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## Transport and Retention of Cadmium, Copper, and Lead in Soils: Miscible Displacement Experiments

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# TRANSPORT AND RETENTION OF CADMIUM, COPPER, AND LEAD IN SOILS: MISCIBLE DISPLACEMENT EXPERIMENTS

A Thesis

Submitted to the Graduate Faculty of the  
Louisiana State University and  
Agricultural and Mechanical College  
in partial fulfillment of the  
requirements for the degree of  
Master of Science

in

The School of Plant, Environmental, and Soil Sciences

by  
Nazanin Akrami  
B.S., Sharif University of Technology, 2012  
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*Dedicated to the part of me that will stay in Louisiana forever...*

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## **ABSTRACT**

Heavy metal contamination is a major concern for soil and water quality. To quantify their potential hazard, it is crucial to understand their mobility and retention in soils. The source of the problem is anthropogenic activities such as mining, smelting, usage of sewage sludge and fertilizers. The objective of this study was to quantify Cd, Cu and Pb transport and retention in three soils having different properties, and evaluate their competitive influence on the mobility of individual heavy metal. The second objective was to quantify Cd, Cu and Pb retention kinetics in the different soils. This study also investigates the extent and distribution of retained Cd, Cu and Pb with depth in soil columns.

In the study, batch experiments were carried out for different range of concentrations in time. The results indicated that retention of Cd, Cu and Pb in Windsor, Mahan and Webster soil is nonlinear. Lead exhibited highest retention among all three metals. Moreover, all three metals exhibited highest affinity in Webster soil, which has a higher clay content (mostly smectite), organic material and cation exchange capacity. Sorption of all metals was also observed to be kinetic when retention time increased from one day to seven days.

Miscible displacement experiments in saturated soil columns were also carried out in two ways. In the first type, consecutive pulses of Cd, Cu and Pb were sequentially introduced to each soil column followed by an extended period of leaching with the background solution ( $\text{KNO}_3$ , 0.005M). In the second type, two consecutive pulses of mixed solution (Cd, Cu and Pb), each followed by leaching with the background solution, were introduced to soil columns. Results indicate that Cd was the most mobile with the highest recovery the effluent solution, whereas Pb was the least mobile with the lowest recovery among all elements and soils. It was also observed that Pb resulted in enhanced mobility of both Cd and Cu.

Efforts to describe results from the column experiments based on a multireaction and transport model (MRTM) showed varied degrees of success. Although the model accounts for several sorption mechanisms including nonlinear equilibrium, kinetics, and irreversible reactions, the model was not successful in predicting the competitive behavior of heavy metals in the soil columns.

## CHAPTER 1 : INTRODUCTION

### 1.1 General Descriptions

As varied as heavy metals can be, so are their definitions; some scientists define heavy metals based on their atomic weights such as Bennet (1986), while others such as Thornton (1995) are inclined to define heavy metals based on their density, which must exceed  $6 \text{ g/cm}^3$  to be in this class. In addition, Harrison and Waites (1998) mentioned a high atomic mass and relative toxicity as criteria in defining heavy metals. However, Duffus (2002) brought up an important issue when it is stated that in order to have a measurement basis for the toxicity of heavy metals, a chemical classification of heavy metals and their compounds is necessary. According to De Vries et al. (2002), elements of the transition group in the Periodic Table which have high density can be termed heavy metals, while most of these groups' elements are more accurately dubbed trace metals due to their low abundance in soils.

Raven and Leoppert (1996) state that atmospheric depositions and soil amendments including fertilizer, sludge, liming materials, compost manures, and pesticides are the main sources of heavy metals that enter the soil. Biogeochemistry processes will then circulate these heavy metals in nature, some of which are essential for biological functions while in excess may become toxic and hazardous to the environment (Friberg and Nordberg, 1986).

In this study we focus on three heavy metals: Cd, Cu and Pb. A brief description of each appears below.

#### 1.1.1 Cadmium

Cadmium (Cd) is an element, with the atomic number 48, and density of  $8.65 \text{ g/cm}^3$ . The following is a partial list of its properties:

- It prefers the oxidation state +2 in most of its compounds rather than +1.
- The average concentration of Cd in the Earth's crust is between 0.1 and 0.5 part per million.
- This metal is soft, malleable, ductile, bluish-white and divalent.
- Cadmium in its metallic form is insoluble in water.

Cd is considered an environmental contaminant and a potential concern (Kabata-Pendias and Mukherjee, 2007). Cd compounds exist in both cationic and anionic forms, such as  $\text{Cd}^{2+}$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{Cd}(\text{OH}_3)^-$ ,  $\text{Cd}(\text{OH}_4)^{2-}$  and  $\text{CdCO}_3$  and other complexes in aquatic systems based on Moore (1991), and as  $\text{CdCl}^+$ ,  $\text{CdOH}^+$ ,  $\text{CdHCO}_3^+$ ,  $\text{CdCl}_3^-$ ,  $\text{Cd}(\text{OH})_4^{2-}$ , and  $\text{Cd}(\text{HS})_4^{2-}$  in the soil (Kabata-Pendias and Sadurski, 2004).

Precipitation of Cd appears to be its dominant retention mechanism in soil when  $\text{S}^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$  are available ions (Naidu, 1977). Potential mobility of Cd has an inverse relationship with pH (Dijkstra, 2004). Strawn and Sparks (1999) state that the mobility of Cd in porous media is influenced by retention/release phenomenon, which might be kinetically controlled.  $K_d$ , or the partitioning coefficient, indicates the ratio of Cd concentration in the soil to the  $\text{Cd}^{2+}$  concentration in the solution. According to Sauve' et al. (2000),  $K_d$  is dependent on organic material, soil solution pH, and total metal content. According to Lee (1996), it also has a linear relationship with pH.

In several investigations, the non-linearity of Cd sorption has been reported: Buchter (1989), Krishnamurti and Naidu (2003) to name a few. The transport and the fate of Cd in the soil are often considered moderately mobile and several equilibrium and kinetic models have been used. According to Selim et al. (1992), time dependent sorption has been observed for several soils.

### 1.1.2 Copper

Copper (Cu) is an element with the atomic number 29 and density of 8.96 g/cm<sup>3</sup>. The following is a partial list of its qualities:

- Cu in its pure form is malleable.
- Its surface has a reddish-orange color if freshly exposed.
- Cu concentration in the Earth's crust is about 50 parts per million (ppm).
- It is an essential element for plants and animals, the concentration of which can affect nitrogen fixation, cell metabolism and valance changes (Kabata-Pendias and Pendias, 2001).
- The range of Cu concentrations in soils is between 20 to 30 mg/kg in the world and in excess is harmful for the environment (Alloway, 1995).

While Cu is used in fertilizers (Holmgren et al., 1993; Mermut et al., 1996), fungicides and bactericides (Epstein & Bassein, 2001), the mobility of Cu is important when agricultural management is considered. According to McBride (1981) and Alloway (1995), Cu can exist as Cu<sup>2+</sup>, Cu<sup>+</sup>, CuCl<sup>2-</sup>, CuSO<sub>4</sub>, Cu(OH)<sub>2</sub>, Cu(Cl) and CuCO<sub>3</sub> in the soil.

Copper shows an affinity to organic materials, clay minerals and metal hydroxides (Adriano, 2001; Kabata-Pendias & Sadurski, 2004; Han, 2007). According to Chen (1999), pH, organic material, CEC, clay content, Mn, Al, and Si oxides would affect Cu retention. Also, based on Selim and Ma's work in 2001, we can use MRM models to describe the nonlinearity of Cu kinetic behavior in soils (Selim& Ma, 2001).

Mathur et al. (1984) showed that there is a significant leaching of Cu in humus poor acidic soils. Sparks (2003) stated that heavy metals' mobility and fate can be presented by the partitioning coefficient,  $K_d$ , which according to Chang et al. (2001) is reported as 5.3 to 9.6  $\text{L kg}^{-1}$  for acidic soils with low CEC.

### 1.1.3 Lead

Lead (Pb) is an element in the carbon group with symbol Pb (from the Latin word: Plumbum), atomic number 82, and density of  $11.34 \text{ g/cm}^3$ . The following is a partial list of its qualities:

- Pb is a malleable and soft metal.
- It is also the heaviest non-radioactive element.
- Metallic Pb does occur in nature, but is rare.
- USEPA (1997) states that Pb may be found in sediment, soil, air and water; it is an essential element concerning plant growth.
- According to Steinnes (2013), automobile exhausts, sewage sludge, mining and smelting, shooting and urban soils are listed as anthropogenic sources of Pb contamination.

Kabata-Pendias and Pandias (2001) stated that Pb is immobile; it often goes from a soluble form, to form complexes with sulfates, phosphates, organic materials and clay minerals. Also if the concentration of Pb in soils exceeds 100 to 500 ppm, it is more than normal range.

Barkouch et al. (2007) in a column experiment showed Pb retention in the soil is dependent on a number of parameters including: water soil surface contact, bed height, bed tortuosity, feed flow rate

and volume of water. Rouff et al.(2002) states that in a Pb sorption experiment, Pb would be sorbed to the surface very fast and then the sorption behavior follows a slow continuous process with time.

## 1.2 Heavy Metals Retention in Soils

The term retention or sorption is used when the process of the bonding mechanism between the heavy metal (adsorbate) and soil particles (adsorbent) is unknown. The equations that have been used to describe the relationship between the sorbed amount to the soil (S) and the concentration in the soil solution are applied to predict the chemical retention of elements. They are referred to as sorption isotherms.

The following equation is used when a direct linear relationship between S and C is assumed:

$$[1.1] \quad S = K_d C$$

$K_d$  is the distribution coefficient ( $L^3M^{-1}$ ), which indicates the affinity of an element to the soil (Selim & Amacher, 1997).

One of the most widely used models to describe nonlinear sorption behavior is the Freundlich equation:

$$[1.2] \quad S = K_f C^b$$

Where  $K_f$  is the distribution coefficient ( $ML^{-3}$ ) and b is a dimensionless reaction order which is an indicator of the shape of isotherm:  $b < 1$  concave,  $b = 1$  linear, and  $b > 1$  convex.

Another approach used to describe nonlinear isotherms is the Langmuir equation:

$$[1.3u] \quad S = \frac{S_{\max} K_l C}{1 + K_l C}$$



In which  $S_{\max}$  is the sorption capacity ( $\text{MM}^{-1}$ ),  $K_l$  is Langmuir coefficient ( $\text{L}^3\text{M}^{-1}$ ), which indicates the binding strength.

Goldberg and Criscenti (2008) stated that Langmuir equation is derived considering these two assumptions neither of which are applicable in soils especially high in metal concentration within the soil solution: first, a finite number of uniform adsorption sites exist, and second, lateral interaction between adsorbed species is ignored.

Equations [1.1], [1.2] and [1.3] do not account for the reaction time because they are used as equilibrium models. While Zhang and Selim (2005) stated that in equation [1.3] when the reaction time is increased, higher  $S_{\max}$  is observed which is important because generally, metals' retention to the soil is time dependent. The reaction time may vary from few seconds to years (Sparks, 2011). First and second order kinetic reaction models are used to describe the time dependency of sorption.

The equations described above are based on single site or reaction assumption; however, we can modify them to multi-site and multireaction models. One of the models that consider metals interaction with soil surface is a multireaction transport model (MRTM), which is capable of describing the kinetic reactivity of the metal and soil profile during the transport phenomenon while other models such as Langmuir and Freundlich are assumed (Selim, 1992; Selim & Amacher, 1997).

The following equations are used in this model:

$$[1.4] \quad S_e = \frac{\theta}{\rho} K_e C^n$$

$$[1.5] \quad \frac{dS_1}{dt} = K_1 \left( \frac{\theta}{\rho} \right) C^n - K_2 S_1$$

$$[1.6] \quad \frac{dS_2}{dt} = [K_3 \left( \frac{\theta}{\rho} \right) C^n - K_4 S_2] - K_5 S_2$$

$$[1.7] \quad \frac{dS_5}{dt} = K_5 S_2$$

$$[1.8] \quad S_{irr} = K_{irr} \left( \frac{\theta}{\rho} \right) C$$

Where  $K_e$  is the equilibrium constant which is dimensionless,  $K_1$ ,  $K_2$ ,  $K_3$ ,  $K_4$ ,  $K_5$  and  $K_{irr}$  ( $T^{-1}$ ) are reaction rates,  $N$  and  $n$  are dimensionless reaction orders (see Figure 1.1).

### 1.3 Heavy Metals Transport in Soils

There are several mathematical models used to describe and predict the transport of metals in soils. Earlier scientists used to assume that solute transport was only due to dispersion (Liu et al., 2006). They obtained retardation factors, dispersion coefficients of Cd and other metals by using linear adsorption with convection-dispersion equations. It is stated by Barrow et al., (1989) that due to existence of different reaction types and affinities, the use of a single reaction and linear equation is not adequate. The convection-dispersion equation (CDE) also known as advection-dispersion equation (ADE) describes one dimensional transport of a non-reactive solute in the soil:

$$[1.9] \quad \frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial z} + \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right)$$

In which  $\frac{\partial C}{\partial t}$  is the net change of concentration with time (t),  $v = \frac{q}{\theta}$  is the average pore water velocity ( $L T^{-1}$ ),  $q$  is the Darcy's velocity ( $L T^{-1}$ ) and  $z$  is the distance (L). The term  $v \frac{\partial C}{\partial z}$  is known as the advection while the term  $\frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right)$  is known as dispersion or diffusion term. For miscible displacement in saturated column experiment it is often assumed that  $q$  and  $\theta$  are constants over space and time under steady-state flow.

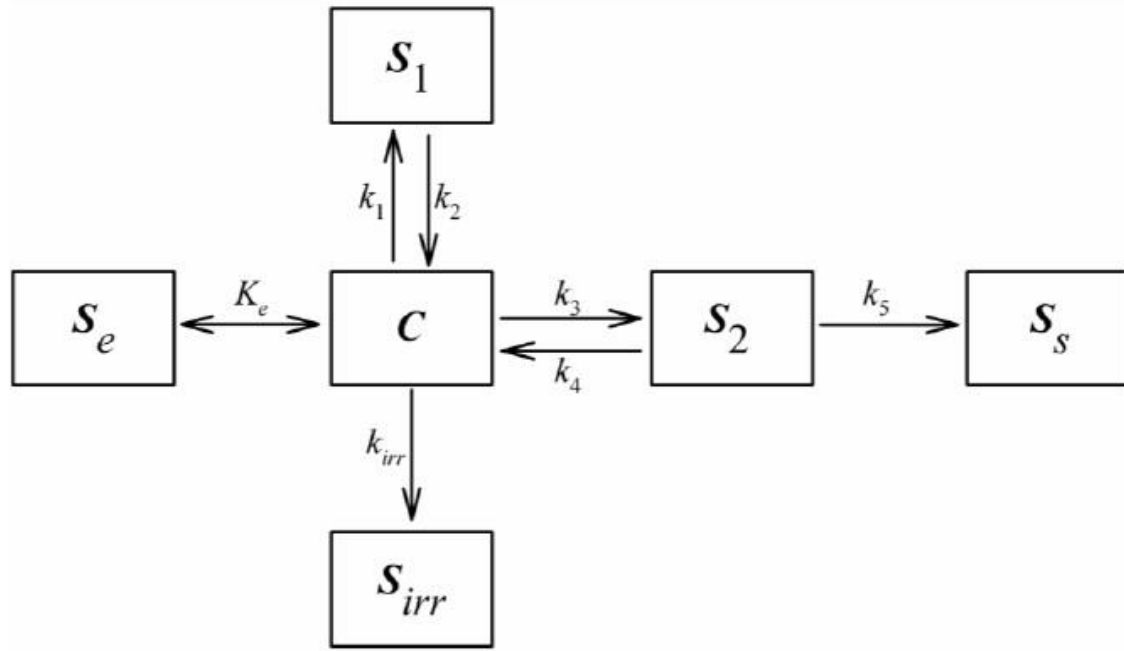


Figure 1.1. A schematic diagram of the multireaction and transport model, where  $C$  is concentration in solution,  $S_e$  represents the amount retained on equilibrium sites,  $S_1$  and  $S_2$  represent the amount retained on reversible kinetic sites,  $S_{irr}$  and  $S_s$  represent the amounts irreversibly retained, and  $k_e, k_1, k_2, k_3, k_4, k_5$  and  $k_{irr}$  are the respective reaction rates.

