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Comparison of equilibrium and non-equilibrium distribution coefficients for the human drug carbamazepine in soil

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HIGHLIGHTS

- Higher flow rates resulted in decreased sorption of carbamazepine.
- Repeated applications of carbamazepine increased potential mobility.
- Carbamazepine mobility was adequately predicted using a 2 h sorption event.

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ABSTRACT

The distribution coefficient (K_D) for the human drug carbamazepine was measured using a non-equilibrium technique. Repacked soil columns were prepared using an Airport silt loam (Typic Natrustalf) with an average organic matter content of 2.45%. Carbamazepine solutions were then leached through the columns at 0.5, 1.0 and 1.5 mL min^{-1} representing average linear velocities of 1.8, 3.5 and 5.3 cm h^{-1} respectively. Each flow rate was replicated three times and three carbamazepine pulses were applied to each column resulting in a total of 9 columns with 27 total carbamazepine pulses. Breakthrough curves were used to determine K_D using the parameter fitting software CXTFIT. Results indicate that as flow rate decreased from 5.3 to 1.8 cm h^{-1}, K_D increased an average of 21%. Additionally, K_D determined by column leaching (14.7–22.7 L kg^{-1}) was greater than K_D determined by a 2 h batch equilibrium adsorption (12.6 L kg^{-1}). Based on these K_D's carbamazepine would be generally characterized as non-mobile in the soil investigated. However, repeated carbamazepine applications resulted in an average 22% decrease in K_D between the first and third applications. Decreasing K_D is attributed to differences in sorption site kinetics and carbamazepine residence time in contact with the soil. This would indicate that the repeated use of reclaimed wastewater at high application rates for long-term irrigation or groundwater recharge has the potential to lead to greater transport of carbamazepine than K_D determined by batch equilibrium would predict.

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1. Introduction

The presence of pharmaceutically active compounds in environmental samples has become a concern. Recently, 40 different rivers and streams in Germany were found to contain 31 different pharmaceutical compounds (Ternes, 2001). It was also found that at least one compound was found in every sample. The presence of pharmaceutical chemicals in water can arise from sources such as livestock feedlots, runoff from agricultural fields where animal manure has been applied, and the disposal of treated sewage effluent.

In North America, a survey of 139 streams found that 80% of streams sampled contained at least one target compound (Kolpin et al., 2002). They also found that an individual sample contained 86% of the target organic wastewater contaminants. Further analysis of individual streams by Kolpin et al. (2004) indicated sewage effluent inflows represent a major source of human pharmaceuticals to surface waters. It was found that during low stream flow periods, when inputs from urban sewage treatment facilities contribute significant flow to the overall stream, the concentration of pharmaceuticals increased downstream from the inputs. These results and others (Castiglioni et al., 2006) indicate that a significant source of pharmaceuticals found in environmental water samples originate from municipal sources.

Abbreviations: K_D, distribution coefficient; D, hydrodynamic dispersion coefficient; R, retardation factor.

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In many arid regions of the world sewage effluent is often viewed as a valuable water resource. Recently the use of treated sewage effluent has been seen as a way to increase water supply by replacing fresh water with reclaimed water for irrigation and groundwater replenishment through artificial recharge. As a result, understanding the environmental fate of wastewater contaminants found in sewage effluent in soil is becoming more important. In particular the fate of pharmaceutically active compounds in soil systems is becoming a topic of research. Previous investigations of pharmaceuticals have focused on river and stream systems and hydrologically connected groundwater (Clara et al., 2004; Kolpin et al., 2002, 2004; Löffler et al., 2005). Conclusions drawn from research on these systems are not directly transferable to terrestrial systems where effluent is applied for irrigation or groundwater recharge. Kinney et al. (2006) reported that the use of reclaimed wastewater for irrigation of turf resulted in the presence of a number of pharmaceutical compounds in the top 30 cm of soil. They also found that the concentration of the individual compounds investigated were less than 15 μg kg^{-1} in the top 30 cm of soil and that most compounds showed no net accumulation in the soil. This indicates that natural inactivation and removal of the compounds were occurring in the top 30 cm of soil through degradation, sorption, leaching or some combination of all three.

Carbamazepine (5*H*-dibenz(b,f)azepine-5-carboxamide) is a commonly prescribed drug used to control seizures in the treatment of epilepsy (Johannessen and Ben-Menachem, 2006) and acute mania or mixed episodes in bipolar disorder type I (Golden et al., 2006). A low estimate of generic carbamazepine production in the United States is approximately 35 000 kg annually and does not include name brand production (Thacker, 2005). Clara et al. (2004) found that a significant portion of the ingested carbamazepine was excreted unchanged in the urine. Carbamazepine has also been found to be very resistant to degradation during sewage treatment. Möhle and Metzger (2001) found that typical treatment processes removed only 7% of the carbamazepine entering the treatment system. They also found that carbamazepine was present in effluent samples from 9 different sewer treatment plants in Germany that were sampled throughout a year. As a result of wide spread use and resistance to degradation in sewer treatment plants carbamazepine has commonly been found in environmental samples at relatively high concentrations. Tixier et al. (2003) detected carbamazepine in surface waters in Switzerland at concentrations up to 0.95 μg L^{-1}. Surface waters directly downstream from treated sewage effluent outfalls have also been shown to have carbamazepine concentrations as high as 0.26 μg L^{-1} (Kolpin et al., 2004).

