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SILVER TRANSPORT AND ADSORPTION-DESORPTION IN SOILS: INFLUENCE OF ZINC

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 Sciences

in

The School of Plant, Environmental, and Soil Sciences

by
Liyun Zhang
B.S., China Agricultural University, 2011
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ABSTRACT

Transport of heavy metals such as Ag is affected by several rate-limiting processes including adsorption and release reactions in soils. In this study, the objective was to qualify adsorption-desorption behavior and transport of silver in the different soils. This study also investigated the influence of the presence of Zn on Ag retention and transport in soils. Kinetic batch adsorption-desorption and column experiments were carried out to investigate the adsorption-desorption and transport of silver in soils having different properties in the presence of Zn. Transport of Ag was carried out using miscible-displacement experiments in water saturated soil columns. For all soils, results indicated that adsorption isotherms for Ag were highly nonlinear with greater affinity for Webster soil. Moreover, the presence of Zn resulted in reduced Ag sorption indicative of competitive behavior. Measured Ag breakthrough results (BTCs) from the column experiments indicated highest Ag mobility in Olivier soil whereas Webster soil exhibited least mobility. This finding is based on the Ag recovered and the retardation of the arrival of Ag in the effluent solution. Furthermore, the presence of Zn resulted in enhanced mobility of Ag. A multireaction and transport model (MRTM) that accounted for nonlinear reversible kinetics and irreversible reactions was capable of describing both Ag and Zn transport in all soil columns.

CHAPTER 1: INTRODUCTION: LITERATURE REVIEW

1.1 General Description

Silver is comparatively rare in the Earth's crust—67th in order of natural abundance of elements. But it is valued as a precious metal, and is used as an investment, to make ornaments, jewelry, high-value tableware, utensils, and currency coins. Furthermore, now the major industrial use of silver was used in the manufacturing of chemicals for photographic products in the USA (Begum, 2003). Other industrial uses of silver include the production of electrical contacts and switching gear, batteries, catalysts and mirrors. Silver has been known since ancient times. It is found in native form very rarely, but more usually combined with sulfur, arsenic, antimony, or chlorine. The principal sources of silver are zinc, copper, gold, lead. Because of its widely use, silver is regarded as one of the most important metals. Much research effort in the last several decades has been devoted to geochemical reaction of Ag in the natural environment.

1.2 Silver in Soil and Its Source

Silver is a rare element, which occurs naturally in its pure form as a white, ductile metal, and in ores. It has an average abundance of about 0.1 ppm in the earth's crust and about 0.3 ppm in soils.

Because of increased use of silver in varieties of industries, discharges containing silver is often reported. The total U.S. annual release of silver to land from production processes and consumptive uses in 1978 was estimated at 1.01 million kg (Scow et al., 1981). Annual silver released to the environment from industrial waste and emissions has been estimated at approximately 2,500 tonnes, of which 150 tonnes gets into the sludge of wastewater treatment plants and 80 tonnes is released into surface waters.

Silver levels in soils are low except in mineral-rich areas where levels as high as 44 mg kg-1 was observed. Plants can absorb Ag with measured levels ranges from 0.03 to 0.5 mg kg^{-1}. The Ag content of surface soils ranges from less than 0.01 to 5 mg kg^{-1}, with most reported values being <1 mg kg^{-1} (Mitchell, 1955; Vanselow, 1966; Boyle, 1968; Bradford et al., 1996; Sterckeman et al., 2002; Murray et al., 2004). However, Ag concentrations in soils impacted by industry (e.g., mean, 2.3 ± 2.2 mg kg^{-1}) or by smelter activity (e.g., up to 2.4 mg kg^{-1}) may be 3-20 times the background (Sterckeman et al., 2002; Murray et al., 2004).

Release from the photographic industry and from disposal of sewage sludge and refuse are the major sources of soil contamination with silver. The major source of elevated silver levels in cultivated soils is from the application of sewage sludge and sludge effluents as agricultural amendments. Additional anthropogenic sources of silver in soils include atmospheric deposition (especially from ore processing); landfilling of household refuse, sewage sludge, or industrial wastes; and leaching of metal tailings (Smith and Carson 1977).

Sorption is considered the dominant process in silver partitioning in water and its mobility in soils and sediments. Silver accumulation in marine algae has been reported mainly because of adsorption rather than uptake (Begum, 2002). Based on a study of environmental factors determining Ag sorption to soils, sorption of Ag is dominated by soil organic matter either through exchange or complexation (Jacobson et al., 2005).

1.3 Environmental Toxicity of Silver

Silver ion is one of the most toxic forms of all heavy metals, surpassed only by mercury and thus has been assigned to the highest toxicity class, together with cadmium, chromium, copper and mercury (Ratte, 1998). Because of extensive research efforts by the photographic industry since the early 1990s, initiated primarily by the Silver coalition and the Silver Council in the US, our knowledge of the environmental fate and toxicity of silver has changed markedly.

The perception of high silver toxicity has long been due to the fact that most laboratory toxicity experiments tested $AgNO_3$, which readily dissolves, releasing the highly toxic free Ag^+ ion. Because of enhanced heavy metal analyses and experimental techniques (e.g., the ultraclean technique), a better understanding of total silver concentrations in various environmental compartments and, in particular, of silver speciation has emerged (Ratte, 1998).The research has demonstrated that apparent toxicity is related to individual silver species rather than total silver concentration. Overall, silver in the environment can be expected to behave predictably. The majority of the silver released into the environment (>94%) remains in the soil or wastewater sludge at emission sites. Silver from industrial and public wastewater is bound to the activated sludge of wastewater treatment plants. The remaining portion of the silver enters the aquatic environment and, under freshwater conditions, will be adsorbed to sediments or suspended particles immediately at the discharge site and thus are immobilized. A small amount of silver will be kept in solution by colloidal and complexed materials, transported downstream, and enter lakes, estuaries, or the sea.

The existence of various silver species depends on physicochemical environmental conditions. Results of laboratory experiments done by Compell in 1995 and 1996 indicated that the biological response elicited by a dissolved metal is a function of the concentration of the free metal ion. However, as reported for other metals, exceptions to this so-called free-ion activity model (FIAM) of bioavailability have been identified that may also apply to silver.

The toxicity of silver in the aqueous environment depends on the concentration of active, free silver ions. Silver sulfide is perhaps the least toxic of all tested silver compounds because of its low solubility and bioavailability. In soils, sewage sludge, and sediments, in which silver sulfide predominates, the toxicity of silver, even at high concentrations, is often low. A second route of exposure, via the particulate phase (which can lead to contact toxicity), needs to be

considered. Silver nitrate is the most toxic silver compound while silver thiosulfate, a highly soluble compound and main component of wastewaters of photo processors, has lower toxicity (e.g., 15,000 -17,000 times less toxic) than silver nitrate (Erickson, 1998; Cobb et al., 1996). This can be attributed to the silver complexed by thiosulfate, which reduces the bioavailability of free silver ions. In natural waters, ionic silver and some silver complexes are readily adsorbed to particulate matter. As a rule, <25% of the total silver measured in natural waters is dissolved as ion, colloid, and complex (Cobb et al., 1996).

Silver ions are very toxic to bacteria, and bioaccumulation can be investigated only in silver-tolerant species or at low concentrations, which are found in sewage treatment works with wastewater from silver end users. In higher plants and fungi, silver accumulation is expected only in areas contaminated with silver, such as tailings from silver mines, areas with cloud seeding, and soils amended with silver-containing sewage sludge. The plants were grown on soils amended with sewage sludge that was experimentally spiked with silver sulfide. Grasses and agricultural crops accumulated silver to a far greater extent in the roots than other parts of the plant (Hirsch, 1998). Mushrooms were found to have a higher bioaccumulation potential if grown with compost amended with silver and sewage. Bioaccumulation of silver by terrestrial animals has been investigated mainly in domestic animals and laboratory models. Silver concentrations detected in the tissues of domestic animals, which also apply to humans, were relatively low. The silver content in the liver of birds feeding on silver-contaminated food was found to be elevated. In terrestrial invertebrates, elevated silver concentrations were sometimes found (e.g., in snails and worms), although there was no bioaccumulations potential in earthworms (Cobb et al., 1996) pointed out that low silver concentrations do not give rise to concern for acute affects but that chronic, sub lethal exposure of biota to low ionic silver

concentrations could lead to accumulations of silver in various compartments of aquatic ecosystems, which for lont-lived organisms, may lead to toxic body burdens (Ratte, 1998).

1.4 Zinc in soil

The simultaneous presence of several heavy metals is common in contaminated soils due to application of fertilizers, sewage sludge, liming materials, and other industrial and waste materials into natural environment (McIlveen and Negusanti, 1994). This situation can create considerable difficulty in assessing the impact of heavy metal contamination if only considering a single element in the contaminated environment.

Zinc, as a plant-essential micronutrient and hence an indispensable ingredient of the soil system, is among the heavy metals that may be present at elevated levels in contaminated soils and in the vicinity of mining areas. It is always found in silver mining (e.g., The McArthur River mine, one of the world's largest zinc, lead and silver mines). The presence of zinc may have an influence on the sorption and transport of silver. A consequence of heavy metal ion competition maybe mutually suppress Ag and Zn adsorption and enhanced mobility in the soil environment.