Selim et al. (1992) proposed a multireaction transport model based on sorption kinetics and soil heterogeneity, which can describe nonlinear kinetic sorption and slowly reversible and/or irreversible heavy metal reactions in the soil. MRTM assumes heavy metals are retained by different sites having different affinities in the soil and incorporates both chemical and physical non-equilibrium in the model. It uses a nonlinear least-square parameter optimization method in the estimation procedure. It has been successful in describing the retention and transport of some heavy metals in the soil (Selim, 1992; Zhang & Selim, 2005; Liao & Selim, 2009). Incorporation of convection-dispersion equation (CDE) [1.9] with equation [1.4] to [1.8] yields [1.10].

$$[1.10] \quad \rho \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t} = \theta D \frac{\partial^2 C}{\partial z^2} - q \frac{\partial C}{\partial z}$$

Where  $S$  is the total amount sorbed

$$[1.11] \quad S = S_e + S_1 + S_2 + S_s + S_{irr}$$

D is the hydrodynamic dispersion coefficient ( $L^2T^{-1}$ ). Criteria for errors are based on coefficient of determination ( $r^2$ ) and the root mean square error (RMSE) to estimate the best fit of the model to the experimental breakthrough curves.

$$[1.12] \quad RMSE = \sqrt{\frac{\sum (C_{obs} - C)^2}{n}}$$

Where  $c$  is the simulated metal concentration at time  $t$ ,  $n_0$  is the number of measurements,  $n_p$  is the number of fitted parameters, and  $C_{obs}$  is the observed metal concentration at time  $t$ .

#### 1.4 Statement of Problem

Cadmium, Copper and Lead mobility like other heavy metals is related to the soil chemical and physical properties. Soil is a heterogeneous system with complex interactions. So the kinetic reactivity and the extent of the mobility of heavy metals are expectantly different in different soils.

Literature studies reveal that Cd and Cu transport and release have been studied in different soils in which the dominant mechanism is equilibrium adsorption (Sidle and L.T. Kardos, 1977; Zhu & A.K. Alva, 1993). There are many studies focused on multi-component batch experiments, there is also a study by Elbana (2013) in which consecutive transport of Pb, Cd and Cu has been studied. However, we were not aware of any other study that investigates the consecutive and concurrent transport of Cd, Cu and Pb in soils.

In this study we focus on the quantification of the transport and retention of Cd and Cu and Pb in three different soils. While Cd, Cu and Pb are known as environmental pollutants, Cu is simultaneously an essential metal for plants, and they all exist in the soil matrix, as was discussed

earlier. Therefore, it is important to evaluate their sorption and transport behavior in the presence of each other.

## 1.5 Objectives

In this study the transport and retention of Cd, Cu and Pb in three different soils, Windsor, Mahan and Webster were carried out. The study is made up of: (i) retention study and (ii) transport study. In the retention study, kinetic batch experiments were used to quantify the time dependent retention of Cd, Cu and Pb in three soils. In the transport study, miscible displacement experiments under steady-state flow conditions were used to quantify the extent of the mobility of Cd, Cu and Pb in soil columns. The transport studies were carried out in two different ways. First we introduced consecutive pulses of Cd, Cu and Pb to a soil column followed by leaching using cation-free solution in order to study the competitive transport of these metals. In the other set of columns, two consecutive pulses of mixed solution (Cd, Cu and Pb) followed by leaching were introduced. We are seeking to investigate the mobility of these heavy metals in a multi-metal system and a pre-polluted soil column. We then described the experimental measurements based on a multireaction nonlinear model, incorporating equilibrium and kinetic reactions with the solute transport equation.

Doing so, we will try to meet the following objectives:

- (i) Quantify time-dependent sorption of Cd, Cu and Pb in Windsor, Webster and Mahan Soils.
- (ii) Measure the retention and transport of Cd, Cu and Pb in these soils.
- (iii) Predict the extent and distribution that retained Cd, Cu and Pb with depth in soil columns.

- (iv) Compare the influence of these heavy metals have on mobility of other metals.

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## **CHAPTER 2 : ADSORPTION OF CADMIUM, COPPER AND LEAD IN SOILS**

### **2.1 Introduction**

Heavy Metals are released to the soil and ground water due to anthropogenic activities. Industrial waste and sewage sludge disposal on land often contains significant amounts of heavy metals such as Cd, Cu and Pb, which create a potential risk for the environment. Kabata-Pendias and Mukherjee (2007) discuss the adverse effects of Cd in the biological processes that occur in humans, animals and plants. Mining, phosphate fertilization lime application, utilization of biosolids amendments are sources for Cd contamination of the soil (Alloway, 1995). Several Studies have been focused on the retention behavior of heavy metals in soils. Physical and chemical processes govern heavy metals' behavior in soil. Dijkstra et al., (2004) state that Cd's potential mobility is at its highest level in acidic soils. With this in mind, Naidu et al., (1997) explains the direct relationship between Cd adsorption and pH. In oxidizing environments, such as alkaline soils, Cu is susceptible to accumulation in the surface layers of soils because it can strongly bind to soil OM, Al, Mn, Fe oxides and clay minerals (Kabata-Pendias & Sadursky, 2004; Ma et al., 2006).

Copper retention, similar to Cd, is often correlated to soil pH, OM, CEC and Mn, Si, Al, Fe oxides, and clay content (Chen et al., 1999; Adriano, 2001; Shaheen et al., 2009). There are also several studies quantifying the competitiveness of heavy metals in a multi- component system especially when Pb is present. For example, in a loamy sandy soil co-contaminated system where transport and sorption of Cr, Cd, Cu, Zn and Pb were studied, results indicate that sorption capacity is lower for a Pb competitive sorption experiment, in comparison to a non-competitive sorption (Fonseca, 2011). Based on Lu and Xu (2009), competitive sorption of Cd, Cu, Zn and Pb is the most strongly sorbed metal.

Strawn and Sparks (1999) state that sorption isotherms must be time dependent. Cadmium partitioning coefficient between soil and solution,  $K_d$  which is the ratio of sorbed Cd to the soil divided by the concentration of Cd in the solution, is influenced by soil organic matter, soil solution pH and metal content (Sauvé et al., 2000). It has been observed that  $K_d$  is in a direct relationship with pH (Lee, 1996). Also Retained Cu in the soil is associated with OM clay carbonates and Fe and Mn oxides (Tessier et al., 1979; Emmerich et al., 1982; Baker & Senft, 1995). In addition, Harter and Naidu (2001) state that ionic strength and competing and counter ions of soil solution is also important in metals adsorption in soils.

Copper adsorption also correlates to pH, CEC, clay content,  $\text{CaCO}_3$ , OM. (Hooda & Alloway, 1998). Meanwhile, Chang et al., (2001) states that in the study of Cd adsorption,  $K_d$  is between 2.71 to 5.04  $\text{L kg}^{-1}$  in acidic soil with low CEC while the  $K_d$  values is between 147.5 to 1699.9  $\text{L kg}^{-1}$  for  $\text{pH} > 7.4$  and high CEC soils. Buchter et al., (1989) describes a strong non-linearity in a calcareous soil's Cd sorption isotherm. These are not the only studies which depict Cd sorption as nonlinear.

Based on Elbana et al., (2014), the batch study of Pb isotherms shows highly nonlinear sorption with a Freundlich exponent parameter  $b$  of 0.240 and 0.249 for Windsor and Olivier soils respectively. They have also run this experiment with presence of Tin and Sn, and show a decrease in Pb sorption for both Windsor and Olivier soils. Based on their findings, Pb had a kinetic behavior where 3 to 15 for Windsor, and 13 to 28 percent for Olivier, were released during desorption.

In this present study, three soils were under consideration: Windsor, Mahan and Webster. The major objective was to quantify the adsorption characteristics of selected heavy metals for different soils having a wide range of physical and chemical properties and to assess the adsorption of heavy metals based on their retention properties in soils.

## 2.2 Materials and Methods

### 2.2.1 Soils

As mentioned above, we used three different soils in this study. 1) Windsor: a fine sandy loam formed on glacial outwash plains, and deltas of the U.S northeast region. It was sampled near Lebanon, New Hampshire. 2) Mahan: a fine-silty, nonacidic soil formed in iron-rich clayey, and found in marine sediments, and 3) Webster: a poorly drained, very deep, moderately permeable soil formed in glacial till or local alluvium derived from the till on uplands. It is collected from Story Country, Iowa.

All soil samples were air-dried and have been passed through 2 mm sieves before running experiments. Soil properties including pH, CEC and particle size analysis are given in Table 2.1.

Table 2.1. Selected Physical and Chemical Properties of the Studied Soils

Soil		Windsor	Mahan	Webster
pH		6.11	6.10	6.92
TOC a	%	2.03	-	4.03
CEC b	cmol kg <sup>-1</sup>	2.00	7.00	27.00
Sand c	%	77.00	49.00	39.00
Silt	%	20.00	20.00	39.00
Clay	%	3.00	31.00	22.00
Selective extraction by Ammonium Oxalate (pH 3.0)				
Fe	g Kg <sup>-1</sup>	0.36	-	0.98
Al	g Kg <sup>-1</sup>	0.69	-	0.89
Citrate-bicarbonate-dithionite				
Fe	g Kg <sup>-1</sup>	3.68	-	4.42
Al	g Kg <sup>-1</sup>	3.65	-	0.77

a TOC = total organic carbon, b CEC = cation exchange capacity, c Grain size distribution: sand (2.00-0.05 mm), silt (0.05-0.002 mm), and clay (<0.002 mm).

### 2.2.2 Adsorption

Adsorption of Cd, Cu and Pb in this study has been carried out using a batch method described by Selim and Amacher (1997). Two duplicates of 3 gram soils were placed in Teflon centrifuge tubes

with a capacity of 40 ml. Subsequently, it was mixed with 30 ml solutions of five known initial concentrations of input solution contaminant including  $\text{Pb}(\text{NO}_3)_2$  (Sigma-Aldrich: 233-245-9),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Sigma-Aldrich: 10022-68-1) and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Fisher Scientific: 10031-43-3) as discussed in Table 2.2.

All solutions were prepared in 0.005 M  $\text{KNO}_3$  background solution to maintain ionic strength at a constant level. Tubes were sealed with Teflon caps and placed on a reciprocal shaker. The tubes were shaken continuously and then centrifuged after one day and seven days of retention for 15 minutes at 4500 RPM. A 7-ml aliquot was sampled from the supernatant, and the metal concentration in the supernatant solution was analyzed with inductively coupled plasma-OES (SpectroCiros Charge-coupled device [CCD], Spectro analytical Instruments, Kleve, Germany).

The difference between the concentrations of the supernatant and the initial solutions concentrations were used to measure the amount of sorbed metal.

Table 2.2. Different Metal Concentrations in Input Solution

Input Solution	Metal Concentration (ppm)				
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	9.188	42.789	83.813	129.478	223.275
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	12.531	55.893	77.464	118.123	333.71
$\text{Pb}(\text{NO}_3)_2$	26.38154	76.5665	146.963	279.684	405.789

## 2.3 Results and Discussion

### 2.3.1 Adsorption Isotherms

In order to assess the retention capability of the soils with regards to Cd, Cu and Pb, adsorption Isotherms were measured. Adsorption isotherms measure the distribution between aqueous and sorbed phases for metals. The set of sorption isotherms shown exhibited strong nonlinear metal retention behavior for all metals and soils. This nonlinear sorption behavior for Cd, Cu and Pb was described using the Freundlich equation:

$$[2.1] \quad S = K_f C^b$$

Where  $K_f$  is the distribution of coefficient ( $ML^{-3}$ ), and  $b$  is a dimensionless reaction order which is an indicator of the shape of isotherm:  $b < 1$  convex,  $b = 1$  linear, and  $b > 1$  concave.

The effect of the time of reaction on the extent has been observed in all Figures and indicates an increased metal retention vs. time for all three soils.

Sheindorf et al., (1981) notes that the exponent  $b$  in the Freundlich model represents the energy distribution of the heterogeneity of the sorption-site, where the highest energy sites are preferentially sorbed at low concentrations, and as the concentration increases lower energy sites become occupied successively.

Also, linear models following equation [2.2] has been used to for day one and day seven in order to predict the retention behavior of metals in the soils.

$$[2.2] \quad S = K_d C$$

Where  $K_d$  is the distribution coefficient ( $ML^{-3}$ ) between the metal concentration in the soil surface and soil solution.

### 2.3.2 Cadmium Adsorption Isotherms

Adsorption isotherms for one and seven day sorption of Cd describe the distribution between Cd in the aqueous solution ( $C$ ) and that which is sorbed ( $S$ ). As shown in Table 2.3, based on the coefficient of determination ( $r^2$ ) and standard error (SE) for the estimated parameter by linear model, the use of linear model was not successful for either one day or seven day sorption isotherms. Whereas the Freundlich equation provided a strong simulation;  $r^2$  are significantly high and  $b$  values are less than 1 for both one day and seven day isotherms which show that Cd sorption by these soils are nonlinear.

Table 2.3. Estimated Linear Parameters for 1 d and 7 d of Cd, Cu and Pb sorption for all three Soils.

Metal	1 d				7 d		
Cd	Soil	$K_d$	SE	$r^2$	$K_d$	SE	$r^2$
	Windsor	5.5937	1.4557	0.2167	7.2126	1.7141	0.3587
	Mahan	14.4449	3.5723	0.3914	16.5014	3.886	0.4464
	Webster	456.9874	66.04	0.7952	473.6064	80.5832	0.5839
Cu	1 d				7 d		
	Soil	$K_d$	SE	$r^2$	$K_d$	SE	$r^2$
	Windsor	4.8128	1.2217	0.353	5.5064	1.7042	0.146
	Mahan	10.7049	2.4883	0.5197	13.3954	3.8249	0.3574
	Webster	1011.824	177.818	0.7494	2237.038	396.6134	0.7459
Pb	1 d				7 d		
	Soil	$K_d$	SE	$r^2$	$K_d$	SE	$r^2$
	Windsor	16.5062	3.918	0.4124	23.8284	5.7235	0.4299
	Mahan	130.7246	27.3847	0.5988	309.9993	70.4685	0.5491
	Webster	--	--	--	--	--	--

$K_d$  values are in ml/g, -- Complete Sorption.

Nonlinearity and competition are often regarded as characteristics of a site-specific adsorption process. Also the b parameter illustrates the extent of heterogeneity of sorption sites which means sorption sites have different affinities for heavy metal retention, where sorption by the highest energy sites takes place preferentially at the lowest solution concentration before those sites of lower energy. Basically, at increasing higher concentration, sorption takes place at sites of decreasing affinities which based on (Selim et al., 2013) results in nonlinear or concentration- dependent isotherms of S vs. C.  $K_f$  values illustrates the extent of metal affinity among different soils. See Figure 2.1.

