RAPID AND SECONDARY SORPTION OF BENZENE AND TOLUENE BY TWO AQUIFER SOLIDS

WILLIAM K. AHLERT and CHRISTOPHER G. UCHRIN

Department of Environmental Science, Cook College, New Jersey Agricultural Experiment Station, Rutgers, The State University of New Jersey, New Brunswick, NJ 08903 (U.S.A.)

Summary

The adsorption and secondary uptake of benzene and toluene on two aquifer solids were examined by static batch and flow-through column studies. Benzene and toluene showed a higher affinity for the aquifer solids with a greater organic matter content. Toluene was found to have a greater affinity then benzene for the two aquifer solids examined.

In long-term batch and flow-through column experiments using the solids with greater organic matter content, the experimental results indicated both a fast and a very slow uptake of solute from the liquid phase. Column studies showed that the secondary uptake rate had little dependence on the percent organic matter of the solids. Conversely, the batch studies showed little to no adsorption or secondary uptake of benzene and toluene on the solids with the lower organic matter content.

Flow-through column results showed that the mass adsorbed during primary adsorption (initial uptake) is finite and reversible. An examination of the solid and liquid phases, after allowing the columns to stand undisturbed for one hundred days, gave evidence that the solutes removed by the secondary process remained in the systems and was not lost through biological or chemical degradation.

Introduction

Contamination of groundwater by spills of hazardous substances leachate migration from landfills and leaking underground storage tanks is a problem of great national and international concern. The so-called "Superfund" has been mandated to clean-up severely contaminated sites in the U.S.A. There are, however, insufficient resources to effect immediate action at all of the sites identified to date, and it is anticipated that there will be more sites added to the list in the future. In recent months, concern has focused on groundwater contamination by leaky gasoline storage tanks at thousands of service stations across the nation. It is necessary to prioritize the sites on the basis of the present and potential seriousness which they repersent. In the case of gasoline, it is important to understand how specific compounds (i.e. benzene and toluene)

will react and move in subsurface systems. Once this is established, compounds can be added together to examine their effects on each other. A variety of factors other than system hydrodynamics contribute to the transport and fate of substances in groundwater systems. Important among these are the sorptive characteristics of dissolved pollutants and the solid matrix material and, also the potential for biochemical degradation. The potential for desorption of solutes adsorbed to the soil matrix is important. Recent work by Lee et al. [1] has indicated that the initial sorption of solutes from the liquid phase to the solid phase is usually rapid and reversible. There is also a much slower secondary process which may reflect stronger solute binding to the soils than in primary sorption.

This paper presents results from ongoing research examining the processes involved in long-term adsorption/desorption static batch and flow-through column experiments. It examines the possibility that secondary pore diffusion is the mechanism for changes that continue to occur after initial, rapid adsorption/desorption processes are completed.

Materials and methods

Sorbents

Naturally occurring soils associated with two major aquifers were studied: soil from the Cohansey (COH) aquifer was taken from an outcrop site located at the Rutgers University Cranberry Culture Experiment Station near Chatsworth, New Jersey and soil from the Towacca (TOW) aquifer was extracted from a subsurface deposit near Hanover, New Jersey. Relevant physical and chemical properties of the Cohansey and Towacca soils are given in Table 1. Organic matter content was determined by the Walkley and Black modification of the rapid dichromate oxidation technique, with organic carbon content

TABLE 1

Soil properties*

Parameter	Cohansey	Towacca
Sand, %	90	92
Silt, %	8	6
Clay, %	2	2
Organic matter, %	4.4	0.2
pH	3.8	8.4
CEC, meq/100 g	5.1	2.3
TKN, mg-N/L	473	<90
USDA texture	sand	loamy sand

*Percentages are given on a weight basis; CEC= Cation Exchange Capacity; TKN is total Kjeldahl N; texture according to the U.S. Dept. of Agriculture classification.

defined as 58% of the organic matter content (Nelson and Sommers, [2]). Soil samples were air-dried and sieved to pass a 1 mm screen.