1.5 Sorption

1.5.1 Sorption Isotherms

Sorption of Ni on minerals, clay fractions and whole soils had been conducted using traditional batch equilibration methods. The relationship between the equilibrium concentration in the aquatic solution and the amount adsorbed on the solid surface, that is, the partition distribution coefficient is commonly described with adsorption isotherms. Linear and nonlinear forms are usually employed to describe the Ni adsorption on mineral and soil surfaces. The linear equation can be expressed as:

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

where S is the metal sorbed on soil at equilibrium given in mg kg^{-1} and C represented the metal concentration in solution at equilibrium given in mg L^{-1}; hence, the units for K_d values are in L kg^{-1}. Although somewhat simplistic, the K_d approach is easy to integrate into various chemical models and allows estimations of metal dissolved in soil solution and prediction of mobility as well as potential leaching losses (Mellis et al., 2004; Sauve et al., 2000). Covelo et al. (2004) employed the linear form to estimate the competitive sorption and desorption of heavy metals in mine soil and correlated K_d value to principal soil components such as organic matter, Fe oxides, CEC, etc.

Modeling metal sorption using a single-valued K_d approach presumes that the sorption capacity of a material is relatively independent of soil physicochemical properties. However, due to the heterogeneity of the soil matrix, the Freundlich model (Echeverría et al., 1998) is commonly used to model equilibrium batch data. The Freundlich equation is defined as:

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

where K_f is the Freundlich distribution constant; and N is a nonlinear coefficient which is often reported less than one. For N = 1, the Freundlich equation reduced to the linear model Eq. 1.1. Buchter et al. (1989) have measured Freundlich parameters (K_f and n) for 11 different soils and 15 trace elements. They explored the correlation of the Freundlich parameter with selected soil properties and found that pH, cation-exchange capacity, and iron/aluminum oxide contents were the most important factors for correlation with the partitioning coefficients.

1.5.2 Sorption Mechanisms

Because of the intrinsic chemical and physical heterogeneity of soils, it is difficult to describe and predict the kinetics of silver adsorption on soil material with their heterogeneity of the sorption sites, differing in affinities for solute retention. It is of great importance for understanding the fate of Ag in contaminated soils.

Sorption is considered the dominant process in silver partitioning in water and its mobility in soils and sediments. Silver accumulations in marine algae have been reported mainly because of adsorption rather than uptake (Begum, 2002). Several studies suggest that several phenomena occur at the solid/liquid interface: 1) cation exchange at the permanent negative sites on the clay fraction (outer-sphere complexes) and or 2) inner-sphere complexes at specific functional group due an Fe, Mn and Al hydrous oxide and organic matter. Published data on the interaction of silver with soil are rare. However, silver is strongly adsorbed by clays and organic matter (Begum, 2002). The peaty-muck soil sorbed Ag more strongly than the mineral soils, confirming that silver sorption to soils is dominated by soil organic matter either through exchange or complexation.

Sorption of silver to soils (Jones et al., 1986) has been modeled using Freundlich isotherms. Soil organic matter (SOM) is known to bind Ag strongly (Jones and Peterson, 1986; Smith and Carson, 1977) and thus may play an important part in controlling its cycling, mobility, and sorption in soils (Presant and Tupper, 1965; Jones et al., 1990). Both humic and fulvic acids have been shown to have strong retentive capacities of up to 30 mg kg^{-1} for silver (Chen et al., 1978; Jones and Peterson, 1986); thus, biologically available Ag is estimated to be <5% of the total silver concentration (Jones et al., 1984). In contaminated soils, however, this may be enough to adversely affect soil microbial populations.

Other studies have shown that silver is strongly complexed to the reduced sulfur groups on organic matter if given its soft, polarizable nature (Benoit and Rozan, 1997; Adams and Kramer, 1998; Bell and Kramer, 1999). Illitic clays and oxides also appear to be important in retaining silver (Jacobson, 2005). In addition, parameters such as pH and silver concentrations, which may affect the chemical interactions, were also studied. Silver removal is favored at low concentrations and basic pH. Begum in 2002 showed that a greater amount of solids required for

maximum removal at low concentrations, indicating that silver is minimally adsorbed onto the concrete surface, in which research, the concrete were obtained from Portmand cements.

1.6 Statement of Problem

The transport and mobility of Ag in soils are highly depended on adsorption and desorption processes and the competitive influence in the presence of several heavy metals. Moreover, in most studies there is less emphasis on the kinetic aspects of silver and its transport in soils. Kinetic adsorption data have the advantage of accounting for the nonequilibrium sorption behavior which may arise from the heterogeneity of sorption sites on soil surface and slow diffusion process on the interface between the liquid phase and soil matrix.

Based on the review of literature, studies on Ag adsorption and desorption, transport under dynamic flow conditions are limited. Moreover, modeling attempts to describe the transport of Ag in heterogeneous soils have been often unsuccessful. This is perhaps due to the time-dependent, concentration dependent, and multi-reactions of Ag sorption processes. In order to predict the fate of Ag in the soil environment, the incorporation of geochemical reactions into the solute transport models is necessary.

1.7 Objective

In this study, kinetic batch and miscible displacement column experiments were carried out to quantify the retention and transport of Ag in soils having different properties. Measured experimental results were subsequently simulated using nonlinear multi reactions models incorporating equilibrium and kinetic reactions. The specific objectives of this study were: (1) to study the adsorption and desorption kinetics of Ag in soils having different properties; (2) to study the transport of Ag in soils based on the miscible displacement experiment and multireaction transport simulation; and 3) to study the sorption and transport of Ag in the presence of Zn in soils.

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CHAPTER 2: ADSORPTION—DESORPTION OF SILVER IN DIFFERENT SOILS IN THE PRESENCE OF ZN: BATCH EXPERIMENTS AND KINETICS

2.1 Introduction

Heavy metals are commonly considered potential pollutants to the soil and groundwater environment. Major sources of heavy metal contamination including industrial and anthropogenic wastes, mining, and smelting. It is recognized that the fate and transport of heavy metals in soils and geological media is significantly impacted by various interactions in the soil systems.

Silver is a nonessential trace metal. The monovalent silver ion is more toxic to fish than copper or mercury, and it is an extremely effective bactericide (Smith and Carson, 1977). Silver is easily accumulated and adsorbed by soils, which causes significant threats to soil and water environment and ecosystem system (Begum, 2002). Such information on reaction mechanisms is needed for the prediction of Ag adsorption and desorption. Several soil properties influence Ag adsorption, desorption and equilibrium between the solid and solution phases. These factors include soil pH, clay content, organic matter (OM), cation exchange capacity (CEC), and Fe/Al oxides. Specifically, chemical and physical processes occurring at different reaction sites in the soil-solution phase control the level of heavy metal in solution and its transport, therefore influence the release of heavy metal ions to water phases (McIlveen and Negusanti, 1994; Sposito, 1989).

Silver sorption has been studied using equilibrium batch experiments conducted within a short period of reaction time (Jacobson et al., 2005). A study investigated Ag adsorption in different soils. Freundlich isotherms have been used to describe Ag retention by different soils (Jones et al., 1986). They found that Ag adsorption isotherms are predominantly nonlinear in nature. Some studies found that SOM, CEC, and oxides have influence on sorption of Ag in soil

(Jacobson, 2005). SOM is known to bind Ag strongly (Jones and Peterson, 1986; Smith and Carson, 1977). Exchange reactions are purported to play an important role in silver soption to soils (Dyck, 1968; Anderson et al., 1973). Several studies showed that in soils with pH > 4 is that Ag sorbs readily to oxides, particularly iron and manganese oxides, largely by exchange processes (Dyck, 1968; Anderson et al., 1973; Smith and Carson, 1977). However, Anderson et al. (1973) found that the amount of silver sorbed to the manganese oxide is more related to the amount of occluded K and/or Na on the mineral rather than its surface area, and that Ag exchange for structural K, Na, and/or Mn in the mineral structure was another important factor governing its sorption. Thus, structural exchange in poorly crystalline oxides may partially explain the increase in Ag sorption to the soils over time.

Models of the Freundlich and Langmuir type are commonly used to describe equilibrium sorption of heavy metals by soils (Tiller et al., 1984; Voegelin et al., 2001). However, the occurrence of kinetic (non-equilibrium) reaction of Ag with mineral (Begum, 2002), and natural soils (Jacobson, 2005) was commonly observed. The utility of results from short duration (equilibrium) studies to accurately describe non-equilibrium behavior of heavy metals in the soil environment were questioned (Srivastava and Brusseau, 1996; Selim et al., 1992).

Nonlinearity of sorption isotherms may be regarded as a characteristic of site-specific adsorption processes, where adsorption occurs preferentially at the sites with the highest adsorption affinities and available sites with lower adsorption potential are occupied with increasing concentration. Nonlinear or concentration-dependent adsorption influences heavy metal transport in soils, where extremely limited mobility at low heavy metal concentrations is expected.

A study focused on silver removal from aqueous solution by adsorption on concrete particles showed that silver removal is favored by low concentration and high pH. When pH is

decreased, there is a greater concentration of H^+ to compete with Ag^+ for these anionic sites, resulting in lower percent removal (Begum, 2002). Cornelis et al. (2011) carried out studies on the retention and dissolution of engineered silver nanoparticles in natural soils, they found that soils are unlikely exposed to unmodified silver nanoparticles (AgNP). But even if soils are exposed to minor concentrations of unmodified AgNP, it is unlikely that these are persistent, because the dissolution in soil suspensions is fast. The adsorption of Ag is influenced by soil pH, IS, and the presence of organic matter.