As shown in Table 2.4,  $K_f$  for one day isotherms are 190.43, 276.92, and 922.97 ml/g for Windsor, Mahan and Webster soil respectively, as well as 190.57, 274.90 and 1028.99 ml/g for seven day isotherm. Which shows that affinity of Cd in different soils for both one day and seven day data follows this trend: Webster > Mahan > Windsor. Webster has the highest pH among the soils which results in more negatively charged sites (Jacobsob et al., 2005). Also it has the highest percentage of

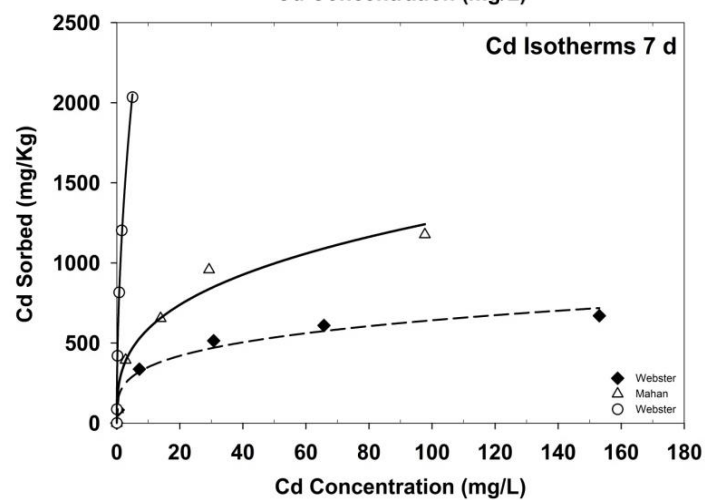
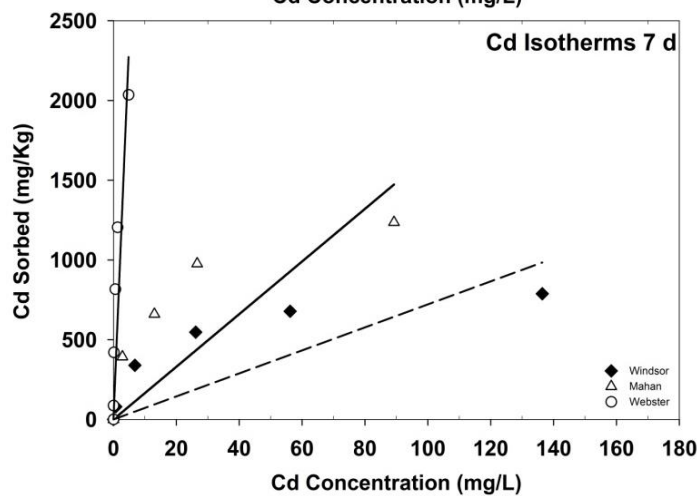
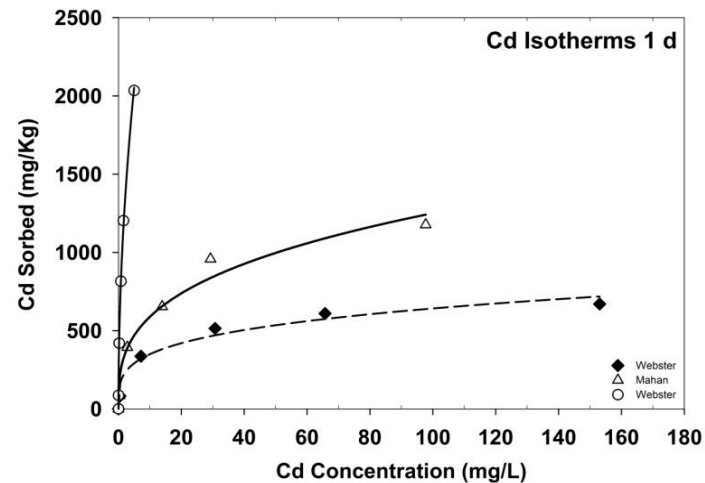
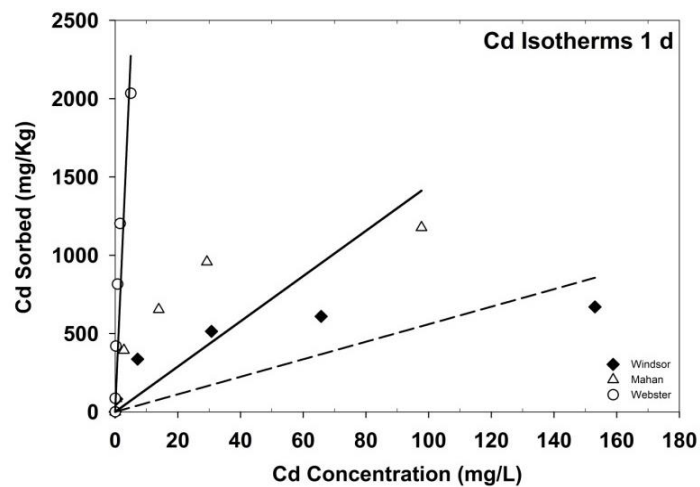


Figure 2.1. Cd sorption isotherms for Windsor, Mahan and Webster after 1d sorption. Solid and dashed lines represent simulations based on linear (left) and Freundlich (right) models



Table 2.4. Estimated Freundlich Parameters for 1 d and 7 d of Cadmium Sorption for all three Soils.

Metal	1 d						7 d				
Cd	Soil	K <sub>f</sub>	SE	b	SE	r <sup>2</sup>	K <sub>f</sub>	SE	b	SE	r <sup>2</sup>
	Windsor	190.4323	34.2086	0.2638	0.042	0.9712	180.5682	31.0473	0.3118	0.0407	0.9788
	Mahan	276.9244	50.0811	0.3273	0.0464	0.9713	274.8013	42.9073	0.3454	0.0407	0.9794
	Webster	922.9724	20.0229	0.498	0.016	0.9984	1028.99	18.2361	0.4405	0.0131	0.9986
Cu	1 d						7 d				
	Soil	K <sub>f</sub>	SE	b	SE	r <sup>2</sup>	K <sub>f</sub>	SE	b	SE	r <sup>2</sup>
	Windsor	167.8744	47.8931	0.3272	0.0607	0.9448	273.4776	71.9947	0.2616	0.0581	0.9149
	Mahan	256.0249	38.7804	0.3663	0.0338	0.9825	537.0418	77.0821	0.2506	0.0338	0.9601
	Webster	1712.332	119.084	0.4651	0.0551	0.9701	2420.551	282.1938	0.5105	0.1077	0.9078
Pb	1 d						7 d				
	Soil	K <sub>f</sub>	SE	b	SE	r <sup>2</sup>	K <sub>f</sub>	SE	b	SE	r <sup>2</sup>
	Windsor	888.8781	159.6757	0.1862	0.0405	0.9339	823.2077	178.2546	0.2402	0.0515	0.9297
	Mahan	1373.546	111.9778	0.2865	0.0275	0.9894	1508.844	221.9792	0.3693	0.0651	0.9427
	Webster	--	--	--	--	--	--	--	--	--	--

K<sub>f</sub> values are in ml/g, -- Complete Sorption

Smectite clay, and it has very high CEC ( $27 \text{ cmol kg}^{-1}$ ) among soils which justifies its great retention quantities of cationic species that Windsor and Mahan.

This is when Windsor with lowest percentage of clay (3%), consequently lowest CEC ( $2 \text{ cmol kg}^{-1}$ ) is showing the less retention among other soils while Mahan with relatively moderate values is in between.

### 2.3.3 Cadmium Sorption Kinetics

Freundlich isotherms show that Cd retention characteristics were affected by increasing equilibrium time from one day to seven day, which led to an increase in value of  $K_f$  or  $b$ , consequently sorbed amount in Webster, Windsor and Mahan soils.

Although the sorption of divalent metal ions such as Cd, onto oxides has been reported to be completed within a few seconds (Voegelin et al., 2001), slow kinetics have also been observed where sorption continued for several days or months (Strawn & Sparks, 1999; Jeon et al., 2003). Numerous mechanisms are suggested that contribute to the kinetics of heavy metal sorption on soils including: 1) slow diffusion through intra-particle micropores (Strawn & Sparks, 1999); 2) heterogeneity of sorption sites; sites having different affinities; 3) slow sorption due to the increase in surface charge upon the inner-sphere complexation of such ions (Jeon et al., 2003); 4) at neutral or basic condition, slow formation of new solid phases such as hydroxides or layered double hydroxides may cause kinetic effects and the immobilization of nickel (Voegelin et al., 2001; Scheidegger et al., 1998; Businelli et al., 2004).

### 2.3.4 Copper Adsorption Isotherms

As shown in Table 2.3 based on the coefficient of determination, ( $r^2$ ) and standard error (SE) for the estimated parameter by linear model, the use of linear model was not successful for both one day

and seven day sorption isotherms. Whereas based on Table 2.4 Freundlich equation provided  $r^2$ 's are significantly high and b values are less than 1 for both one day and seven day isotherms therefore, Cu sorption by all three soils is nonlinear.

As shown in Table 2.4,  $K_f$  for one day isotherms are 167.87, 256.02 and 1712.33 ml/g for Windsor, Mahan and Webster soil respectively as well as 273.4776, 537.04 and 2420.55 mg/L for seven day isotherm. Which shows that affinity of Cu in different soils for both one day and seven day data follows this trend: Webster > Mahan > Windsor, and is in the same line with Cd retention properties. Webster has the highest percentage of clay; also it has very high CEC ( $27 \text{ cmol kg}^{-1}$ ) among soils which justifies its great retention quantities of cationic species than that of Windsor and Mahan soils. See Figure 2.2.

### 2.3.5 Copper Sorption Kineticsc

Freundlich isotherms show that Cu retention characteristics were affected by increasing equilibrium time from one day to seven day which led to increase in value of  $K_f$  in Webster, in Windsor and Mahan where Cu shows a much higher affinity. Such two-stage reaction is characteristic of the sorption of several heavy metals on clays, oxide surfaces and soils as suggested by Voegelin et al., (2001), Jeon et al., (2003), Bruemmer et al., (1988) and Scheidegger et al., (1998).

### 2.3.6 Lead Adsorption Isotherms

As shown in Table 2.3, based on the coefficient of determination, ( $r^2$ ) and standard error (SE) for the estimated parameter by linear model, the use of linear model was not successful for both one day and seven day sorption isotherms. Also, Freundlich modeling was not applicable for the simulation of Pb retention in Webster soil. Whereas based on Table 2.4 the Freundlich equation provides strong simulation as was expected for Windsor and Mahan, as well as Cd and Cu,  $r^2$  are significantly

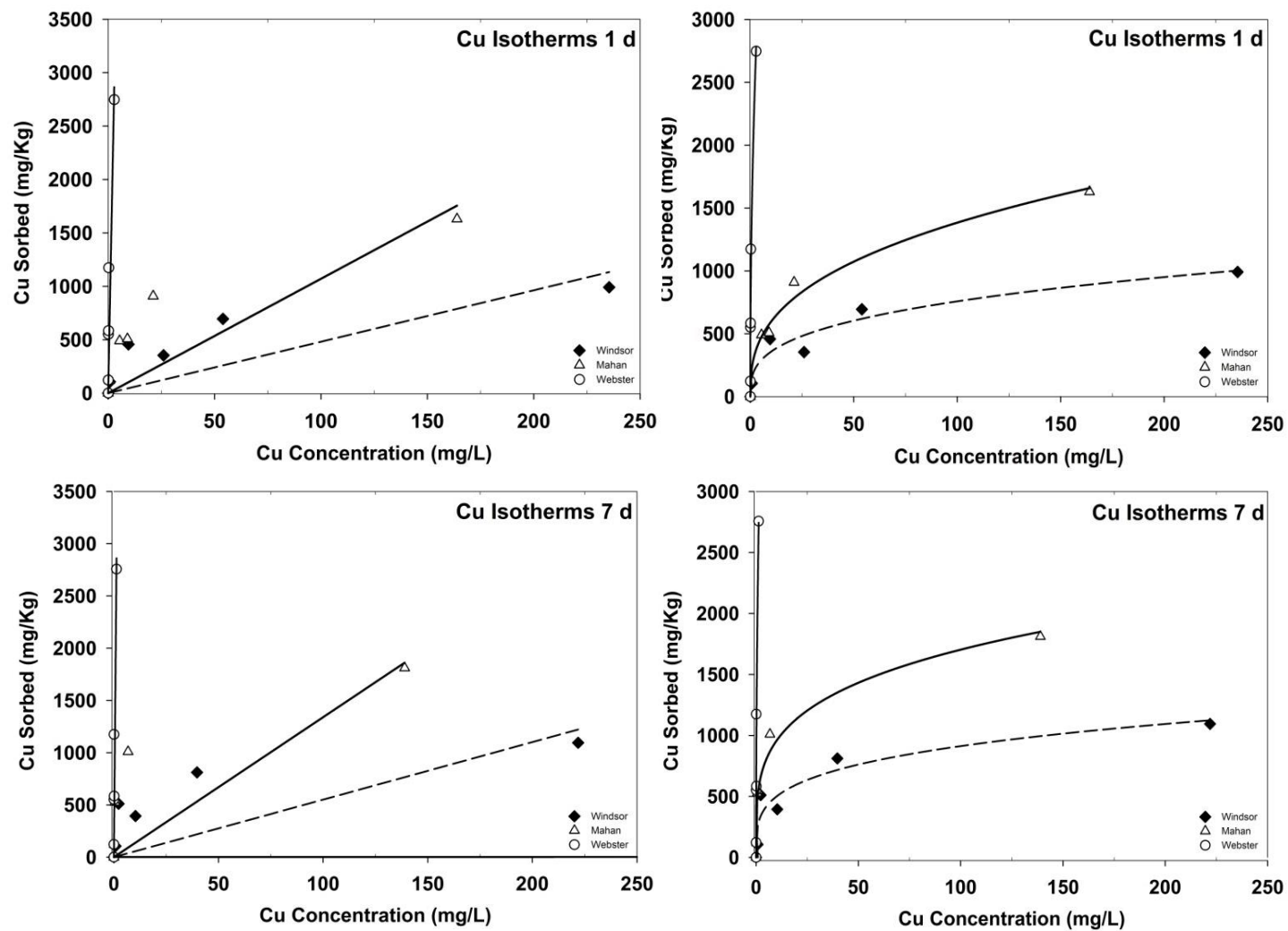


Figure 2.2. Cu sorption isotherms for Windsor, Mahan and Webster after 1d sorption. Solid and dashed lines represent simulations based on linear (left) and Freundlich (right) models.

high and  $b$  values are less than 1 for both one day and seven day isotherms which show that Pb sorption by Mahan and Windsor are nonlinear. As shown in Table 2.4  $K_f$  for one day isotherms are 888.88 and 1373.54 ml/g for Windsor and Mahan soil respectively as well as 823.20 and 1508.84 mg/L for seven day isotherm. Which shows that the affinity of Pb in different soils for both one day and seven day data follows this trend: Mahan>Windsor, and is in the same line with Cd and Cu retention properties. According to what was discussed earlier, Mahan has the higher percentage of clay in comparison to Windsor as expected.

#### 2.3.7 Lead Sorption Kinetics

Freundlich isotherms show that in Mahan Soil, Pb retention characteristics were affected by increasing equilibrium time from one day to seven day. This led to an increase in the value of  $K_f$ . Whereas in Cd shows a much higher affinity. See Figure 2.3.

#### 2.3.8 Summary

Cd, Cu Sorption behavior in Windsor, Mahan and Webster is highly nonlinear, the highest affinity toward retention of Cd and Cu follows this trend: Webster> Mahan>Windsor, which is due to there being the highest percentage of clay in a Webster soil and thus such a behavior is anticipated. Lead Sorption in Windsor and Mahan soils follows the same trend as in Cd and Cu. Due to the complete sorption of Pb in the Webster soil, Freundlich modeling for Pb data was not applicable. Copper sorption in all three soils was highly kinetic. At the same time, Cd sorption for Webster, and Pb sorption in Mahan, was kinetic as well.