Organic chemicals

The two chemicals used in this study, toluene and benzene, have been found in abundance in New Jersey groundwaters (Fusillo and Voronin, [3]). Both compounds are present in commonly used mixtures, i.e., gasoline, cleaning solvents, etc; spills or poor disposal practices provide pathways to the environment. Both chemicals were purchased from Fischer Scientific (Springfield, NJ) in reagent grade purity.

Analytical instrumentation

A Gow-Mac Model 740p gas chromatograph (GC), equipped with a flame ionization detector (FID) was employed to determine toluene and benzene concentrations in aqueous solutions. A direct aqueous injection technique was employed and external standards were used for calibration of the GC. This technique involved withdrawing a 4.0 μl aliquot from the reactor vessel and injecting it directly into the GC column. A 0.1% SP-1000 on 80/100 Carbopack C, packed in a 1.8 m long by 2 mm diameter glass column, purchased from Supelco Inc. (Bellefonte, PA.), was used to separate the components of the aqueous solution.

Batch adsorption rate studies

Predetermined masses of air-dried soil were introduced into 50-ml glass vials and sealed with Teflon-crimp tops to minimize losses due to volatilization. One vial was kept free of soil, but filled with 50 mL of solute in water to act as a control. One vial was filled with water alone to act as a blank. Another vial was filled with a given mass of soil and solute-free water to determine whether the soil had been contaminated previously. The remainder of the vials were filled with a given mass of soil and a known volume of solution with a specific concentration of benzene or toluene in water. The vials were sealed immediately and agitated. Samples were withdrawn for analysis, with a 10 μl syringe, at time intervals of 1, 2, 4, 6, 12, 24, 48 and 72 hours. Some of the experiments were conducted for three to four weeks to examine long-term changes in the systems. Care was taken to eliminate headspace in the vials. Analysis of the blanks demonstrated that losses due to volatilization and/or sorption by the glassware were less than analytical error and, thus, were negligible. Analytical error was computed to be less than 10% based on an analysis of 15 replicates of known standards of the two compounds.

Adsorption equilibrium studies

An identical procedure for the rate studies was employed except that a matrix consisting of three different soil masses (5, 10, and 15 g) and three differ-

ent solute concentrations (25, 50, and 100 mg/L) was used. Vials were agitated until equilibrium could be assumed, as determined from the rate studies, after which samples were withdrawn and analyzed.

Column studies

Column studies were designed based on modifications of techniques suggested by McCarty et al. [4], Enfield and Carsel [5], Van Genuchten et al. [6], Rao and Davidson, [7], and Davidson et al. [8]. This type of flow study uses a column to focus on the mechanism of sorption. Column studies were conducted in 5-cm I.D. glass columns, purchased from Ace Glass Co. (Vineland, NJ) and operated in a downward, gravity flow mode. All interconnecting tubing and fittings were made of glass, teflon or stainless steel to minimize losses due to sorption by the apparatus. The experiment consisted of four columns run in pairs. Each pair consisted of a column filled with a quantity of Towacca soil measuring approximately 30.5-cm in depth (after packing) or a quantity of Cohansey soil, also measuring approximately 30.5-cm in depth (after packing).

The literature and past work [9–11] led to expectations that the extent of sorption occurring in the system would be proportional to the mass of organic matter present. Based on those expectations it was necessary to measure the mass of soil used in each column.

Before the columns were packed, a support phase of glass wool and glass was placed at the bottom of each unit. The volume of solids to be used was poured (all at once) into the columns directly onto the support phase. Gentle tapping of the sides was used to ensure uniform of the soils. A layer of glass beads was placed at the top of each column to prevent the formation of an impervious layer due to soil disruption during the introduction of liquid feed. Each pair of columns was fed from the same influent solution source, ensuring common influent concentrations for each column.

Soil systems were saturated and column hydraulics were observed by passing distilled water in a gravity mode through the columns after a constant flow of water was achieved, a solution of the appropriate solute at a specific concentration was applied to each pair of columns. Influent solutions as well as effluent solutions were contained in collapsible Teflon bags to prevent volatilization losses. The bags were fitted with septa, so that samples could be withdrawn for analysis by use of a syringe. All columns were equipped with in-line sampling ports, just above and just below each end of the column, so that influent and effluent concentrations could be determined at any time. All influent solutions contained 0.02 N CaCl$_2$ to maintain a constant flow rate and soil structure and, also, act as a tracer to determine an appropriate dispersion coefficient. Effluent samples were analyzed for the solute in question, pH, and chloride concentration. The volume of each sample was measured to determine flow rate. Temperature was recorded at each sampling period.