A literature search revealed that information on the sorption rate of Ag on soils is limited and most of the studies focused on short-term adsorption. Only a few studies have investigated release or desorption of Ag from minerals and soils.

In this present study, two acidic soils (Olivier loam, Windsor sand) and one non-acidic soil (Webster loam) were used. The major objective was to qualify Ag adsorption-desorption kinetics for soils having different properties. A second object was to assess Ag adsorption in the presence of Zn for different soils.

2.2 Materials and Methods

2.2.1 Soils

Three surface soils having different properties were used in this study. Olivier loam is a fine-silty alluvial soil occurring in the lower Mississippi River basin in Louisiana and southern Mississippi. 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. All 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.

Table 2.1 Selected physical and chemical properties of the soils studied.

Soil		Olivier Loam	Webster Loam	Windsor Sand
Taxonomic classification		fine-silty, mixed, thermic Aquic Fragiudalf	Fine-loamy, missed, mesic Typic Haplaquoll	Mixed, mesic Typic Udipsamment
pH		5.80	6.92	6.11
TOC[a]	%	0.83	4.02	2.03
CEC[b]	cmol kg^{-1}	8.6	27.0	2.0
$CaCO_3$	%	-	3.7	-
Sand[c]	%	5	39	77
Silt	%	89	39	20
Clay	%	6	22	3
Clay mineralogical composition (fraction < 2um)[d]	%	Kaolinite(31%), Illite(30%), Smectite (28%), Quartz(11%)	Smectite (73%), Quartz(11%), Kaolinite(9%), Illite(7%),	Illite(33%), Kaolinite(29%), Chlorite(15%), Smectite (12%), Quartz(10%)
Selective extraction by				
Ammonium oxalate (pH 3.0)				
Fe	g kg^{-1}	0.32	0.98	0.36
Al	g kg^{-1}	0.08	0.89	0.69
Citrate-bicarbonate-dithionite (CBD)				
Fe	g kg^{-1}	4.09	4.42	3.68
Al	g kg^{-1}	1.29	0.77	3.65

[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 and Desorption

Adsorption and desorption of Ag in three different soils was studied using the batch method described by Selim and Amacher (1997). Two duplicate 3-g samples of each soil were placed in 40 ml Teflon centrifuge tubes, and then mixed with 30 ml solutions of 5 known initial $AgNO_3$ concentrations, which were 20, 50, 100, 150, and 200 mg L^{-1}. All solutions were prepared in 0.005 M $Ca(NO_3)_2$ background solution to maintain constant ionic strength. The

tubes were sealed with Teflon screw caps and placed on a reciprocal shaker. The mixtures were continuously shaken and then centrifuged after 1 and 7 days of retention time at 5000 ×g for 10 minutes. After 1 and 7 days of retention time, a 4-ml aliquot was sampled from the supernatant; the total concentration of Ag of the samples was analyzed with inductively coupled plasma-atomic emission spectrometry (Spectro Ciros charge-coupled device[CCD], Spectro Analytical Instruments, Kleve, Germany). Amounts of Ag sorbed by the soil matrix were determined by the difference between the concentrations of the supernatant and that of the initial solutions.

Desorption or release experiments were conducted to assess the release of Ag as well as the extent of kinetic behavior by the different soils. The extent of release or desorption was performed using the batch method described above.

Desorption commenced immediately after the 7-d adsorption step. Tubes in which $AgNO_3$ concentration were 100, 150, and 200 mg L^{-1} were conducted for desorption. Each desorption step was carried out by replacing all the supernatant with 0.005 $Ca(NO_3)_2$ background solution and then shaking for 3 days. The supernatant left in the tube was taken out carefully after samples needed to be analyzed were collected.The silver concentration in the supernatant was measured using inductively coupled plasma-atomic emission spectrometry (Spectro Ciros charge-coupled device [CCD], Spectro Analytical Instruments, Kleve, Germany). The fraction of silver desorbed from each soil was calculated based on the change in concentration of the supernatant solution (before and after each desorption step). Ten desorption steps were conducted. In the last reaction, 8-mL aliquots were collected and no replacement of the background solution was performed.

2.2.3 Competitive Kinetics of Ag and Zn Adsorption and Desorption in soils

To study the influence of Zn on Ag adsorption and desorption, the previously mentioned Ag batch experiments were also carried where with different levels of zinc (Zn) was added in the

solution. Three levels of Zn were used, namely, 50, 100, and 200 mg L^{-1} in three different soils. The form of Zn used was $Zn(NO_3)_2$ in 0.005 M $Ca(NO_3)_2$ as the background solution.

2.3 Results and Discussion

2.3.1 Silver adsorption among different soils

Adsorption isotherms for silver which describe the distribution between Ag in the aqueous solution (C) and that sorbed (S) are presented in Fig. 2.1. These isotherms illustrate the different affinities for Ag, where the lowest sorption was observed for Olivier soil and the highest sorption for Webster soil. This is consistent with other studies that reported strong complexation of Ag by humic and fulvic acids, and by SOM, especially thiol groups (Sillen and Martell, 1964; Boyle, 1968; Smith and Carson, 1977; Jones and Peterson, 1986). Webster soil indicated strong Ag retention which is likely due to the high percentage of clay (22%), total organic matter (4.02%), and amorphous Fe and Al and the presence of carbonates (Table 2.1). Windsor has a higher TOC (2.03%) than Olivier (0.83%) which leads to a higher sorption of Ag. Furthermore, soil pH (Webster Soil: pH = 6.92 , Windsor Soil: pH = 6.11, Olivier Soil: pH = 5.80) also has an influence on the silver sorption of the three soils, higher pH results in more negatively charged sites (Jacobson et al., 2005). Another important reason for Ag immobility in soils is that Ag sorbs readily to oxides, particularly iron and manganese oxides, largely by exchange process (Dyck, 1968; Anderson et al., 1973; Smith and Carson, 1977).

Silver adsorption isotherms describing the distribution between aqueous and sorbed phases for 24 h and 7 d of reaction time are presented in Fig. 2.1-Fig. 2.8. For all three soils, Ag isotherms are highly nonlinear and depict strong affinities or sorption. The Freundlich equation was used to describe these adsorption isotherms as indicated by the solid and dashed. The Freundich equation is one of the oldest nonlinear sorption models and has been used widely to

describe solute retention by soils (Helfferich 1962, Sposito 1984, Travis and Etnier 1981, Murali and Aylmore 1983).

$$S = K_F C^N \qquad [2.1]$$

where S is the (total) amount of solute retained by the soil (mg kg^{-1}), C is the solute concentration in solution (mg L^{-1}), K_F is the Freundich partitioning coefficient (L kg^{-1}), and N is a dimensionless reaction order commonly less than one (Buchter et al., 1989). The distribution coefficient describes the partitioning of a solute species between solid and liquid phases over the concentration range of interest and is analogous to the equilibrium constant for a chemical reaction. The dimensionless parameter N may be regarded as a representation of energy distribution of the heterogeneity of sorption-site, where the highest energy sites are preferentially sorbed at low concentrations, and as the concentration increases, successively lower energy sites become occupied (Sheindorf et al., 1981). In other words, sorption by the highest-energy sites takes place preferentially at the lowest solution concentration. Estimates for the Freundlich parameters N and K_f along with r^2 values are presented in Table 2.2.

Silver isotherm results were described using the Freundlich model of Eq. [2.1] and are shown as the solid and dash curves in Fig. 2.1. The Freundlich model provided a good fit to the data for isotherms with high r^2 values. Based on parameter estimates of the nonlinearity parameter N of Eq. 2.1 given in Table 2.2, silver isotherms are highly nonlinear, with N values ranging from 0.20 to 0.57. Pérez-Novo et al. (2011) has reported a range of N values of 0.42 to 0.60 for acid soils. Nonlinearity and competition are often regarded as characteristics of site-specific adsorption processes. The parameter N represents the order of the nonlinear or concentration-dependent reaction and illustrates the extent of heterogeneity of sorption sites on soil matrix surfaces.

For the 1 d adsorption, K_F values of silver when there were no presences of zinc of the three soils have the order: Windsor (86.11 mL g^{-1})< Olivier (132.37 mL g^{-1})< Webster (208.12 mL g^{-1}). K_F value illustrates the extent of heavy metals affinity among various soil types. It illustrates the extent of Ag affinity among the three different soils. Webster soil with high pH and high CEC soils retained greater quantities of the cationic species than Windsor and Olivier soils. Whereas Olivier has a lower pH 5.80 and CEC 8.6 cmol kg^{-1}, Windsor has a pH 6.11 and CEC 2.0 cmol kg^{-1}, which lead to their lower K_F value and lower sorption. Olivier and Windsor have lower CECs due to their relative low organic matter and clay content dominated by kaolinite and illite and less smectite (Table2.1). Whereas the N values of silver when there were no presences of Zn of the three soils are: Olivier (0.222) < Windsor (0.458) < Webster (0.570). N is a measure of the extent of heterogeneity of the sorption sites having different affinities for solute retention by matrix surfaces. This means that sorption sites have different affinities for heavy metal retention by matrix surfaces, where sorption by the highest energy sites takes place preferentially at the lowest solution concentrations before sites of lower energies. At increasing higher concentration, sorption takes place at sites of decreasing affinities, which results in nonlinear or concentration-dependent isotherms of S vs. C (Selim, 2013). Differences of K_F and N between Olivier and Windsor may be due to differences in pH and CEC.