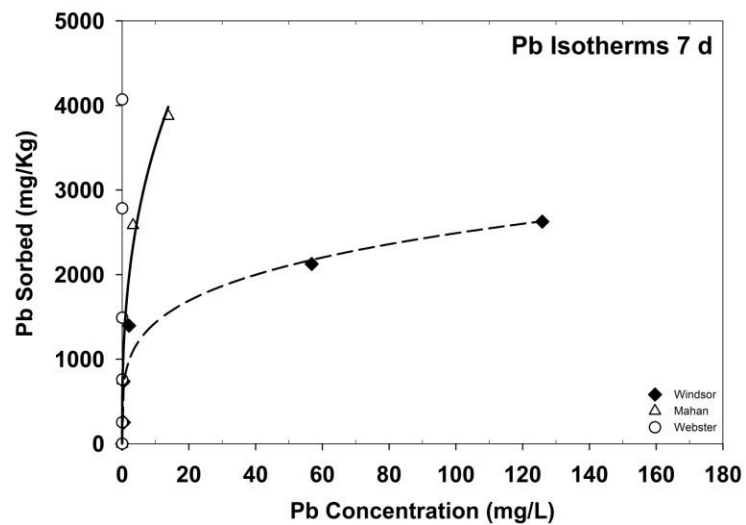
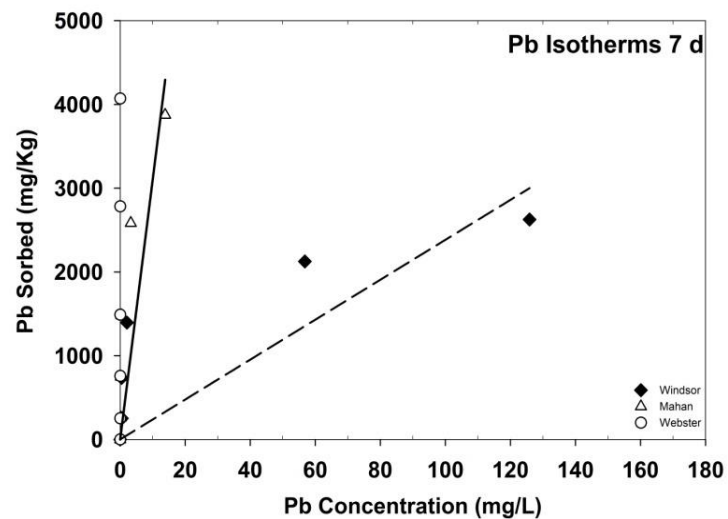
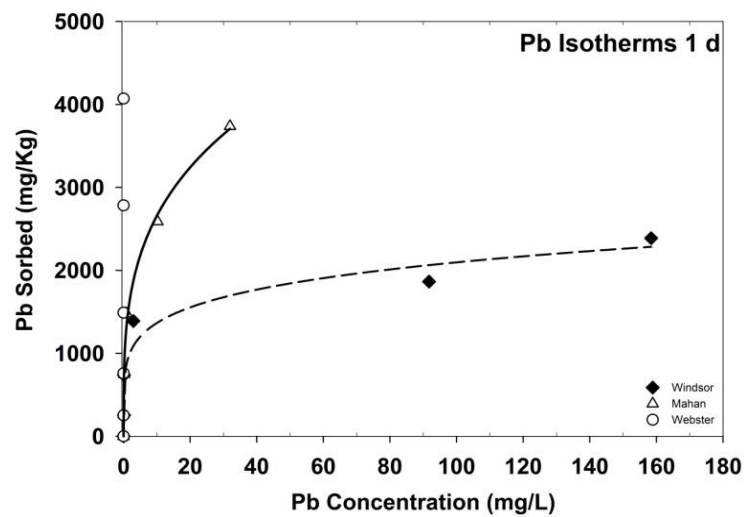
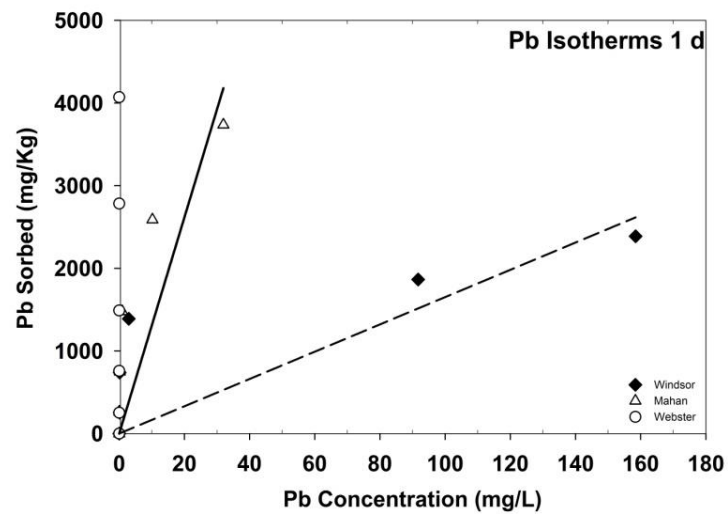


Figure 2.3 Pb sorption isotherms for Windsor, Mahan and Webster after 1d sorption. Solid and dashed lines represent simulations based on linear (left) and Freundlich (right) models.

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## **CHAPTER 3 : TRANSPORT OF CADMIUM, COPPER AND LEAD IN SOILS; MISCIBLE DISPLACEMENT COLUMN EXPERIMENTS AND KINETIC MODELING**

### **3.1 Introduction**

Heavy metal contamination is a major concern for the quality of soil and ground water and toxicity to plants and the ecosystem in general. Industrial and anthropogenic activities such as mining, smelting, usage of sewage sludge and fertilizers are different sources of contamination. Therefore, it is essential to understand their mobility and retention in soils in order to quantify their potential contamination. In order to do so, we must consider that the pollution potential is affected by properties of soil solution and the strength of the bond between heavy metals and soil surface (Filgueiras et al., 2002).

In order to describe and predict the transport of heavy metals in the soil, several mathematical models have been developed. Barrow et al., (1989) emphasized that the use of a single reaction and linear equations which were used are not adequate since different reaction sites with different affinities exists for heavy metals and soils. A multireaction transport model based on soil heterogeneity and sorption kinetics has been proposed for the purpose of describing time-dependent nonlinear sorption and irreversible or slowly reversible reactions of heavy metals in soil environment (Selim et al., 1992). This multipurpose model assumes that heavy metals in the soil environment are retained by different sites having different affinities, which incorporates both chemical and physical non-equilibrium in the transport model. The estimation procedure uses a nonlinear least-squares parameter optimization method. It successfully describes the retention and transport of some heavy metal ions in soils (Selim et al., 1992; Zhang & Selim, 2006; Liao et al., 2009).

Having a multicomponent system may result in enhanced or retarded ion mobilities in the soil solution. It has been discussed by Agbenin and Olojo (2004) that categorizing and separating sorbed metals into higher and lower affinity types can help with understanding the competitive sorption.

The competitive degree of sorption among different ions depends on the sorption site's vacancy quantities and the extent of saturation of such sites by competing ions (Tsang and Lo, 2006). There are a few studies focused on competitive transport of heavy metals during miscible displacement experiment (Tsang & Lo, 2006; Voegelin et al., 2001; Voegelin & Kretzschmar, 2005). It has been reported by Atanassova (1999) that Cu specific sorption, as a result of competition with Zn, Cd and Ni, decreased for low affinity sites at high percentage saturation of CEC. Conversely it has been reported by Antoniadis et al., (2007) that Ni mobility increases in the presence of Zn and Cu in a column infiltration technique.

Cadmium is considered an environmental contaminant and a potential concern (Kabata-Pendias & Mukherjee, 2007). Strawn and Sparks (1999) state that the mobility of Cd in porous media is influenced by a retention/release phenomenon, which may be kinetically controlled. Kabata-Pendias (2001) introduces copper as an essential micronutrient required by plants and soils, so it is important for plant nutrition management. However at high concentrations Cd is considered harmful according to Alloway (1995), therefore, knowledge of Cu mobility is important.

Kabata-Pendias and Pandias (2001) stated that Pb is immobile; it often goes from a soluble form, to form complexes with sulfates, phosphates, organic materials and clay minerals. Also if the concentration of Pb in soils exceeds 100 to 500 ppm, it is considered more than normal range. There are some studies such as Aringhieri et al., (1985), Selim et al., (1992) and Strawn & Sparks

(1999), in which scientific evidence of time-dependent sorption in many soils have been observed for Cd transport. CDE has been applied to predict Cd mobility in several sludge applications by Moradi et al., 2005, also in the description of Cu, Zn and Cd movement in a sludge-treated forested soil Sidle and Kardos(1977) used the convection-dispersion equation as well, while the retention process was considered a nonlinear equilibrium type in other words Freundlich. Also the simulation of Cd BTC in acidic soils by linear sorption isotherms was successful (Gerritse, 1996).

Based on Elbana and Selim (2010), Multi Reaction Transport Model was successful in describing Cd arrival time in effluent and its concentrations during leaching from the soil column.

Based on Chang et al., (2001) that performed Cu and Cd miscible displacement experiments on a silty-clay soil, Cd BTCs (Break-Through Curves) better simulated when using Freundlich compared to linear modeling. Elbana and Selim (2011) shows that Multireaction Transport Model (MRTM) was successful in describing the BTCs for soil columns with acidic soils. They also mentioned that irreversible reactions were dominant in case of alkaline soils, based on model simulations. There are also numerous studies carried out to quantify the competitive effect of several heavy metals on Pb retention and mobility in soils. Fonseca et al., (2011) in the study of the sorption and transport of Cr, Cd, Cu, Zn and Pb to evaluate the co-contamination of a loamy sand soil by single and multiple heavy metals, results for Pb showed that the soil exhibited higher sorption capacity for noncompetitive compared with Pb competitive sorption; Although Pb exhibited a slightly higher retardation in the competitive experiment under flow conditions than in the noncompetitive sorption (Fonseca et al., 2011).

Elbana (2013) has studied the Pb mobility in an alkaline soil and the subsequent influence of Cd and Cu on Pb release and showed that Pb recovery was less than 0.5 percent meaning it is heavily sorbed. It also reveals that the influence of subsequent Cd and Cu pulse applications did not result in Pb release from both surface and subsurface soils. The affinity of metals in their study has been evaluated as:  $Pb > Cu > Cd$ .

A thorough literature review reveals there are only a few studies focused on multicomponent transport systems with more than two heavy metals. The objective of this study was to: 1) Measure the retention and transport of Cd, Cu and Pb in three different soils. 2) Quantify the mobility of Cd, Cu and Pb in three different soils while considering the influence they have on other metals mobility. 3) Predict the extent and distribution of retained Cd, Cu and Pb with depth in soil columns.

### **3.2 Modeling Heavy Metals Retention**

The Multireaction Transport Model (MRTM) is a conceptual model used to describe the kinetic retention behavior and the transport of heavy metals in soils. See Figure 3.1. This model accounts for several interactions so it proves useful for heavy metals with soil matrix surfaces (Selim, 1992). Also, it is perhaps one of the earliest models that have a multisite approach for describing the retention and transport behavior of reactive solutes in porous media. Based on the assumptions that the solute species in the soil environment which is made up of different constituents (soil minerals, OM, Fe, and aluminum oxides) is likely to react with various constituents (sites) by different mechanisms, several phases representing heavy metal retained by the soil ( $S_e$ ,  $S_k$ ,  $S_s$  and  $S_{irr}$ ) is depicted in the following schematics.

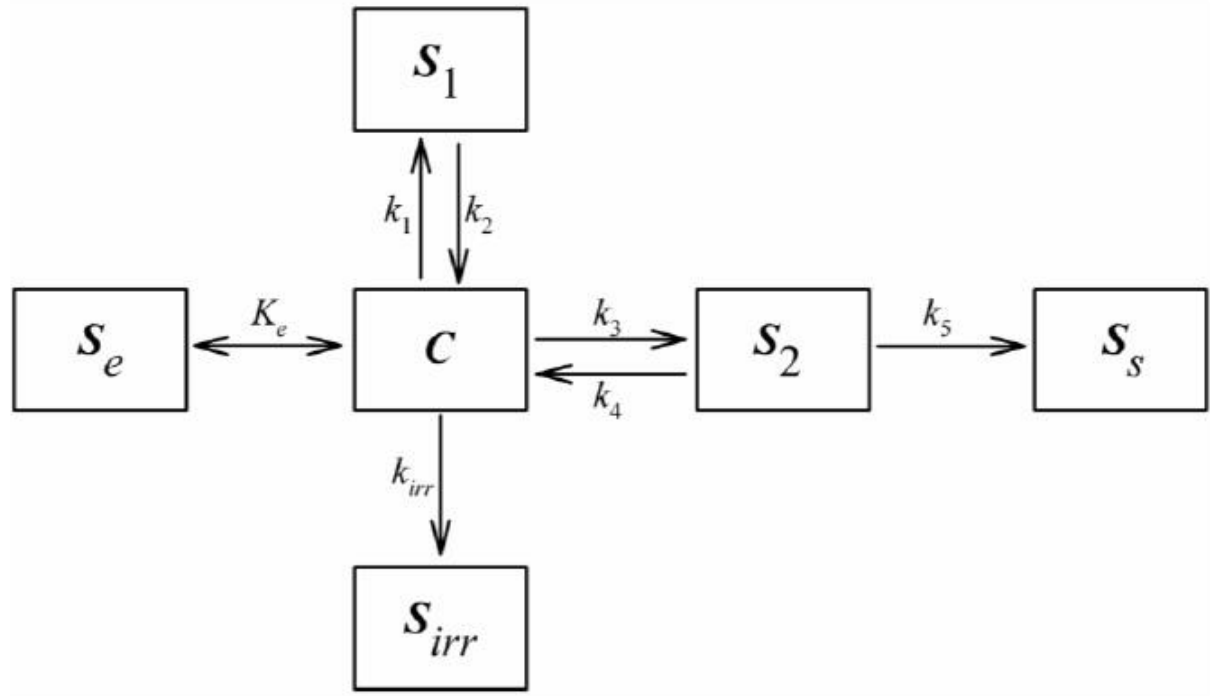


Figure 3.1. A schematic diagram of the multireaction and transport model, where  $C$  is concentration in solution,  $S_e$  represents the amount retained on equilibrium sites,  $S_1$  and  $S_2$  represent the amount retained on reversible kinetic sites,  $S_{irr}$  and  $S_s$  represent the amounts irreversibly retained, and  $k_e, k_1, k_2, k_3, k_4, k_5$  and  $k_{irr}$  are the respective reaction rates.

The multireaction model used here assumes that a fraction of the total sorption sites is kinetic in nature while the remaining fractions interact rapidly or instantaneously with reactive chemicals in the soil solution (Selim, 2012). The model accounts for reversible as well as irreversible sorption of the concurrent and consecutive types.

The retention reactions associated with MRTM are,

$$[3.1] \quad S_e = K_e \frac{\theta}{\rho} C^n$$

$$[3.2] \quad \frac{\partial S_k}{\partial t} = k_1 \frac{\theta}{\rho} C^m - (k_2 + k_s) S_k$$

$$[3.3] \quad \frac{\partial S_s}{\partial t} = k_s S_1$$

$$[3.4] \quad \frac{\partial S_{k\text{irr}}}{\partial t} = k_{\text{irr}} \frac{\theta}{\rho} C$$

where  $S_e$  is the amount retained on equilibrium sites ( $\text{mg kg}^{-1}$ ),  $S_k$  is the amount retained on kinetic sites ( $\text{mg kg}^{-1}$ ),  $S_s$  is the amount retained irreversibly by consecutive reaction ( $\text{mg kg}^{-1}$ ),  $S_{\text{irr}}$  is the amount retained irreversibly by concurrent type of reaction ( $\text{mg kg}^{-1}$ ),  $C$  is concentration in solution ( $\text{mg l}^{-1}$ ),  $\rho$  is the soil bulk density ( $\text{g cm}^{-3}$ ),  $\theta$  is the water content ( $\text{cm}^3 \text{ cm}^{-3}$ ),  $n$  and  $m$  are dimensionless reaction order commonly less than 1,  $K_e$  is a dimensionless equilibrium constant,  $k_1$  and  $k_2$  ( $\text{h}^{-1}$ ) are the forward and backward reaction rates associated with kinetic sites, respectively,  $k_{\text{irr}}$  ( $\text{h}^{-1}$ ) is the irreversible rate coefficient associated with the kinetic sites, and  $k_s$  ( $\text{h}^{-1}$ ) is the irreversible rate coefficient associated with solution. For the case  $n = m = 1$ , the reaction equations become linear. In the above equations we assumed  $n = m$  since there is no known method for estimating  $n$  and/or  $m$  independently.

The total amount of solute retention on soil is  $S$ :

$$[3.5] \quad S = S_e + S_1 + S_2 + S_s$$

representing the sum of all sorbed phases retained by the soil matrix.

The MRTM model has been applied successfully to simulate the soil retention of many environmental contaminants (e.g., Amacher et al., 1988; Selim et al., 1992; Barnett et al., 2000). Eq. [1] through [4] were incorporated into the one-dimensional reactive convective-dispersive transport equation (CDE) under steady water flow.

$$[3.6] \quad \rho \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t} = \theta \frac{\partial^2 C}{\partial z^2} - q \frac{\partial C}{\partial z}$$

Where S is the total amount sorbed, D is the hydrodynamic dispersion coefficient ( $\text{cm}^2 \text{h}^{-1}$ ), q is Darcy's water flux density ( $\text{cm h}^{-1}$ ), and z is distance (cm).

### 3.2.1 Linear Modeling

To describe transport results from the miscible displacement column experiments for tritium, we utilized a linear model, named CXTFIT, as described by Toride et al., (1995). This analytical model was employed to solve the inverse problem based upon the CDE where linear equilibrium sorption was assumed. To account for irreversible reactions, the CXTFIT version selected includes a sink term, which was referred to as first-order degradation or decay in CXTFIT. The CDE used after the incorporation of a first-order decay (sink) term is,

$$[3.7] \quad R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \mu C$$

Where R is a dimensionless retardation factor ( $R = 1 + \rho K_d / \theta$ ), and  $K_d$  is a partitioning coefficient ( $\text{ml g}^{-1}$ ). In Eq. [14] the term R accounts for linear equilibrium sorption. The rate coefficient  $\mu$  ( $\text{h}^{-1}$ ) associated with the sink term ( $\mu C$ ) captures irreversible retention (or removal) of a chemical directly from the soil solution based on first-order decay.