Initial adsorption–desorption experiment

While flow rate was being stabilized, influent solutions were prepared in teflon bags and allowed to sit overnight, to ensure solution stability. Just prior to start-up, the liquid in the bags was sampled and analyzed to determine initial concentrations. After starting the adsorption phase of the experiment, samples were taken after 12, 16 and 20 hours to ensure that breakthrough was monitored, thereafter, samples were withdrawn daily. The adsorption portion of the experiment was run until a constant effluent concentration was reached in all the columns. Steady-state was assumed established when influent and effluent concentrations stayed relatively constant for three to four days. In retrospect, steady-state was never actually reached, instead a low-rate change continued to occur. This small change continued but did not become apparent until much of data were compiled. Once all four columns had reached an apparent steady-state, the desorption phase of the experiment was started. The chloride concentration in the effluent samples, prior to $CaCl_2$ addition, was the same as that of the distilled water used to prepare the influent solutions. The influent solutions were switched to 0.02 N $CaCl_2$ in distilled water. The desorption portion of the experiment was continued until effluent solute concentrations were below detection limits in all columns.

Second adsorption–desorption experiment

Once the intial desorption phase was completed a second adsorption–desorption experiment was started. In this experiment, the flow rates and organic solute concentrations for each column were kept the same as in the first experiment. The adsorption phase was allowed to run an additional two weeks past the pseudo-steady-state to examine the effects of secondary sorption, which is believed to occur at a much slower rate than the primary sorption. Once this part of the experiment was completed the desorption phase was initiated. After all columns had reached non-detectable solvent levels in the effluent, the flow was stopped and the columns were sealed, completely filled with water. Samples were withdrawn just prior to sealing and withdrawn again two months later to determine whether very slow desorption was occurring. The columns were allowed to sit upright in complete darkness, at room temperature, for the two-month period. During this period, mass balances were performed on each column and percent recoveries determined.

Results

Batch rate studies

Experiments were performed to estimate the time to equilibrium for the sorption of benzene and toluene onto a sand (Cohansey) and a loamy sand (Towacca). The results of these studies, presented in Figs. 1 and 2, suggest that, for both benzene and toluene with the Towacca soil, little or no sorption occurred over a seventy-two hour period. Conversely, benzene and toluene have a moderate affinity for the Cohansey soil. An apparent steady-state occurred

in both benzene/Cohansey and toluene/Cohansey systems in approximately seventy-two hours. Small additional changes were evident up to 148 h for the toluene/Cohansey soil system.

In an effort to determine when a specific steady-state concentration occurred, longer term rate studies were conducted. Two different concentrations of benzene and toluene (50 and 100 mg/L) were used with the Cohansey soil, for two-hundred hours. Results are shown in Figs. 3 and 4. The benzene/Cohansey system displayed no change after the first seventy-two hour period. The toluene/Cohansey system, after the initial uptake, continued to show small changes throughout the two-hundred hour period. It appeared that secondary changes were due to processes other than primary adsorption. Equilibrium batch studies were conducted for time periods between seventy-two and ninety-six hours, based on the results of these intial batch rate studies.
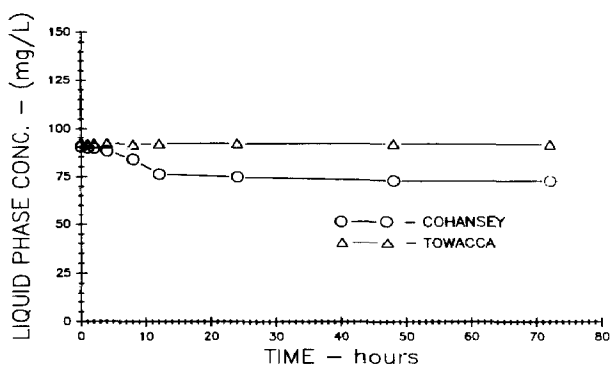

