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EFFECT OF SOLUTION AND SOIL COMPOSITION ON SORPTION OF IONIZABLE AND NONIONIC COMPOUNDS

By

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ABSTRACT

EFFECT OF SOLUTION AND SOIL COMPOSITION ON SORPTION OF IONIZABLE AND NONIONIC COMPOUNDS

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Solution and soil composition affect sorption of ionizable (primisulfuron) and nonionic (TCE and toluene) compounds. Sorption of primisulfuron increased with decreasing pH. At pH 4.5, primisulfuron sorption increased with increasing OC. In soils with less than 1% OC, sorption at pH 4.5 increased with increasing Fe oxide content. Surfactant caused increased sorption in a soil with 0.7% OC, but decreased sorption in a soil with 1.7% OC. About 50% of sorbed primisulfuron did not desorb during a single 24-h batch desorption. Sorption estimates based on log-log relations between water solubility and K_{oc} overestimated K_{oc} by a factor of 4 to 40, even when K_{oc} was corrected for ionization of primisulfuron. Sorption of TCE and toluene by a soil with 2.1% OC decreased log-linearly with increasing volume fraction methanol, although deviations from log-linear behavior were noticed. Without accurate prediction of solubility enhancement, it is impossible to predict sorption in cosolvent solutions.

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Effect of Soil Properties and Surfactant on Primisulfuron Sorption

ABSTRACT

Soil properties affect the environmental fate of herbicides. Little is known about how soil organic matter and pH affect sorption and fate of the sulfonylurea primisulfuron (2-[3-(4,6-bis(difluoromethoxy)-pyrimidin-2-yl]-benzoic acid methyl ester). Primisulfuron sorption and desorption by six soils with different organic carbon (OC), iron oxide, and clay contents were investigated using batch reaction at controlled pH. Sorption was measured at a soil:solution ratio of 1:2 with 0.01 M $CaCl_2$ as a background electrolyte. Sorption and desorption isotherms were linear. When pH was adjusted to values between 4 and 6.5, sorption coefficients decreased with increasing pH. At pH 4.5, sorption coefficients increased with increasing OC and ranged from 0.6 for a soil with 0.2 % OC to 15.5 for a soil with 48 % OC. Surfactant (Triton X-77, 0.25% v v^{-1}) caused primisulfuron sorption to increase in a low-OC soil but caused decreased sorption in a soil with 1.7 % OC. Sorption coefficients were correlated with dithionite-extractable iron in soils with less than 1 % OC, but not in soils with greater OC. Desorption coefficients at native soil pH were up to five times greater than were sorption coefficients; about 50 % of sorbed primisulfuron did not desorb during a single 24-h batch desorption reaction. Primisulfuron is most likely to leach in soils with high pH or low organic matter contents.

INTRODUCTION

Primisulfuron, trade name Beacon (CGA-136872), is a relatively new sulfonylurea herbicide used to control grass and broad-leaved weeds in corn. In order to predict primisulfuron fate in the environment, it is essential to understand the effect of soil properties on primisulfuron sorption. Sorption may affect leaching, chemical and microbial degradation, and carryover to subsequent crops. Primisulfuron is a moderately weak acid with a pK_a of 5.1 (U.S. Environmental Protection Agency, 1990) and a low, pH-dependent water solubility (Fig. 1).

Primisulfuron sorption depends on the affinity of soil for both the neutral molecule, which predominates when $pH<pK_a$, and the anionic species, which is dominant when $pH>pK_a$. Neutral primisulfuron may be sorbed by soil organic matter, whereas the anionic species may be sorbed by protonated hydroxyl groups on iron and aluminum oxides. As pH increases, the proportion of neutral primisulfuron decreases, which causes sorption by soil organic matter to decrease. The proportion of anionic primisulfuron increases, yet the concentration of positively charged sorption sites decreases, which may cause sorption of anionic primisulfuron to decrease as pH increases. Thus, net sorption of primisulfuron should decrease as pH becomes less acidic.

No comprehensive, systematic studies of the effect of soil properties on primisulfuron sorption appear to have been published, but more is known about sorption of chlorsulfuron, an older sulfonylurea herbicide with pK_a near 3.7 (Zahnow, 1982; Shea, 1986). When soil pH was increased by long-term liming, chlorsulfuron sorption decreased with increasing pH (Nicholls and Evans, 1985). A similar decrease in sulfonylurea sorption with increasing pH has been reported when pH was adjusted to values between 4 and 8 (Mersie and Foy, 1985; Shea, 1986; Wehtje et al., 1987; Borggaard and Streibig, 1989).

Sorption of nonionic herbicides generally increases with increasing soil organic carbon (OC) content, but the relationship between OC and sorption of weakly acidic

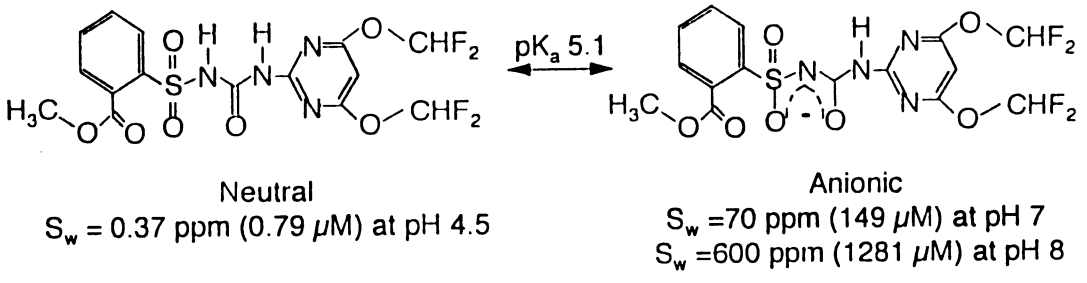

Figure 1. Structure of neutral and anionic forms of primisulfuron, showing delocalization of electron density in the anionic species.

herbicides such as sulfonylureas is more complex. Humic acid sorbs chlorsulfuron strongly at low pH (K_s = 35 at pH 4.2), but sorption decreases exponentially with increasing pH, paralleling the decrease in both neutral herbicide and in undissociated functional groups on humic acid (Borggaard and Streibig, 1988). Some authors have reported a positive correlation between chlorsulfuron sorption and soil OC in soils of varying pH (Mersie and Foy, 1985; 1986; Walker et al., 1989). In these studies, however, soil OC generally increased as soil pH decreased (Mersie and Foy, 1985; 1986; Walker et al., 1989), and there was no trend when soils with > 20 % organic matter were excluded (Walker et al., 1989). Even for soils at the same pH, chlorsulfuron sorption was greater in a soil with 0.8 % organic matter than in a soil with 1.3 % organic matter (Nicholls and Evans, 1985). The absence of a relationship between chlorsulfuron sorption and soil organic matter indicates that soil components other than soil organic matter likely play an important role in chlorsulfuron sorption.

To determine the effect of soil OC and of Fe and Al oxides, Borggaard and Streibig (1989) measured chlorsulfuron sorption by ten soil samples at pH 4.2 and 7 after a series of sequential extractions to remove Fe and Al incrementally. Multiple regression analysis showed that sorption coefficients at each pH depended on soil Fe and Al concentrations, as well as on soil OC (Borggaard and Streibig, 1989). On a mass basis, amorphous $Fe(OH)_3$ sorbs ten times as much chlorsulfuron as does goethite, but only one-fourth as much as does humic acid (Borgaard and Streibig, 1988).

Because sulfonylurea sorption depends in part on interactions between the neutral herbicide and soil organic matter, particularly at pH < 5, sorption may be affected by surfactants (wetting agents) that are used in the field to increase herbicide foliar absorption and water solubility. If surfactants cause substantial increases or decreases in herbicide sorption, then sorption coefficients measured without surfactant would lead to incorrect predictions of herbicide mobility and availability in the field. Sun and Boyd (1993) have reported that surfactants cause decreased sorption of compounds with low

water solubility and high sorption coefficients, but cause increased sorption of compounds with higher water solubilities and lower sorption coefficients. In soils with little organic carbon, sorption of the surfactant itself may substantially increase soil organic C and thus cause an increase in herbicide sorption (Sun and Boyd, 1993).