Carbamazepine is also very stable in the environment. Clara et al. (2004) found that no appreciable reduction of carbamazepine occurred over 120 d during groundwater recharge and that small reductions in the concentration of carbamazepine in the groundwater were linked to dilution effects. Carbamazepine has also been found to have an environmental dissipation half life of 328 d and was classified as highly persistent (Löffler et al., 2005). This dissipation half life was determined for a water sediment system likely to be the terminus for a sewage treatment facility outfall (i.e. river or stream) and can explain the prevalence of carbamazepine in the environment. Because of carbamazepine's persistence in the environment it has been used as a marker for anthropogenic influences on aquatic systems (Clara et al., 2004).

Kinney et al. (2006) found that the total mass of carbamazepine in soils irrigated with reclaimed water increased over a growing season. Their data also indicated that throughout the winter when there was no irrigation the concentration of carbamazepine was reduced. It was postulated that the reduction over the winter was due to precipitation (21.5 cm), leaching the carbamazepine below 30 cm. However, recent sorption data would suggest that according to the index developed by McCall et al. (1980) carbamazepine would be classified as non-mobile in surface soils with elevated organic matter (Williams et al., 2006; Chefetz et al., 2008). It is therefore important to better understand the potential mobility of carbamazepine in soil.

Typically batch equilibrium sorption techniques have been used to determine the potential mobility of organic compounds (Altfelder et al., 2001; Lee et al., 1988; MacIntyre et al., 1991). Others have suggested that column investigations are a better indicator of a compounds leachability (Jackson et al., 1984; and Maraqa, 2007, 2001). Reduced mobility of a compound is related to the overall sorption potential of the compound for the solid phase in a soil system. Sorption within column systems can be viewed as either an instantaneous equilibrium process described by equilibrium sorption or as a non-equilibrium process where sorption occurs at different rates depending on sorption "sites" or where transport occurs in different "regions". When non-equilibrium processes dominate, the explanations for observed solute transport can be either physical or chemical in nature.

Physical non-equilibrium is often described as a "two region" model. The two region model can be thought of as occurring when water occupies different flow regions, with one region being relatively stagnant and the other more mobile. This might be envisioned as a soil having a few large pores which conduct water and dissolved chemicals much more rapidly than the smaller pores in the soil. In such a case, the "region" of the soil comprised of the large pores dominates the transport process, and may result in a breakthrough of dissolved chemicals from the bottom of the column much sooner than might be expected if all the pores had relatively equal contributions to the flow. This early breakthrough of chemical would be considered to result from a physical non-equilibrium process. Generally, a non-interacting tracer, such as bromide, is used to identify the extent of physical non-equilibrium; that is, identify the portion of the conducting pores which contain "mobile" water.

Chemical non-equilibrium is often described as being represented by a "two site" model. Conceptually the two site model describes sorption occurring at different rates depending on the sorption site, with one rate being instantaneous and all other sites having rates lower than instantaneous.

The one dimensional equilibrium convection dispersion equation (CDE) for transport of a conserved sorbing solute can be used to describe carbamazepine's transport, due to carbamazepine's recalcitrance and is given by the following equation (Jury et al., 1991):

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} \tag{1}$$

where C is the solute concentration, t is time, D is the hydrodynamic dispersion coefficient, R is the retardation factor, z is the distance the solute has moved and v is the average pore water velocity. When non-equilibrium processes dominate, the explanations for observed solute transport are either chemical or physical in nature. The two site and two region non-equilibrium models can be reduced to Eq. (2) by using dimensionless parameters when there is no chemical degradation or transformation (see Toride et al., 1999):

$$(1-\beta)R\frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) \tag{2}$$

where T is dimensionless time [time × (average pore-water velocity/column length)], C_1 and C_2 are the concentration of sorbent in the equilibrium and non-equilibrium sites respectively, β and ω are coefficients relating to chemical and physical non-equilibrium. If the non-equilibrium is physical in nature β is the partitioning coefficient related to the fraction of solute in the mobile fraction of soil water and ω is the exchange rate coefficient for sites with

rate limited sorption. On the other hand if the non-equilibrium is chemical in nature then β is the partitioning coefficient related to the fraction of sites with instantaneous sorption and ω is the exchange rate coefficient related to the rate of exchange of the solute between water that is mobile and water that is immobile (Nkedi-Kizza et al., 1984). When all water is mobile and all sorption sites are instantaneous, $\beta = 1$ so that $\omega = 0$, and thus the solution to Eq. (1) can be reduced to the solution for the equilibrium CDE (Toride et al., 1999).