Fig. 1. Benzene adsorption rate studies (batch).
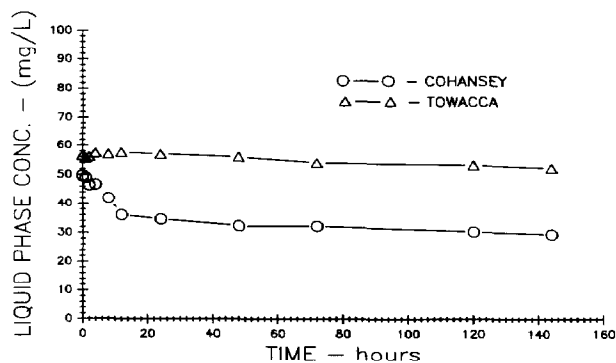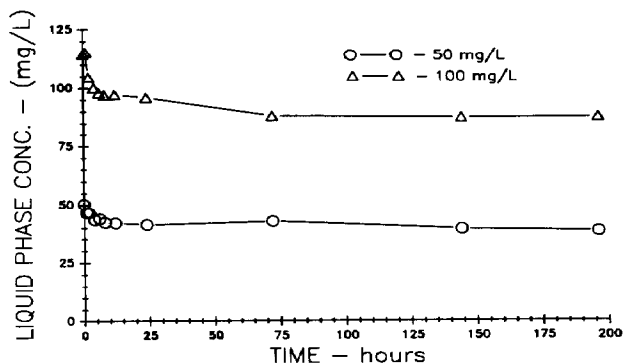

Fig. 2. Toluene adsorption rate studies (batch).

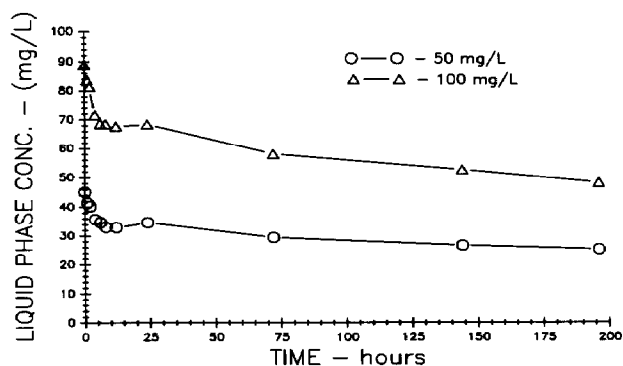Fig. 3. Benzene/Cohansey soil rate studies (batch).

Fig. 4. Toluene/Cohansey soil rate studies (batch).

Batch equilibrium studies

Batch equilibrium studies were not performed with the Towacca soil, since the kinetic studies showed that both benzene and toluene did not adsorb appreciably. Batch equilibrium studies were conducted on the Cohansey soil with both benzene and toluene and Freundlich isotherms obtained by regression of the adsorption data acquired from these studies. These isotherms are presented in Fig. 5 and 6.

The Freundlich isotherm is given by:

$$q_e = kC_e^{1/n} \tag{1}$$

where k and n are empirical parameters, C_e is the liquid phase concentration (mg/L) at equilibrium, and q_e is the mass of benzene or toluene adsorbed per unit mass of soil (μg/g) at equilibrium (Freundlich, [1]. The q_e term was calculated by the formula:
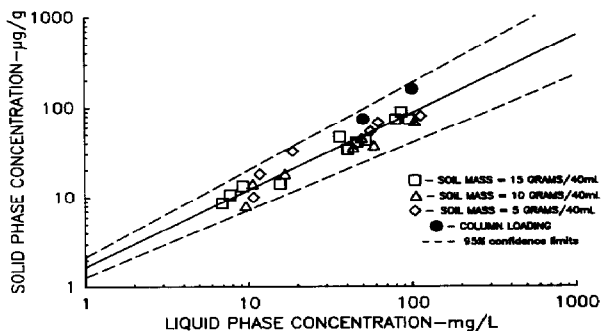
$$q_e = (C_i - C_e)\ V/M \tag{2}$$

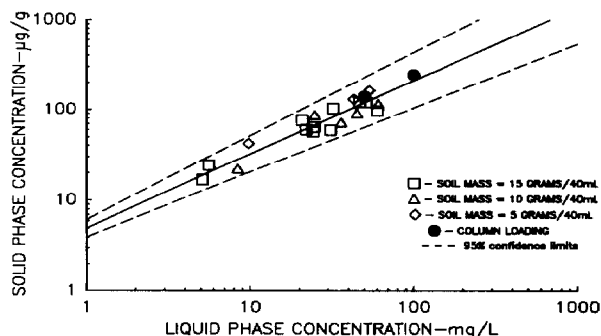Fig. 5. Benzene/Cohansey soil Freundlich isotherm.

