# Slow desorption of volatile organic compounds from soil: evidence of desorption step limitations

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## Abstract

Transient adsorption and desorption of 1,2 dichloroethane and toluene on dry Yolo silt loam soil were studied by continuously measuring the composition of the effluent from a soil-packed chromatography column with a mass spectrometer. After obtaining complete breakthrough at approximately 30% relative saturation of one chemical in nitrogen, pure nitrogen feed was initiated and maintained for several hours. Of the material adsorbed at breakthrough, 9.7% of the 1,2 dichloroethane and 14.2% of the toluene were highly resistant to desorption and remained sorbed on the soil even after 5 h of nitrogen flow. When a second chemical with a higher adsorption affinity was introduced into the soil column (water following toluene or toluene following 1,2 dichloroethane), the majority of the first chemical was quickly desorbed and began leaving the soil column before breakthrough of the second chemical. Conversely, when a second chemical with a smaller adsorption affinity was introduced into the soil column, only a small amount of the first chemical was displaced and began leaving the soil column after breakthrough of the second chemical. The results of this study indicate that the desorption step itself may be the rate-limiting step for sorbate which remains after prolonged exposure to sorbate-free gas. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In the vadose zone, vapor-phase sorption is an important process which controls the movement of volatile organic compounds (VOCs). Recently, a number of studies have found that after a VOC adsorbs on soil, a significant portion does not readily desorb

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[1–4]. This phenomena, which we refer to as slow desorption, has been described in the literature by a variety of other terms such as recalcitrant, rate-limiting, slowly reversible, nonequilibrium, hysteresis, and irreversible adsorption.

At this time, the majority of the studies in the literature dealing with slow desorption have used soils that are either water saturated or contain significant amounts of water. An excellent review of these studies is presented by Pignatello and Xing [1]. Although studies dealing with dry soils are less abundant, slow desorption has been observed with dry soils. In this paper, dry soil is used in order to avoid the complications introduced by the presence of water so the mechanism of slow desorption in dry soils may more clearly be understood.

In the literature, slow desorption on dry soils has been attributed to either a slow intraparticle diffusion process or the actual desorption step. Although possible in dry soils, slow intraparticle diffusion is more likely to be responsible for slow desorption in water saturated soils because liquid-phase diffusivities are approximately four orders of magnitude smaller than vapor-phase diffusivities [5]. This difference was clearly seen by Grathwohl and Reinhard [2] who found that even after a long venting time, the removal rate of VOCs from columns of wet soil was independent of the carrier stream's flow rate while for oven-dry soil it was proportional to the carrier stream's flow rate. Intraaggregate limitations were much greater in the wet soil columns than in the dry soil columns. It has also been shown that the micropores of many clays have sheets of molecular dimensions [6] which could severely restrict diffusion leading to diffusion limitations. Satterfield et al. [7] showed that a molecule to pore diameter ratio of 0.2 can cause a 59% reduction in the diffusion rate. Differences in sorbate molecular sizes may also be important in the lamellae region. Keyes and Silcox [8] suggest that dodecane does not penetrate the lamellae of montmorillonite but toluene does. For this reason, toluene was thought to desorb more slowly, perhaps due to a chemical adsorption process or restrictive diffusion in the lamellae region.

Tognotti et al. [3] found a considerable amount of slow desorption of toluene vapor from oven-dry Spherocarb (Foxboro Analabs). Montmorillonite was also found to exhibit slow desorption of toluene, although to a lesser extent while Carbopack did not.

Using carbon tetrachloride and the same sorbents, Spherocarb was again found to have a significant amount of slow desorption but montmorillonite and Carbopack did not. Tognotti et al. [3] found that the slowly desorbing sorbate constituted less than a monolayer of coverage in these sorbents and hypothesized that this sorbate was more strongly bound and therefore more slowly desorbed due to capillary condensation and intercalation of sorbate molecules in micropores.

Another possible cause of slow desorption is kinetic limitations from certain adsorption sites. Pinnavaia and Mortland [9] have shown with spectroscopic evidence that toluene adsorption on montmorillonite clays is caused by chemical adsorption due to coordination through the $\pi$-electrons of the aromatic rings [9]. It has also been found that clay surfaces may behave as Lewis acids and therefore can strongly interact with organic species containing either double bonds or aromatic rings [10]. Intercalated organic species have also been shown to often exhibit multiple types of adsorption sites with different bonding [11]. The higher adsorption energies associated with chemical adsorption could result in much slower desorption compared to physical adsorption.

In a spectroscopic study of the rate of accumulation of 1,2 dichloroethane (DCA) on dry montmorillonite and dry kaolinite, Aochi and Farmer [4] showed that the DCA becomes associated with the minerals in both a liquid and a labile vapor state. It was further shown that there is a third sorbed species which accumulates at a much different rate than the other two sorbed species. They hypothesized that this additional sorbed species is sorbed in areas of the mineral to which access was limited. For this reason, accumulation of this species was somewhat delayed and increased with time even after desorption was initiated [4].

Dogu et al. [12] found a significant amount of slow desorption when studying benzene adsorption on dry soil. They determined, based on adsorption energy calculations, that the reversible fraction of the adsorption was physical while the irreversible binding was caused by either chemisorption or entrapment in soil micropores.

Keyes and Silcox [8] studied the desorption of toluene from montmorillonite particles. Toluene exhibited a considerable amount of slow desorption which they concluded was caused by either a slow desorption process related to breaking chemical bonds in the lamellae region or by a slow diffusion process. They concluded that local desorption kinetics in pores larger than those in the lamellae region was not rate-limiting because the desorption was found to be independent of particle size.

At this time, the rate-limiting mechanism which causes slow desorption in dry soil, is poorly understood. However, the importance of slow desorption can be seen from a study in which 1,2 dibromoethane (EDB) was detected in agricultural topsoil 19 years after application even though it is degradable and volatile [13]. Although this study involved soil with significant amounts of water, the implications of organic chemicals remaining decades after exposure are clear.

In this paper, the fundamental cause of slow desorption from dry soil is investigated. Adsorption of two common VOCs, 1,2 dichloroethane (DCA) and toluene, on dry Yolo silt loam soil was studied using both batch and chromatographic experiments. The effect of exposing a soil with a slowly desorbing VOC to a second VOC or water is also examined.