The objectives of this study were to determine the effect of pH, organic matter, variable-charge minerals, and surfactant (Triton X-77) on primisulfuron sorption by several soils. Careful selection of soils and choice of reaction pH permits unambiguous interpretation of the effect of soil pH and OC on primisulfuron sorption. Desorption was measured at native soil pH to determine the amount of sorption hysteresis.

MATERIALS AND METHODS

Materials

^{14}C-phenyl-labeled primisulfuron with a specific activity of 52.4 μCi mg^{-1} and a radiochemical purity of 94.3 % was obtained from Ciba-Geigy (Greensborough, NC). Non-radioactive analytical grade (99% pure) primisulfuron also was obtained from Ciba-Geigy. Triton X-77, a non-ionic surfactant typically applied with primisulfuron in the field (0.25% v v^{-1}) was obtained from Valent Corp. All other chemicals were analytical grade.

Samples of Kalamazoo sandy clay loam A and B horizons (fine-loamy, mixed, mesic Typic Hapludalfs), Misteguay clay A horizon [fine, mixed (calcareous), mesic Aeric Haplaquepts], and Houghton muck (euic, mesic Typic Medisaprists) were collected from Michigan State University research farms. Samples of two Oxisol B horizon samples [fine (siliceous), isothermic Typic Haplorthoxes, and very-fine (oxidic), isothermic Typic Haplorthoxes] were collected in Lavras, Brazil and provided by Dr. J. M. Lima (Univ. Fed., Lavras). These soils were selected to provide a range of OC and iron oxide concentrations (Table 1). The soils were air-dried and passed through a 2-mm

sieve. Organic carbon (OC) was determined by the Walkley-Black method (Nelson and Sommers, 1982), dithionite-extractable Fe (Fe_{DCB}) was determined using the method of Jackson et al. (1986), and clay content was determined by the hydrometer method (Gee and Bauder, 1986).

Batch Sorption Isotherms

The effect of soil OC and extractable Fe on primisulfuron sorption was determined by batch sorption experiments at pH 4.5. This pH was chosen in part because four of the six soil samples had supernatant solution pH values near 4.5 when neither acid nor base was added, and in part because neutral primisulfuron composes 80% of total solution-phase primisulfuron at this pH. The effect of pH on primisulfuron sorption by four of the soils was determined by adjusting suspension pH to a range of values between 4 and 6.5. The amounts of acid or base required to bring suspension pH to the desired value were determined in preliminary experiments. To measure primisulfuron sorption, 5.0-g subsamples of each soil (1.0 g for the muck soil) were weighed into screw-top, 25-mL glass Corex centrifuge tubes in triplicate for each herbicide concentration and pH. Solutions were prepared by adding either HCl or NaOH to 0.01 M $CaCl_2$ solutions so that each soil suspension would be at the desired pH after the solutions and soils were shaken for 24 h; $CaCl_2$ was used as a background electrolyte to minimize dissolution/dispersion of organic matter. Ten mL of appropriate solution was added to soil subsamples in the centrifuge tubes to give a 1:2 soil:solution ratio (1:10 for muck soil). Tubes then were sealed with teflon-lined caps and shaken for 1 h to bring each soil suspension to the desired pH before primisulfuron was added. For each soil and pH, four of the tubes were centrifuged, the supernatant solution pH was measured, and soil was resuspended using a vortex mixer. Finally, aliquots of 1000 mg L^{-1} analytical grade primisulfuron and 5.0 μL of 100 mg L^{-1} ^{14}C-primisulfuron (both in methanol) were added to all tubes to give total radioactivity of 2.6 μCi L^{-1} and eight initial herbicide

concentrations ranging from 0.05 to 1.0 mg/L (for pH < 5.5; 0.11 to 2.13 μM) or 0.05 to 5 mg L^{-1} (for pH 5.5 to 6.5; 0.11 to 10.67 μM). The lowest initial primisulfuron concentration was equivalent to 100 μg kg^{-1} soil (0.21 μmol kg^{-1}), a typical field application rate. For each concentration and pH, a tube with solution only (that is, soil-free "blank") was prepared. For each soil and pH, triplicate samples were also prepared with no primisulfuron so that the concentration of dissolved and colloidal organic C (DOC) could be measured without releasing ^{14}C-CO_2 into the laboratory air. Methanol-containing samples explode in the high-temperature C analyzer, so no methanol was added to these samples. The tubes were placed on a reciprocating shaker and shaken for 24 h at 23 ± 2 °C. Loss of primisulfuron from soil-free blank solutions during shaking and centrifugation was negligible. A preliminary kinetic study showed that steady state was reached in 24; within experimental error, the concentration of primisulfuron sorbed after longer reaction times (up to 5 d) was the same as that sorbed after 24 h. The supernatant solutions were separated from the sorbents by centrifuging for 10 min at 8000 x g.

A 1-mL aliquot from each sample supernatant and "blank" solution was added to 5.5 mL of toluene-based scintillation cocktail and counted with a Packard 1500 Tricarb Liquid Scintillation Analyzer (Packard Inst. Co., Downer's Grove, IL). The pH of the remaining supernatant solution was measured. The supernatant solution was decanted, and the tubes were reweighed to determine the mass of solution entrained in the soil pastes at the bottom of each tube. Samples were saved for desorption experiments. The DOC concentration in the supernatant solution of samples with no ^{14}C was determined using a Dohrmann DC-190 high-temperature TOC analyzer (Rosemount Analytical, Santa Clara, CA).

To assess the effect of surfactant on primisulfuron sorption by two agricultural soils at three suspension pH values, primisulfuron sorption by the Hapludalf and Haplaquept A

horizon samples was measured as described above, except that the surfactant Triton X-77 was added to all 0.01 M $CaCl_2$ solutions at a rate of 0.25 % (v v^{-1}).

Batch desorption isotherms

To determine whether primisulfuron exhibits sorption hysteresis at natural soil pH, primisulfuron desorption was measured in those samples to which no acid or base had been added. Ten mL of herbicide-free 0.01 M $CaCl_2$ were added to the soil pastes that remained in the tubes after the sorption experiments, and the suspensions were shaken for 24 h and centrifuged as described above. A 1-mL aliquot was removed from each tube and counted by liquid scintillation counting.

Data analysis

The concentration of sorbed primisulfuron (x_s; mg kg^{-1}) was calculated with the equation:

$$x_s = (C_{blank} - C_e)V_e M^{-1} \quad [1]$$

where C_{blank} and C_e are the "equilibrium" primisulfuron concentrations (mg L^{-1}) in the soil-free blank and the sample supernatant solutions, respectively, V_e is the volume (L) of sample solution reacted with the sorbent, and M is the dry mass (kg) of soil used in the experiment. Sorption isotherms were constructed by plotting x_s vs. C_e. Sorption isotherms were linear at the primisulfuron concentrations used in these experiments, so sorption data were fit by linear regression to give the sorption coefficient K_s (L kg^{-1}), which is the slope of the regression line.

For the desorption experiments, the concentration of primisulfuron not desorbed in 24 h (x_d) was calculated with the equation:

$$x_d = [(x_s M + C_e V_{ent}) - C_d V_d)] M^{-1} \quad [2]$$

where V_{ent} is the volume (that is, mass) of solution entrained after the sorption experiment, C_d is the primisulfuron concentration in the desorption supernatant solution,

and V_d is the volume of entrained solution plus the volume of 0.01 M $CaCl_2$ solution added during the desorption experiment. Desorption isotherms were constructed by plotting q_d vs. C_d. The linear desorption coefficients (K_{desorp}) were determined from the slope of the desorption isotherms.

RESULTS AND DISCUSSION

Effect of OC on Sorption at pH 4.5

At pH 4.5, 80% of solution-phase primisulfuron is neutral, and primisulfuron sorption coefficients generally increased as soil OC increased (Table 1). There is a correlation between K_s and OC, even when the muck soil is omitted and only the mineral soils are included ($P = 0.037$; Fig. 2), which suggests that soil organic matter is important for primisulfuron sorption. However, the non-zero intercepts for the K_s vs OC correlation lines and the ten-fold increase in the OC-normalized sorption coefficient, K_{oc}, with decreasing OC (Table 1) suggest that primisulfuron sorption is more complex than predicted by partition theory.