## 3.3 Materials and Methods

### 3.3.1 Soils

Three surface soils having different properties were used in this study. Windsor sand is a fine, sandy loam formed on glacial outwash plains, deltas of the U.S northeast region; it was sampled near Lebanon, New Hampshire. Webster is a very deep, poorly drained, moderately permeable soil



formed in glacial till or local alluvium derived from till on uplands, it is collected from Story County, Iowa. Mahan is a fine-silty, nonacidic soil formed in iron-rich, clayey, marine sediments that are moderately high in siderite. Soil samples were air-dried and pass through 2 mm sieves before experiments. Soil properties such as soil pH, cation exchange capacity (CEC), and particle size analysis are given in Table 2.1.

### 3.3.2 Miscible Displacement Experiments

To quantify the mobility of Cd, Cu and Pb in the mentioned soils, miscible displacement column experiments that are described by Zhang and Selim (2006) were carried out. Air-dry soils were uniformly packed into acrylic columns (5-cm in length and 6.4-cm of inner diameter), and then the columns were saturated with background solution ( $\text{KNO}_3$ , 0.005M) where upward flow was maintained. Each column was weighed before and after packing. Soil bulk density and water content were calculated based on weight and volume of the column. A piston pump (FMI lab pump, Model QG 6, Fluid Metering Inc., Oyster Bay, NY) was used to ensure the solution constant flux in the soil column. To ensure saturation, each column received 15 to 20 pore volumes of background solution prior to the introduction of pulses. Column effluent was collected using an ISCO fraction collector (model Retriever II, Teledyne Isco Inc., Lincoln, NE). The samples collected were analyzed by ICP-OES (SpectroCItros CCD, model CCD; Spectro Analytical Instruments, Kleve, Germany).

Two set of miscible displacement column experiments were performed:

a) Consecutive pulses of Cd, Cu and Pb were sequentially introduced to each soil column followed by an extended period of leaching with the background solution ( $\text{KNO}_3$ , 0.005M).

The volume of each applied pulse, along with associated soil parameters for each column in both sets is presented in Tables 3.1 and 3.2. To obtain independent estimates for the dispersion coefficient ( $D$ ) separate pulses of a tracer solution were applied to each soil column in the second set after the last leaching step.

b) Two consecutive pulses of mixed solution (Cd, Cu and Pb) each followed by leaching with the background solution ( $\text{KNO}_3$ , 0.005M) were introduced to soil columns as shown in Table 3.2.

The tracer used was tritium ( $^3\text{H}_2\text{O}$ ) and the collected samples were analyzed using a Tri- Carb liquid scintillation  $\beta$  counter (Packard 2100TR, PerkinElmer, Waltham, MA). The tracer pulse was applied to assess flow characteristics by obtaining independent values for the hydrodynamic dispersion coefficient ( $D$ ) of the classical CDE. Estimates for  $D$  values were obtained using CXTFIT (Toride et al., 1999) and are given in Table 2.3.

### 3.3.3 Distribution in Soil Versus Depth

Complete recovery of applied heavy metals in the soil columns due to the strong affinity of metals to soils was not expected. The distribution of heavy metals retained by the soil matrix vs. soil depth provides important information on the extent of their mobility in the soil profile. Following the termination of each column experiment, the column was sectioned into 10 equal sections of 0.5 cm in length. The soil was then dried by air and the amount of Cd, Cu and Pb retained by each soil in different depths was determined by using an Innov-X Delta Premium PXRF as a screening method (USEPA, 2007).

Table 3.1. Experimental conditions of the miscible displacement column experiments, where three consecutive pulses were applied: Cd, followed by Cu, followed by Pb pulses.

	Bulk	Moisture	Pore Water	Pulses and Leaching Volume				Dispersion
Soil	Density	Content	Velocity	(P.V.)				Coefficient*
	( $\rho$ , g cm <sup>-3</sup> )	( $\theta$ , cm <sup>3</sup> cm <sup>-3</sup> )	(cm h <sup>-1</sup> )	Cd	Cu	Pb	KNO <sub>3</sub>	(D, cm <sup>2</sup> h <sup>-1</sup> )
Windsor	1.382	0.479	0.549	15.58	16.16	16.18	34.78	0.29
Mahan	1.229	0.536	0.454	15.02	15.96	14.17	29.41	0.45
Webster	1.108	0.582	0.424	15.07	15.43	14.82	30.48	0.32

\*Estimated using CXTFIT 2.0

Table 3.2. Experimental conditions of the miscible displacement column experiments, where two consecutive pulses of a mixed solution (Cd+Cu+Pb) were introduced into each column.

	Bulk	Moisture	Pore Water	Pulses and Leaching Volume				Dispersion
Soil	Density	Content	Velocity	(P.V.)				Coefficient*
	( $\rho$ , g cm <sup>-3</sup> )	( $\theta$ , cm <sup>3</sup> cm <sup>-3</sup> )	(cm h <sup>-1</sup> )	Pulse <sup>a</sup>	KNO <sub>3</sub>	Pulse <sup>a</sup>	KNO <sub>3</sub>	(D, cm <sup>2</sup> h <sup>-1</sup> )
Windsor	1.164	0.561	0.406	15.49	15.89	16.26	21.47	0.29
Mahan	1.237	0.533	0.488	15.62	16.5	15.56	26.84	0.45
Webster	1.212	0.543	0.452	20.86	14.95	14.8	16.42	0.32

\*Estimated by CXTFIT 2.0, a: Pulse is mixed solution of (Cd+Cu+Pb)

### 3.4 Result & Discussion

#### 3.4.1 Tritium Transport

BTCs for tritium pulses from the miscible displacement columns for Windsor, Mahan and Webster soil. are presented as relative concentration  $\left(\frac{C}{C_0}\right)$  versus pore volume  $\left(\frac{V}{V_0}\right)$ , where  $V_0$  is the volume of the entire pore space of each soil column ( $\text{cm}^3$ ). Tritium ( $^3\text{H}_2\text{O}$ ) was considered a conservative tracer and was applied in order to assess flow characteristics by obtaining independent values for the hydrodynamic dispersion coefficient (D) of the classical CDE,

$$[3.8] \quad \frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial z} + \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right)$$

Where R ( $R = 1 + \rho K_f / \theta$ ) is the retardation factor (dimensionless). Other experimental parameters such as the soil bulk density ( $\rho$ ) and soil moisture content ( $\theta$ ) are given in Tables 3.1 and 3.2.

After the pulse application of tritium and subsequent leaching by the tritium free solution, the percent of recovery for the applied tritium in the column effluent were 87, 94 and 76% for Windsor, Mahan and Webster soil respectively.

For all tritium results, the BTCs appear almost symmetrical. Such results are indicative that the diffusional mass transfer of tritium was rapid, Such as when equilibrium conditions are dominant. However, for the Mahan and specially Webster soil column, some degree of tailing of tritium BTCs was observed. Such tailing is evidence of physical non-equilibrium and most likely due to intra-particle diffusion and the presence of immobile water regions (Brusseau, 1992). These tritium BTCs were described using CXTFIT along with nonlinear least-square optimization as described in Toride et al. (1995) in order to obtain best-fit values for D and R parameters for each soil. Values of D were

subsequently used in the MRTM model to predict metals transport in the different soil columns. See Tables 3.1, 3.2, and Figure 3.2.

#### 3.4.2 Consecutive Transport of Cd, Cu and Pb in Soils

Results for Cd, Cu, and Pb concentrations in the effluent solution in Windsor, Mahan and Webster soil are presented as relative concentrations  $\left(\frac{C}{C_0}\right)$  versus effluent pore volumes eluted  $\left(\frac{V}{V_0}\right)$ . In this chart C is the concentration in the effluent and  $C_0$  is that of the input pulse solution, V is the total volume of effluent ( $\text{cm}^3$ ) at any time t, and  $V_0$  represents the volume of soil-pore space within the soil column ( $\text{cm}^3$ ).

#### 3.4.3 Consecutive Transport of Cd, Cu and Pb in Windsor Soil

Based on Table 3.1, a pulse of 15.58 pore volume of Cd was applied to the column followed by 16.16 P.V. of Cu, then 16.18 P.V. Pb and then leached with 34.17 P.V. of background solution. Based on the effluent Cd concentrations 94.12% of Cd has been recovered. This indicates that only 5.88% was retained by the Windsor soil which clearly states the low affinity of Windsor for Cd. Moreover the peak concentration for Cd results show 0.98 for Cd. Moreover the peak concentration for Cd results show 0.98 for  $\left(\frac{C}{C_0}\right)$ , which is followed by extensive tailing of BTC depicting slow release during leaching. Cadmium BTC shows a rapid increase in the effluent concentration where about 16 P.V. of Cu pulse was applied. It also shows a shoulder when Pb was applied. This type of Cd behavior in Windsor is different from the data presented in Elbana and Selim (2010), which described the mobility of Cd in Windsor soil. Their results indicate that only 21% of Cd was recovered after 30 P.V. (which is 73.12% less than in this study). Also, an early

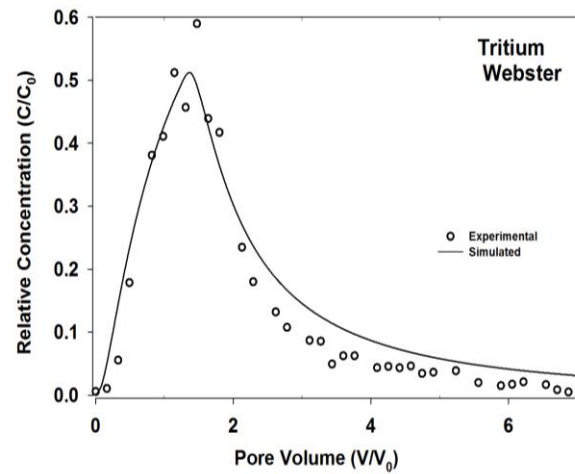
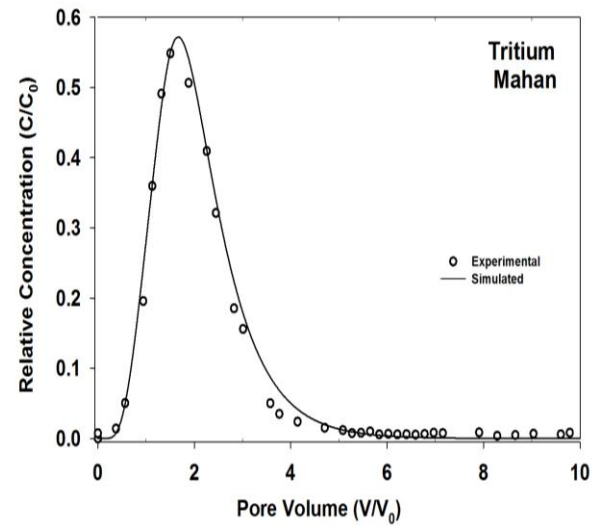
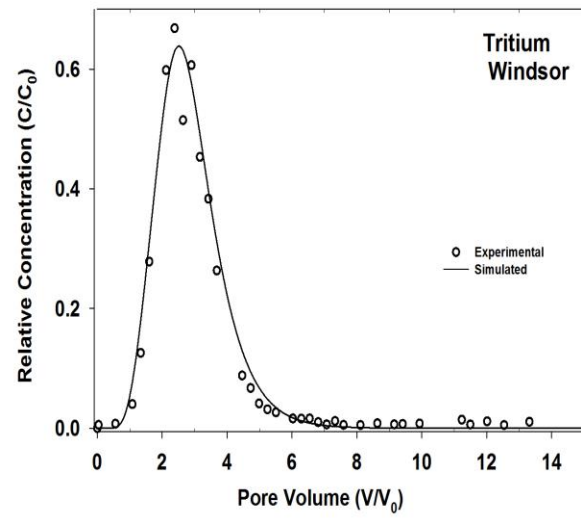


Figure 3.2. Tritium breakthrough curves (BTCs) from the Windsor, Mahan and Webster soil columns. Circle symbols denote measured data. Solid curves are simulations using the CXTFIT model.

arrival of Cd was detected in their study, which might be due to the influence of increasing the applied P.V. from 7.5 (in their study) to 15.58 (in this study). In an effort to describe Cd BTC data has been modeled with MRTM. The best MRTM prediction was realized when accounting for the dominance of equilibrium sorption,  $S_e$  with  $K_f=6.239$  ( $r^2=0.9833$ ;  $RMSE=0.044$ ). See Table 3.3.

Copper pulse was applied after an application of about 15 P.V. of Cd and it exhibits an early arrival. Copper increase in mobility in Windsor has been observed by Elbana and Selim (2011) as a result of increase in the applied pore volume about 40 P.V. of the metal and therefore has caused a significant increase in the recovery percentage. The peak maximum concentration for Cu is  $0.76 \frac{C}{C_0}$  and 72.62% of applied Cu has been recovered in the effluent after 83 P.V. Numerous studies showed that Cu retention with Fe and Al oxides are dominant mechanisms in acidic soils such as Windsor. (Chen et al., 1999, Shaheen et al., 2009). Similar to Cd, extensive tailing has been observed for Cu BTC. See Figure 3.3.

Application of Pb pulse at 32 P.V. has caused a constant concentration of Cu in the effluent for about 10 P.V. when Pb concentration is increasing in the effluent. MRTM best prediction to explain the behavior of copper in this system shows that  $S_{irr}$ ,  $S_1$  and  $S_e$  sites need to be taken into account. And suggest that irreversible, reversible kinetic, and equilibrium sorption are dominant mechanisms.  $S_{irr}$  represents the direct precipitation from the solution. This is when Selim and Ma (2001) suggested that  $S_s$  irreversible phase should be taken into account for surface precipitation reactions of Cu in soils with high contents of Al and Fe oxides such as Windsor soil. However this was the best fit we could accomplish. ( $r^2=0.9890$ ,  $RMSE=0.0318$ ) the rest of parameters is shown in Table 3.3.

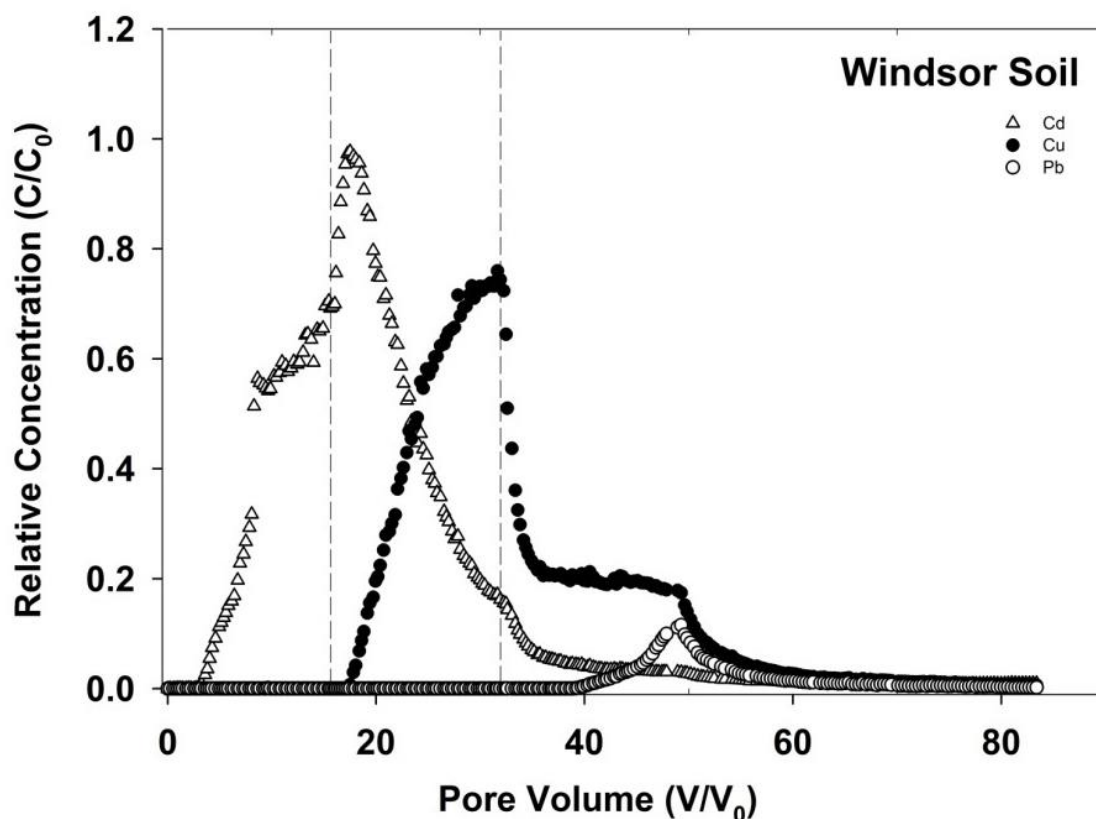


Figure 3.3. Breakthrough results of Cd, Cu, and Pb from the Windsor soil column; vertical dashed lines indicate introduction of Cu and Pb pulses, respectively.