## 2. Experimental materials and methods

### 2.1. Soil and sorbates

The Yolo silt loam soil used in all experiments was obtained from a site near Davis, CA which has never been treated with pesticides or other organic chemicals. This soil is a mixed fine-silty, non-acidic, thermic, typic xerorthent. The characteristics of this soil as determined by the Division of Agricultural and Natural Resources (DANR) Analytical Laboratory at the University of California at Davis and from Amali et al. [14] are given in Table 1. The soil was first ground to pass through a 2.0 mm sieve. The soil was then further sieved and soil aggregates passing through a 0.589 mm sieve but retained by a 0.495 mm sieve were collected and used in all experiments. The solid phase density of the soil was determined by air pycnometry to be 2.67 g/ml. The soil's aggregate porosity was determined to be 0.467 by using small glass beads (3M superbrite No. 500)

Table 1
Characteristics of Yolo silt loam soil

| Characteristic | Yolo silt loam soil |
| --- | --- |
| EGME surface area (m$^2$/g) | 80.6[a] |
| Organic carbon (%) | 1.73 |
| pH | 7.3 |
| EC (mmho/cm) | 0.77[a] |
| CEC (meq/100 g) | 21.1[a] |
| Sand (%) | 34 |
| Silt (%) | 51 |
| Clay (%) | 15 |

[a] From Amali et al. [14].

to resemble a fluid surrounding, but not entering the pores of the aggregates. By measuring the increase in volume when aggregates with a known weight and solid phase density are added to the beads, the aggregate density and porosity were easily determined. This method has been used successfully elsewhere to measure soil aggregate porosities [15].

Three sorbates were used in this study: DCA, toluene, and water. These sorbates were chosen because they have a wide range of physical properties and are present in many environmental situations. The toluene and DCA used were ACS certified and used as received from Fisher Scientific. The characteristics of the sorbates are listed in Table 2. The nitrogen used in the column experiments was industrial grade (99.99% pure) and was passed through tubes of Drierite® and activated carbon before use in order to remove any residual traces of water and organic chemicals.

## 2.2. Microbalance experiments

Equilibrium experiments were conducted using the gravimetric apparatus shown in Fig. 1. A Cahn RG 2000 electrobalance with an accuracy of 0.1 microgram located inside a balance chamber was used to measure the weight change of approximately 0.5 g of soil during adsorption. A Pfeiffer Balsars Model TPH 050 turbomolecular pump in line with a Leybold-Heraeus Type D2A direct drive mechanical pump provided vacuum down to $10^{-5}$ Torr. Before each experiment, the soil was exposed to a vacuum of

Table 2
Physical properties of the chemicals used in experiments

| Chemical | Boiling point (°C) | Molecular weight | Vapor pressure (Torr) |
| --- | --- | --- | --- |
| Water | 100.0[a] | 18.016[a] | 23.75[a] |
| TCE | 87.2[a] | 131.40[a] | 77.5[b] |
| DCA | 83.7[a] | 98.97[a] | 118.0[b] |
| Toluene | 110.8[a] | 92.13[a] | 21.8[a] |

[a] From Perry's Chemical Engineering Handbook [16].
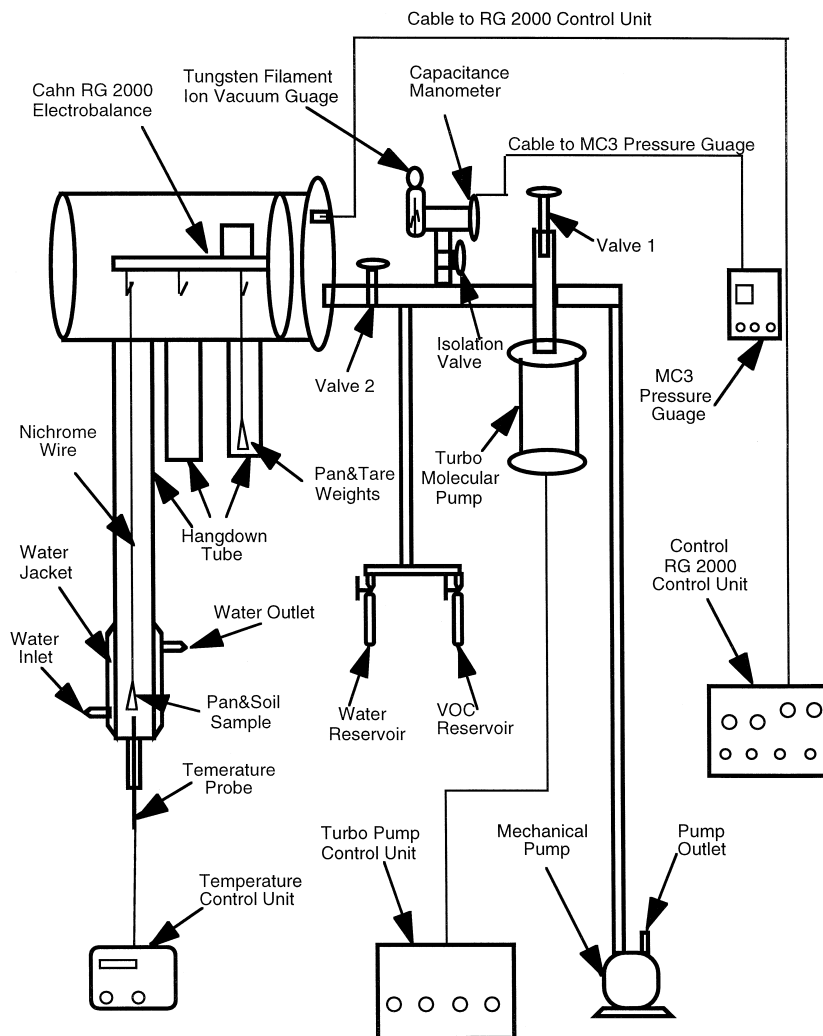[b] From CRC Handbook of Thermochemical Data [17].

Fig. 1. Microbalance experimental apparatus.

$10^{-5}$ Torr which removed nearly all of the water adsorbed on the soil. This procedure resulted in a soil that was dryer than that which could be obtained by oven-drying the soil and prevented possible soil structural changes sometimes caused by heating.

The temperature of the soil on the sample pan was kept constant by circulating water from a water bath through a jacket surrounding the balance chamber. A thermocouple located just below the sample pan was used to assure that there were no significant temperature changes during an experiment. A high-vacuum needle valve was used to isolate the liquid VOC in the VOC reservoir from the soil sample until an experiment was started. Once the needle valve was opened, the VOC in the reservoir evaporated

into the balance chamber. The vapor pressure of the VOC inside the balance chamber was measured using an Inficon model CM3 capacitance manometer and could be easily controlled by opening and closing the needle valve as needed.

The kinetic adsorption experiments were performed by first drying the soil as described above. The needle valve which isolates the VOC from the soil was then opened long enough to attain the desired partial pressure of the VOC. The weight of the soil was continuously recorded during the entire adsorption and desorption processes. Equilibrium was assumed to be reached when no weight gain had been detected for 2 h after which the adsorption phase of the kinetic experiments were terminated. The desorption phase of the kinetic experiments was conducted immediately after the completion of the adsorption phase by turning on the vacuum pump in order to evacuate the VOC initially in the balance chamber and as it desorbed from the soil. This process was continued until the weight of the soil remained constant for 2 h after which, the VOC remaining was considered to be slowly desorbing.