Green and Karickhoff (1990) have suggested that partition theory (Karickhoff et al., 1979; Karickhoff, 1981; Chiou et al., 1979; 1983) should be used to predict K_{oc} only if an herbicide's water solubility is less than about 1 mM and a soil's clay:OC ratio is less than 40. When the clay:OC ratio is greater than about 40, sorption by minerals should cause the measured K_{oc} to be greater than K_{oc} calculated from partition theory. According to these criteria, partition theory should provide a reliable estimate of K_{oc} in the muck soil but not in the other five soils, where the clay:OC ranges from 39 to 94.

To determine whether partition theory gives reasonable estimates of K_{oc} for any of the soils at pH 4.5, K_{oc} was calculated with an equation adapted from Chiou et al. (1983):

$$\log K_{oc} = -0.813 (\log S_{scl} + \log V) - 0.993 + \log 1.74 + \log (C_0 C_{tot}^{-1}) \qquad [3]$$

Table 1. Primisulfuron sorption coefficients (K_s) and K_{oc} values at pH 4.5±0.1, and relevant soil properties (n=3).

Soil	K_s †	K_{oc} ‡	OC §	Fe_{DCB} ¶	Clay	DOC †
	—— L kg^{-1} ——		%	g kg^{-1}	%	mg L^{-1}
Medisaprist (muck)	15.47±0.90	32	47.7	8.9	N.D.#	150±15
Haplauqept	1.56±0.13	93	1.67	5.0	60	85±10
Oxidic Oxisol	0.80±0.04	101	0.79	84.8	74	30.8±0.8
Hapludalf A	0.55±0.05	83	0.66	11.6	26	57±8
Hapludalf B	0.67±0.04	279	0.24	32.6	23	26.7±0.6
Siliceous Oxisol	0.67±0.05	319	0.21	38.1	42	20±3

† Sorption coefficient K_s determined from slope of isotherm ± 95% confidence interval

‡ $K_{oc} = K_s (0.01 \times \% OC)^{-1}$. Predicted K_{oc} is 1325; see text for explanation

§ SD < 0.03 % OC for mineral soils; 0.3 % OC for muck soil

¶ SD ≤ 0.2 g Fe kg^{-1}

Not determined. Ash content of muck soil was 18 %

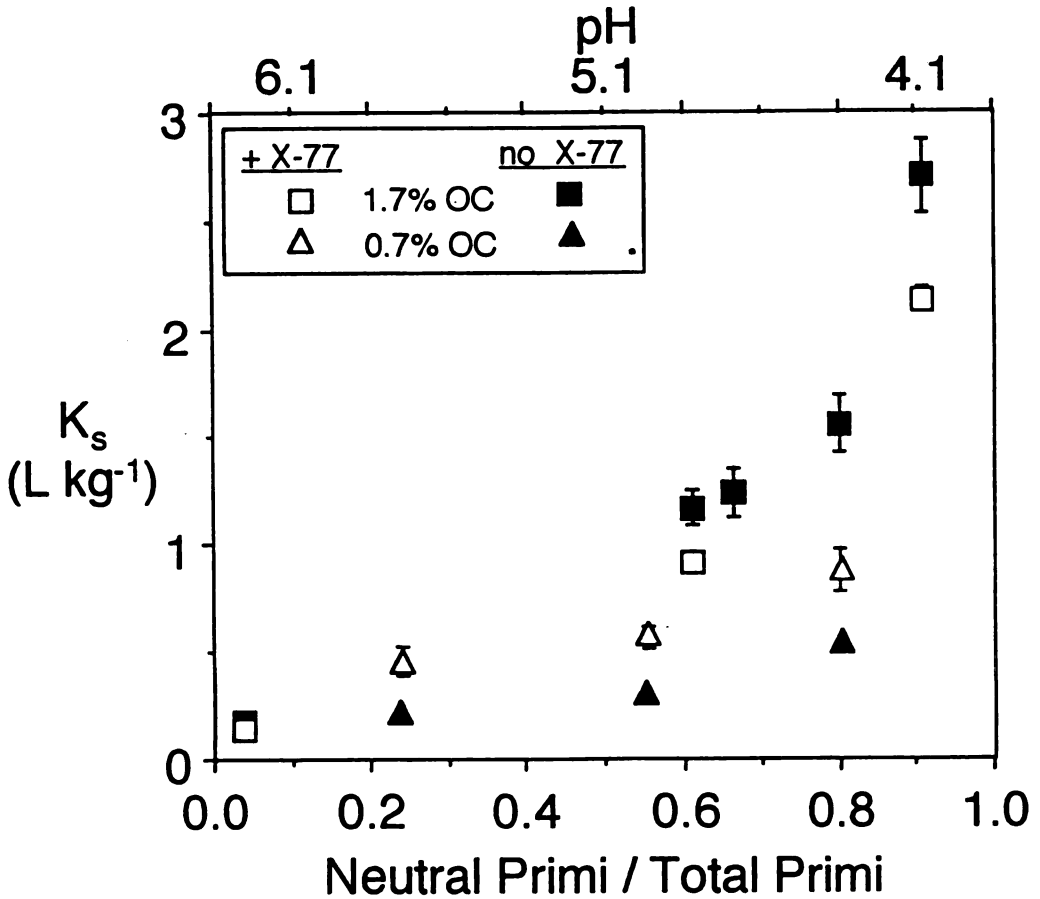

Figure 2. Sorption coefficient K_s as a function of soil organic C concentration for the five mineral soils. Error bars represent 95% confidence limits of the slope of sorption isotherms and generally are smaller than the size of data points.

where S_{scl} is the water solubility of primisulfuron as a hypothetical supercooled liquid, V is primisulfuron's molar volume (0.289 L mol^{-1}), log 1.74 converts from log K_{om} to log K_{oc}, and log (C_0 C_{tot}^{-1}) adjusts for the fraction of primisulfuron that is neutral at pH 4.5. The solubility of the hypothetical supercooled liquid may be calculated as (Chiou et al., 1982)

$$\log S_{scl} = \log S + \frac{\Delta H_f}{2.303\,R}\left(\frac{T_m - T}{T_m\,T}\right) \qquad [4]$$

where S is the measured solubility of solid primisulfuron, ΔH_f is the enthalpy of fusion, T_m is the melting temperature (476.1 K), and T is temperature. With the approximation that ΔH_f (cal) = 13.5 T_m (Chiou et al., 1982) and setting T = 298 K, Eq. [3] simplifies to

$$\log K_{oc} = -0.813\,(\log S + \log V) - 0.00805\,(T_m - T) - 0.849. \qquad [5]$$

At pH 4.5, Eq. [5] gives K_{oc} equal to 1325, which is 4 to 40 times greater than the measured K_{oc} values (Table 1). The discrepancy between measured and calculated K_{oc} is greatest for the muck soil, the only soil for which partition theory was expected to be valid. No other solubility-based equation in the literature gave a better estimate of K_{oc} than did Eq. [5]. Furthermore, the discrepancy between measured and calculated K_{oc} was even worse (that is, the calculated K_{oc} is near 49,100) if corrections for the solid-liquid phase transition, molar volume, and (C_0 C_{tot}^{-1}) were omitted. The less-than-predicted K_{oc} values at pH 4.5 cannot be caused by primisulfuron sorption by minerals because additional sorption sites on minerals should cause measured sorption to be greater, not less, than predicted from partition theory.

Dissolved and colloidal organic C (DOC) can enhance the affinity of large, insoluble organic compounds for the solution phase and cause sorption to decrease with increasing DOC. Dissolved OC concentrations measured in supernatant solutions after the sorption experiment (Table 1) were greatest for the soils with large OC concentrations

and small K_{oc}, a result that is consistent with the hypothesis that the decrease in K_{oc} with increasing soil OC was caused by DOC-primisulfuron interactions. However, even the largest DOC concentration, 150 mg/L, is only about 7 times S_{sol} for primisulfuron (21 mg L^{-1}) and is probably not large enough to affect primisulfuron sorption, based on data reported by Chiou et al (1986; 1987). The DOC concentrations reported in Table 1 do not include methanol, which was the solvent for the primisulfuron stock solutions. Methanol contributed an additional 155 to 450 mg DOC L^{-1} and increased with increasing primisulfuron concentration. The total DOC concentration still was only 8 to 25 times S_{sol} for primisulfuron.