Fig. 6. Toluene/Cohansey soil Freundlich isotherm.

where C_i is the initial concentration (mg/L) of benzene or toluene, measured at the time the spike was added, C_e is the equilibrium concentration (mg/L) measured at ninety-six hours, V is the volume (mL) of liquid in the batch system and M is the mass (g) of solids used in the experiment. A comparison of Fig. 5, describing the benzene/Cohansey system and Fig. 6, describing the toluene/Cohansey system indicates that toluene has a higher affinity for the Cohansey solids. The "so-called" solids effect, observed for other substances [13,14] and by other investigators [15,16] where increases sorption is noted for decreasing solids concentrations, was not evident in these experiments.

Column studies

Each column was fed with a 100 mg/L solution of benzene or toluene in water, at a continuous flow of 0.5 L/day. Effluent and influent concentrations are plotted against empty bed volumes in Figs. 7–10. For purposes of computation, empty bed volumes were assumed to be proportional to the macro pore volumes of the solids. The sum of the mass differences are presented on Figs.

7–10, also. The results in all cases showed qualitatively similar responses. All the columns started with a rapid uptake of solute in the initial adsorptive phase. In some cases, the fast uptake reached an apparent steady-state, in others it diminished to a very slow rate, assuming steady removal. Once an "apparent" steady-state had been reached in all columns, the desorption phase was initiated. Initial desorption was very rapid in all cases, promptly coming to an apparent steady-state. After the first desorption phase, a small mass of solute was retained on the solid phase or had disappeared from the systems.

In the second adsorptive phase, a rapid initial uptake reaching a solute loading on the solids equal to that after the rapid uptake portion of the first adsorptive phase, was repeated. After the rapid uptake in the second adsorptive phase, solute uptake continued at a much slower rate. The second adsorptive phase was run much longer than the first, in an effort to reach equilibrium in the systems. When continuously increasing mass differentials made it apparent that equilibrium could not be reached, the second desorption phase was started. As with the first desorption phase, the second desorption phase was very fast, quickly coming to the pseudo steady-state. The mass of solute de-
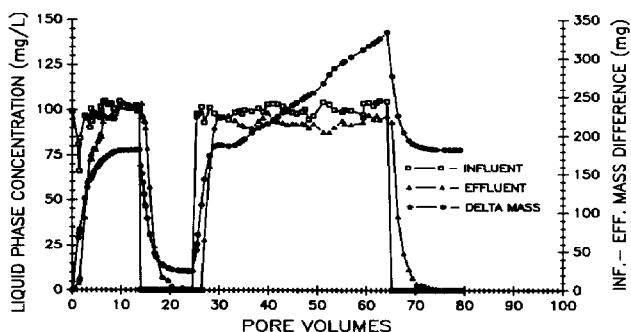

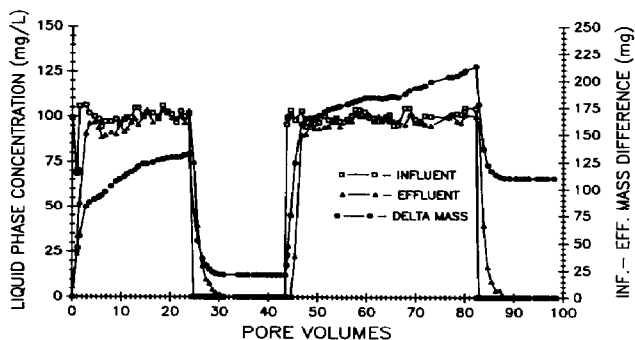Fig. 7. Column 1 Cohansey/100 benzene (flow-through).