Equilibrium experiments were conducted in a similar manner as kinetic adsorption experiments. Dry soil was exposed to step increases in sorbate concentration and allowed to reach equilibrium at each step. The sorbate adsorbed at each step corresponds to a point on the adsorption isotherm. Desorption experiments were not conducted on soil samples used to determine adsorption isotherms.

## 2.3. Chromatographic experiments

Chromatographic experiments were conducted using the apparatus shown in Fig. 2. The apparatus consists of three main sections. The first section is the sparging section where pure nitrogen is sparged through a liquid VOC or water and then mixed with a stream of pure nitrogen in order to create a vapor with the desired sorbate concentration. Target concentrations were 25% of the saturation concentration to prevent condensation.

The second section is the chromatographic section where a switching valve allows the introduction of either the pure nitrogen or the nitrogen plus sorbate into a packed soil column. The space between the valve and the inlet to the soil column was minimized in order to minimize the dispersion of the step input before its introduction into the soil column. A soil column made of glass and Teflon with a diameter of 0.9 cm and a length of 12.0 cm (Safe-Lab, model C-2508) was used in all chromatographic experiments. Pressure gauges were placed before and after the soil column and the pressure drop across the column was found to be small (0.1 atm or less). The experimental apparatus was designed so the VOC/nitrogen vapor only contacts Teflon, glass and a minimal amount of stainless steel. Experiments with empty columns and with the soil column replaced with Teflon tubing showed there was no detectable adsorption to the walls of the confinement.

The third section of the apparatus is the detection section where the concentration of the effluent leaving the soil column was measured. A mass spectrometer (MS) built into a Hewlett-Packard model 5890A GC/MS was used as a continuous, multispecies detector. The Teflon tubing between the outlet of the soil column and the MS was minimized to reduce the time lag between the sorbate leaving the soil column and detection. A precision flow splitter was used to maintain a constant flow rate of
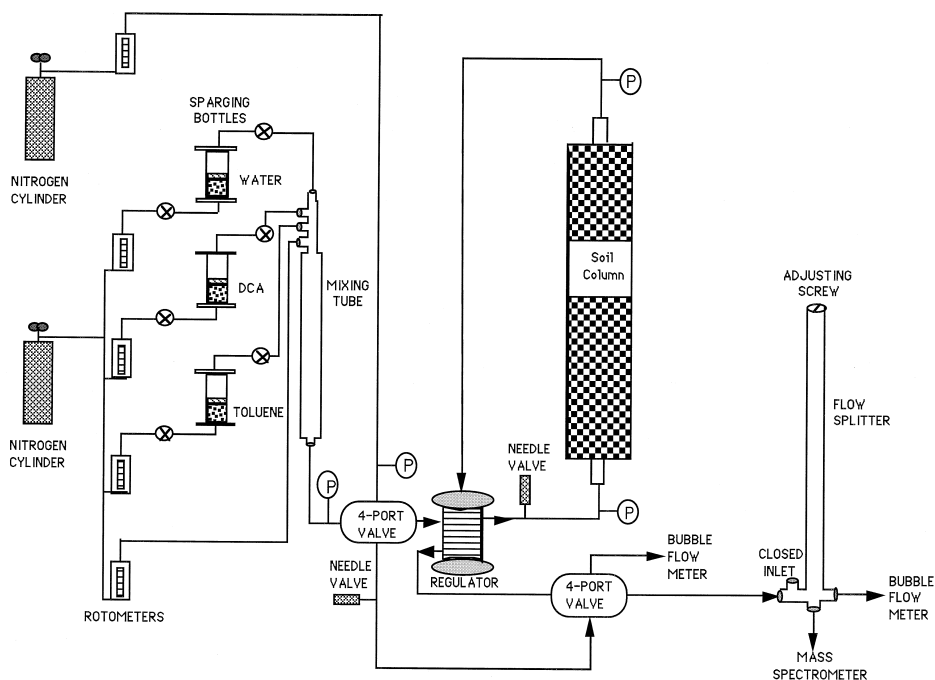
Fig. 2. Chromatographic experimental apparatus.

1 ml/min into the MS throughout all experiments while the remaining effluent was vented.

The packed soil columns used in experiments were dried by passing a dry nitrogen stream through them for 24 h. It was found that drying soil in this manner resulted in slightly lower water content than oven drying and problems associated with adsorption of water during column packing were avoided. Drying the soil column longer than 24 h was found not to result in any additional drying of the soil based on weight measurements taken at 24, 48, and 72 h.

Experiments were conducted by first drying virgin soil as described above. The soil was then exposed to a step input of one VOC in nitrogen. The sorbate was continuously introduced into the soil column and the column effluent was continuously measured until complete breakthrough was obtained. Breakthrough was considered to be complete when the concentration of the sorbate leaving the column was the same as the concentration of the sorbate entering the column. After breakthrough was complete, desorption was initiated by introducing a feed of pure nitrogen rather than the sorbate/nitrogen mixture. The column effluent was continuously measured until the effluent maintained a very low constant concentration, typically 0.1% or less of the inlet concentration, for at least 3 h. In some experiments, this process was continued for 2 days during which the baseline did not significantly decrease. The remaining adsorbed sorbate was considered to be slowly desorbing. At this point, a mixture of a second sorbate in nitrogen was introduced and passed through the column until breakthrough

occurred. During this breakthrough and desorption, the column effluent was measured simultaneously for both the first and the second sorbates.

## 3. Results and discussion

### 3.1. Microbalance equilibrium studies

After exposing a virgin soil to a given partial pressure of a VOC and then allowing the VOC to desorb, it was found some of the adsorbed VOC did not desorb. When exposed a second time to the same partial pressure, the soil was able to adsorb only as much as was desorbed after the first exposure. Fig. 3 shows the adsorption isotherm when virgin soil was exposed to toluene and the apparent isotherm for the second exposure. The term 'apparent isotherm' is used because this isotherm uses the initial weight of the soil (including any sorbate which was not desorbed) as the baseline. Subsequent apparent isotherms were nearly identical to the apparent isotherm obtained on the second exposure. As can be seen in Fig. 3, the soil adsorbed much less toluene on
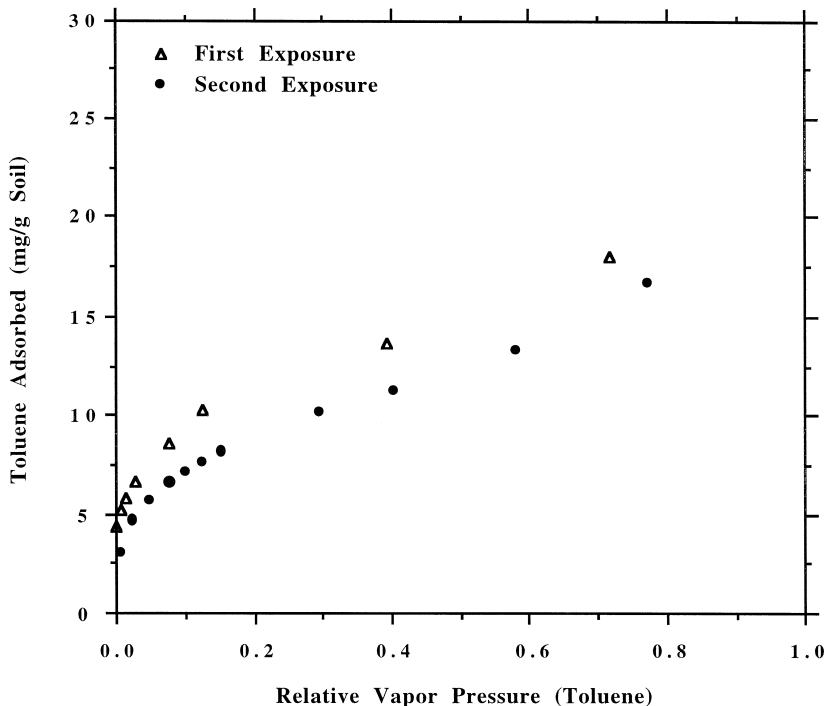


