant migration in the contaminated soil wthen they are in mixture.

IV. Conclusions

(1) The Langmuir and Freundlich adsorption models were used to evaluate the single-solute and multisolute adsorption data. Both of the models fit the experimental data well.

(2) The mixture effect was evaluated using the phenol adsorption in both single-solute and mixture studies. Phenol adsorbed less in the mixtures than in the single-solute system. This effect was more significant in the Mississippi soil (acidic soil, low organic carbon) than in the Texas soil (basic soil, higher organic carbon).

(3) Phenol adsorbed more in a high organic carbon content and basic soil (Texas Soil) than in a low organic carbon content and acidic soil (Mississippi soil).

(4) The adsorption of 2,4,6-trichlorophenol was related to the pH of the soil. 2,4,6-trichlorophenol adsorbed in the Mississippi soil twice as much as in the Texas soil, even though the Texas soil had a relatiely high organic carbon content. The 2,4,6-trichlorophenol was neutral in the Mississippi soil and anionic in the Texas soil. This implies that the ionic status of the compound was more important than organic carbon content in adsorption of 2,4,6-trichlorophenol.

(5) 2,4-dichlorophenol and 2,4,6-trichlorophenol competed for sorption in hight concentrations but not in low concentrations.

(6) Brucine adsorbed strongest and thiourea adsorbed weakest of the five compounds used in both soils. Brucine is a polycyclic aromatic compound. Thiourea is an aliphatic compound. The other three were monocyclic aromatic compounds.

Acknowledgements

References

1. Abdul A. S., Gibson, T. L., and Rai, D., 1986, The Effect of Organic Carbon on the Adorption of Fluorene by Aquifer Materials, Hazardous Waste & Hazardous Materials, Vol. 3, No. 4, pp. 429–439.

2. Benefield, L. D., Judkins, J. F. Jr., and Weand, B. L., 1982, Process Chemistry for Water and Wastewater Treatment, Prentice-Hall, Inc., NJ, p. 200.

3. Chiou, C. T., Porter, P. E., and Schmedding, D. W., 1983, Partition Equilibria of Nonionic Organic Compounds betteen Soil Organic Matter and Water, Environmental Science & Technology, Vol. 17, No. 4, pp. 227-231.

4. Dean, J. A., 1985, Lange's handbook of Chemistry, 13rd Ed., McGaw-Hill Book Co., pp. 5:13-5:38

5. Elliott, H. A., Liberati, M. R., and Huang, C. P., 1986, Competitive Adsorption of Heavy Metals by Soils, Journal of Environmental Quality, Vol. 15, No. 3, pp.214-219.

6. Federal Register, Appendix-IX Groundwater Monitoring List (1987), Vol. 52, No.131.

7. Federal Register, Hazardous Wasted Management System, 40 CFR Part 261 (1984), Vol. 49, No. 247.

8. Kennedy, J. B., and Neville, A. M., 1986, Basic Statistical Methods for Engineers and Scientists, 3rdEd., Harper & Row, NY., pp. 314-320.

9. Mathews, A. P., and Su, C. A., 1983, Prediction of Competitive Adsorption Kinetics for Two Priority Pollutants, Environmental Progress, Vol. 2, No. 4, pp. 257-261.

10. Murin, C.J., and Snoeyink, V.L., 1979, Competitive Adsorption of 2,4-Dichlorophenol and 2,4,6-Trichlorophenol in the Nanomolar to Micromolar Concentration Range, Environmental Science & Technology, Vol. 13, No. 3, pp.305-311.

11. Nkedi-Kizza, P., R^{ao}, P.S.C., Hornsby, A. G., 1987, Influence of Organic Cosovents on Leaching of Hydrophobic Organic Chemical through Soils, Environmental Science & Technology, Vol.21, No.11, pp. 1107-1111.

12. Nkedi-Kizza, P., Rao, P.S.C., Sherwood, J.M., and Delfino, J. J., 1984. Sorption of Organic Chemicals by Soils from Multi-sorbate Mixtures, American Society of Agronomy 76th Annual Meeting, Las Vegas, Nov. 25-30.

13. Rao, P.S.C., Hornsby, A. G., Kilcrease, D. P., and Nkedi-Kizza, P., 1985, Sorption and Transport of Hydrophobic Organic Chemicals in Aqueous and Mixed Solvent Systems : Model Development and preliminary Evaluation, Journal of Environmental Quality, Vo.,14, No.3, pp. 376-383.

14. Ward, T. M., and Getzen, F.W., 1970, Influence of pH on the Adsorption of Aromatic Acids on Activated Carbon, Environmental Science & Technology, Vol. 4, No.1, pp. 64-647.

15. Westall, J. C., Leuenberger, C., and Schwarzenbach, R. P., 1985, Influence of pH and Ionic Strength on the Aqueous-Nonaqueous Distribution of Chlorinated Phenols, Environmental Science & Technology, Vol. 19, No.2, pp. 193-198

16. Zachara, J.M., Alnsworth, C.C., Cowan, C.E., and Thomas, B.L., 1987, Sorption of Binary Mixtures of Aromatic Nitrogen Heterocyclic Compounds on Subsurface Materials, Environmental Science & Technology, Vol., 21, No. 4, pp. 397-402.