Carbamazepine, and two other drugs (naproxen and diclofenac) were reported by Chefetz et al. (2008) to have distribution coefficients that were linked to their transport in soil with differing properties. They found that breakthrough curves of the drugs could be qualitatively explained based on distribution coefficient for soils with different textures and organic carbon (OC) contents. However, no quantitative comparison was made between R determined by the distribution coefficients and R calculated from their column experiments.

Currently, the leaching potential of pharmaceuticals in the environment are based on equilibrium partition coefficients (K_D). This assumption may not be accurate due to kinetic factors. An equilibrium K_D may not necessarily match the effective K_D of a solute being transported through soil. The extent to which they match is dependent upon the velocity of the solute transported through the soil and the kinetics of the sorption processes involved. However, no quantitative link between batch measured partition coefficients and column breakthrough curves have been established for carbamazepine. The purpose of this study was to determine if batch equilibrium distribution coefficients can adequately predict the transport of carbamazepine in a non-equilibrium flow through system.

2. Materials and methods

Soil columns were constructed using 4.7 cm (id) by 5.0 cm glass tubes. The soil was collected from the surface 18 cm of an Airport silt loam (Typic Natrustalf) located in Davis County, Utah. Soils were air-dried, sieved to 2.0 mm, and some of their physical properties measured by standard techniques (Table 1). Columns were constructed by tightly packing 1-cm of 0.595–0.841 mm, combusted and washed Ottawa sand to a bulk density of 1.8 g cm^{-3}. The sand was used to ensure that the flow was evenly distributed across the entire surface of the soil layer. Following the sand 1-cm of soil was packed to a bulk density of 1.4 g cm^{-3} followed by another 1-cm of sand. Both ends of the column were sealed using silicone stoppers inserted to a depth of 1-cm with one hole through which 1/8″ (0.318 cm) Teflon tubing was passed. The column and stoppers were placed in a clamping mechanism that prevented internal pressure from pushing the stoppers out of the columns. After packing, columns were leached under saturated conditions for 24 h with a water solution made by adding NaCl and $CaCl_2$ to 18 MΩ water to create an electrical conductivity (EC) of 1 dS m^{-1} and a sodium adsorption ratio (SAR) of 2 (Williams et al., 2002). The column design for this study is to allow direct comparison of K_D values obtained with those obtained from previous work with batch equilibrium studies. Specifically, the column pulses were designed to apply carbamazepine to the soil at the rate of 0.10 μg g^{-1} soil. Williams et al. (2006) determined K_D's based on batch equilibrium systems with initial carbamazepine application concentrations between 0.05–0.15 μg g^{-1} soil. Thus, the K_D determined by using the non-equilibrium system is directly comparable to the K_D determined by batch equilibrium since the ratio of carbamazepine to potential sorption sites is the same for both systems.

Table 1
Soil physical properties of Airport silt loam (Aquic Natrixeroll).

pH	7.0
SAR	0.60
EC (dS m^{-1})	0.49
% Sand	43
% Silt	32.5
% Clay	24.5
% Organic carbon[a]	1.42

[a] Walkley–Black procedure used (Nelson and Sommers, 1982).

Water solutions were applied to the soil columns using a Dionex[1] GP40 pump with all PEEK components (Dionex Co., Sunnyvale, CA). The pump allowed for precise flow control and solution switching without flow disruptions. Column effluent was collected using a fraction collector. Fractions were collected in 22 mL increments. Treatments consisted of three linear velocities (1.8, 3.5 and 5.3 cm h^{-1}) and three consecutive pulses of 10 μg L^{-1} carbamazepine. In all cases columns were leached under saturated conditions. The carbamazepine pulses were timed such that a total of 10 μg of carbamazepine was applied in each pulse which resulted in pulse durations of 240, 120, and 80 min for the respective 1.8, 3.5, and 5.3 cm h^{-1} velocities. Prior to, and following each carbamazepine pulse, a 10 mg L^{-1} Br^- pulse was applied to the column. Each flow rate was replicated three times for a total of 9 columns with 27 carbamazepine pulses and 54 bromide pulses.

The parameter fitting software CXTFIT v. 2.1 (Toride et al., 1999) was used to determine non-equilibrium K_D's by fitting the CDE to observed breakthrough curves. Fitting the CDE was accomplished using bromide breakthrough curves before and after each carbamazepine pulse and assuming that any observed non-equilibrium transport would be due to physical non-equilibrium, as bromide is a non-reactive tracer (Williams et al., 1999). For bromide K_D is negligible and R was assumed to be 1 and the software was allowed to independently fit the non-equilibrium form of the CDE equation by optimizing the hydrodynamic dispersion coefficient (D), the instantaneous solute retardation (β) and the mass transfer coefficient (ω). A complete description of the theory and procedures can be found in the literature (e.g., see Graber et al., 1997 and Veeh et al., 1994). In general β and ω describe the degree of either chemical or physical non-equilibrium. CXTFIT was then used to fit the retardation factor, β and ω for carbamazepine breakthrough curves. This procedure involved using the results for D from the Br^- curves and allowing R, β and ω to be optimized. The resulting R was used to calculate K_D based on the following equation (Jury et al., 1991):

$$R = 1 + \frac{\rho K_D}{\theta} \tag{3}$$

where ρ is the soil bulk density and θ is the volumetric water content.