Another possible explanation for the decrease in K_{oc} with increasing soil OC is that the polarity of organic matter in the soils with low OC may "match" the polarity of primisulfuron, which contains 59% O, N, S, and F by weight. In contrast, the muck soil's organic matter is highly humified and possibly less polar than is primisulfuron, making the muck soil a poor sorbent for primisulfuron. Although further research is needed to verify this last hypothesis, our results clearly show that partition theory cannot reliably predict sorption of primisulfuron, even at an acidic pH where most of the herbicide is nonionic.

Effect of Iron Oxides on Sorption

At pH 4.5, where 20% of solution-phase primisulfuron is anionic, there is a correlation between K_s and dithionite-extractable Fe (Fe_{DCB}) in soils with less than 1% OC (Table 1; $P < 0.01$). In contrast, the relation is not significant when soils with greater than 1% OC are included ($P = 0.45$). Minerals may play an important role in sorption of polar organic compounds when soil OC is less than about 0.5% or when the clay:OC ratio is high (Green and Karickhoff, 1990). The data in Table 1 show that primisulfuron sorption depends on both OC and Fe_{DCB}; Al oxides may also play a role, as shown previously for chlorsulfuron (Borggaard and Streibig, 1988; 1989). Our results indicate that even when pH is held constant and is $< pK_a$, primisulfuron K_s values cannot be

predicted from any single soil property. Previous research has shown that K_s values for chlorsulfuron sorption by humic acid are four or five times greater than for Fe oxides, even when the anion is the predominant solution-phase sulfonylurea species (Borggaard and Streibig, 1988). Thus, at pH 4.5, organic C is probably a more important sorbent for primisulfuron than are minerals, particularly because 80% of dissolved primisulfuron is uncharged.

Effect of pH on Sorption

Primisulfuron sorption coefficients decreased with increasing equilibrium supernatant solution pH values in all of the soils used in these experiments (Table 2). Other researchers have reported similar pH effects for other sulfonylureas (Mersie and Foy, 1985; Shea, 1986; Wehtje et al., 1987; Borggaard and Streibig, 1989). As pH increases, sorption of neutral primisulfuron decreases because the proportion of the neutral species decreases. In addition, sorption of the anionic form also decreases as pH increases and surface charge on Fe and Al oxides becomes less positive.

Measured K_s values exhibit a non-linear dependence on the fraction of neutral primisulfuron ($C_0\ C_{tot}^{-1}$) with the steepest slope at low pH (Fig. 3). The nonlinear dependence of K_s on ($C_0\ C_{tot}^{-1}$) may be caused by strong sorption of the anion on positively charged oxides at low pH, or by a greater affinity of organic matter for primisulfuron at low pH, where organic matter has a smaller net negative charge.

Effect of Surfactant on Sorption

When primisulfuron-soil suspensions at pH 4.5 contained the surfactant X-77, K_s for primisulfuron sorption by the Hapludalf A horizon soil (0.7% OC) was twice that measured in surfactant-free solutions. The addition of X-77 caused K_s for the Hapludalf to increase by a constant amount, about 0.25 L kg^{-1}, at all pH values between 4.5 and 5.6 (Table 2; Fig. 3). For the Haplaquept soil (1.7% OC), however, X-77 caused a slight decrease in K_s at pH 4.1 and had a negligible effect at pH 6.5, the natural soil pH. When

Table 2. Primisulfuron sorption coefficients (K_s; L kg^{-1}) at various pH, with and without surfactant (X-77).

	Surfactant (X-77)	
pH	Absent	Present
	Medisaprist (muck)	
4.5	15.47 ± 0.90[†]	N.D.[§]
5.8[‡]	5.43 ± 0.34	N.D.
	Haplaquept	
4.1	2.71 ± 0.17	2.14 ± 0.06
4.5	1.56 ± 0.13	N.D.
4.8	1.24 ± 0.11	N.D.
4.9	1.17 ± 0.08	0.92 ± 0.03
6.5[‡]	0.18 ± 0.03	0.14 ± 0.02
	Hapludalf (A Horizon)	
4.5[‡]	0.55 ± 0.05	0.88 ± 0.10
5.0	0.29 ± 0.05	0.56 ± 0.05
5.6	0.23 ± 0.03	0.46 ± 0.07
	Hapludalf (B Horizon)	
3.9[‡]	1.62 ± 0.11	N.D.
4.3	0.90 ± 0.04	N.D.
4.4	0.67 ± 0.04	N.D.
5.0	0.39 ± 0.03	N.D.

[†] slope of isotherm ± 95% confidence interval

[‡] Indicates supernatant pH when no pH adjustment

[§] N.D. = not measured

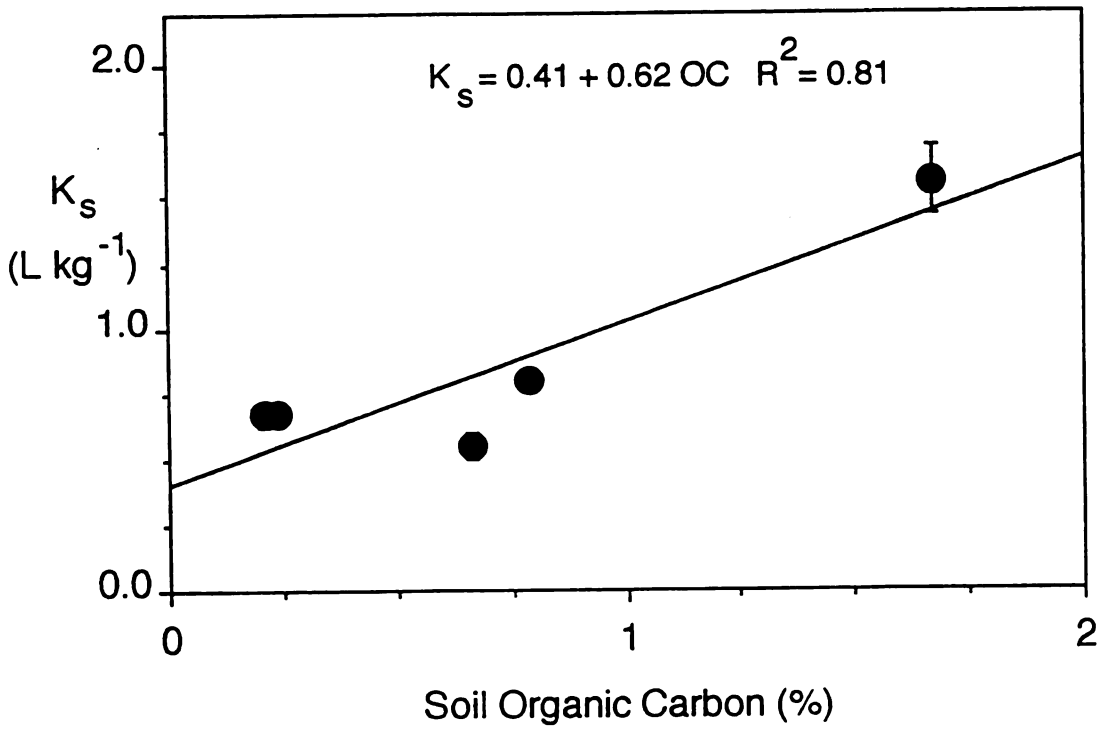

Figure 3. Effect of pH (top axis), fraction of neutral primisulfuron (bottom axis), and X-77 surfactant on primisulfuron sorption coefficients for Haplaquept (1.7% OC) and Hapludalf (0.7% OC) soil samples. Error bars represent 95% confidence limits of the slope of sorption isotherms.

pH was less than the pK_a of primisulfuron, the increase in K_s for the soil with 0.7 % OC and the decrease in K_s for the soil with 1.7 % OC can be understood readily in terms of a model proposed by Sun and Boyd (1993). In this model, addition of surfactant creates two new phases with which primisulfuron may associate: surfactant that is sorbed to the soil, and surfactant that is in the water. Sorbed surfactant increases the affinity of an herbicide for the soil, whereas "aqueous phase" surfactant increases an herbicide's affinity for the solution. The net effect of surfactant (that is, increased or decreased herbicide sorption) depends upon whether sorption enhancement or solubility enhancement is more important. For a single herbicide-surfactant combination in different soils, the mass ratio of sorbed surfactant to natural soil organic matter should determine whether a surfactant enhances or inhibits sorption of the solute, because the solubility-enhancement effect of the surfactant should be the same for all soils.