Lead pulse was applied following of Cd and Cu pulses. The maximum Pb concentration in the effluent was  $0.11 \frac{C}{C_0}$  and the recovery percentage was only 5.72% of that applied. Application of Pb affected Cu BTC; a major drop in Cu and a minor drop in Cd concentration occurred. Also a change of slope in Cd BTC was observed. This is a clear consequence of the competitiveness of Pb free ions with Cd and Cu sorbed form. The extremely low recovery percentage of Pb shows that it is strongly sorbed to the soil and is depicting a high affinity for Pb in the soil. This is consistent with the work of Lu and Xu (2009) who measured the competitive adsorption of four heavy metals Cd, Cu, Zn and Pb and found that Pb was the most



Table 3.3. Model versions for Cd, Cu and Pb retention by the standard errors (SE), root mean square error (RMSE), and coefficient of determination ( $r^2$ ) values.

Experiment	Soil	Metal	$r^2$	RMSE	$k_f$ (h <sup>-1</sup> )	SE	$k_1$	SE	$k_2$ (h <sup>-1</sup> )	SE	$k_{irr}$ (h <sup>-1</sup> )	SE
Consecutive	windsor	Cd	0.9833	0.0445	6.2398	0.0652	-	-	-	-	-	-
		Cu	0.9890	0.0318	9.2007	2.1493	10.4188	0.3054	0.0232	0.0110	0.0078	0.0026
		Pb	0.8187	0.0133	-	-	14.0096	0.1441	0.0324	0.0002	0.4036	0.0044
	Mahan	Cd	0.8425	0.1135	0.4330	0.0123	199.3672	4.4102	0.2259	0.0060	-	-
		Cu	0.9229	0.0659	-	-	13.2177	1.5499	0.0456	0.0069	0.0350	0.0053
		Pb	-	-	-	-	-	-	-	-	-	-
	Webster	Cd	0.8647	0.0060	322.8794	3.9045	-	-	-	-	0.3668	0.0073
		Cu	-	-	-	-	-	-	-	-	-	-
		Pb	-	-	-	-	-	-	-	-	-	-
Concurrent	Windsor	Cd	0.7524	0.3433	-	-	2.7765	1.0551	0.0206	0.0122	0.0057	0.0051
		Cu	0.7075	0.5404	5.3662	8.5302	4.3972	0.5349	0.0048	0.0009	-	-
		Pb	0.6392	0.1262	-	-	9.0707	0.7798	0.0058	0.0013	0.0515	0.0185
	Mahan	Cd	0.6033	0.4077	-	-	102.0714	6.3077	0.8422	0.0492	0.0303	0.0010
		Cu	0.5289	0.3576	156.7359	36.6094	-	-	-	-	-	-
		Pb	0.4135	0.1978	-	-	8.5707	2.1659	0.0096	0.0046	0.1165	0.1165
	Webster	Cd	0.7881	0.2813	5.9043	6.1777	3.0758	0.5183	0.0092	0.0021	-	-
		Cu	0.7675	0.1687	16.4703	4.2533	2.7022	0.2223	0.0034	0.0004	-	-
		Pb	0.6557	0.0374	0.5683	0.0173	13.5571	0.2356	0.0051	0.0001	-	-

strongly sorbed metal in their study. The MRTM prediction for Pb BTC shows that the sorption mechanism is dominant with the kinetic and irreversible type phases.

#### 3.4.4 Consecutive Transport of Cd, Cu and Pb in Mahan Soil

A pulse of 15 P.V. of Cd was applied to the Mahan soil column followed by 15 P.V. of Cu, then 14 P.V. Pb and leached with 29 P.V. of the background solution. Based on the effluent Cd concentrations 65.02% of Cd has been recovered, which shows a 29.1% decrease in comparison to Windsor Soil. This shows a higher Cd affinity by Mahan than that of Windsor soil. Moreover the peak concentration for Cd results show 0.83 for  $\frac{C}{C_0}$ , which is followed by extensive tailing of BTC depicting slow release during leaching just like the scenario in the Windsor.

Similar to Windsor Soil, Cd BTC shows a rapid increase in the effluent concentration where the Cu pulse has been applied. In an effort to describe Cd BTC data has been modeled with MRTM. The best MRTM prediction was realized when accounting for the dominance of the kinetic and equilibrium phase types, ( $r^2=0.8425$ ;  $RMSE=0.0113$ ). Note that the b value of 0.32, which was used in this study, is in line with that of the Cd sorption data, which was fitted by Freundlich equation presented in chapter 2, see Table 2.4.

A Copper pulse was applied following the application of 15 P.V. of Cd and is exhibiting a later arrival in comparison to that of Windsor. The peak maximum concentration for copper was 0.71 ( $\frac{C}{C_0}$ ) and 45.85% of applied Cu has been recovered in the effluent after a total 69 P.V. which is lower than that of Windsor. Similar to Cd, extensive tailing has been observed for Cu BTC as well. Application of Pb pulse at 29.28 P.V. has changed the trend of tailing, which is indicative of the fact

that the addition of Pb resulted in enhanced release of Cu. Therefore, Cu is extremely weakly sorbed compared to Pb. See Figure 3.4.

MRTM was utilized to explain the behavior of copper in this system. Best prediction shows that  $S_{irr}$ ,  $S_1$  sites are needed in order to be taken into account, and suggests that irreversible, reversible kinetic sorption are dominant mechanisms ( $r^2=0.9229$ ,  $RMSE=0.0659$ ). See Table 3.3.

Lead pulse has been applied after 29 pore volume of Cd and Cu. the recovery percentage is only 0.008% of that of applied which shows an extreme affinity of soil for Pb. Application of Pb influenced Cu BTC. A major drop in Cu was observed, which is a clear consequence of the competitiveness of Pb free ions with the Cd and Cu that has already sorbed. The extremely low recovery percentage of Pb shows that it is strongly sorbed to the soil and is depicting a high affinity for Pb on the soil. MRTM prediction was not applicable for Pb due to lack of BTC.

In general, Mahan soil exhibited higher affinity for all three metals in comparison to Windsor, which can be explained by the 28% higher percentage of clay content in the Mahan soil. Also, CEC is higher in Mahan, which will increase the higher sorption of metals on the soil.

#### 3.4.5 Consecutive Transport of Cd, Cu and Pb in Webster Soil

A pulse of 15.07 pore volume of Cd was applied to the column followed by 15.43 P.V. of Cu, then 14.82 P.V. Pb and then leached with 30.48 P.V. of background solution. Based on the effluent Cd concentrations 24.73% of Cd was recovered. This shows a major decrease in comparison to Windsor and Mahan Soil. This indicates a higher Cd affinity by Webster than that for Windsor and Mahan soil. The peak concentration results for Cd was only 0.05 for  $\frac{C}{C_0}$ . Late arrival for Cd was observed. However, similar to Windsor Soil, Cd BTC shows an increase in the effluent

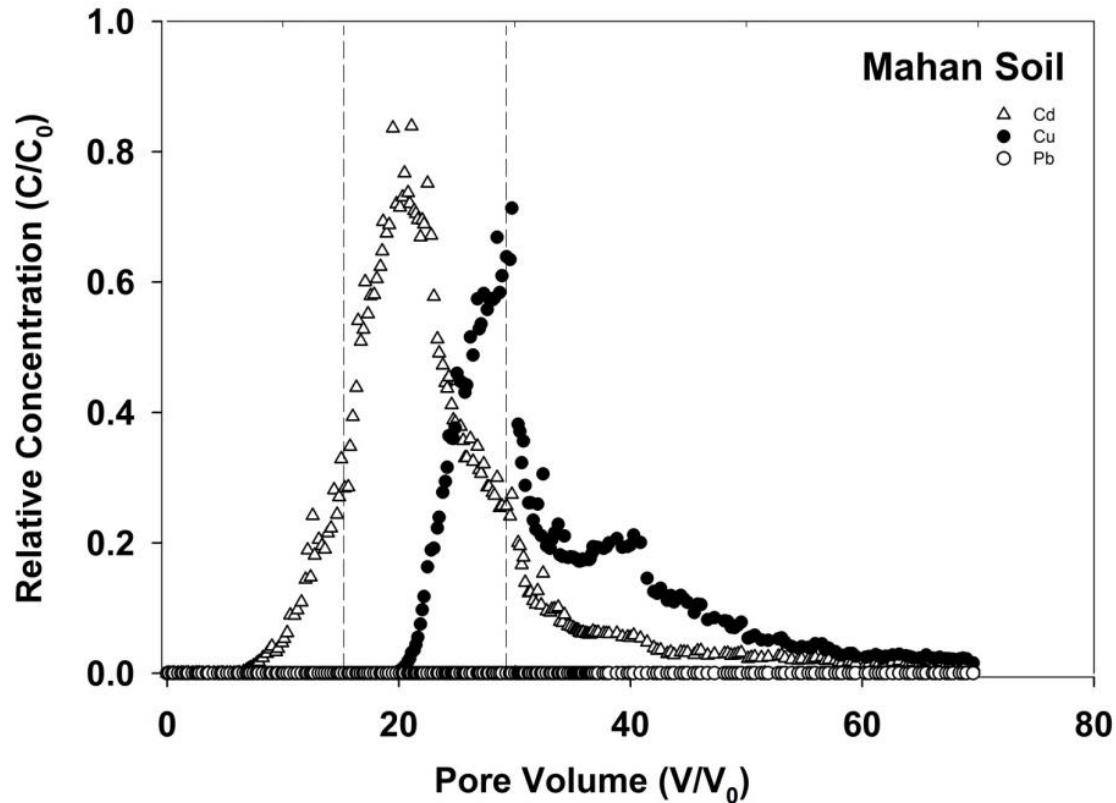


Figure 3.4. Breakthrough results of Cd, Cu, and Pb from the Mahan soil column; vertical dashed lines indicate the introduction of Cu and Pb pulses, respectively.

concentration where the Cu pulse has been applied. In an effort to describe Cd BTC data has been modeled with MRTM. The best MRTM prediction was realized when accounting for the dominance of irreversible and equilibrium phase types, ( $r^2=0.8647$ ; RMSE 0.006).

Copper pulse was applied after application of 15 pore volume of Cd and is exhibiting an early arrival as explained in the case of Windsor soil. The amount of Cu found in the effluent was 0.24% of that of applied which is very low and indicates a very strong retention of Cu by the soil. Also adding Cu solution to the system appears to increase Cd mobility. Due to strong sorption, MRTM modeling was not applicable.

Lead pulse has been applied after Cd and Cu application. The recovery percentage was only 0.03% of that of applied which shows an extreme affinity of soil for the Pb. Application of Pb has affected Cu BTC; a major drop in Cd due to the introduction of Pb pulse was observed, which follows by an increase in the mobility of Cd ions at around 40 pore volumes (a clear consequence of competitiveness of Pb free ions with Cd which has already sorbed). The extremely low recovery percentage of Pb indicates that it is strongly sorbed to the soil and is depicting high affinity for Pb on the soil. MRTM modeling was not applicable for Pb. See Figures 3.5 and 3.6.

In general Webster shows a higher affinity for all three metals which can be explained by the high percentage of clay in the Webster soil which is mostly composed of smectite. Also CEC and TOC are higher in Webster, which will increase the higher sorption of metals on the soil. Similar observation of strong heavy metal affinity for Webster soil was reported by Selim (2012).

#### 3.4.6 Concurrent Transport of Cd, Cu and Pb in Soils

In this set of experiments two mixed pulses of Cd Cu and Pb solution was introduced to the soil column followed by leaching. The results are presented as relative concentrations  $\left(\frac{C}{C_0}\right)$  versus effluent pore volumes eluted  $\left(\frac{V}{V_0}\right)$ . In this charts C is the concentration in the effluent and  $C_0$  is that of the input pulse solution, V is the total volume of effluent ( $\text{cm}^3$ ) at any time t, and  $V_0$  represents the volume of soil-pore space within the soil column ( $\text{cm}^3$ ).

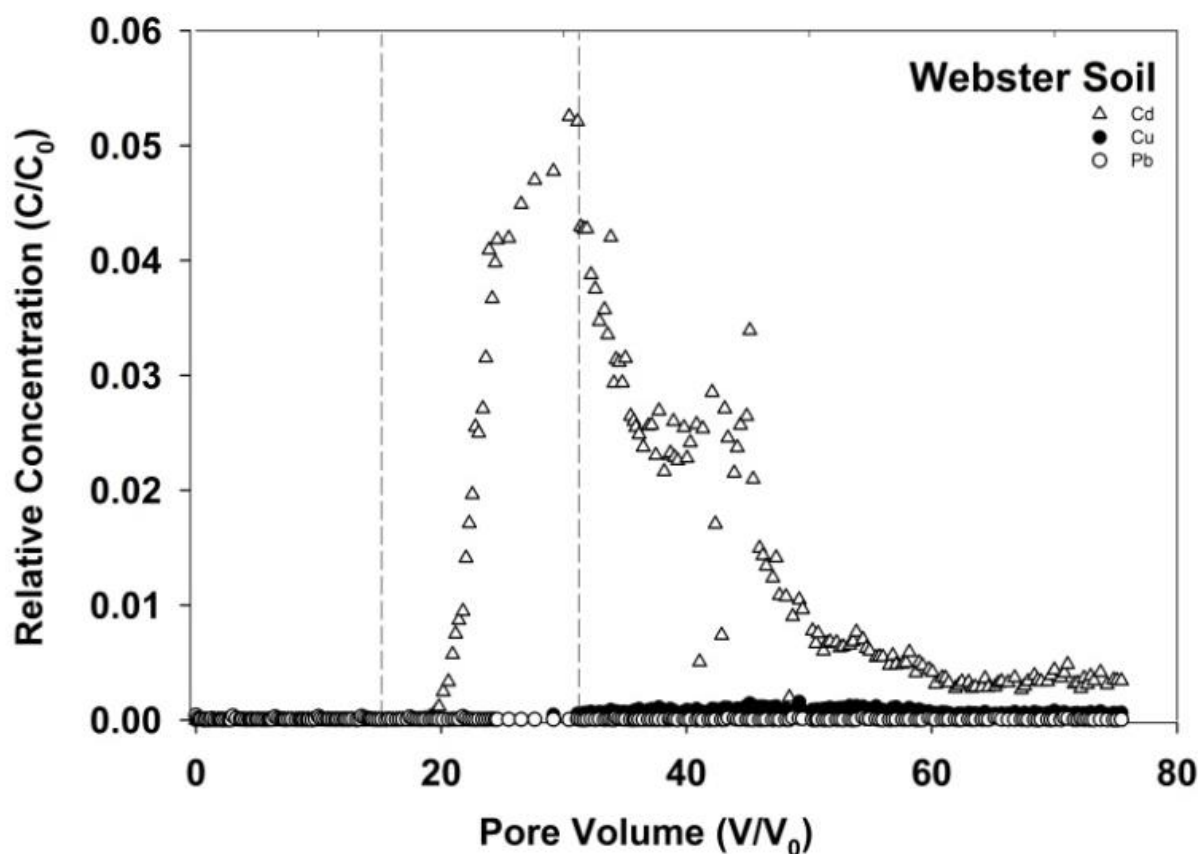


Figure 3.5. Breakthrough results of Cd, Cu, and Pb from the Webster soil column; vertical dashed lines indicate the introduction of Cu and Pb pulses, respectively.

#### 3.4.7 Concurrent Transport of Cd, Cu and Pb in Windsor Soil

Based on Table 3.3, two pulses of 15 and 16 pore volume of mixed solution was applied to the column, each followed by 15 and 21 pore volume of background solution. Based on the effluent Cd concentrations, 87% of total Cd recovered was 66% of the first pulse and 96% of the second pulse.