Solid phase extraction (SPE) was used for column effluent sample concentration and clean up prior to analysis. Oasis HLB© (Waters Co., Milford, MA) SPE cartridges were preconditioned in succession with 5 mL of MTBE, 5 mL of MeOH and 5 mL of water followed by air drying for 5 min. Cartridges were loaded with 20 mL of leachate followed by 5 min drying. Carbamazepine was eluted using two successive 2 mL aliquots of MTBE. Samples were then evaporated to less than 0.25 mL and brought to 1 mL with acetonitrile.

Carbamazepine analysis was performed using a Waters 616 LC system equipped with a Waters 2996 photo-diode array detector (Waters Co., Milford, MA). Separation was carried out using a 3.9 × 150 mm Nova-Pak© C18 column with a 4.0 μm stationary phase (Waters Co., Milford, MA). Operating conditions were an

[1] Trade names included for the benefit of the reader and imply no endorsement or preferential treatment of the product listed by the USDA.

injection volume of 20 μL with an isocratic mobile phase of acetonitrile (19%), methanol (37%), and water (44%) and a constant flow of 0.75 mL min^{-1}. These conditions resulted in a total run time of 6 min and a carbamazepine retention time of 3.6 ± 0.1 min. Carbamazepine was quantified using photo-diode array absorbance at 210 nm. Bromide was analyzed using a Dionex AS4A-SC (Dionex Co., Sunnyvale, CA) column with an isocratic mobile phase of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ at a constant flow rate of 2.24 mL min^{-1} followed by electrochemical suppression and conductivity detection. Total run time was 15 min and Br− eluted at 2 min.

Distribution coefficients determined using a non-equilibrium technique were compared to equilibrium batch results found in Williams et al. (2006). Leaching K_D's were compared between treatments using JMP 10.0 (SAS Institute, Cary, NC) for ANOVA using a balanced two factor design with pulse number and linear velocity as the two factors. Replicates were included in the error term and the interaction between linear velocity and pulse was evaluated. Means comparisons were made using Tukey–Kramer HSD.

3. Results

An initial sorption experiment found there was no measurable sorption of carbamazepine to the washed sand. Additionally, a column was constructed using only sand and the CDE was fitted to three successive carbamazepine breakthrough curve using CXTFIT. The average R was 1.01 with a standard error of 0.02. This would indicate that the K_D measured by the non-equilibrium method is due to the soil and not the sand in the column.

Fig. 1 is a representative series of breakthrough curves for a single column with a linear velocity of 3.5 cm h^{-1}. The solid lines represent the fitted results from CXTFIT and the individual data points are the measured values. The coefficient of determination for the regression of observed points versus predicted values for the Br^- breakthrough curves were greater than 0.99 for all columns and flow rates. A Br^- pulse was also applied immediately before and immediately following each carbamazepine application. Note that the x-axis (dimensionless time) is not consistent and there are three distinct regions. The first and last regions correspond to the Br^- pulses and have the same time scale and can be compared across the six different Br^- pulses. The middle regions correspond to a carbamazepine pulse and have a time scale approximately five times larger than the Br^- pulse. As a result the carbamazepine breakthrough curves are comparable to each other but not to the Br^- curves. Following the carbamazepine pulse, leachate carbamazepine concentrations were measured until they were below detection (0.1 μg L^{-1}) then the second Br^- pulse was applied. After the second Br^- pulse an additional 4 L of carbamazepine free water was applied before the next combination of Br^-, carbamazepine, Br^- pulses were applied.

Observed concentrations for Br^- were used as input for CXTFIT with the retardation factor set to 1 and D, β and ω were then optimized (Fig. 1). In all cases the results of the optimization indicated that β was close to 1 and ω was close to zero so that the equilibrium CDE could be used. This indicates that the transport of the non-adsorbing tracer Br^- behaved conservatively and there was no solute exchange between mobile and immobile regions within the column (Veeh et al., 1994; Toride et al., 1999). When all values of D for the replications of a specific column at a specified flow rate