In the soil with 0.7 % OC, the dominant effect of surfactant apparently is to increase the solid-phase OC concentration and thus to enhance primisulfuron sorption. In contrast, for the soil with 1.7% OC, surfactant sorption likely causes soil OC to increase by a smaller proportion of total OC, and the dominant effect of surfactant appears to be smaller K_s values because of increased affinity of primisulfuron for the aqueous phase.

Desorption

Desorption isotherms were linear over the entire concentration range (not shown). Primisulfuron desorption coefficients (K_{desorp}) at natural soil pH were greater than the corresponding sorption coefficients (Table 3). In most of the soils, about 50 % of sorbed primisulfuron did not desorb during a single 24-h batch desorption reaction, but 90% did not desorb in the soil with the highest pH and lowest K_s (Table 3). Irreversible sorption of nonionic organic compounds has been reported by numerous authors (for example, Pignatello, 1989; Scribner et al., 1992; Brusseau and Rao, 1989) and attributed to a diffusion-controlled process rather than to chemical transformation or chemisorption. In the present study, we cannot state with certainty whether the "irreversibly sorbed" primisulfuron is nonionic or anionic,

Table 3. Primisulfuron sorption (K_s) and desorption (K_{desorp}) coefficients at natural soil pH.

Soil	OC	Supernatant pH	K_s	K_{desorp}
	%		L kg^{-1}	L kg^{-1}
Medisaprist (muck)	47.7	5.8	5.43 ± 0.34†	9.00 ± 0.94
Haplaquept	1.67	6.5	0.18 ± 0.03	0.67 ± 0.13
Oxidic Oxisol	0.70	4.6	0.80 ± 0.04	1.00 ± 0.10
Hapludalf A horizon	0.66	4.5	0.55 ± 0.05	0.61 ± 0.09
Hapludalf B horizon	0.24	3.9	1.62 ± 0.11	2.09 ± 0.29
Siliceous Oxisol	0.21	4.4	0.67 ± 0.05	1.17 ± 0.11

† Slope of isotherm ± 95% confidence interval

yet the large fraction of irreversibly sorbed primisulfuron for the pH 6.5 soil may be caused by strong retention of anionic primisulfuron. Additional research is needed to determine the effect of soil properties on primisulfuron sorption hysteresis.

CONCLUSIONS

In summary, primisulfuron sorption coefficients increase with increasing OC and dithionite-extractable Fe, and with decreasing pH. At constant pH, both OC and Fe oxides are important sorbents in soils with less than 1% OC, but OC is dominant in soils with higher OC. Sorption estimates based on log-log relations between water solubility and K_{oc} overestimate K_{oc} by a factor of 4 to 40, depending on the soil. When pH is varied, a ten-fold change in $[H^+]$ in any one soil has a greater effect on K_s than does a ten-fold change in OC at constant pH. Sorption of primisulfuron is also affected by the surfactant, X-77. Addition of X-77 to soil suspensions caused primisulfuron sorption to increase in a soil with less than 1% OC but to decrease in a soil with greater than 1% OC. Our results show that K_s cannot be predicted from partition theory, and that accurate estimation of herbicide sorption and mobility requires that sorption be measured in the surfactant solutions normally used in weed-control applications, not in surfactant-free aqueous solutions.

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Chapter 2.
Methanol Cosolvent Effects on TCE and Toluene Solubility and Sorption

ABSTRACT

Solution composition can affect the environmental fate of hydrophobic organic compounds (HOCs). Other researchers have proposed log-linear relationships to describe the effect of cosolvents on HOC solubility and sorption. The solubility and sorption of trichloroethylene (TCE) and toluene were investigated in low volume fraction (f_c) methanol solutions. Sorption was measured in two soils with low and medium organic C using batch reaction. Solubility of TCE and toluene increased log-linearly with increasing methanol fraction, although data for toluene might be better described with a nonlinear relationship. Values obtained for the cosolvency power, σ, of methanol for TCE and toluene were 1.6±0.2 and 1.4±0.2, respectively. Toluene and TCE sorption coefficients for a soil with 2 % organic C soil could be fit with a log-linear dependence on methanol f_c, although the plots exhibited some nonlinearity. Deviations from log-linear behavior may be due to increasing solubility enhancement effects with increasing volume fraction cosolvent. Methanol f_c had no effect on toluene sorption by a soil with 0.7% organic C.

INTRODUCTION

Sorption is an important process in determining the fate and transport of hydrophobic organic compounds (HOCs) in the subsurface environment. These chemicals may occur in a mixture of solvents (water plus an organic cosolvent). In other cases, cosolvents may used to facilitate groundwater remediation. Research results from aqueous systems may not be appropriate in some situations to describe HOC sorption and transport in solvent-containing environments.

A number of researchers have studied the effect of cosolvents on HOC solubility and sorption. Yalkowsky et al. (1972) proposed that the solubility of an HOC in aqueous (S_w) and mixed (S_m) solvents can be related by the equation:

$$\log S_m \text{ (moles/L)} = \log S_w \text{ (moles/L)} + \sigma f_c \qquad [1]$$

where f_c is the volume fraction of organic cosolvent and σ is the cosolvency power. The value of σ is unique for every solute/solvent combination and is the slope of a plot of log S_m vs. f_c.

Nkedi-Kizza et al. (1985) found that σ could be related to a solute's hydrocarbonaceous surface area (HSA, $Å^2$) by the equation:

$$\sigma = \Delta\gamma^c \, HSA/kT \qquad [2]$$

where $\Delta\gamma^c$ is the interfacial free energy ($J\ Å^{-2}$) of the solvent at the hydrocarbonaceous surface area of contact with the solute, k is the Boltzmann constant ($1.38 \times 10^{-23}\ J\ K^{-1}$), and T is the absolute temperature. Woodburn et al. (1986) found $\Delta\gamma^c$ was independent of solute and determined a value of $2.30 \times 10^{-22}\ J\ Å^{-2}$ for water/methanol mixtures. Morris et al. (1988) found that σ could be related to a solute's octanol-water partition coefficient (K_{ow}) by the equation:

$$\sigma = a \ \log K_{ow} + b \qquad [3]$$

where a and b are regression parameters unique for every solvent (for methanol a = 0.68 and b = 1.07).

Most researchers who found a log-linear relationship between S_m and f_c used f_c values in the range of 0.1 to 1.0 (Fu and Luthy, 1986a, Yalkowsky et al., 1972, Yalkowsky et al., 1976). Kimble and Chin (1994) found that the solubilities of three polynuclear aromatic hydrocarbons deviated from the log-linear relationship in methanol/water mixtures at low f_c. Pinal et al. (1990) found slight deviations from the log-linear relationship for trichloroethylene and toluene at $f_c > 0.3$.

Using the fact that sorption of HOCs can be related to solubility, Rao (1985) expanded Yalkowsky's theory to relate sorption coefficients in aqueous solution (K_w) and mixed solution (K_m):

$$\log K_m \text{ (L/kg)} = \log K_w \text{ (L/kg)} - \alpha\sigma f_c \qquad [4]$$

where α represents the effect of solvent/sorbent interactions on $\log K_m$, and σ is independent of sorbent. If α is greater than 1.0, a cosolvent causes sorption to decrease more than expected from the increase in HOC solubility alone. If α is equal to 1.0, solvent-sorbent interactions do not affect the sorption coefficient. If α is less than 1.0, the decrease in HOC sorption with increasing f_c is less than predicted based on increased solubility. Therefore, solvent-sorbent interactions cause greater sorption in cosolvent mixtures than in water. Most researchers have found α values less than 1.0 in methanol/water mixtures (Fu and Luthy, 1986, Walters and Guiseppi-Elle, 1988, Wood et al., 1990, Brusseau et al., 1991, Kimble and Chin, 1994).