2.3.2 Silver adsorption with time

Fig. 2.2 is silver adsorption isotherms for three soils for 1 and 7d reaction times. The set of sorption isotherms show increased sorption of Ag with time of reaction, the extent of which varied somewhat among the different soils. As a result the K_F values increased with reaction time for all soils (see table 2.2). For example, the Windsor soil and Webster soil exhibited a strong

Table 2.2. Estimated Freundlich Parameters for 24 h and 7 d of Silver Sorption for all Three soils with different Zn Concentrations

	Ag	Freundlich Parameters									
		1 d					7 d				
	Zn(Ci, mg/L)	K_F mL/g	SE mL/g	N	SE	r^2	K_F mL/g	SE mL/g	N	SE	r^2
Olivier	0	132.37	6.13	0.222	0.011	0.9990	188.37	21.86	0.236	0.029	0.9939
	50	118.94	5.64	0.230	0.011	0.9989	152.00	7.62	0.202	0.012	0.9985
	100	118.98	35.68	0.327	0.069	0.9577	129.87	28.86	0.338	0.052	0.9779
	200	139.74	27.63	0.295	0.046	0.9748	162.02	40.32	0.274	0.059	0.9557
Windsor	0	86.11	27.75	0.458	0.079	0.9824	242.44	18.43	0.285	0.021	0.9976
	50	104.12	6.91	0.376	0.016	0.9990	131.98	18.26	0.367	0.035	0.9955
	100	112.80	5.84	0.435	0.012	0.9991	148.70	24.49	0.398	0.041	0.9892
	200	106.17	11.88	0.444	0.027	0.9950	157.77	20.07	0.370	0.031	0.9903
Webster	0	208.12	21.05	0.570	0.035	0.9944	565.19	20.04	0.273	0.014	0.9974
	50	493.53	23.57	0.361	0.020	0.9967	589.35	35.80	0.321	0.027	0.9895
	100	493.98	81.11	0.401	0.063	0.9701	633.68	36.77	0.343	0.025	0.9949
	200	424.43	35.89	0.429	0.031	0.9935	611.85	32.27	0.337	0.021	0.9960

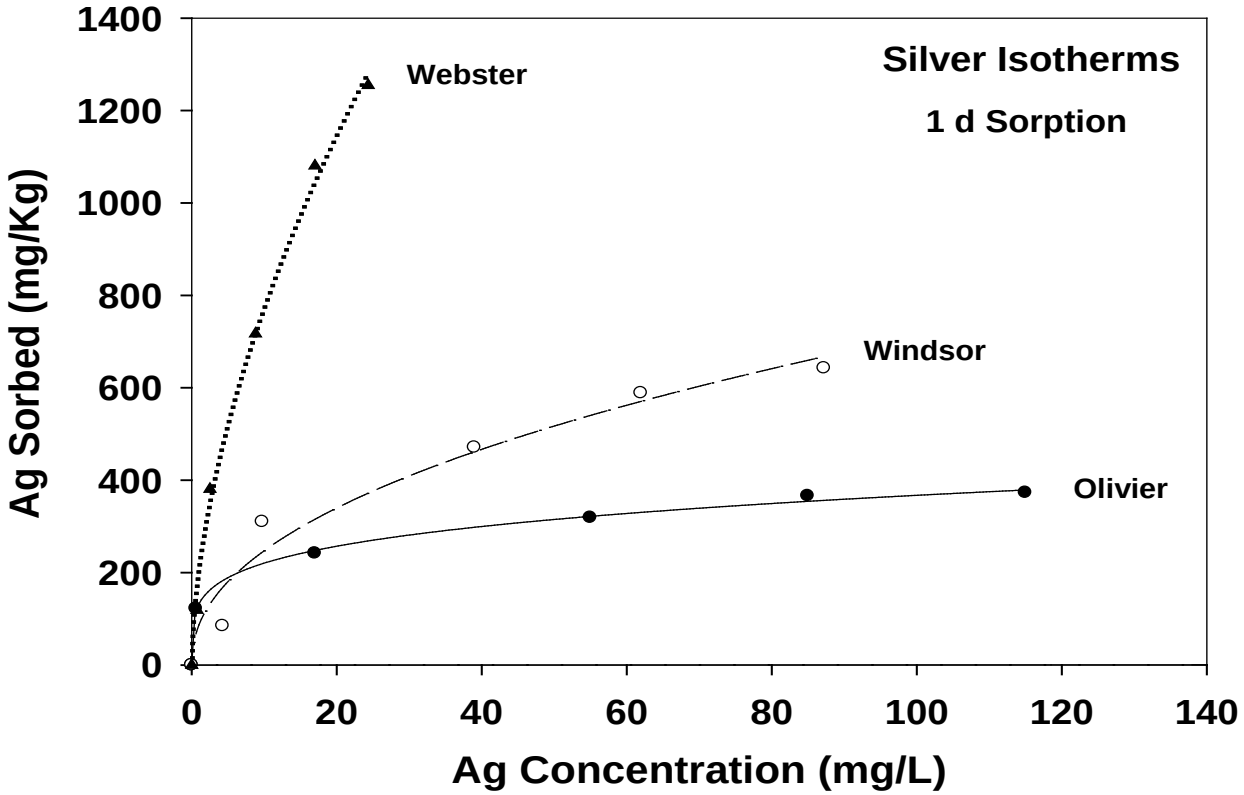

Figure 2.1 Adsorption isotherms for Ag after 1 d for Olivier, Windsor, and Webster soil at Zn = 0 ppm. Curves are simulations using the Freundlich equation.

kinetic behavior, where after 7 d, the K_F value of Windsor soil increased from 86.1 to 242.44 mL g^{-1} and the K_F value of Webster soil increased from 208.12 to 565.19 mL g^{-1}. In contrast, for Olivier soil the K_F value increased from 132.37 to 188.37 mL g^{-1}. Since the parameter N represents the order of the nonlinear reaction and illustrates the extent of heterogeneity of sorption sites on soil matrix surfaces. The decrease of parameter N for Webster may be because after 1 d adsorption, the concentration of the solution in the batches decreased significantly because of the high silver sorption in this soil. Although the sorption of divalent metal ions onto oxides has been reported to be completed within few seconds (Voegelin et al., 2001) and first-order kinetic reactions have been used to quantify various irreversible (sink/source) reactions in soils, including precipitation/dissolution, mineralization, immobilization, biological transformations, volatilization, and radioactive decay, the problem of identifying the fate of solutes in soils must account for retention reactions and transport of the various species in the soil environment (Theis, 1988; Barrow, 1989). Several mechanisms are suggested to be considered as contributions to the kinetics of heavy metal sorption on soils: (1) slow diffusion through intra-particle micropores (Strawn and 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 hydrosides may cause kinetic effects and immobilization of silver. Among the sorption mechanisms mentioned above, the main cause of the difference of silver sorption at different time may be the heterogeneity of sorption sites.