Fig. 3. Comparison of adsorption of toluene on Yolo silt loam soil on first and second exposures.

the second exposure. The difference, which was nearly the same over the entire range of relative pressures tested, was considered to be the slowly desorbing portion of the adsorbed toluene. DCA showed similar behavior with a nearly constant difference in mass between the first and second exposures.

Fig. 4 shows the adsorption isotherms, on virgin soil, of the three sorbates used in this study. The data of Fig. 4 are presented in terms of moles adsorbed and absolute pressure. Although this type of representation is nontraditional, it more easily allows a direct comparison of the three sorbates without the bias caused by different molecular weights and saturation pressures. From this figure, it can clearly be seen that at the same absolute pressure, far more water is adsorbed than either toluene or DCA. Toluene sorption slightly exceeds DCA. Adsorption strengths are related to the amount adsorbed at equilibrium and for that reason, the strength of adsorption of the sorbates are ordered as water $\gg$ toluene > DCA.
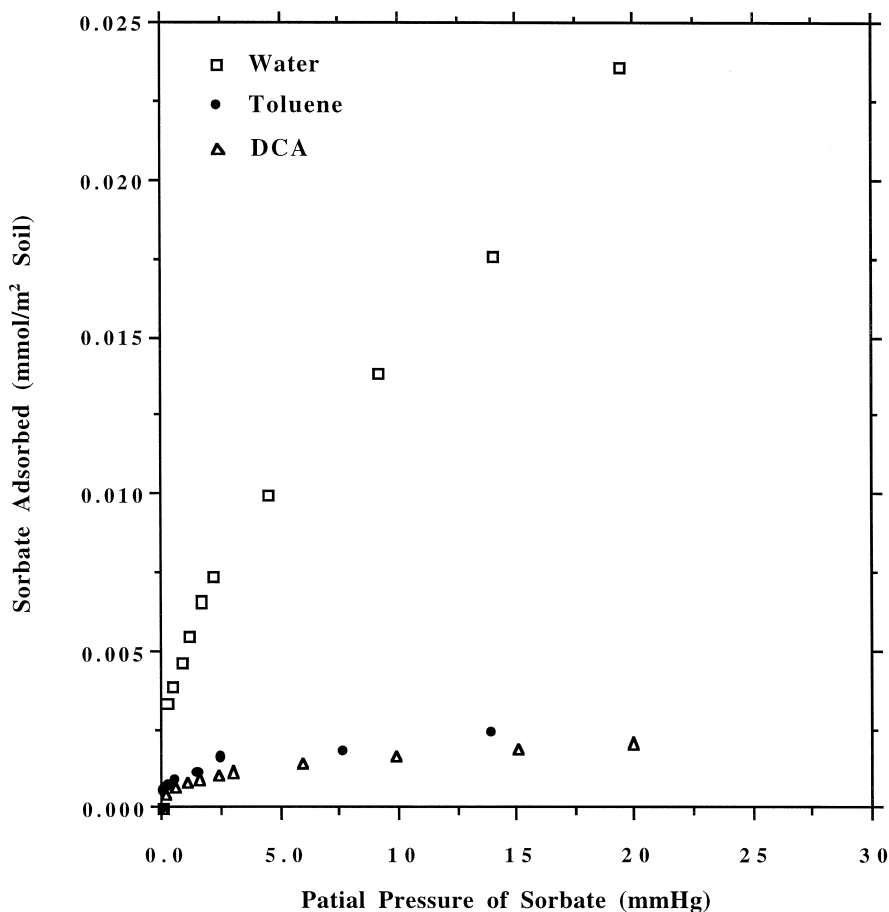


Fig. 4. Adsorption isotherms of sorbates on virgin soil at 25°C.

## 3.2. Microbalance kinetic studies

When kinetic experiments were conducted on the microbalance, both adsorption and desorption occurred on two distinct time scales. Fig. 5 shows an experiment where toluene at 48.0% relative vapor pressure was adsorbed on and then desorbed from virgin Yolo silt loam soil at 25°C. The majority of the adsorption occurred quickly with 79% occurring in the first 2 min. The remainder of the adsorption occurred on a much slower time scale taking an additional 135 min to complete. In the same amount of time (2 min) 34% of the toluene which had been adsorbed was desorbed. An additional 49.7% of the toluene desorbed during the next 117 min. After 117 min, 16.3% of the toluene remained sorbed on the soil but the desorption had slowed to an immeasurable rate. The experiment was continued for 2 h beyond the last data point shown on Fig. 5 during which no additional toluene desorbed. The fast phase is believed to be diffusion-limited desorption of physically adsorbed toluene while the slower phase is rate-limited by the actual desorption step of strongly sorbed sorbate or by diffusion limitations in micropores. Note that a significant amount of the adsorbed toluene never desorbed in these
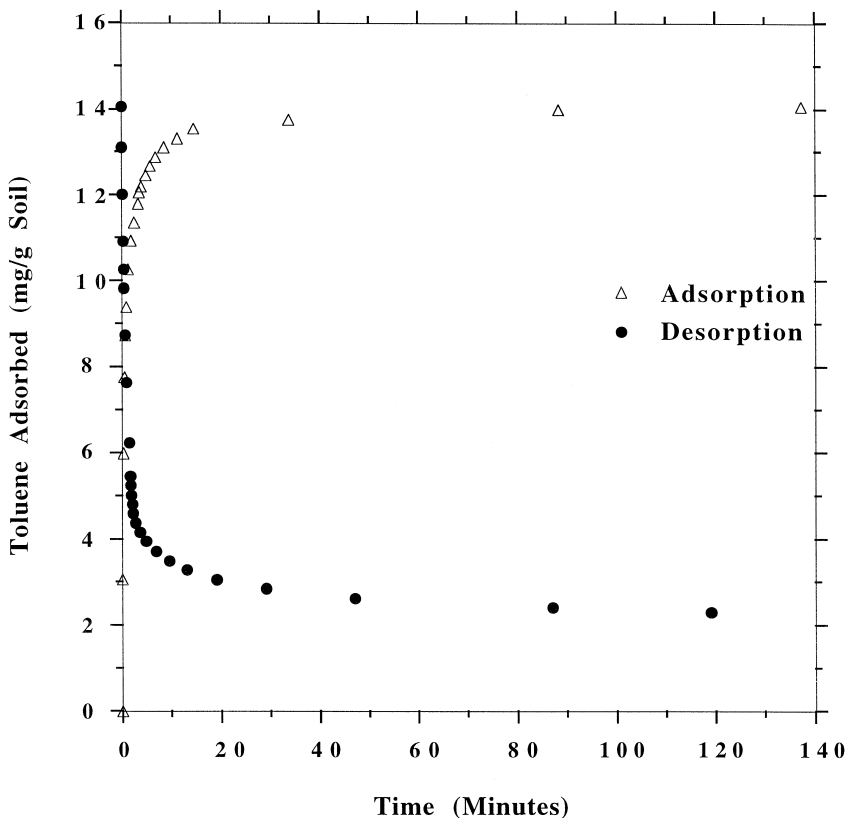
Fig. 5. Adsorption and desorption of toluene on Yolo silt loam soil.