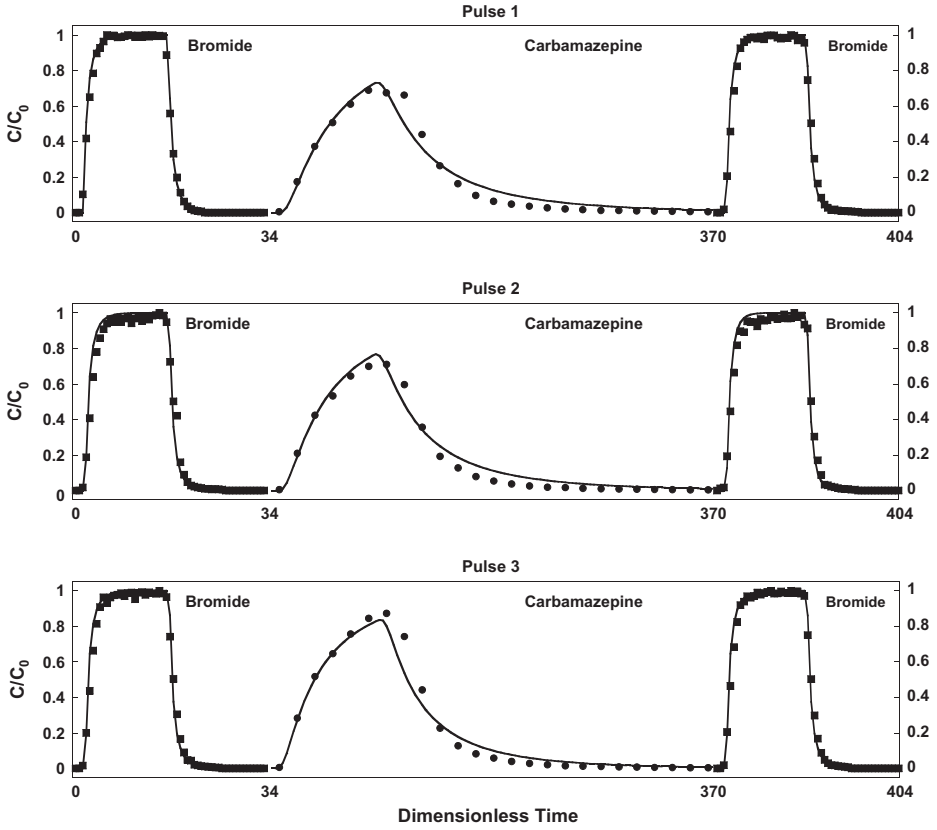

Fig. 1. Solute breakthrough curves obtained from an Airport silt loam for Br^- and carbamazepine at a flow rate of 1.8 cm h^{-1}. Breakthrough curves are from successive pulses of Br^- and carbamazepine through the same soil column. Pulses followed the sequence Br^-, carbamazepine, Br^- with two separate Br^- pulses between each carbamazepine pulse. Data points represent measured concentrations and the solid lines are the fitted curves obtained from CXTFIT. The x-axis is dimensionless time [time × (average pore-water velocity/column length)] for all pulses but the time scale for each carbamazepine pulse is approximately 10 times greater than the Br^- pulses.

Table 2
Average dispersion coefficient for a Br^- pulses through Airport silt loam. Each value is the average of six columns calculated using CXTFIT. Numbers in parentheses equal 1 standard error of the mean.

Linear velocity (cm h^{-1})	Dispersion coefficient, D (L^2 T^{-1}) [a]		
	Column 1	Column 2	Column 3
1.8	46.2 (7.1)	61.5 (4.4)	43.7 (9.9)
3.5	48.8 (3.5)	59.5 (11.2)	53.9 (11.8)
5.3	91.5 (6.7)	92.1 (4.3)	96.9 (3.0)

[a] L is dimensionless length and T is dimensionless time (see Toride et al., 1999).

Table 3
Distribution coefficients for carbamazepine transport through Airport silt loam. Averages are from three replicates calculated using CXTFIT. Numbers in parentheses equal 1 standard error of the mean.

Linear velocity (cm h^{-1})	K_D (L kg^{-1})		
	Pulse 1	Pulse 2	Pulse 3
1.8	23.0 (0.4)	20.3 (0.2)	17.4 (0.3)
3.5	20.5 (1.2)	18.0 (0.9)	16.1 (0.2)
5.3	19.1 (1.2)	15.9 (0.3)	14.7 (0.1)

were compared it was found that there was no statistically significant difference ($p < 0.01$), and an average D was calculated (Table 2).

A retardation factor for each carbamazepine pulse was fit using CXTFIT. The average value of D for each column obtained from the Br^- breakthrough curves was used as a fixed value and the value of R, ω and β were optimized. The coefficient of determination for the regression of observed points versus predicted values for the carbamazepine breakthrough curves were greater than 0.92 for all columns and flow rates. A K_D was then calculated using Eq. (3) and the values are reported in Table 3. In general K_D decreased with increasing linear velocity and repeated carbamazepine applications.

Fig. 2 is a representative series of breakthrough curves for the first pulse through different columns at different flow rates. The advantage of using the dimensionless form of the CDE in CXTFIT is that direct graphical comparisons can be made between breakthrough curves at different flow rates. In Fig. 2 the Br^- breakthrough curve for the column with a linear velocity of 1.8 cm h^{-1} represents a total of 500 min, while the same Br^- breakthrough curve for the 5.3 cm h^{-1} represents a total of 165 min. However, when the Br^- curves are compared in Fig. 2 there are no differences in breakthrough curves for the different flow rates. Similarly, the breakthrough curves for carbamazepine represent 30 h for a linear velocity of 5.3 cm h^{-1} compared to 91 h for 1.8 cm h^{-1}.