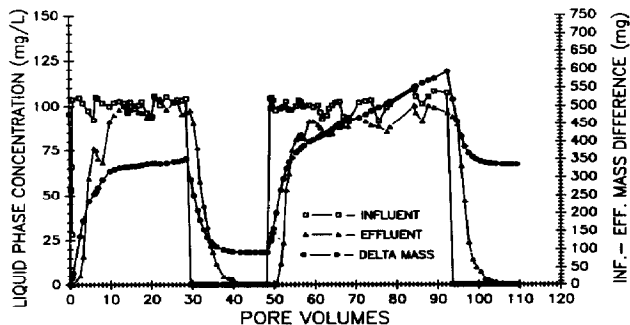Fig. 8. Column 2 Towacca/100 benzene (flow-through).

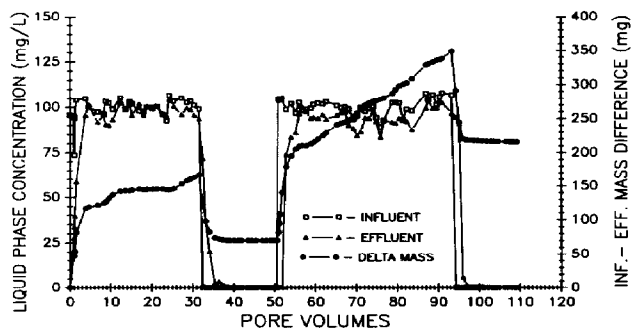Fig. 9. Column 3 Cohansey/100 toluene (flow-through).

Fig. 10. Column 4 Towacca/100 toluene (flow-through).

sorbed in the second phase was equivalent to the mass desorbed in the first phase. The mass desorbed was also comparable to the initial mass loadings in both adsorptive phases.

Initial results from the column studies indicated that primary adsorption of benzene and toluene to both the Cohansey and Towacca soil was very rapid. Mass loadings calculated from the column experiments, using primary adsorption data, fall within a 95% confidence interval of the lines regressed through both benzene and toluene batch isotherm data. These results are presented on Figs. 5 and 6. Results also suggested that desorption of rapidly adsorbed solute is very fast and complete. There are two distinct processes occurring in each system: 1) the simple adsorption and desorption of solute by means of weak physical (Van der Waals) forces, and 2) a very slow removal of solute due to hydrogen bonding, chemical reactions or pore condensation.

Stationary column studies

Once the flow-through column experiments were completed the columns were allowed to sit stationary in darkness for one hundred days. This was done in

an effort to determine if the process involved in the removal of solute from the liquid phase was due to slow adsorption. It was hypothesized that if secondary adsorption occurs and is reversible over time, the liquid phase would reach a new equilibrium. At the end of the stationary period the liquid and solid phases were analyzed. The liquid phases were analyzed for pH, dissolved oxygen, and benzene or toluene. Samples of the soil were carefully extracted from the top and bottom of each column using a spatula. The solid phases were examined for the two solutes by headspace analysis.

These results revealed a large difference in the nature of the solids. In all cases the Cohansey soil showed a substantial amount of solute remaining in the solid. In the case of the Towacca soil none of the solid matrices showed any detectable amount of solute present. Examination of the liquid phases showed that the Towacca systems had sizable concentrations of benzene or toluene. These results indicate that the binding potential of the two soils was very different. The solute adsorbed during the slower process was bound very tightly in the case of the Cohansey systems, and was removed only through heating the solids during the headspace analyses. Solute adsorbed to the Towacca soil during the slower process was released to the liquid phase over time. These results imply that toluene has a much higher affinity for the Cohansey solids than does benzene.

Discussion

The batch rate studies showed the affinity for benzene and toluene to be far greater for solids with a higher percentage of organic matter. Both benzene and toluene were moderately adsorbed on Cohansey soil while no measurable adsorption of either solute onto Towacca soil was found. The mass of toluene sorbed to the Cohansey soil matrix was greater than the mass of benzene sorbed.

Long-term batch studies indicated that for some systems a slow loss of solute occurred with time. This was the first evidence that a secondary process was occurring. All experiments were run in darkness to eliminate the possibility of photodegradation. Thermal recovery (of solids) seemed to match mass deficit and suggested minimal loss due to biodegradation. In most cases, the systems reached an apparent steady-state within 96 hours; systems were assumed to be at equilibrium, so that isotherm analysis could be performed. Isotherm analysis showed no evidence for the so-called solids effect, where increased adsorption is noted for decreasing solid concentration.