experiments. This is the material which we refer to as slowly desorbing because we have no evidence that it is irreversibly bound although its desorption rate is immeasurable small under the experimental conditions. As shown below, this material is rapidly desorbed under other experimental conditions.

Other studies have found similar differences between the time required to adsorb and the time required to desorb VOCs. Tognotti et al. [3] found that these differences depend on the sorbate. Spherocarb was found to take 17.5 times longer to desorb 50% of the adsorbed toluene than was required to adsorb the same amount of toluene. The same study found that the same desorption only took 1.3 times as long as adsorption on montmorillonite. For comparison, in the experiment shown in Fig. 5, 50% of the adsorption occurred in the first 0.33 min. Of the total adsorption that occurred, 50% desorbed in 1.07 min. If we ignore the 16.3% of sorbate which never desorbed, it took 0.88 min to desorb 50% of the amount that actually desorbed.

Tognotti et al. [3] also found significant differences related to the sorbate when studying toluene and carbon tetrachloride adsorption on montmorillonite and Spherocarb. With Spherocarb, the ratio of desorption time to adsorption time decreased for carbon tetrachloride relative to toluene, however, the opposite was found with montmorillonite.

Although slow desorption has been observed in many studies, it has not been observed with all sorbates. Tognotti et al. [3] found Spherocarb and montmorillonite exhibited slow desorption of toluene while Carbopack did not. Grismer et al. [18] have shown that sorption of toluene on bentonite exhibits negligibly slow desorption. The soil used in our study is composed of a number of sorbents with montmorillonite being the most important component with respect to adsorption. Since montmorillonite has been found to exhibit slow desorption in other studies, it could be expected in this study as well.

## 3.3. Column breakthrough and desorption

Chromatographic breakthrough and desorption for toluene are shown in Fig. 6. In this experiment, the inlet toluene concentration was 26.4% of the saturation concentration and was introduced at an apparent velocity of 7.89 cm/s. Breakthrough occurred at approximately 10 min and the effluent concentration rapidly rose to approximately 92% of the feed concentration within 15 min. Over the next 65 min, the effluent concentration slowly rose to the feed concentration. At this time, pure nitrogen feed was introduced. Although desorption was much slower than adsorption, approximately 82% of the concentration decrease occurred in the first 15 min after which the effluent concentration displays a very long tail. This type of tailing has been observed in other studies with soils and VOCs [19]. Although the concentration of the column effluent slowly decreased and reached a concentration lower than the MS could accurately measure (approximately 0.04% of the toluene inlet concentration) at 280 min, it remained at a detectable concentration. Desorption experiments have been conducted as long as 2 days after complete toluene breakthrough and toluene was detected throughout this time. Since toluene is continuously released from the soil, the amount of adsorption that is attributed to slow desorption is somewhat arbitrary. The values reported here
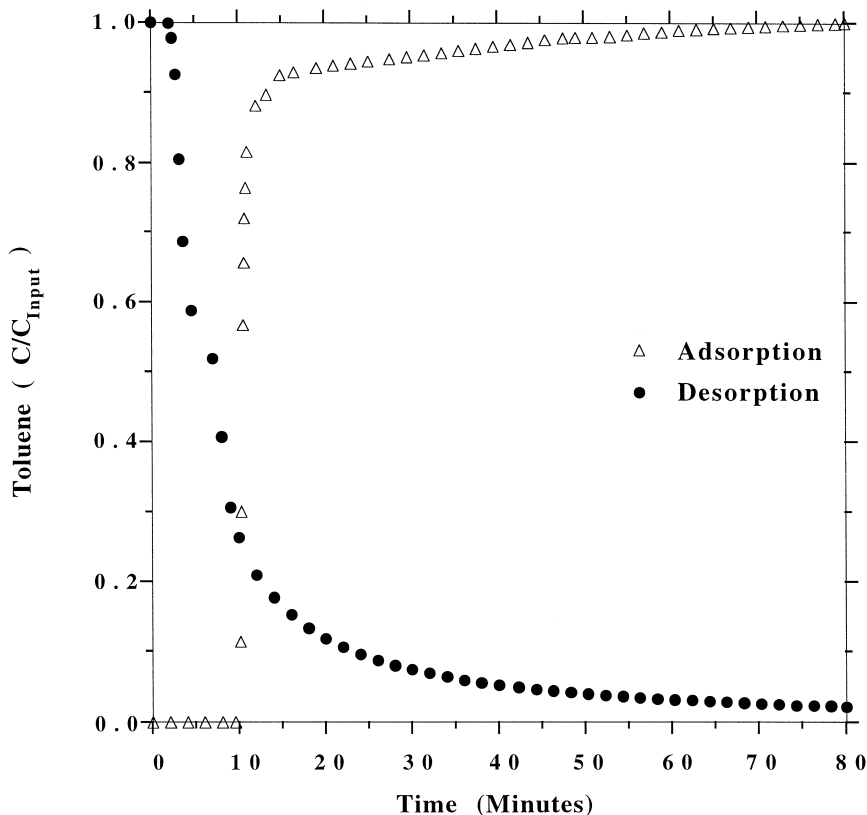
Fig. 6. Chromatographic breakthrough and desorption of toluene on Yolo silt loam soil.

correspond to the amount adsorbed when the observed concentration dropped below the level which the MS could accurately measure. At concentrations below this level, accurate measurements are impossible because of the effect of background noise on the analytical method used in the experiments. When using this method to calculate the amount of slow desorption, changing the time beyond which adsorption is considered to be due to slow desorption, even by hours, has only a small effect on the results.