The peak concentration ( $\frac{C}{C_0}$ ) of Cd BTCs was 1.4 and 1.2 for first and second peak respectively. The recovery percentage of the first peak (66%) decreased significantly in comparison to the recovery of the single Cd peak in Windsor (94%). This indicates that the existence of Pb and Cu ions in the input solution along with Cd has significantly impacted the amount of Cd in the effluent and its

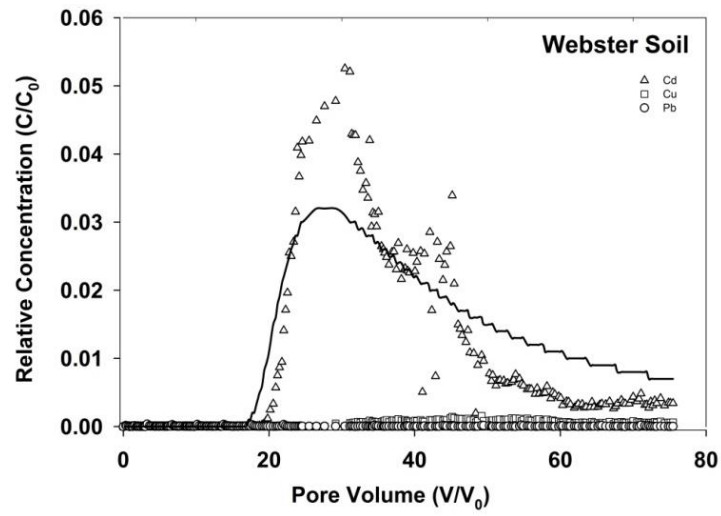
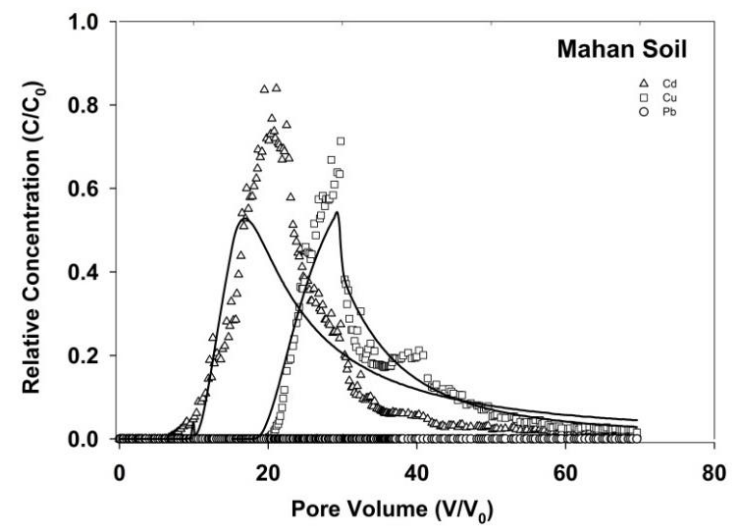
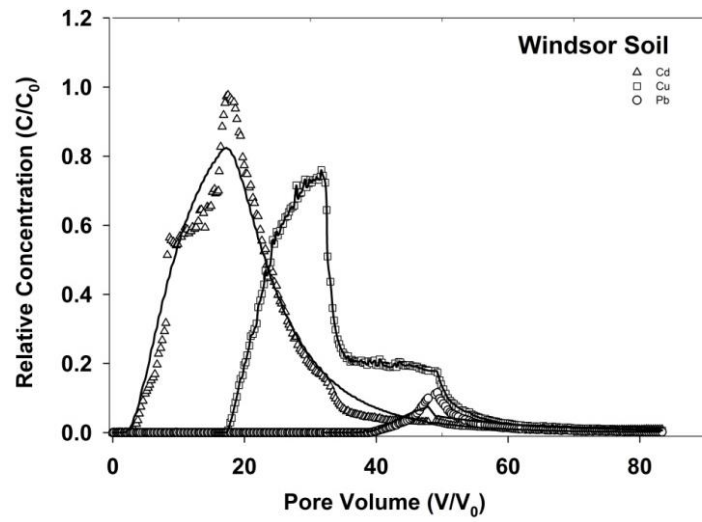


Figure 3.6. Breakthrough results of Cd, Cu, and Pb from the Windsor, Mahan and Webster soil column; Solid curves are multireaction and transport model (MRTM) simulations.

mobility. Also, Cd is retained strongly in the soil, which clearly is the result of ions competing for available sites. In making a comparison between first and second BTC, second Cd peak shows a significant early arrival. Also, a higher mobility and a greater recovery were observed. The reason being, in the first pulse application, the soil retained Cd to some extent, and when introducing the second pulse, many sites were not available. What has been explained in the case of Cd is true for Cu and Pb as well. Both Cu and Pb are showing a lower recovery percentage in comparison to the single ion experiment, and they are showing a higher mobility when applied to a pre-polluted soil as opposed to the soil that is devoid of these metals. They also show a very early arrival in the second peak, which is indicative of fewer available sites. See Figure 3.7.

In an effort to describe Cd BTC data was modeled with MRTM. The best MRTM prediction was realized when accounting for the dominance of irreversible and kinetic sorption. See Table 3.3.

For copper, MRTM's best prediction in explaining the behavior of Cu in this system indicates that  $S_e$ ,  $S_1$  need to be taken into account, and it suggests that equilibrium and kinetic sorption are the dominant mechanisms. ( $r^2=0.7075$  RMSE=0.5404) the rest of the parameters are shown in Table 3.3.

The MRTM prediction for Pb BTC shows that the sorption mechanism is dominant with kinetic type phase and irreversible type, which is the same mechanism discussed earlier for Windsor soil when consecutive pulses were applied.

#### 3.4.8 Concurrent Transport of Cd, Cu and Pb in Mahan Soil

Based on Table 3.1 two pulses of 15 pore volume of mixed solutions were applied to the column, each followed by 16 and 26 P.V. of background solution. Based on the effluent Cd concentrations, 83% of total Cd was recovered, whereas the recovery percentage during the first pulse was 88% and



during the second pulse was 75%. The peak concentration ( $\frac{C}{C_0}$ ) for Cd indicates 1.3 and 1.1 for first and second peak respectively. Unlike Windsor soil, first. pulse recovery percentage (88%) increased in comparison to the single Cd peak in Windsor, which shows only 65% recovery.

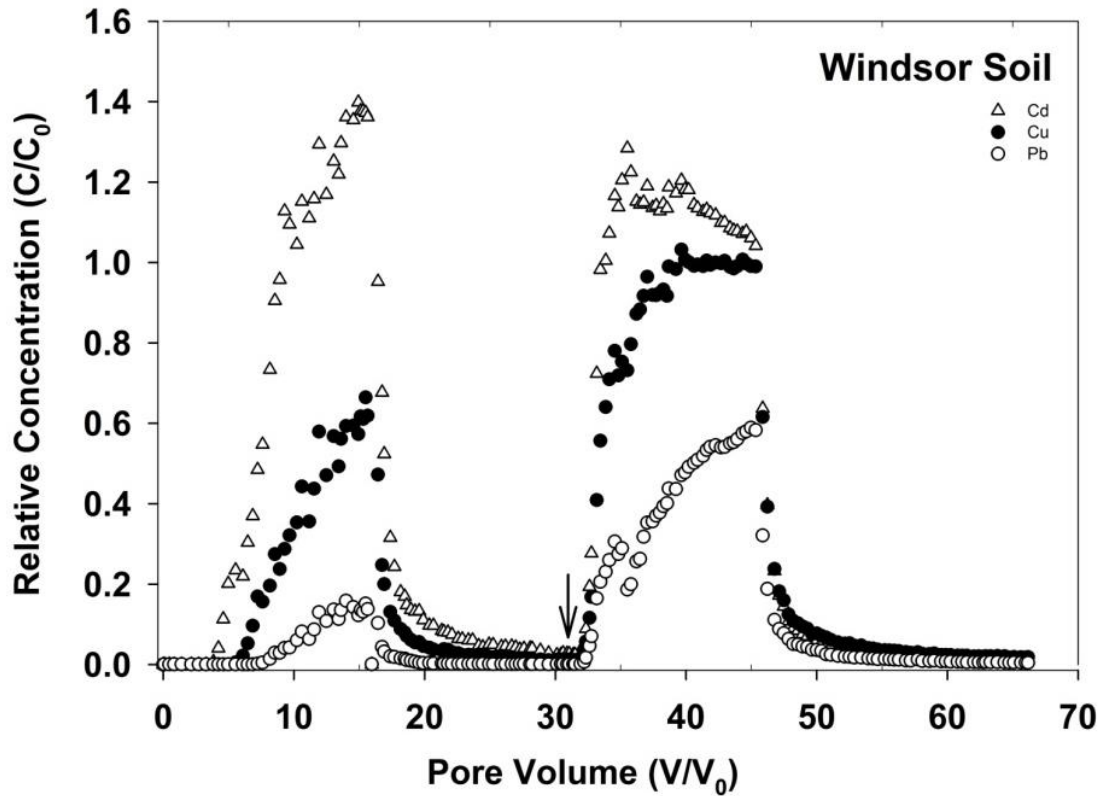


Figure 3.7. Breakthrough results of Cd, Cu, and Pb from the Windsor soil column when two mixed pulses (Cd+Cu+Pb) were applied. The arrow indicates when the second pulse started.

This points to the fact that the existence of Pb and Cu ions in the input solution along with Cd increased the amount of Cd in the effluent and its mobility. Because Cd is retained strongly in the soil, we can conclude that there is a competition among ions toward available sites in Mahan soil. When making a comparison between first and second peak, Cd peak shows a significant early arrival. Also, you can see a lower mobility and recovery for Cd in the second peak which shows a different trend.

In an effort to describe Cd BTC data was modeled with MRTM. The best MRTM prediction was realized when accounting for the dominance of the irreversible and kinetic sorption, the parameters of MRTM modeling of data is shown in Table 3.3. ( $r^2=0.6033$  RMSE=0.4077). In general the trend is moderately different from what was seen in the Windsor soil.

Copper shows a total 63% recovery, 49% in the first pulse and 74% in the second pulse. The recovery of Cu for the first pulse (49%) shows no significant difference from that of a single Cu pulse in the consecutive experiment (45.85%). This shows that the competition between ions did not significantly affect the mobility of Cu. However, we see that the mobility of Cu during the second pulse application and leaching, demonstrates a significant increase in comparison to that of the first one, which is due to the limitation in available sites during the second pulse application. The recovery percentage of Cd and Cu and also their highest concentration in the effluent is very similar to each other, which highlights their similar mobility when applying a mixed pulse to a pre-polluted system. See Figure 3.8.

Copper MRTM prediction shows that only  $S_e$  needs to be taken into account, and it suggests that equilibrium sorption is the dominant mechanism. The parameters are shown in Table 3.3.

Similar to Cd and Cu, Pb exhibited similar trend with a first pulse recovery of only 6.8%, while second pulse recovery of 39% is observed. The first pulse recovery percentage shows a major difference in comparison to consecutive experiment (0.008%). This fact points to the influence of competitiveness on the mobility of Pb. Also results show that although Pb is a heavily sorbed metal in comparison to Cd and Cu, it gets sorbed much less when applied in a competitive system.

The MRTM prediction for Pb BTC shows that the sorption mechanism is dominant with a kinetic type phase and an irreversible type. More information can be found in Table 3.3.

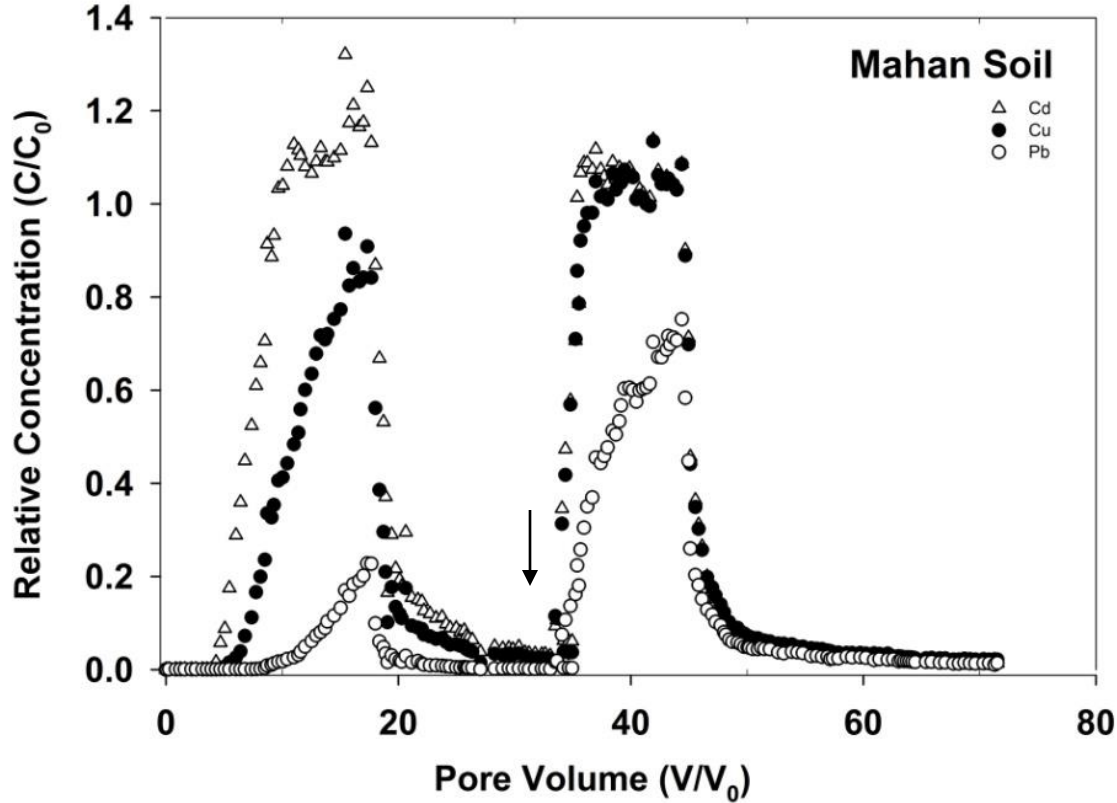


Figure 3.8. Breakthrough results of Cd, Cu, and Pb from the Mahan soil column when two mixed pulses (Cd+Cu+Pb) were applied. The arrow indicates when the second pulse started.

#### 3.4.9 Concurrent Transport of Cd, Cu and Pb in Webster Soil

Based on Table 3.2 two pulses of 20 and 14 pore volume of mixed solution has been applied to the column, each followed by 15 and 16 P.V. of background solution. See Figure 3.9. Based on the effluent Cd concentrations 77% of total Cd has been recovered, 60.2% during the first pulse and 99% in the second pulse. The peak concentration results for Cd are 0.89 and 1.33 for first and second peak respectively for  $\frac{C}{C_0}$ .

Unlike Windsor soil, the first peak recovery percentage (77%) was higher than the single Cd peak in Webster soil (24.13% recovery). This means that the presence of Pb and Cu ions in the input solution along with Cd increased the amount of Cd in the effluent and its mobility in the soil. Also, Cd is retained strongly in the soil, which is as a clear result of competing among ions toward available sites in the Webster soil. When making a comparison between first and second peak, Cd peak has an early arrival. In the second peak, it also illustrates a higher mobility and a greater recovery. This points to the fact that the soil has already retained some of the Cd which was applied in the first pulse, therefore when introducing the second pulse, most of the sites are not available.