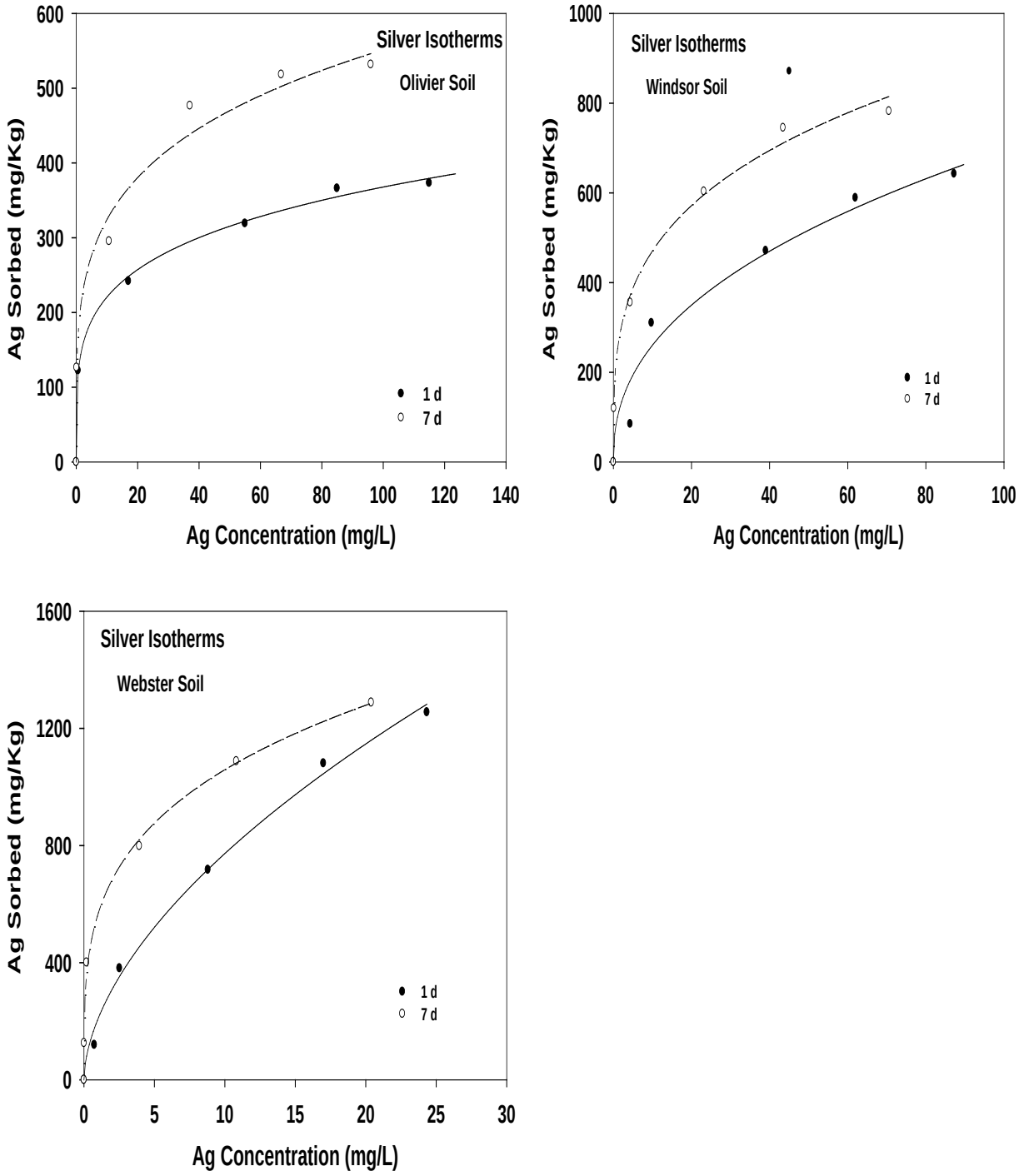

Figure 2.2 Adsorption isotherms of Ag at 1 d and 7 d for Olivier, Windsor, and Webster. Curves are simulations using the Freundlich equation.

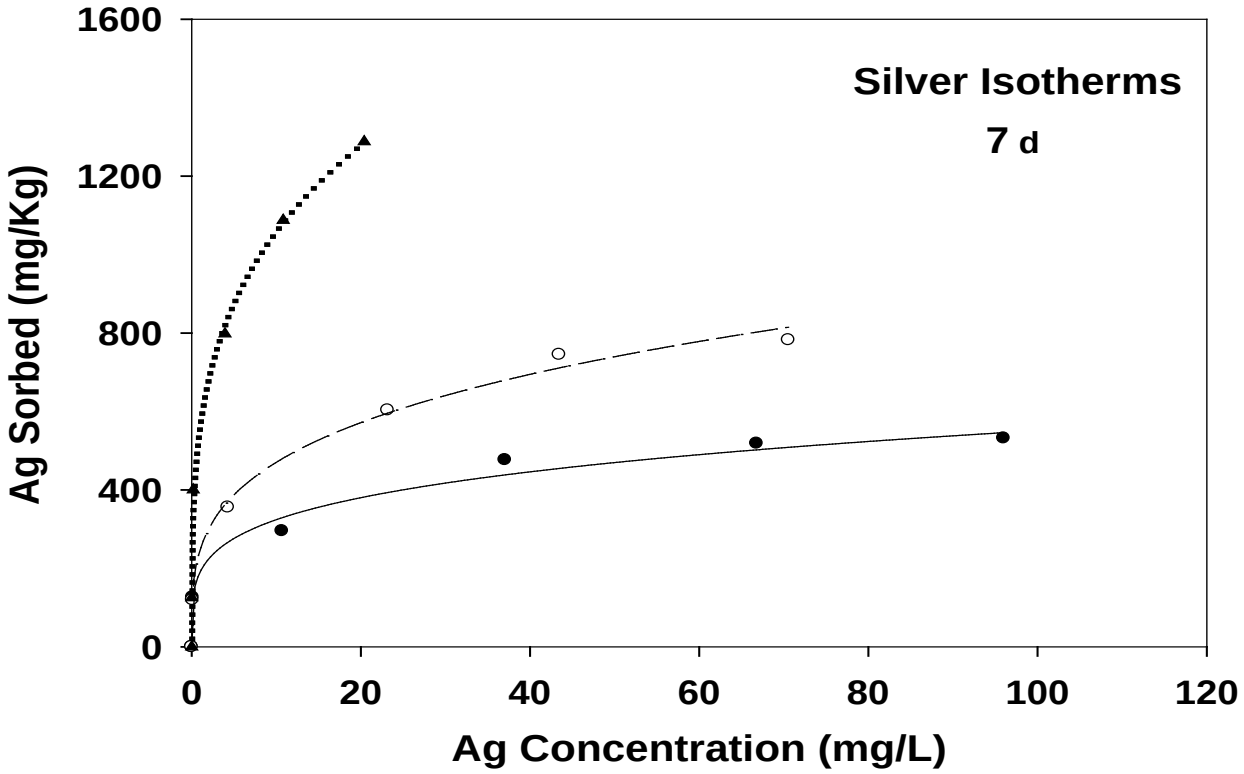

Figure 2.3 Adsorption isotherms for Ag after 7 d for Olivier, Windsor, and Webster soil at Zn = 0 ppm. Curves are simulations using the Freundlich equilibrium.

2.3.3 Ag adsorption in the presence of Zn

The family of isotherms shown in Fig. 2.4 represents Ag sorption in the presence of different initial Zn concentrations (100 mg/L and 200 mg/L) for all soils. The influence of Zn on increased Ag sorption was clearly manifested in the isotherms, where similar trends were observed for acidic soils (Olivier loam and Windsor sand) and neutral soil (Webster loam).

Ion exchange involves electrostatic interactions between a counterion in the boundary layer between the solution and a charged particle surface and counterions in a diffuse cloud around the charged particle. It is usually rapid, diffusion-controlled, reversible, and stoichiometric, and in most cases there is some selectivity of one ion over another by the exchanging surface. Polarization must be considered in examining the selectivity of different ions. Helfferich (1926) has given a selectivity sequence for some of the common cations, in

which Zn^{2+} is easier to be selected than Ag^{+} does. After 1 d adsorption, Olivier, Windsor, and Webster soils sorbed 635.08, 842.34, and 1668.62 mg kg^{-1} silver with initial input Ag concentration 182.9 mg kg^{-1} when there was 100 mg kg^{-1} zinc in the input solution, while it sorbed 601.25, 829.88, and 1621.82 mg kg^{-1} silver with initial input silver concentration 185.2 mg kg^{-1} when there was 200 mg kg^{-1} zinc in the input solution. The presence of Zn decreased the Ag adsorption by soils.

The silver sorption in Webster soil decreased the most when there was zinc added in. The rate of ion exchange in soils is dependent on the type and quantity of inorganic and organic components and the charge and radius of the ion being considered (Sparks, 2003). For Webser soil, TOC and CEC are both higher than Olivier and Windsor soils. Higher percentage of clay also results in the more influence of Zn in the Ag sorption. With clay minerals like kaolinite, where only external exchange sites are present, the rate of ion exchange is rapid. Nevertheless, this still needs to be further concerned.

Figures 2.5 – 2.7 show adsorption isotherms for Ag after 1 d and 7 d for Olivier, Windsor, and Webster soils at Zn = 50 mg/L, Zn = 100 mg/L, and Zn = 200 mg/L. We can find the differences between Ag sorbed amount between 1 d and 7 d are the largest when Zn is 0 mg/L. With the increase of Zn concentration added in, the isotherms for Ag after 1 d and 7 d are closer and closer. This indicates the presence of Zn has an influence on Ag sorption in soils. Compare fig. 2.5, 2.6, and 2.7, we can find that the differences between 1 d and 7 d sorption of Webster soil (alkaline soil, less Kaolinite) in different Zn concentrations did not vary as much as that of Olivier and Windsor soils (acidic soils, more kaolinite).

Compare the parameters K_F and N in Table 2.2, we can notice that K_F values increased with addition of Zn in the solution, illustrating that Zn increased the amount of Ag adsorption in all the three soils. This is consistent with the data from batch experiment in Fig. 2.3. While N

values for the three soils did not vary very much with different Zn concentrations, they are all in a small range: Olivier soil (0.200 – 0.327); Windsor soil (0.389 – 0.444); Webster soil (0.361 – 0.570.