Column studies confirmed that organic matter was a major factor in the affinity of benzene and toluene for the soils. For all twelve columns, the mass adsorbed after each adsorptive phase was greater for the columns containing Cohansey soil, as compared to the Towacca soil. The column studies also confirmed that the initial uptake of solute from the liquid phase was very rapid. Results indicated that the mass adsorbed during primary adsorption (initial

uptake) is finite. Solute loading after the first primary sorption phase was equal to the net loading after the second primary sorptive phase.

By using the loading results from the Cohansey soil, an average mass/bed mass was calculated for the benzene (100 mg/L) and toluene (100 mg/L) systems. This provided four more isotherm points; these were added to the equilibrium data. The toluene loading points fit on the line regressed through the toluene batch isotherm data. The benzene loading points fit within the 95% confidence interval on the line regressed through the benzene batch isotherm data. This suggests that the batch studies effectively describe the primary adsorption of benzene and toluene onto Cohansey soil.

The kinetic batch studies on the Towacca soils showed little or no adsorption of benzene and toluene, whereas the column studies revealed that a significant amount of primary adsorption had occurred. For ion sorption, large solids/liquid ratios are required for batch experiments. Column experiments with solids ratios of about 5–6 permit more reasonable (analytically accurate and precise) data.

The first and second desorptive phases were very rapid and complete. The mass of solute desorbed during the first phase was equal to the mass of solute adsorbed in the initial rapid uptake. This was true for the second adsorptive and desorptive phases, also. This suggests that solute adsorbed in the initial or primary uptake phase is held by weak "physical forces" and is easily removed during the desorptive phase.

The column studies demonstrated that references to a secondary process that removes solute from solution are well founded. Once the experiments were completed, an examination of the solute masses retained in the systems show that the slow loss of solute was not an artifact of the experiments.

Possible mechanisms of removal are biochemical activity, chemisorption, condensation or secondary pore diffusion. Biochemical activity could explain the increased activity during the second adsorptive phase. The biological communities may have become acclimated in the systems, once acclimated the communities settled into a first-order decay mode with benzene and toluene as the source of carbon.

The stationary column studies gave more evidence that the secondary loss of solute was secondary pore diffusion. Solute was recovered from all the columns through headspace analysis of liquid and soil. While this analysis was not fully quantitative, these data combined with recovery data, with some mass balances close to 100%, eliminating biochemical activity as a probable mechanism of removal.

The stationary studies revealed a large difference in the nature of the two soils examined. In all cases, the Cohansey solids showed a substantial mass of solute remaining on the surface, while none of the Towacca soils showed the presence of either solute. Examination of the liquid phases showed that the Towacca cases had significant masses of benzene or toluene present. These

results showed that the binding potential of the two soils was very different. The Cohansey systems, which showed a higher affinity for the two solutes, bound any contaminant adsorbed during the secondary process very tightly. The solute was released from the Cohansey solids only through heating. On the other hand, solute adsorbed to the Towacca systems during the slower process was readily released to the liquid phase over time.

A difference in the nature of the two solutes examined was confirmed by the stationary studies. As was shown in batch studies and flow-through column experiments, toluene has a much higher affinity for the Cohansey soils than has benzene. No difference was observed with the Towacca soil, suggesting that the amount of organic matter present was a controlling factor.

Conclusions

The following three conclusions can be drawn:

(1) For both batch and flow-through column experiments the organic matter present in the solids matrix was the major factor in the affinity of benzene and toluene to the soils examined.

(2) Column studies showed that two distinct uptake phases exist, an initial rapid adsorptive phase which is followed by a much slower secondary uptake phase.

(3) Results obtained show that the mass adsorbed during primary adsorption (initial uptake) was finite and reversible. The solute loading after the first primary adsorption phase was equal to the loading after the second primary adsorptive phase (repeatability). The masses adsorbed during the primary adsorption phases were equal to the masses desorbed during the desorption phases (reversibility).

Acknowledgements

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