In the experiment described above, 14.2% of the adsorbed toluene did not desorb due to slow desorption. Similar results have been found when DCA was used in place of toluene. It was found that 9.3% of the adsorbed DCA after complete breakthrough at 27.4% of the saturation concentration did not desorb due to slow desorption. These results as well as the other experimental results are summarized in Table 3.

### 3.4. Column studies with a second sorbate

An interesting phenomena was observed when a second sorbate was introduced into a soil column from which all but the slowly desorbing fraction of the first sorbate had been removed by nitrogen desorption. When toluene was the first sorbate introduced,

Table 3
Summary of experimental results

|  | Vapor saturation (%) | Slowly desorbing (%) | Displaced by DCA (%) | Displaced by toluene (%) | Displaced by water (%) |
|---|---|---|---|---|---|
| DCA | 27.4 | 9.7 | – | 8.3 | – |
| DCA[a] | 17.2 | 9.8 | – | – | – |
| Toluene | 26.0 | 14.2 | Small | – | 11.4 |
| Toluene[a] | 48.0 | 16.3 | – | – | – |

[a] Indicates microbalance experiment.

introducing DCA into the soil column until complete breakthrough was obtained slightly increased the rate of release of toluene from the soil column (Fig. 7). The concentration of the toluene in the column effluent first increased by approximately 10 times slightly after the first DCA appeared in the column effluent. The toluene concentration then decreased until it maintained a nearly constant level approximately 5 times the original concentration. An increased concentration of toluene was observed in the column effluent the entire 7 h that DCA was introduced into the column although the concentration decreased slightly with time. Within 2 min after the DCA feed was
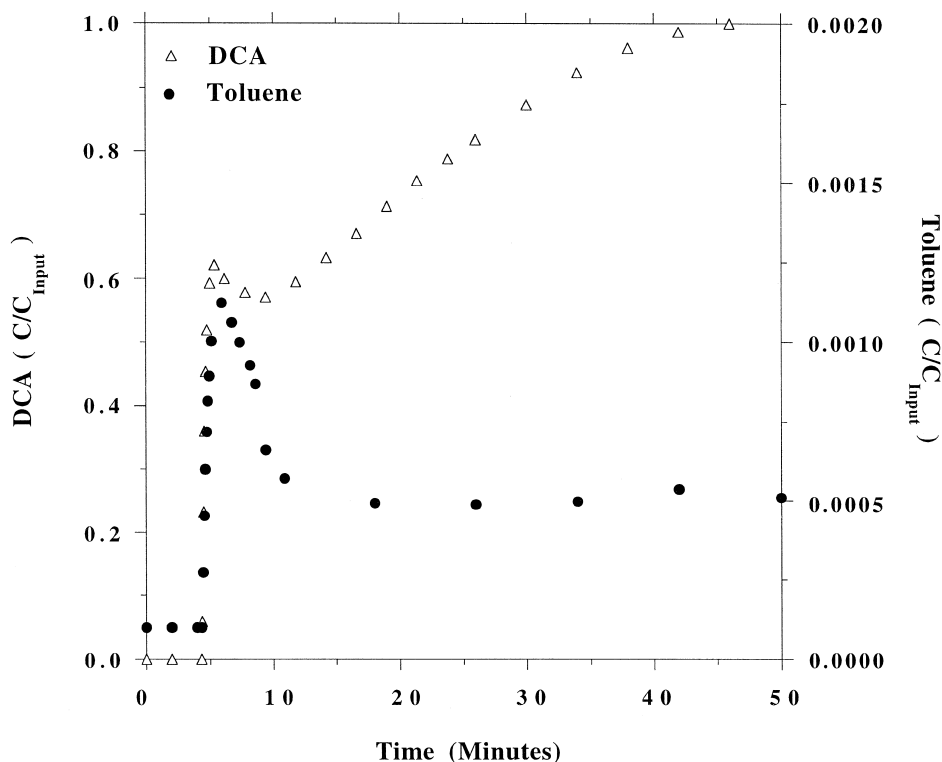


Fig. 7. Breakthrough of DCA and effect on release of previously sorbed toluene.

replaced with pure nitrogen, the toluene concentration dropped to a level which was lower than the original concentration. The speed with which the toluene concentration dropped after DCA was no longer introduced into the column indicates that the high concentration of DCA in the gas-phase was the cause of the toluene desorption.

The DCA breakthrough exhibited a very small peak at the same time the that the first toluene came out of the column. This phenomena is believed to have occurred because as the DCA was introduced it was present in excess and quickly filled many of the monolayer adsorption sites. The toluene molecules, which we believe are involved in a very slow kinetically controlled desorption process, are continuously desorbing (although at an extremely slow rate) and due to a lack of available monolayer adsorption sites, were much less likely to readsorb. As the desorbed molecules move through the column, they displace adsorbed DCA molecules and keep DCA molecules slightly ahead of the toluene front. For this reason, the DCA was observed leaving the column first and both DCA and toluene displayed small peaks. However, since there was only a small amount of toluene adsorbed on the soil, the toluene peak was small.

If, instead of introducing DCA, water is introduced after the toluene, a dramatically different effect is observed. Fig. 8 shows an example of this type of experiment. In this experiment, the apparent velocity of the gas was 7.86 cm/s, the water input concentra-
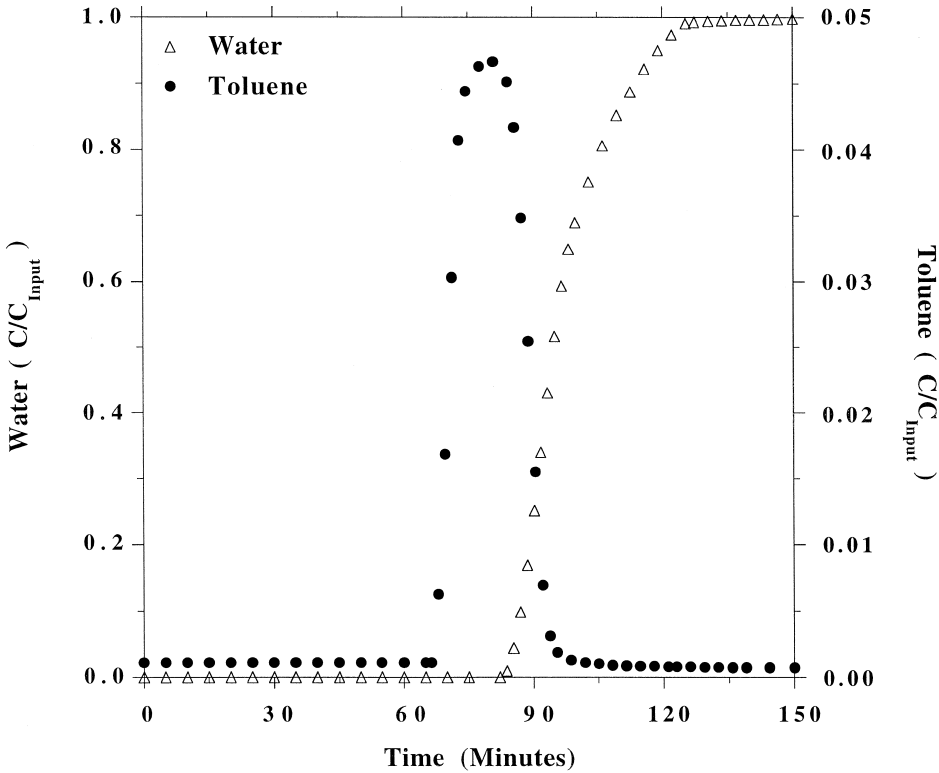


Fig. 8. Breakthrough of water and effect on release of previously sorbed toluene.

tion was 26.2% of saturation and the starting time was 386 min after the last toluene was introduced into the column.