4. Discussion

Typical batch equilibrium K_D's are determined using contact times from 2 h up to days and even months. These various times are usually based on a time series of sorption experiments to determine when no further sorption will occur. For the purpose of using K_D to determine leaching potential this would be equivalent to the sorption that occurs during the interval between water application events (irrigation, groundwater recharge, or rain events). However, in most arid regions the initial sorption and mobility of a compound would occur during a leaching event (irrigation or

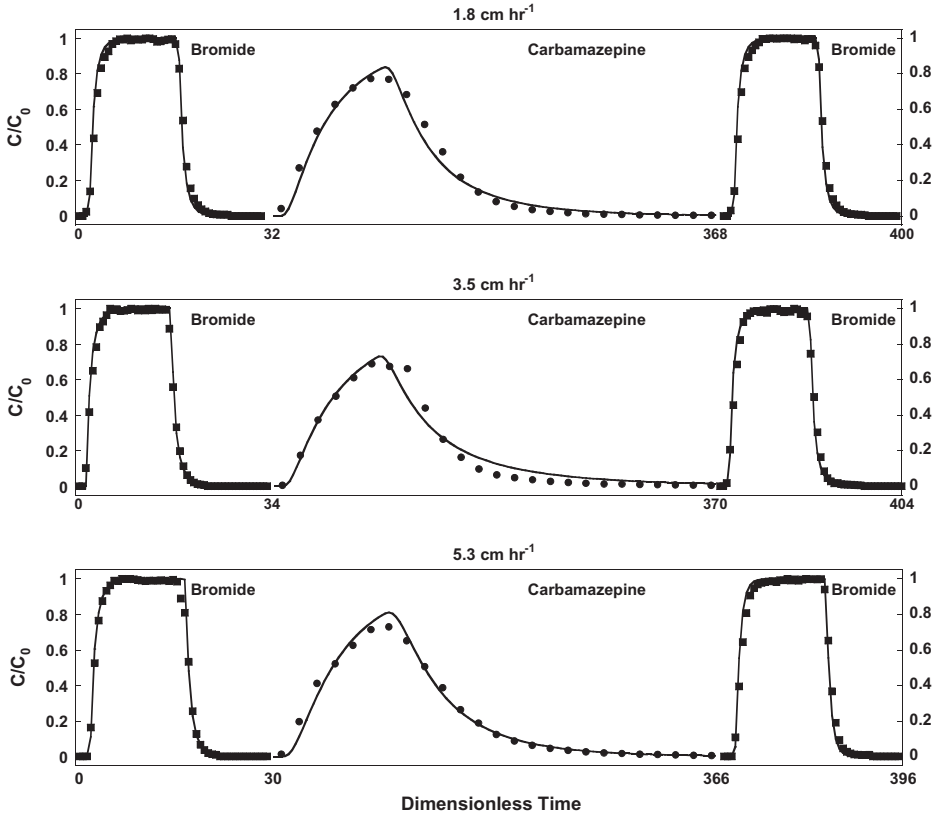

Fig. 2. Solute breakthrough curves obtained from the first pulse of carbamazepine through an Airport silt loam at different flow rates. Each carbamazepine pulse was preceded and followed by a Br^- pulse. Data points represent measured concentrations and the solid lines are the fitted curves obtained from CXTFIT. The x-axis is dimensionless time [time × (average pore-water velocity/column length)] for all pulses but the time scale for each carbamazepine pulse is approximately 10 times greater than the Br^- pulses and the scales between flow rates are slightly different.

Table 4
Distribution coefficients for carbamazepine sorption to Airport silt loam determined by batch techniques (Williams et al. (2006)).

	K_D (L kg^{-1})
Adsorption	12.6
First desorption	20.3
Second desorption	36.9
Third desorption	47.8

groundwater recharge) more similar to the non-equilibrium method described here. The water and compound would transport through the surface rapidly and then once the leaching event is over the compound would be able to reach an equilibrium K_D.

Williams et al. (2006) reported carbamazepine sorption and desorption coefficients using 2 h equilibrium batch techniques for the same Airport silt loam soil used in the current study (Table 4). Briefly, the adsorption coefficient was determined by adding carbamazepine free soil to an aqueous solution containing carbamazepine and allowing equilibrium to be established. The desorption coefficients resulted from removing a portion of the equilibrium solution and adding carbamazepine free water to the system and allowing for a new equilibrium to be reached. This process was repeated three times for a total of four K_D's (1 adsorption and 3 desorption) ranging from 12.6 to 47.8 with the adsorption K_D being lowest and the third desorption being the highest. The difference between adsorption and desorption is hysteresis and has been observed to occur with other organics (Boivin et al., 2005; Koskinen et al., 2006; Taylor et al., 2004). Comparing the K_D's from column leaching (Table 3) and batch sorption indicates that the batch system was not at equilibrium after 2 h as indicated by the fact that the adsorption K_D is lower than the K_D's from the flowing systems. The present study resulted in K_D's higher than a 2 h adsorption event, but equal to or lower than the corresponding 2 h desorption events. Thus, carbamazepine mobility through the soil would be over predicted based solely on K_D estimates derived from batch systems considering only a 2 h adsorption event.

