



# 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<sup>-1</sup> representing average linear velocities of 1.8, 3.5 and 5.3 cm h<sup>-1</sup> 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<sup>-1</sup>,  $K_D$  increased an average of 21%. Additionally,  $K_D$  determined by column leaching (14.7–22.7 L kg<sup>-1</sup>) was greater than  $K_D$  determined by a 2 h batch equilibrium adsorption (12.6 L kg<sup>-1</sup>). 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  $15 \mu\text{g kg}^{-1}$  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  $0.95 \mu\text{g L}^{-1}$ . Surface waters directly downstream from treated sewage effluent outfalls have also been shown to have carbamazepine concentrations as high as  $0.26 \mu\text{g L}^{-1}$  (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):

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

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):

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

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

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