The toluene concentration leaving the soil column began to increase 66.6 min after the first introduction of water. The water, however, did not begin leaving the soil column until 83.0 min after its first introduction—16.4 min after the toluene began leaving the column and slightly after the toluene peak which occurred at approximately 80 min. The toluene came out in a nearly perfect bell shaped curve with the peak occurring near the first appearance of water. Most of the toluene had left the column by 95 min, however, the concentration of the toluene did not return to a nearly constant concentration until approximately the same time that water breakthrough was complete. After the large peak of toluene came out, the concentration of the toluene in the column effluent dropped to a concentration which, although it could not be accurately measured, appeared to be approximately one-half of that before the water was introduced into the column.

Of the 14.2% of toluene adsorbed due to slow desorption, 11.4% came out while the water was introduced into the column. This left an additional 2.8% of the toluene adsorbed on the soil which was observed slowly leaving the column at a barely detectable concentration.

Experiments in which breakthrough and desorption of DCA at 27.4% of saturation were first conducted followed by introduction of toluene into the soil column were also performed. In the experiment represented by Fig. 9, the apparent velocity of the gas was 10.91 cm/s, the inlet concentration of the toluene was 28.1% of saturation, and the toluene was introduced starting at 312 min after the last DCA was introduced into the column. At the start of the experiment shown in Fig. 9, there was 9.7% of DCA adsorbed due to slow desorption. When toluene was introduced, 8.3% of the DCA was desorbed during the toluene breakthrough which left 1.4% of the DCA still adsorbed on the soil which proceeded to come out of the column at a barely detectable concentration.

DCA began leaving the column 0.5 min before the first toluene began leaving the column and came out in a small peak followed by a tail which returned to a nearly constant concentration at approximately the same time that toluene breakthrough was complete. Although accurate measurements were not possible, the concentration of DCA after complete breakthrough of toluene appeared to be approximately 20 times lower than the concentration of the DCA before toluene was introduced.

The slow desorption observed in these experiments and those of other investigators could be caused by very slow intraparticle diffusion or by a rate-limiting desorption step. Biodegredation could also cause the illusion of slow desorption. However, the possibility that the observed slow desorption was caused by biodegredation has been ruled out because experiments performed after a soil sample's first exposure to the sorbate did not exhibit a loss of sorbate. Had biodegradation been the cause of the slow desorption, sorbate would have been lost on each sorbate exposure and the sorbate would be permanently lost rather than slowly desorbing from the soil. In addition, the experiments were conducted under very dry conditions, with no oxygen, and for relatively short times, all making biodegredation unlikely.

In all of the experiments presented here, there was a significant amount of the first sorbate remaining in the column due to slow desorption when the second sorbate was
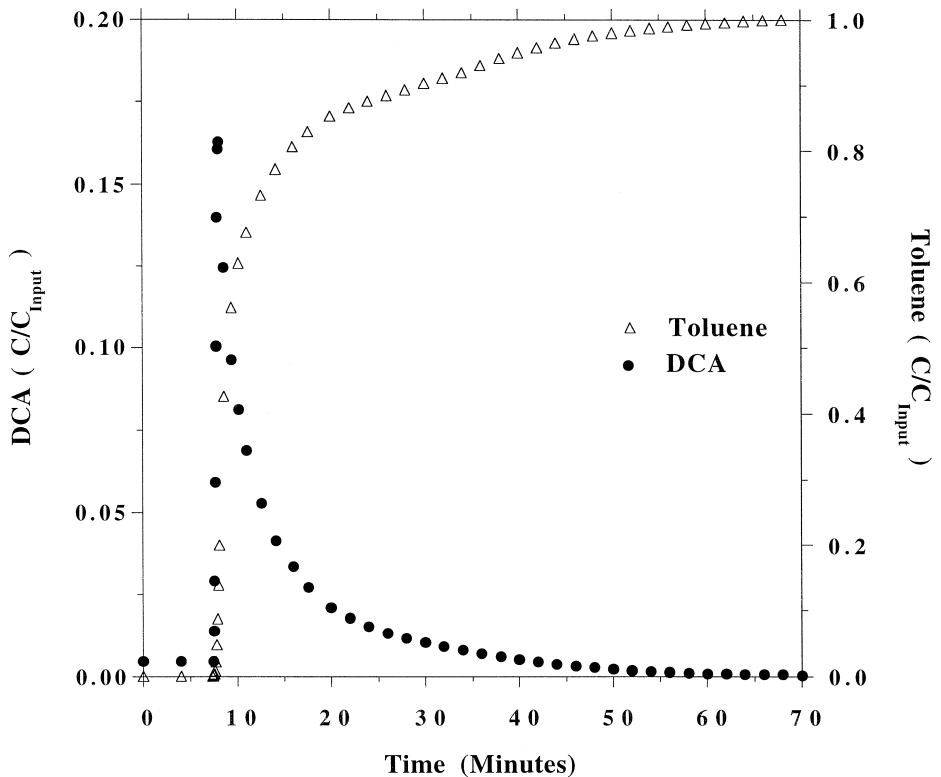
Fig. 9. Breakthrough of toluene and effect on release of previously sorbed DCA.

introduced into the column. However, depending on the order of introduction of the sorbates, different results were obtained. According to Adamson [20] and assuming that adsorption is occurring only on monolayer adsorption sites, the adsorption rates are related to the concentration of the sorbate in the gas phase ($P$), the number of monolayer adsorption sites ($S_m$), the number of occupied adsorption sites ($S$) and an adsorption rate constant ($a$), according to Eq. (1) and desorption rates are related to the adsorption energy ($Q_{ad}$,), a desorption rate constant ($b$), and $S$ according to Eq. (2).

$$\text{Rate of Adsorption} = aP(S_m - S) \tag{1}$$

$$\text{Rate of Desorption} = b\text{EXP}\left(\frac{-Q_{ad}}{RT}\right)S \tag{2}$$

Before a second sorbate is introduced into the column containing the first sorbate undergoing slow desorption, it is likely that any of the bound sorbate molecules that desorb will quickly readsorb on other sorption sites. This readsorption greatly retards the release of the slowly desorbing sorbate from the column. However, when a second

sorbate is introduced into a column containing a slowly desorbing sorbate, the second sorbate has a much higher concentration in the gas phase. It is therefore believed that the second sorbate molecules quickly fill many of the empty monolayer sorption sites according to Eq. (1). Therefore, when molecules of the first sorbate desorb, the most likely sorption sites for readsorption are multilayer sorption sites. These sorption sites have characteristic desorption rates similar to evaporation rates which are much larger than the characteristic desorption rates from soil surface sorption sites which have larger binding energies [21]. Previous studies have shown that desorption from multilayer adsorption sites occurs much more quickly than from monolayer adsorption sites [2,19].