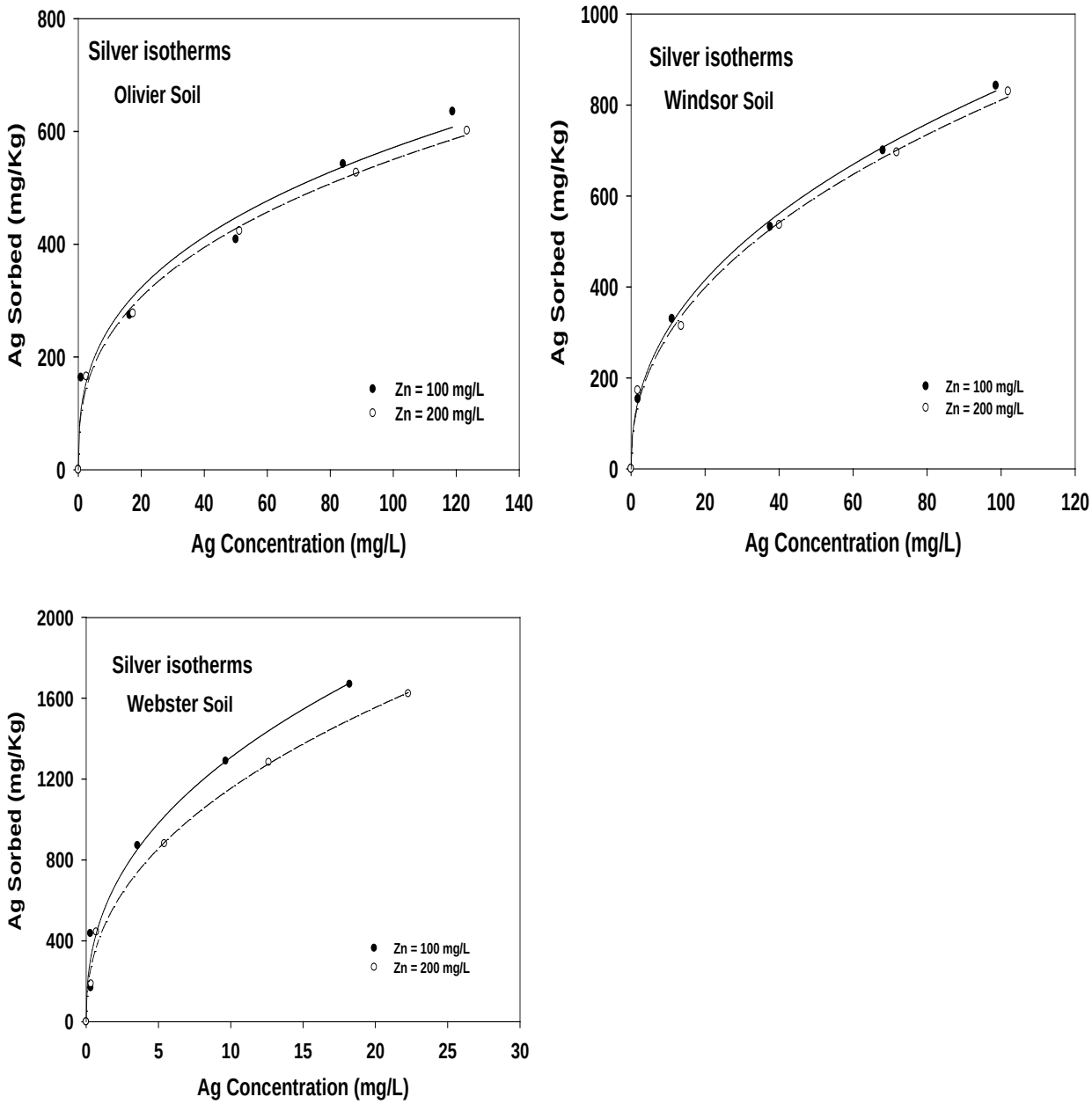

Figure 2.4 Adsorption Isotherms of Ag after 1 d in the presence of different Zn concentrations for Olivier, Windsor, and Webster. Curves are simulations using the Freundlich equilibrium.

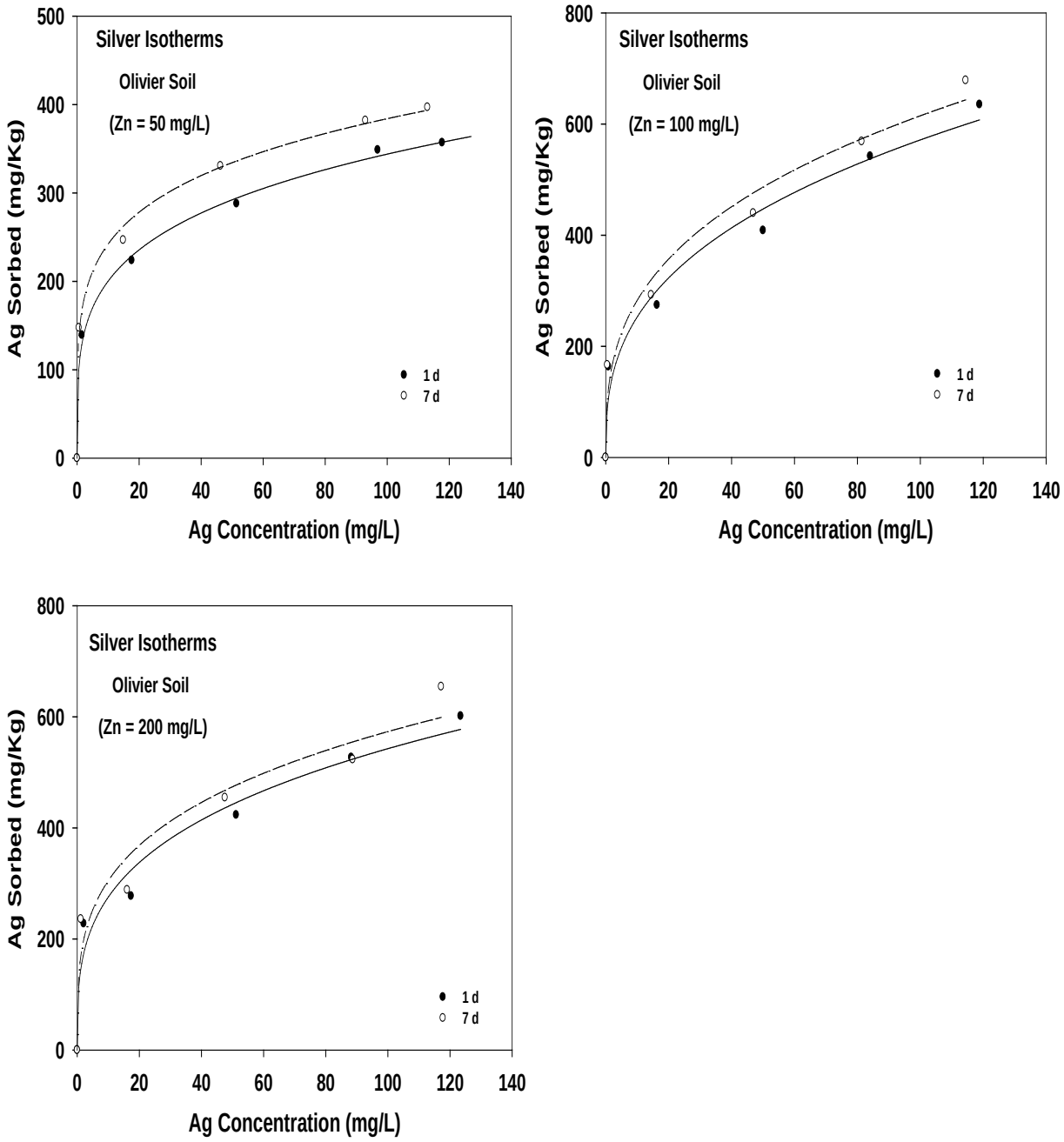

Figure 2.5 Adsorption isotherms for Ag after 1 d and 7 d for Olivier soil at Zn = 50 mg/L, Zn = 100 mg/L, and Zn = 200 mg/L.

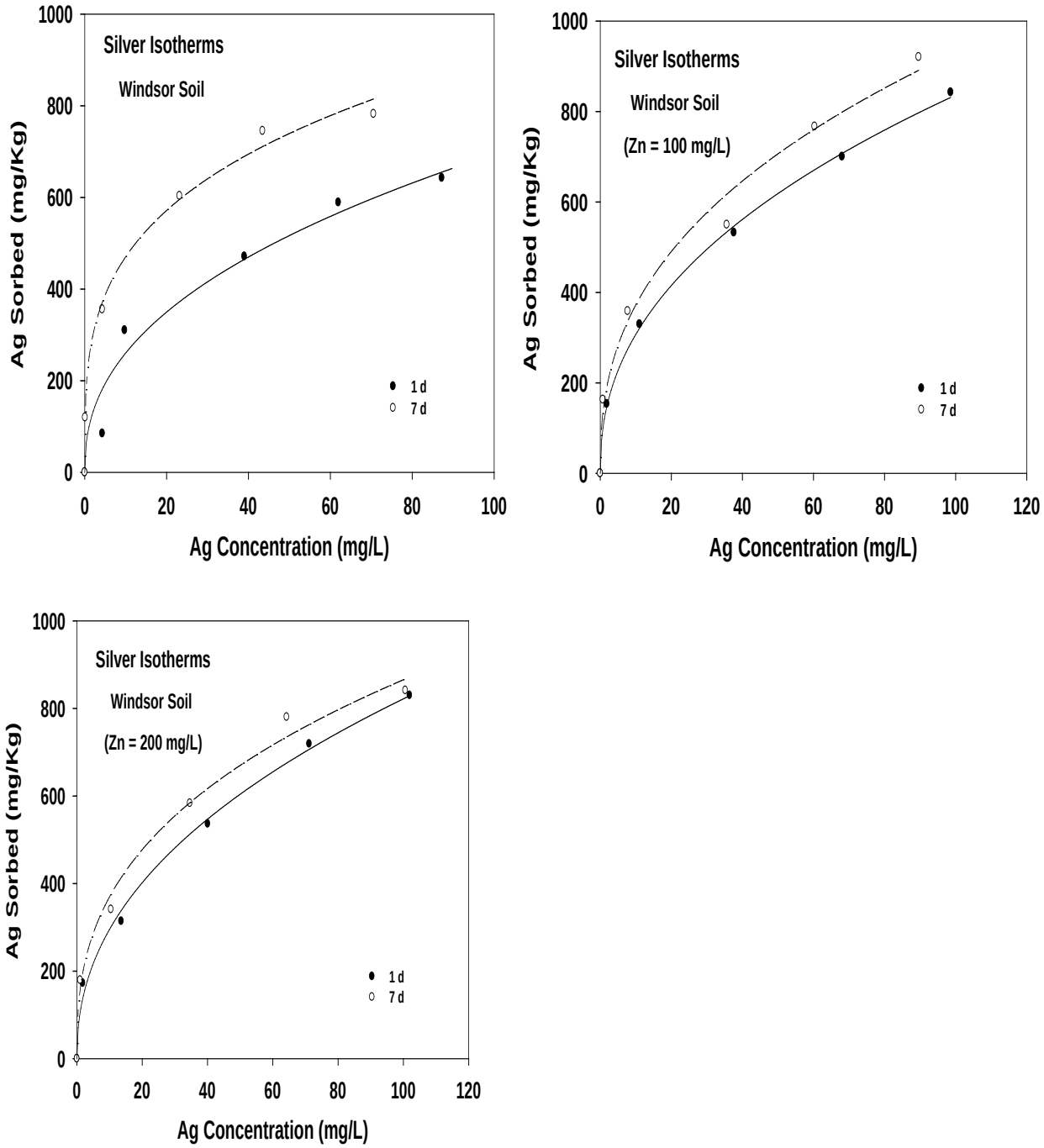

Figure 2.6 Adsorption isotherms for Ag after 1 d and 7 d for Windsor soil at Zn = 50 mg/L, Zn = 100 mg/L, and Zn = 200 mg/L.