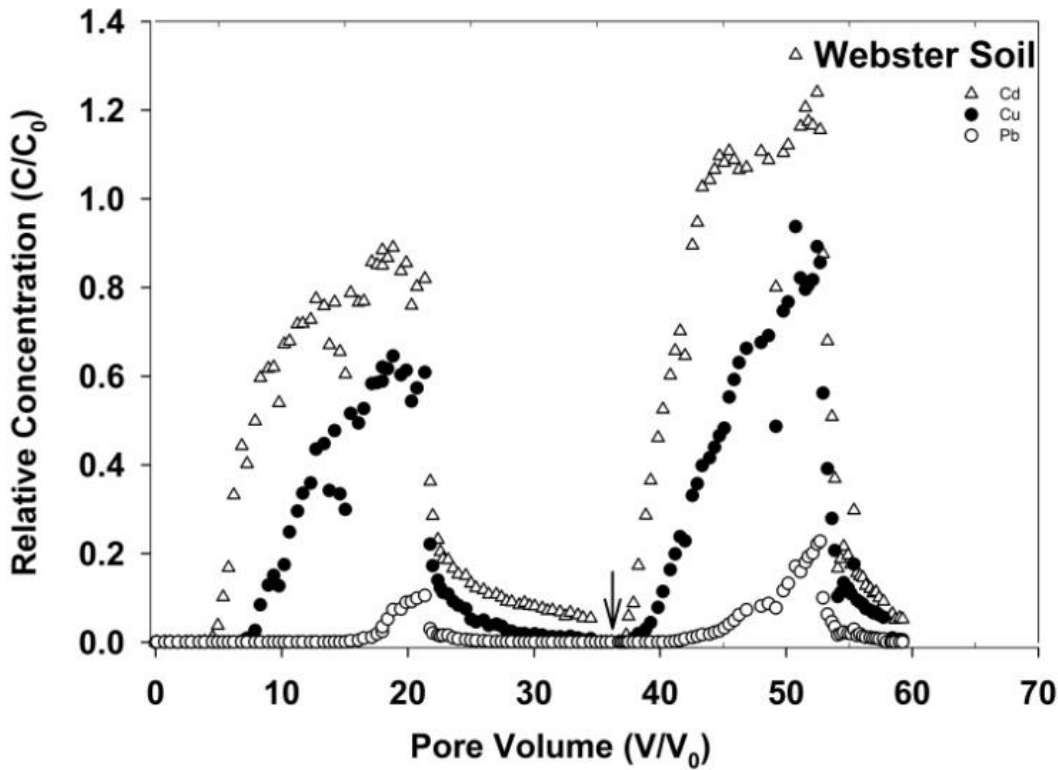


Figure 3.9. Breakthrough results of Cd, Cu, and Pb from the Webster soil column when two mixed pulses (Cd+Cu+Pb) were applied. The arrow indicates when the second pulse started.

In an effort to describe Cd BTC data has been modeled with MRTM. The best MRTM prediction was realized when accounting for the dominance of an irreversible and kinetic sorption, the MRTM modeling parameters of data is shown in Table 3.3. ( $r^2=0.6033$ , RMSE=0.4077). In general the trend is moderately different from what was seen in the Windsor soil.

Copper shows a total of 39% recovery (30% in the first peak and 53% in the second peak). we see that the mobility of Cu during the second pulse application and leaching shows a significant increase in comparison to that of the first one which is due to the limitation of available sites during the application of the second pulse.

MRTM best prediction to explain the behavior of Cu in this system shows that only Se is needed to be taken into account, and it suggests that equilibrium sorption is the dominant mechanism. The parameters are shown in Table 3.3.

Similar to Cd and Cu, Pb is showing a similar trend with a first pulse recovery of 1.83%, while the second is 7.19%. The first pulse recovery percentage shows a major difference with Pb in the first consecutive experiment. This indicates the competitiveness influence on Pb mobility. Also, results show that although Pb is a heavily sorbed metal in comparison to Cd and Cu, it gets sorbed much less when applied in a competitive system. Lead BTC shows a gradual increase in the second peak, which illustrates its slower release in comparison to Cd and Cu, because it has a higher retention capability.

In general, the mobility of elements in Webster decreased in comparison to Windsor and Mahan Soil. Higher percentage of clay content, higher TOC and higher CEC values in the Webster soil might explain this observation as discussed earlier.

MRTM's best prediction to explain the behavior of Cd, Cu and Pb in this system shows that equilibrium and kinetic sorption mechanisms are dominant. More information is provided in Table 3.3 and Figure 3.10.

All three elements were observed to have higher mobility when applied to the soil with retained Cd, Cu and Pb in comparison to the untreated soil. This is due to limitation of available sites on the soil surface.

### **3.5 Distribution of Elements with the Depth**

The distributions of sorbed Cd, Cu and Pb vs. depth in the Windsor, Mahan and Webster soil was measured. The sorbed Cu distribution in almost all three soils for both consecutive and concurrent transport experiment has not changed much with the depth.

Whereas in the consecutive experiment, 46 and 73% of total sorbed Cd, and in the concurrent experiment 58 and 58% of total sorbed Cd has been found in the last one centimeter of the column in Windsor and Mahan soils respectively. In the Webster soil, 69 and 41% of the total Cd sorbed has been found in the first 2 cm of the soil surface in consecutive and concurrent experiment respectively.

Lead data also shows: 52, 67 and 85 % of the total Pb has been found in top 2 cm of the Windsor, Mahan and Webster soil respectively in the consecutive experiment. Result shows 49, 49 and 80 % for Windsor, Mahan and Webster soil in the concurrent transport, This decrease in percentage of lead found in the surface in the concurrent experiment in comparison to the consecutive experiment is explained by the fact that lead observed to have higher mobility in the concurrent experiment.

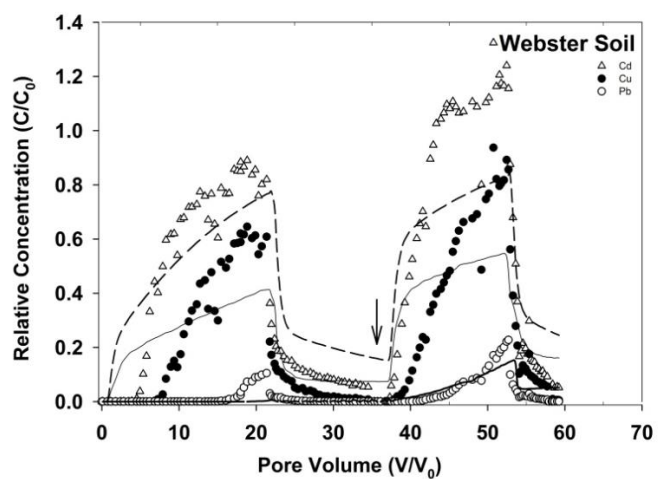
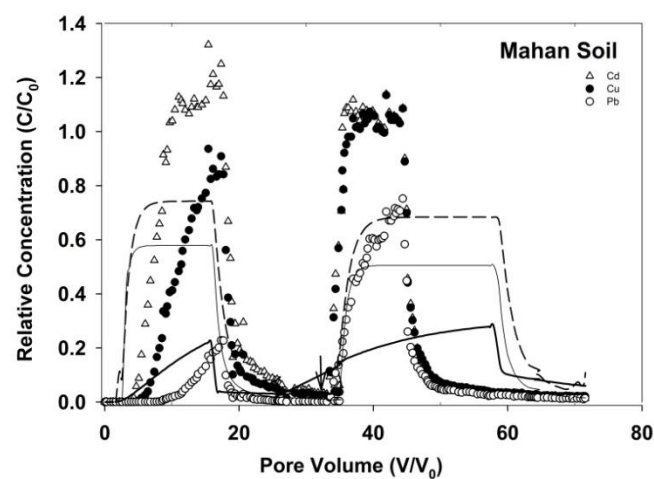
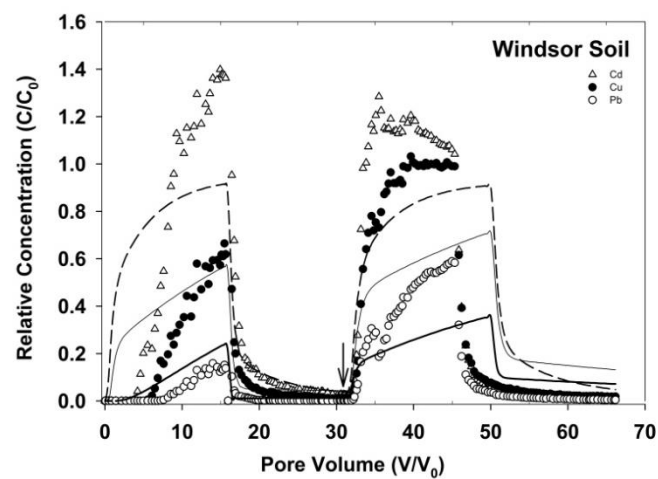


Figure 3.10. Breakthrough results of Cd, Cu, and Pb from the Windsor soil column when two mixed pulses (Cd+Cu+Pb) applied. Solid arrows indicate when the second pulse started. Solid curves indicate multireaction and transport model (MRTM) simulations.

In general Pb in all experiments has been primarily found in the top 2 cm of the surface which shows a low mobility of that in the soil, this is when both sorbed Cd and Cu in Windsor and Mahan soil mostly located in the last one cm of the soil profile (4 to 5 cm) and for Webster they have been mostly found in the top 2 cm of the profile. This means that Cd and Cu are less mobile in the Webster soil in comparison to Windsor and Mahan. See Figures 3.11 and 3.12.



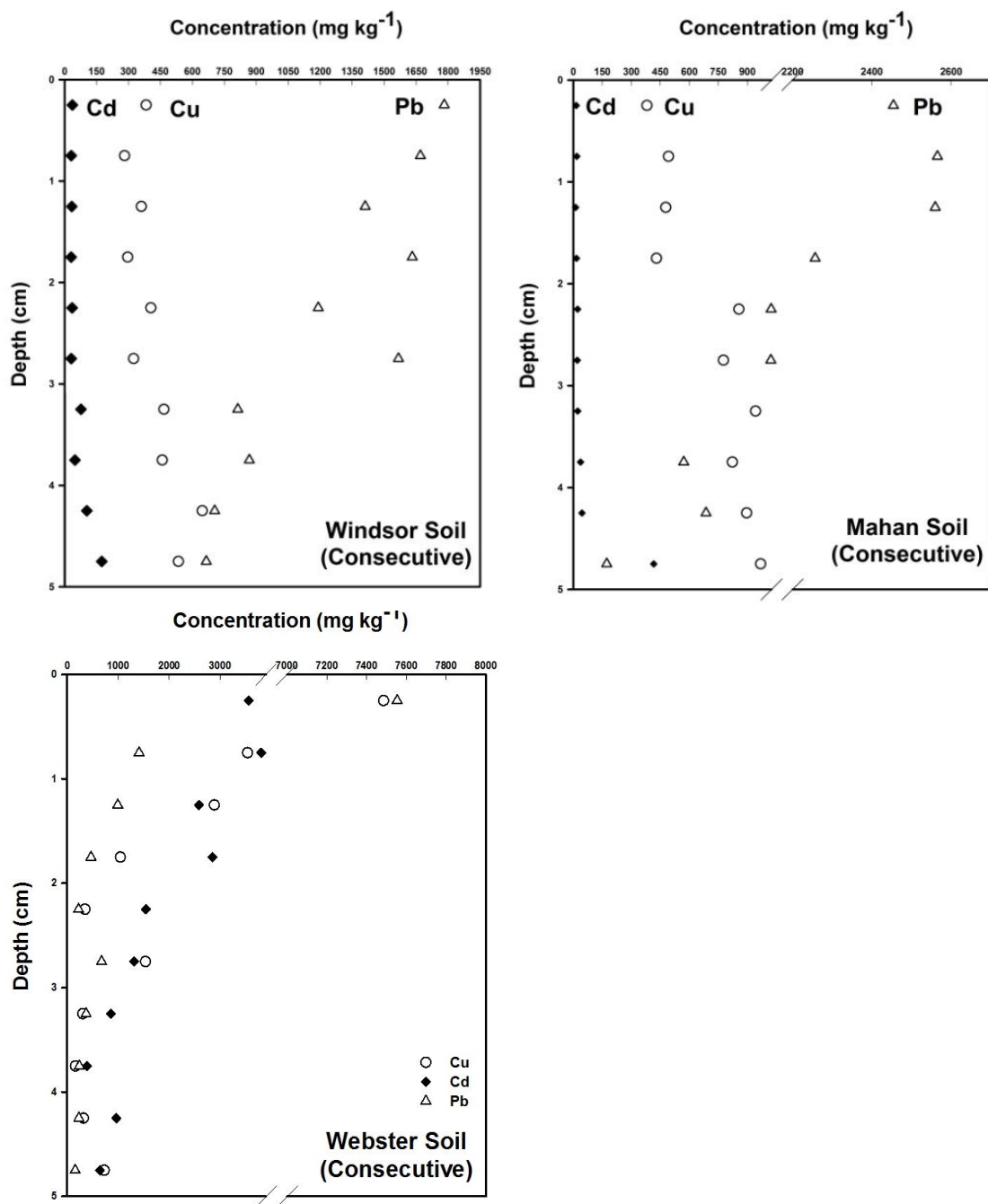


Figure 3.11. Cd, Cu and Pb sorbed vs. column depth based on XRF measurements for Windsor, Mahan and Webster soil columns (Consecutive pulses of Cd, followed by Cu which was followed by Pb applied)

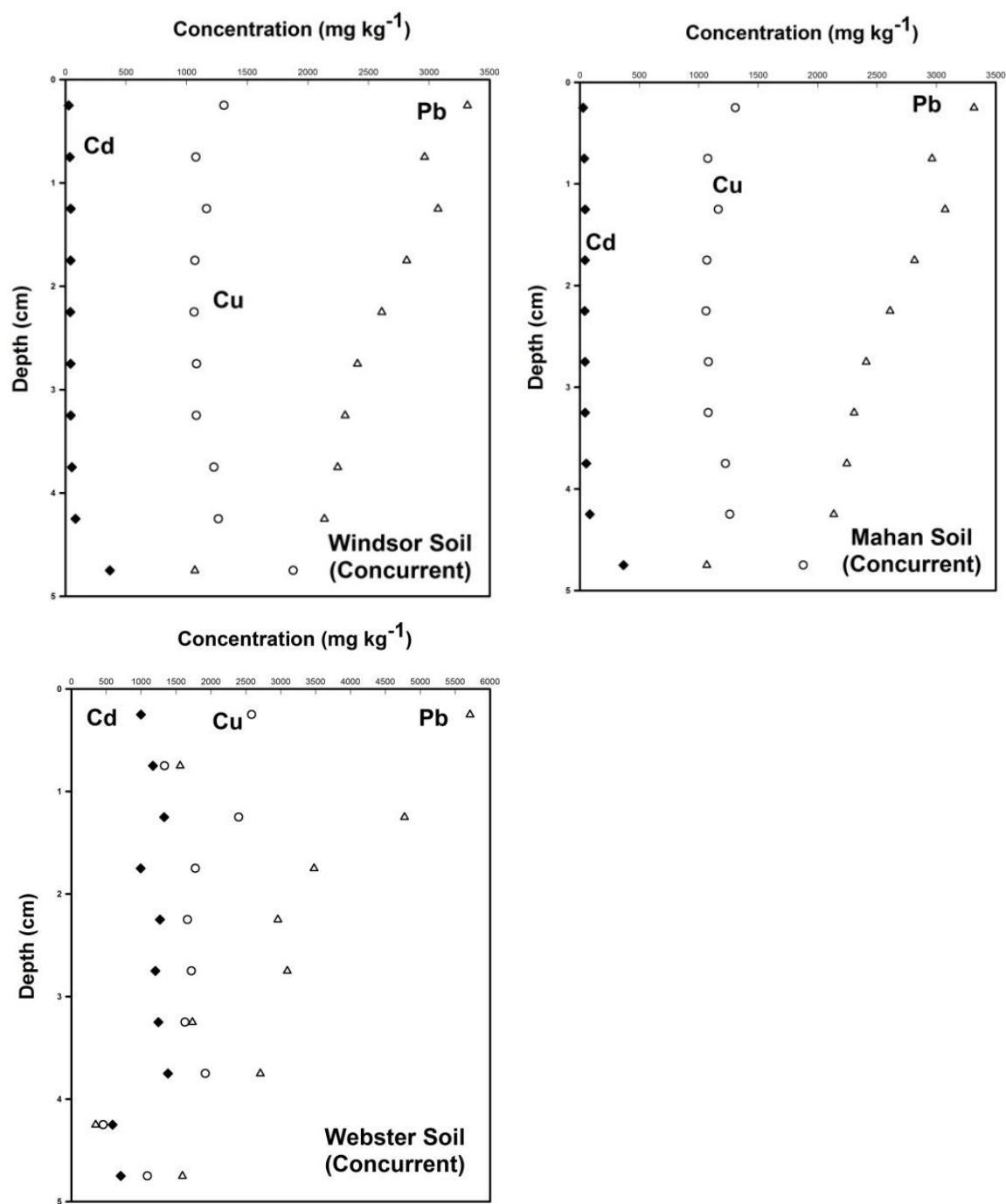


Figure 3.12. Cd, Cu and Pb sorbed vs. column depth based on XRF measurements for Windsor, Mahan and Webster soil columns (two concurrent pulses (Cd+Cu+Pb) applied).

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