Analysis of variance indicated a statistically significant difference ($p < 0.05$) between the K_D resulting from different linear velocities in soil columns. A linear velocity of 5.3 cm h^{-1} had a significantly lower K_D than 3.5 and 1.8 cm h^{-1}. Others have reported the same relationship between reduced K_D at increased pore-water velocity (Schulin et al., 1987; Brusseau, 1992; Kim et al., 2006; Theis et al., 1988). According to the non-equilibrium CDE there are two potential explanations to describe a change in K_D due to pore-water velocity. First, according to the two region model, the presence of an immobile water phase would result in the solute more rapidly passing by any individual physical point within the column including locations where the mobile and non-mobile phases come together. These interfaces are where solute must pass from one region to another via physical processes such as diffusion. Faster pore-water velocities will result in less time at the interface for solute to transfer from the mobile to immobile phase. For the column leaching experiments reported here this explanation is not very likely due to the lack of deviation of Br^- from the equilibrium CDE during the tracer pulses, as indicated by the ω and β estimates from CXTFIT for the Br^- breakthrough curves. These results are in agreement with previous studies where repacked soil columns were leached under saturated conditions (Maraqa et al., 1998).

The second possible explanation for higher K_D's found at lower pore-water velocity is related to the two site model regarding differences in sorption kinetics. Here the Br^- data is unable to provide any insight due to its lack of sorption. However, the presence of sorption sites with different kinetic characteristics is likely. Pignatello and Xing (1996) linked slow sorption to a combination of organic matter diffusion and sorption-retarded pore diffusion. Organic matter diffusion is the process by which the organic solute must first diffuse through the organic matter prior to site-specific sorption, while sorption-retarded pore diffusion is a result of inhibited diffusion through small pores. The inhibited diffusion is caused by physical or chemical processes similar to chromatography that slow the solute prior to reaching the sorption site. The experimental design was such that the same mass of carbamazepine was exposed to the same soil surface area but for different times resulting in the same number of sorption sites being exposed to the same mass of sorbent for different times. This would lead to sites with instantaneous sorption being equal for all pore-water velocities but the sites with slower kinetics being exposed for different times resulting in different K_D's.

Table 5
List of abbreviations and symbols.

Abbreviation or symbol	
CDE	Convection dispersion equation
OC	Organic carbon
EC	Electrical conductivity
SAR	Sodium adsorption ratio
SPE	Solid phase extraction
K_D	Distribution coefficient
C	Solute concentration
t	Time
D	Hydrodynamic dispersion coefficient
R	Retardation factor
z	Distance
T	Dimensionless time
β	Fraction of instantaneous sorption sites
ω	Mobile water mass transfer coefficient

Distribution coefficients decreased as a result of successive applications of carbamazepine with a statistically significant difference ($p < 0.05$) between the K_D from the third pulse of carbamazepine when compared to the first and second pulses (Table 3). Differences in K_D from pulse 1 to pulse 3 were greatest for a linear velocity of 5.3 cm h^{-1} with a reduction of 23.0% and least for 1.8 cm h^{-1} with a reduction of 19.7%. These results are consistent with the reduction in K_D being due to differences in sorption kinetics. Regitano et al. (2006) found that the longer a sorbing organic is in contact with a sorbent the more tightly it is held by the sorbent. Xing and Pignatello (1997) also showed that steric hindrances to sorption sites would lead to a slow approach to equilibrium. As the number of pulses increases the time the soil sorption sites are exposed to carbamazepine increases and would result in slow filling of the sites due to incomplete emptying of the same site from the previous pulse. The combination of increased pore-water velocity and periodic applications would then lead to a quasi steady-state being reached where the K_D reaches a value in equilibrium with the slow sites as they fill and empty.

Breakthrough concentrations for carbamazepine are plotted in Fig. 3 for the first (Fig. 3a) and third (Fig. 3b) carbamazepine pulse at each flow rate. Statistically there was no difference in K_D for pulse 1 (Fig. 3a) at any of the three flow rates, however, there is evidence of kinetic differences in sorption between the flow rates. The 1.8 cm h^{-1} breakthrough curve for pulse 1 has a similar center of mass as the 3.5 and 5.3 cm h^{-1} flow rates but the peak tail is shifted to the left and the maximum concentration is higher indicating that the lower flow rate underwent slightly lower dispersion than the 3.5 and 5.3 cm h^{-1} flow rates. Since all six of the Br^- breakthrough curves were similar for all of the packed columns the differences in carbamazepine breakthrough must be due to differences in sorptive behavior consistent with the two site model. Elucidating this difference is beyond the scope of the current research but warrants further investigation.