Therefore, we believe the amount of retardation of desorbing first sorbate molecules is much less when a second sorbate is present. However, even when a second sorbate is present, we believe the rate of release of the first sorbate is limited by the rate of the actual desorption step which is slow. It is for this reason that we believe a slightly increased amount of strongly bound toluene was observed leaving the column when DCA was introduced into the column following toluene.

In the cases where toluene followed DCA and water followed toluene, a much larger amount of the slowly desorbing sorbate was observed quickly leaving the column. In these cases, as in the cases described above, the second sorbate was present in excess and therefore, we believe, caused an increase in the rate of release of the slowly desorbing sorbate. However, this alone cannot explain the much greater amount of the first sorbate that was observed leaving the column. These cases differ in that the second sorbate is more favorably sorbed than the first sorbate. It is therefore energetically favorable for the second sorbate to occupy high energy adsorption sites which we believe are responsible for the observed slow desorption. It is clear from the experimental results that the second sorbate is actually displacing the first sorbate which was slowly desorbing.

The order in which the sorbates leave the column is also important. When the second sorbate is less preferentially adsorbed than the first sorbate, the initial increase in the first sorbate leaving the column occurs slightly after the second sorbate begins leaving the column. We believe this is caused by most of the soil sorption sites first being filled by the second sorbate and then the slowly desorbing sorbate molecules making their way out past the filled sorption sites. Conversely, when the second sorbate is preferentially sorbed, the initial increase in the first sorbate leaving the column occurs before the second sorbate begins leaving the column. This shows that the second sorbate displaces the slowly desorbing sorbate keeping it ahead of the second sorbate's front as it moves through the column. After the majority of the first sorbate is displaced by the second sorbate, the concentration of the first sorbate is lower than that before the second sorbate was introduced. This is likely caused by a small amount of the first sorbate remaining which is released at an exceedingly slow rate.

The experiments presented here demonstrate that most of a slowly desorbing sorbate on dry soils can be quickly desorbed when a second, more tightly bound sorbate is introduced into the column. This indicates that the slow desorption is not caused by a slow intraparticle diffusion process. If it were caused by a slow intraparticle diffusion process, introducing a second sorbate would not cause the first sorbate to be so quickly removed from the soil and to elute ahead of the front of the second sorbate. However, if

the slow desorption is actually caused by the chemical rate of the desorption step, then introducing a second sorbate would cause the rate of release of the first sorbate to be increased as was observed in the experiments presented here. Further support for this hypothesis comes from the finding that, except for the first exposure, adsorption was reversible. If slow diffusion were the cause of the slow rate of release, subsequent exposures to the sorbate would result in an increased amount of slowly desorbing sorbate. We therefore believe that with dry soils, most of the slow desorption is caused by a slow desorption step. From the speed with which the first sorbate is desorbed, it is believed that the majority of the sorption sites causing slow desorption are in areas of the aggregates that are readily available to the second sorbate. Therefore, we believe that the majority of the sorption sites causing slow desorption are located on the external surfaces, the macropores, or the short micropores of the aggregates.

## 4. Conclusions

The data presented in this work demonstrate that desorption of toluene, water, and DCA on Yolo silt loam soil occurs on two distinct time scales, one very fast and one much slower. Upon first exposure, up to 16.3% of the adsorbed sorbate is involved in a slow desorption process. Subsequent exposures do not cause a significant increase in the amount of slowly desorbing sorbate. The sorbate retained due to slow desorption is highly resistant to desorption into dry nitrogen or a vacuum.

Introduction of a second, preferentially sorbed sorbate into a soil column containing a slowly desorbing sorbate quickly results in the displacement of the majority of the first sorbate. However, the rate of release of a more tightly bound sorbate was only slightly increased by introducing a less tightly bound sorbate. These findings indicate that the cause of the observed slow desorption is a very slow chemical desorption step.

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## References

[1] J.J. Pignatello, B. Xing, Environ. Sci. Technol. 30 (1996) 1.
[2] P. Grathwohl, M. Reinhard, Environ. Sci. Technol. 27 (1993) 2360.
[3] L. Tognotti, M. Flytzani-Stephanopoulos, A.F. Sarofim, Environ. Sci. Technol. 25 (1991) 104.
[4] Y.O. Aochi, W.J. Farmer, Environ. Sci. Technol. 29 (1995) 1760.
[5] W.J. Lyman, W.F. Reehl, D.H. Rosenblatt, Handbook of Chemical Property Estimations Methods, ACS, Washington DC, 1990.
[6] R.M. Barrer, Zeolites and Clay Minerals as Sorbents and Moleular Sieves, Academic Press, London, 1978.

[7] C.N. Satterfield, C.K. Colton, W.H. Pitcher, AIChE J. 19 (1973) 628.

[8] B.R. Keyes, G.D. Silcox, Environ. Sci. Technol. 28 (1994) 840.

[9] T.J. Pinnavaia, M.M. Mortland, J. Phys. Chem. 75 (1971) 3975.

[10] D.H. Solomon, Clays Clay Miner. 16 (1968) 31.

[11] J.J. Gibbons, R. Soundararajan, Am. Lab. (1988) 38.

[12] T. Dogu, C. Cabbar, G. Dogu, AIChE J. 39 (1993) 1995.

[13] S.M. Steinberg, J.J. Pignatello, B.L. Sawhney, Environ. Sci. Technol. 21 (1987) 1201.

[14] S. Amali, L.W. Petersen, D.E. Rolston, J. Haz. Mat. 36 (1994) 89.

[15] W.B. Voorhees, R.R. Allmaras, W.E. Larson, Soil Sci. Am. 30 (1966) 163.

[16] R.H. Perry, D. Green (Eds.), Perry's Chemical Engineering Handbook, 6th edn., McGraw-Hill, New York, 1984.

[17] D.R. Lide, H.V. Kehianian, CRC Handbook of Thermochemical Data, CRC Press, New York, 1994.

[18] M.E. Grismer, E. Labolle, T. Raihala, J. Ewiss, ASTM STP 1261 (1995) .

[19] C. Thibaud, C. Erkey, A. Akgerman, Environ. Sci. Technol. 26 (1992) 1159.

[20] A.W. Adamson, Physical Chemistry of Surfaces, Wiley-Interscience, New York, 1967.

[21] K. Goss, S.J. Eisenreich, Environ. Sci. Technol. 30 (1996) 2135.