Values of α less below 1.0 may be caused by swelling of organic matter in cosolvent solutions, which makes nonpolar sorption regions more accessible to a solute (Wood et al., 1990). Freeman and Cheung (1981) have shown that the Hildebrand solubility parameter (δ) of organic matter is between 8 and 15, and likely is near 10, at least for nonpolar sorption regions of organic matter. Swelling of cross-linked polymers increases as the solubility parameter of the solvent approaches that of the cross-linked solid. Thus, as the volume fraction methanol (δ=15) increases relative to water (δ=23) in a cosolvent mixture, the solubility parameter of the solvent becomes closer to that of

organic matter, which facilitates swelling and may expose additional sorption domains (Wood et al., 1990).

Increased swelling of organic matter may also explain why sorption and/or desorption rate constants increase as the fraction of cosolvent increases (Walters and Guiseppi-Elle, 1988, Nkedi-Kizza et al., 1989, Brusseau et al., 1991) because solute diffusion through swollen organic matter is faster than through the more densely entangled structure of unswollen organic matter (Freeman and Cheung, 1981). Intraorganic matter diffusion is believed to be the rate limiting step in obtaining sorption equilibrium (Freeman and Cheung, 1981; Brusseau and Rao, 1989). Consequently, sorption and desorption are faster in the presence of cosolvents that promote swelling of nonpolar regions of organic matter.

The addition of cosolvent can help researchers not only by decreasing time to reach equilibration, but also can be useful in determining the water solubility (S_w) or sorption from water (K_w) for a highly hydrophobic compound. Results from solubility or sorption experiments using several different fractions of a cosolvent can be extrapolated to an f_c = 0.0, to predict S_w or K_w. A K_{oc} value extrapolated from dioxin sorption isotherms using methanol as a cosolvent agreed well with values predicted from S_w (Wood and Guiseppi-Elle, 1988).

Due to the fact that cosolvents can increase solubility, decrease sorption, and decrease nonequilibrium sorption constraints, addition of cosolvents to ground water would increase the amount of HOCs present in the liquid phase relative to the soil at contaminated sites (Augustijn et al., 1994). This may enhance *in situ* remediation techniques such as bioremediation or pump and treat technologies, depending on the cosolvent fraction and properties.

The purpose of this research was to determine the effect of methanol on the solubility and sorption of trichloroethlyene (TCE) and toluene by soils with a range of

organic C contents and to determine if equations 1-4 hold true for low (f_c<0.20) concentrations of methanol.

MATERIALS AND METHODS

Materials

The two soils selected for this study were chosen to have a range of organic carbon contents, because the effect of cosolvents on organic matter swelling should increase with increasing organic matter content. The first soil used in this study was an A-horizon sample of Capac loam (fine-loamy, mixed, mesic Aeric Ochraqualfs) that contained 2.1% organic C. The second soil was an A-horizon sample of Kalamazoo sandy clay loam (fine-loamy, mixed, mesic Typic Hapludalfs) that contained 0.66% organic C. Soil was air-dried and passed through a 2-mm sieve. The two solutes used in the experiment were trichloroethylene (TCE) and toluene. Selected properties of the solutes are shown in Table 1. The cosolvent chosen for the experiments was methanol. All organic chemicals were HPLC grade.

Table 1. Solute Properties.

Solute	Density† (g/mL)	K_{oc}† (mL/g)	log K_{ow}†	S_w† (mol L^{-1})	HSA (Å^2)
toluene	0.866	300	2.73	5.59×10^{-3}	127‡
TCE	1.465	126	2.38	8.37×10^{-3}	ND§

† Pavlostathis and Mathavan (1992).
‡ Woodburn et al. (1986).
§ Not determined.

Solubility Enhancement Experiments

The solubility of TCE and toluene was measured in systems composed of 0 to 0.2 volume fraction methanol in aqueous 0.01 M $CaCl_2$ with 0.05% NaN_3 added as a biocide. Duplicate 5-mL aliquots of these mixtures were added to screw-top, 25-mL glass Corex

centrifuge tubes. Liquid TCE or toluene was added dropwise to the tubes until phase separation was obtained. All tubes were sealed with teflon-lined caps and shaken for 36 h at 25±1°C, then centrifuged at 10,000 rpm for 10 min. A 10-μL aliquot was removed from the aqueous phase of each tube, diluted to 5 mL with deionized water, and analyzed by gas chromatography. Although solubility enhancement experiments did not occur in zero headspace, this method was considered reliable based on good agreement between values measured for water solubility (volume fraction methanol = 0, no salt or biocide) and those previously reported (Table 1).

Batch Sorption Isotherms

Sorption of TCE and toluene from water and from mixed methanol-water cosolvent solutions was measured in batch sorption experiments. Sorption of TCE and toluene by Capac soil was measured in solutions that contained 0. 0.04, 0.08, 0.12, and 0.20 volume fraction methanol in 0.01 M $CaCl_2$ with 0.05% NaN_3 to inhibit microbial activity. Sorption of toluene by Kalamazoo sandy clay loam was measured at 0, 0.04, 0.08, and 0.12 volume fraction methanol. For each soil and cosolvent composition and each of eight initial TCE and toluene concentrations, duplicate 5.0±0.05-g subsamples of soil (dry weight) were weighed into 16-mL glass septum vials. The vials were then filled to zero headspace with the appropriate aqueous or cosolvent solution. Each vial was sealed with a teflon-lined septum and an aluminum crimp seal. The vials were then weighed to determine the solution volume. Aliquots (1 to 8 μL) of 10,000 μg mL^{-1} TCE or toluene in methanol were injected into each vial to give the appropriate initial solution concentration. The volume of methanol added was negligible (<0.075% v v^{-1}). For each TCE, toluene, and cosolvent fraction, eight soil-free blank solutions were prepared with zero headspace and treated identically to the soil-containing samples. Vials were shaken at room temperature for 24 h, after which the suspensions were centrifuged at 3,000 rpm for 10 min. A 5-mL aliquot of the liquid phase was transferred with a syringe to a headspace vial and analyzed for TCE or toluene by gas chromatography.

Gas Chromatography

Solute analyses were performed with a Perkin-Elmer gas chromatography autosystem. Samples were heated to 90 °C for 25 min using an HS40 headspace sampler. Injector temperature was set at 250 °C. A 30m, 0.53mm I.D., 3.0 μm film thickness, liquid cyano-methyl-phenylsilicone column was used to provide resolution for TCE and toluene. The carrier gas was helium and the temperature program was 60-100 °C at 10 °C per min. Solutes were detected with a flame ionization detector set at 250 °C. Samples were calibrated against a standard curve from obtained known quantities of solutes dissolved in the same solvent (volume fraction methanol, salt and biocide) as the samples.

Data Analysis

The concentration of solute sorbed (x_s, mg kg^{-1}) was calculated with the equation:

$$x_s = (C_{blank}V_{blank} - C_eV_e)\, M^{-1} \qquad [5]$$

where C_{blank} and C_e are the concentrations (mg L^{-1}) of solute in the "equilibrated" soil-free blank and sample supernatant solutions, respectively, V_{blank} and V_e are the volumes (L) of soil-free blank and sample solutions, respectively, and M is the dry mass (kg) of soil used in the experiment. Sorption isotherms were constructed by plotting x_s vs. C_e. The linear sorption coefficient (K; L kg^{-1}) was determined from the slope of the isotherm. Standard errors for each K value were calculated using the regression data analysis tool in Microsoft Excel.

RESULTS

Solubility Enhancement Experiments

The solubilities of TCE and toluene increased log-linearly with increasing methanol fraction (Figs. 1 and 2), although data for toluene might be better described with a nonlinear relationship. Using Eq. 1, values of σ for TCE and toluene were 1.6±0.2 and 1.4±0.2, respectively. These values are significantly less then the values of 2.7 and 2.9 for TCE and toluene, respectively, predicted from Eq. 3. By contrast, Eq. 2 gives $\sigma = 7.1$ for toluene, which is almost 2.5 times greater than calculated from Eq. 1.

Kimble and Chin (1994) suggested that the log-linear relationship between S_m and f_c could be divided into two regions, low (f_c<0.2) and high (f_c>0.2) cosolvent concentrations. This would give each solute two σ values. They proposed that σ for low methanol concentrations could be related to the HOC's aqueous activity coefficient (γ) by the equation:

$$\sigma = 1.03 \log (\gamma) - 3.56 . \qquad [6]$$

The aqueous activity coefficient calculated from the inverse liquid mole fraction solubilities gives γ values of 6640 and 9440 for TCE and toluene, respectively. Using these values, Eq. 6 predicts σ values of 0.38 and 0.56 for TCE and toluene, respectively, significantly less that what was found in our experiments. Clearly, published equations for calculating σ give values that differ by greater than a factor of 10; the values determined from Eq. 1 in the present experiments are well within the broad range of predicted values.