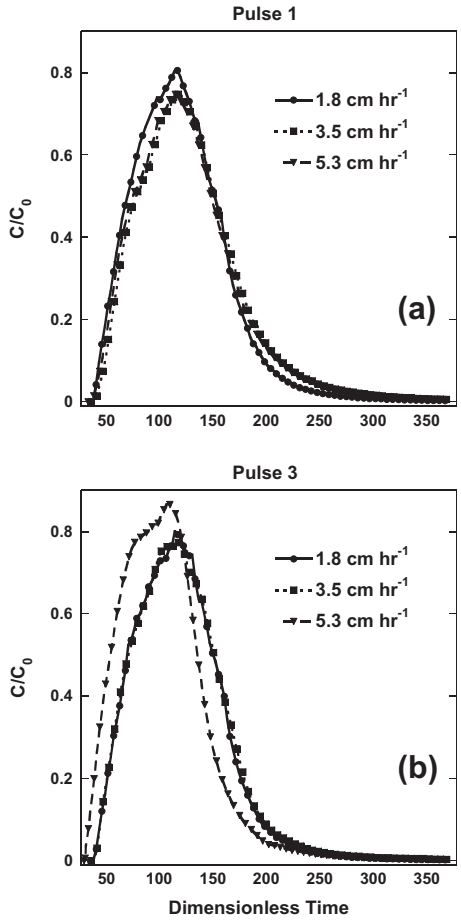

Fig. 3. Actual breakthrough curves for the first (a) and third (b) carbamazepine pulses leached through an Airport silt loam from 3 different columns at flow rates of 1.8, 3.5 and 5.3 cm h^{-1}.

There is a statistically significant difference in K_D between the flow rates by the third pulse that is evident in Fig. 3b. At this point the entire breakthrough curve for the 5.3 cm h^{-1} pulse has been shifted to the left resulting in increased mobility. To directly compare the breakthrough curves dimensionless time was used in Fig. 3. This means that even though the center of mass for the 3.5 and 1.8 cm h^{-1} breakthrough curves are shown eluting at the same time, in real time, the 3.5 cm h^{-1} curve eluted in half the time as the 1.8 cm h^{-1}. Based on this carbamazepine had three times longer to equilibrate with the soil in the column with 1.8 cm h^{-1} flow rate than the column with 5.3 cm h^{-1} rate. This would indicate that by the third pulse the fastest flow rate had a different apparent equilibrium than the other two flow rates and would account for the potential increased mobility of carbamazepine. These results indicate that repeated inputs of carbamazepine in wastewater used for irrigation or groundwater recharge may increase environmental transport.

The current study used carbamazepine concentrations far greater than those found in typical wastewater effluent. Average carbamazepine concentration from five wastewater treatment plants in Spain was reported as 0.55 μg L^{-1} (Calderon-Preciado et al., 2011; Santos et al., 2009) To achieve a carbamazepine application of 0.10 μg g^{-1} soil would require approximately 51 m of water with a carbamazepine concentration of 0.55 μg L^{-1}. Typical groundwater recharge scenarios can average 0.1 m d^{-1} annually (Williams and McLain, 2012). Under these conditions it would take approximately 1.4 years to apply 51 m of water and since carbamazepine is resistant to degradation there is a potential for accumulation over long time periods. Recharge facilities are designed for long term recharge (>25 years), therefore, the results from the non-equilibrium technique described here can be applicable to situations with long-term, high frequency wastewater application.

5. Conclusions

Chefetz et al. (2008) reported that carbamazepine would be characterized as non-leaching in higher OC surface soils but that it would leach in underlying soils that had lower OC content. Our results also indicate that carbamazepine would be characterized as non-leaching in a higher OC surface soil based solely on a single K_D. The sorption coefficient of carbamazepine to an Airport silt loam determined by batch equilibrium was 12.6 L kg^{-1} and ranged from 14.7 to 22.7 L kg^{-1} when determined by the non-equilibrium technique indicating that carbamazepine would be characterized as non-mobile in the surface of the Airport soil. The column experiments used flow rates equivalent to typical irrigation or recharge rates (1.7–5.2 cm h^{-1}) and applied three successive pulses of carbamazepine. It was found that at higher flow rates, which resulted in increased pore-water velocity, the mobility of carbamazepine was increased. Repeated applications of carbamazepine also increased potential mobility by reducing K_D by an average of 23% from the first to third pulse. This would indicate that the use of reclaimed wastewater for long-term irrigation or groundwater recharge has some limited potential for movement of carbamazepine to ground water over an extended period of time. Carbamazepine mobility will depend on amount of water application beyond evaporative demand, soil OC content, degradation rates, and depth to groundwater. Results also indicate that carbamazepine mobility was adequately predicted in the Airport soil by using a combination of a 2 h sorption event followed by a 2 h desorption event even though absolute equilibrium may not have been achieved. The non-equilibrium technique also provided a quantitative link between equilibrium K_D and mobility of carbamazepine.

Appendix

Table 5.

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