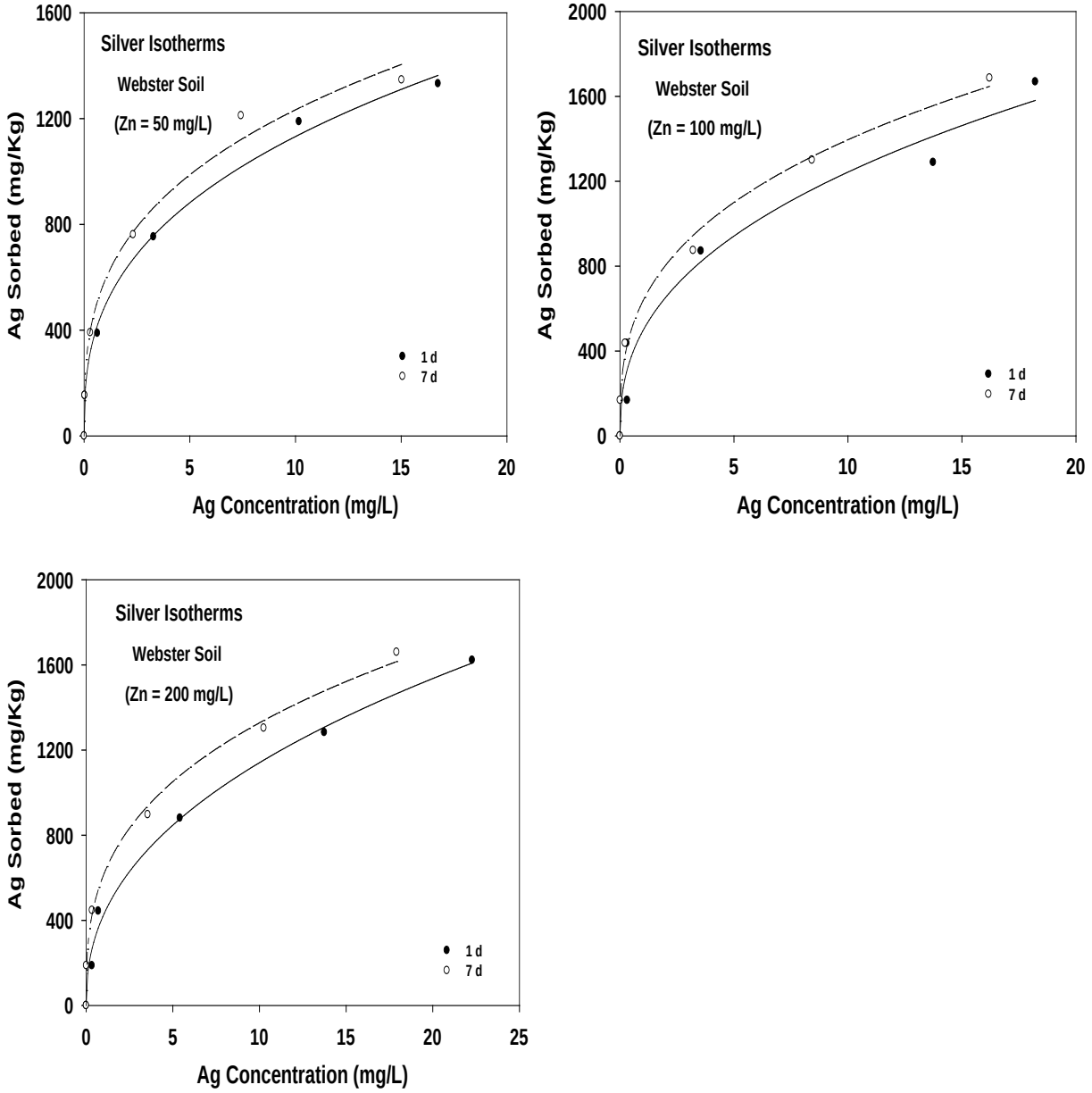

Figure 2.7 Adsorption isotherms for Ag after 1 d and 7 d for Webster soil at Zn = 50 mg/L, Zn = 100 mg/L, and Zn = 200 mg/L.

2.3.4 Ag Desorption

In Figure 2.8, we present the amount of Ag retained vs. reaction time to illustrate the kinetics of Ag desorption for the three soils for the various initial concentrations (C_0) used. As illustrated in the figures, Ag desorption exhibited strong time-dependent behavior as depicted by the continued decrease of the amount sorbed with time. For the Olivier and Windsor soils, the

rate of Ag desorption was initially rapid and followed by gradual or slow reactions. In contrast, the Webster exhibited slow kinetics, as manifested by the slow release of Ag with time. Figure 2.9 shows Ag concentrations in soil solution versus time during adsorption for Olivier, Windsor, and Webster soils. For Olivier and Windsor soils, the concentrations in the soil solution were high at the beginning, and then decrease rapidly. While for Webster soil, the concentrations at the beginning was much lower than Olivier and Windsor soils. They decrease relatively slower with the time. This indicates that a fraction of Ag was strongly or irreversibly sorbed in Webster soil and was predominantly bound via inner sphere surface complexation (Sposito, 1984; Sparks, 2003). While it was weakly sorbed by the Olivier and Windsor soils via ion exchange or outsphere surface complexation.

Figure 2.10, 2.12, 2.14 show Ag sorbed amount in Olivier, Windsor, and Webster soils vs. time during desorption for various initial Ag concentrations when Zn = 50, 100, and 200 mg/L. Figure 2.11, 2.13, 2.15 show silver concentration in soil solutions vs. time during desorption for various initial Ag concentrations when Zn = 50, 100, and 200 mg/L.

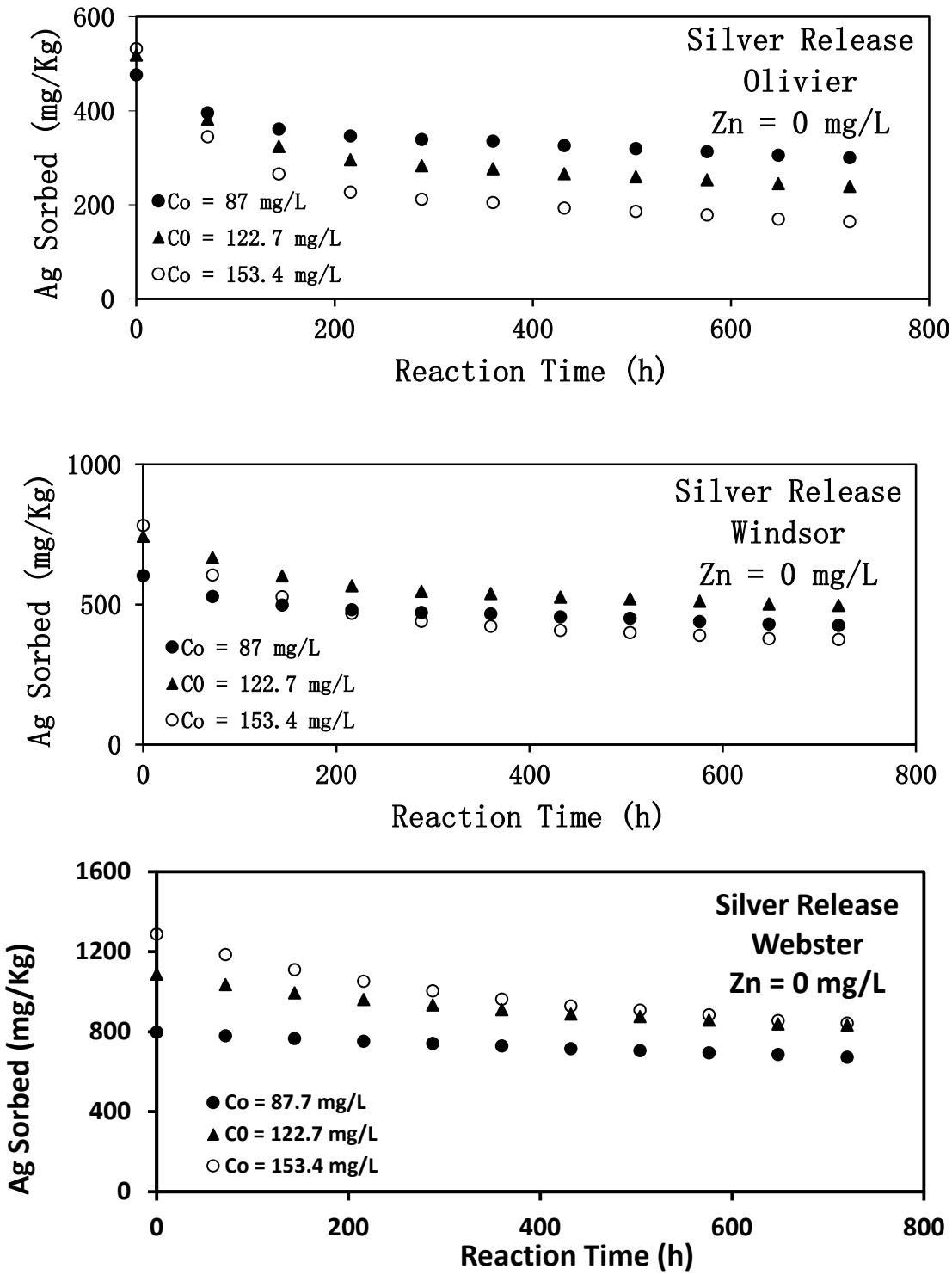

Figure 2.8 Silver sorbed in Olivier, Windsor, and Webster soils vs. time during desorption for various initial Ag concentrations when Zn = 0 mg/L.