One possible explanation for the wide range of σ values is that methanol solubility-enhancement effects are nonlinear over the entire concentration range. Banerjee and Yalkowsky (1988) hypothesized that at low f_c, each solute molecule interacts with only one hydrated cosolvent molecule in low cosolvent/water mixtures. As f_c increases, the cosolvent molecules can associate with one another, significantly increasing solubility enhancement effects. If this hypothesis is true, then solubility enhancement effects should increase over the entire range of cosolvent concentrations. This would yield a nonlinear dependence of log S_m on f_c. There need not be a sharp increase in solubility enhancement at a certain concentration as in a critical micelle concentration for surfactants or as proposed for cosolvency by Kimble and Chin (1994).

A nonlinear increase in solubility enhancement effect can be seen in our data for toluene as well as in data from other researchers previously reported as linear (Fu and Luthy, 1986a, Morris et al., 1988, Pinal et al., 1990). These researchers may have mistaken nonlinear trends as linear by focusing on medium ranges of cosolvent (f_c=0.2 to 0.8) and ignoring data for low and high f_c, where nonlinearity is most pronounced.

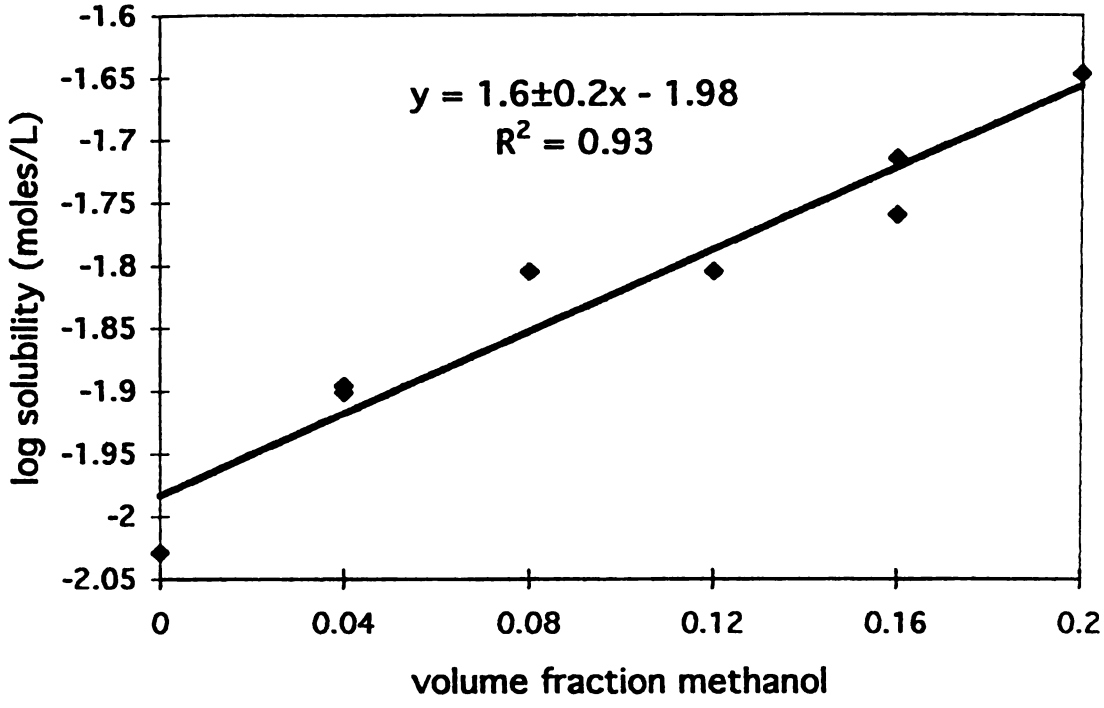

Figure 1. Log solubility of TCE as a function of volume fraction methanol.

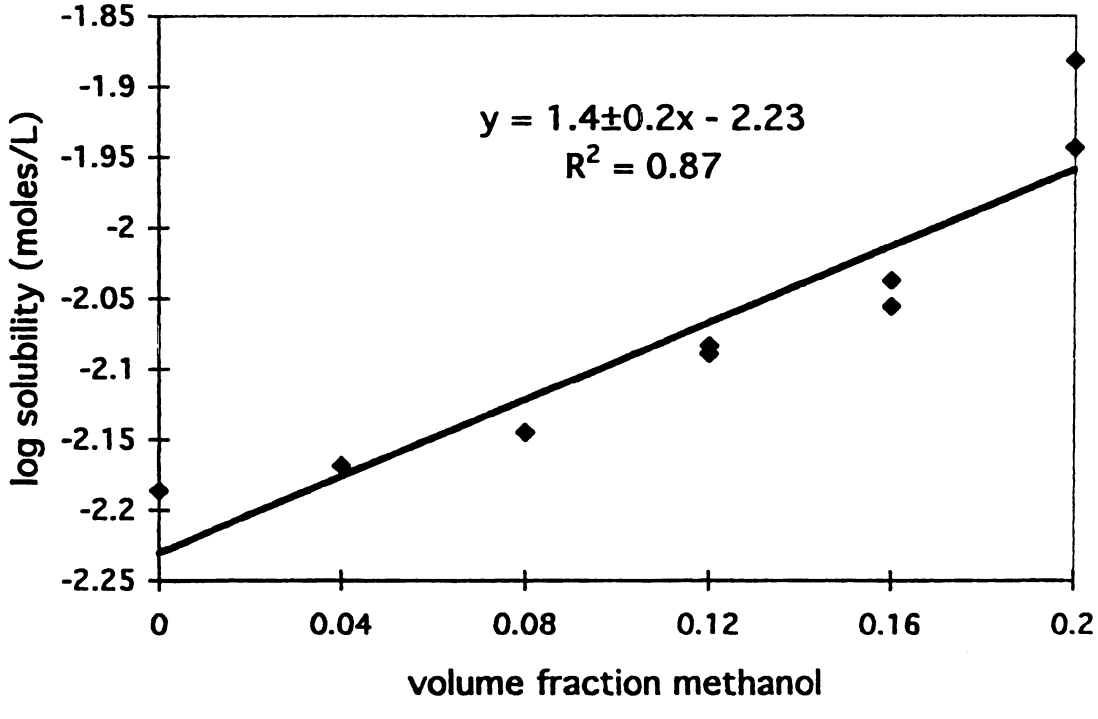

Figure 2. Log solubility of toluene as a function of volume fraction methanol.

Batch Sorption Isotherms

Trichloroethylene and toluene sorption coefficients for by Capac soil at methanol volume fractions from 0 to 0.20 are presented in Table 2. Sorption of TCE and toluene decreased log-linearly with increasing methanol fraction (Figs. 3 and 4). The data for TCE might be better described with a nonlinear relationship, although most published reports have shown similar nonlinearity but regarded the data as log-linear (Fu and Luthy, 1986b, Walters and Guiseppi-Elle, 1988, Wood et al., 1990). Using Eq.4 and σ values calculated from corresponding solubility enhancement experiments, α values for TCE and toluene were 0.9±0.3 and 0.7±0.2, respectively. Because α represents cosolvent/sorbent interactions and is independent of solute, the value for α should be constant. There has been a wide range of α values (0.35-0.89) published for water/methanol mixtures (Fu and Luthy, 1986b, Pinal et al., 1990, Wood et al., 1990, Kimble and Chin, 1994). Because α is calculated from the slope of K_m vs. f_c (slope = $-\alpha\sigma$), an incorrect value for σ would yield an incorrect α. Further, if σ increases as f_c increases, then log K_m vs. f_c would be nonlinear, and the calculated value of α would depend on the f_c range included in the study.

Table 2. TCE and toluene sorption coefficients (K_m) by Capac soil at low volume fractions (f_c) of methanol.

f_c	K_m (L kg^{-1}) toluene	K_m (L kg^{-1}) TCE
0.00	1.44±0.08†	1.17±0.07
0.04	1.29±0.11	1.12±0.06
0.12	1.17±0.06	0.93±0.12
0.20	0.91±0.15	0.58±0.03

† Slope of sorption isotherm ± standard error.

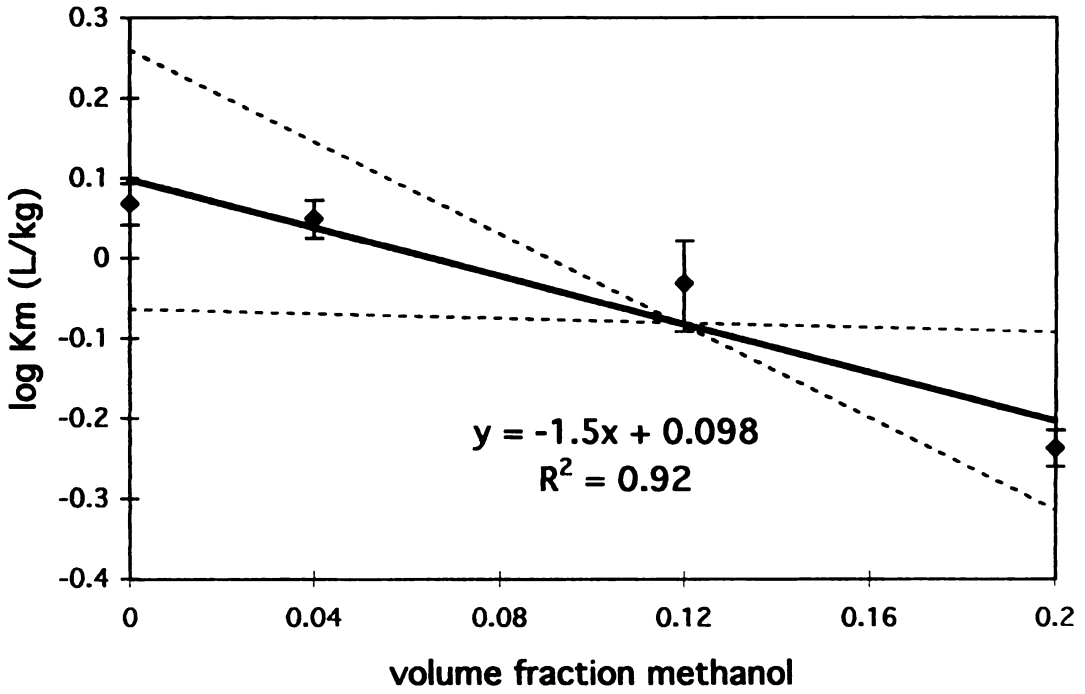

Figure 3. Log TCE sorption coefficient K_m for Capac soil as a function of methanol f_c. (dotted lines represent 95% confidence levels)

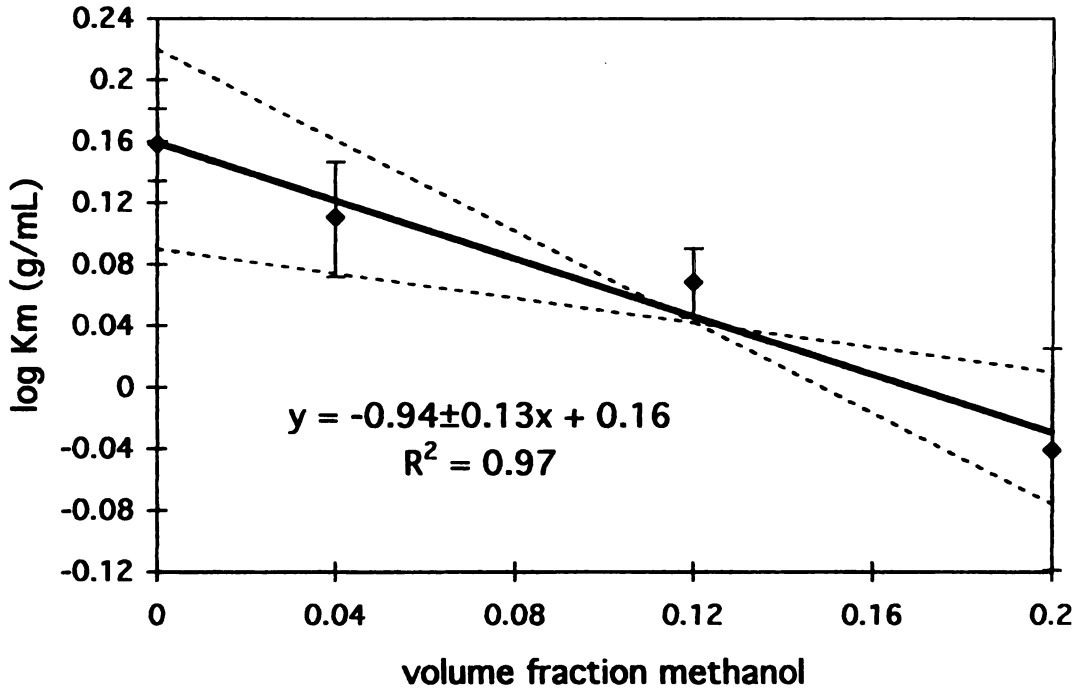

Figure 4. Log toluene sorption coefficient K_m for Capac soil as a function of methanol f_c. (dotted lines represent 95% confidence levels)

Toluene sorption coefficients for Kalamazoo soil at methanol volume fractions from 0 to 0.12 are presents in Table 3. Volume fraction of methanol had no significant effect on sorption. This may be due to the low amount of organic matter in the soil and subsequent low sorption of toluene by the soil even at $f_c = 0$. Methanol may be sorbed by the organic matter, increasing the affinity of toluene for the soil. This increase in sorption may counteract the decrease in sorption due to enhanced water solubility.

Table 3. Toluene sorption coefficients (K_m) by Kalamazoo soil at low volume fractions (f_c) of methanol.

f_c	K_m (L kg^{-1}) toluene
0.00	0.58±0.13†
0.04	0.62±0.09
0.08	0.49±0.08
0.12	0.59±0.02

† Slope of sorption isotherm ± standard error.

CONCLUSIONS

In summary, TCE and toluene solubility increased log-linearly with increasing methanol f_c, and sorption decreased log-linearly with increasing f_c, although deviations from log-linear behavior were noticed. Values obtained for σ were within the range of those calculated from previously published equations. The wide range of reported σ values may be due to an incorrect assumption of a linear relationship between log S_m and f_c used in the equations proposed by other authors. Therefore σ may not be a constant value, as solubility enhancement effects may increase as f_c increases. This may also explain the wide variability of α values found in our experiments as well as those reported by other authors. Volume fraction of methanol had no significant effect on sorption of toluene by a low organic C soil.

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Chapter 3.
Conclusions

Sorption is an important process in determining the fate and transport of organic compounds in the subsurface environment. It was shown that solution and soil composition affect sorption of ionizable (primisulfuron) and nonionic (TCE and toluene) compounds. Sorption of primisulfuron increased with decreasing pH because of increased fraction of the molecular form which can be sorbed by organic matter. At pH 4.5 primisulfuron sorption increased with increasing OC. In soils with less than 1% OC, primisulfuron sorption at pH 4.5 increased with increasing Fe oxide content. The presence of surfactant increased sorption of primisulfuron in a soil with 0.7% OC, but decreased in a soil with 1.7% OC. About 50% of sorbed primisulfuron did not desorb during a single 24-h batch desorption reaction. Sorption estimates based on log-log relations between water solubility and K_{oc} overestimated K_{oc} a factor of 4 to 40, depending on the soil, even when K_{oc} was corrected for the ionization of primisulfuron.

Sorption of TCE and toluene by a soil with 2.1% OC decreased log-linearly with increasing volume fraction methanol, although deviations from log-linear behavior were noticed. Cosolvency power of methanol was within the broad range of those predicted by equations proposed by other authors. Without an accurate prediction of solubility enhancement it is impossible to predict sorption increases with increased volume fraction methanol using a proposed equation. More research is needed (especially on the molecular level) in order to better predict the effect of soil and solution properties on sorption of organic compounds. This first step is necessary in order to determine the fate and transport of organic compounds in the subsurface environment.