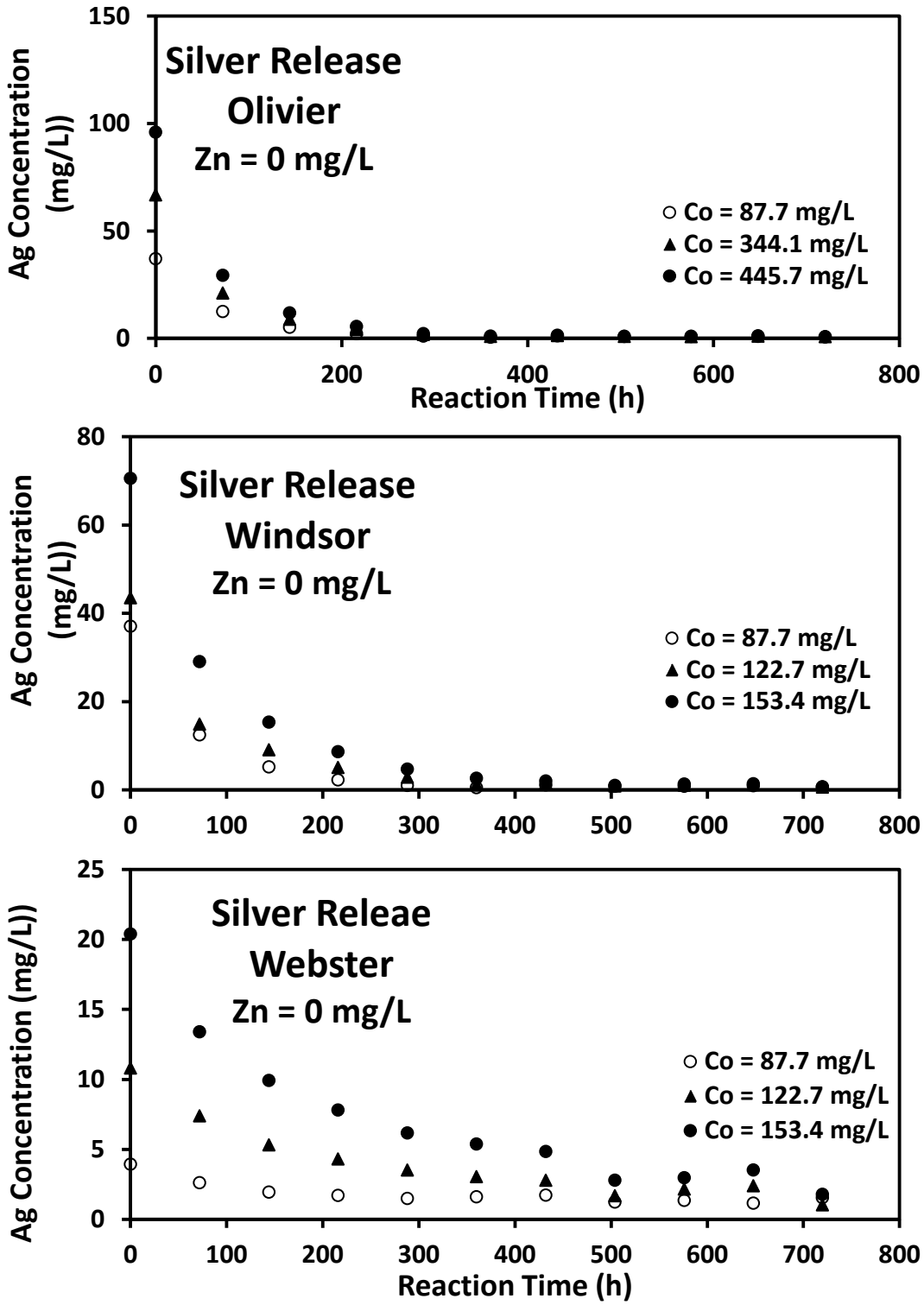

Figure 2.9 Silver concentration in soil solutions vs. time during desorption for various initial Ag concentrations when Zn = 0 mg/L.

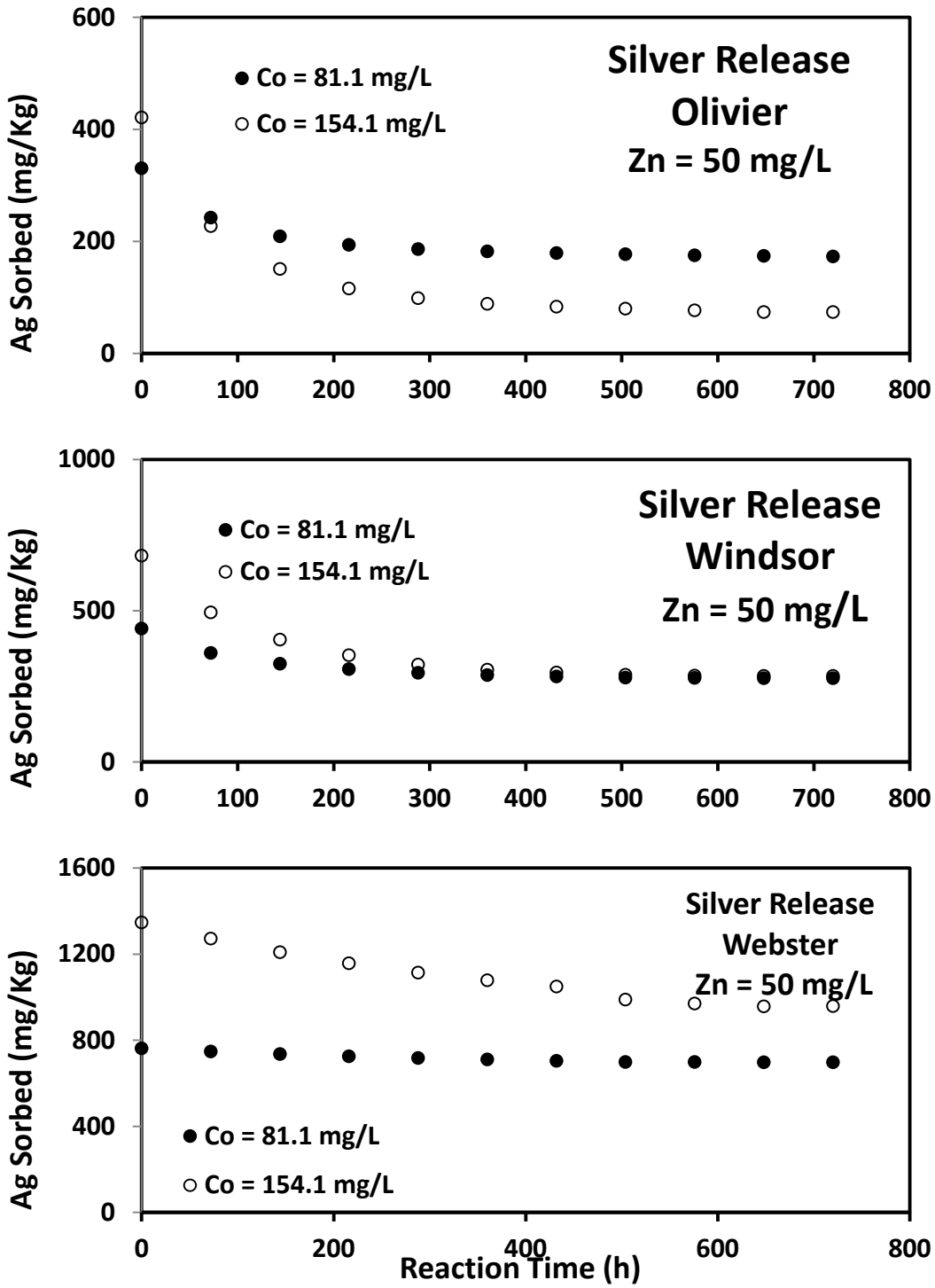

Figure 2.10 Silver sorbed in Olivier, Windsor, and Webster soils vs. time during desorption for various initial Ag concentrations when Zn = 50 mg/L.

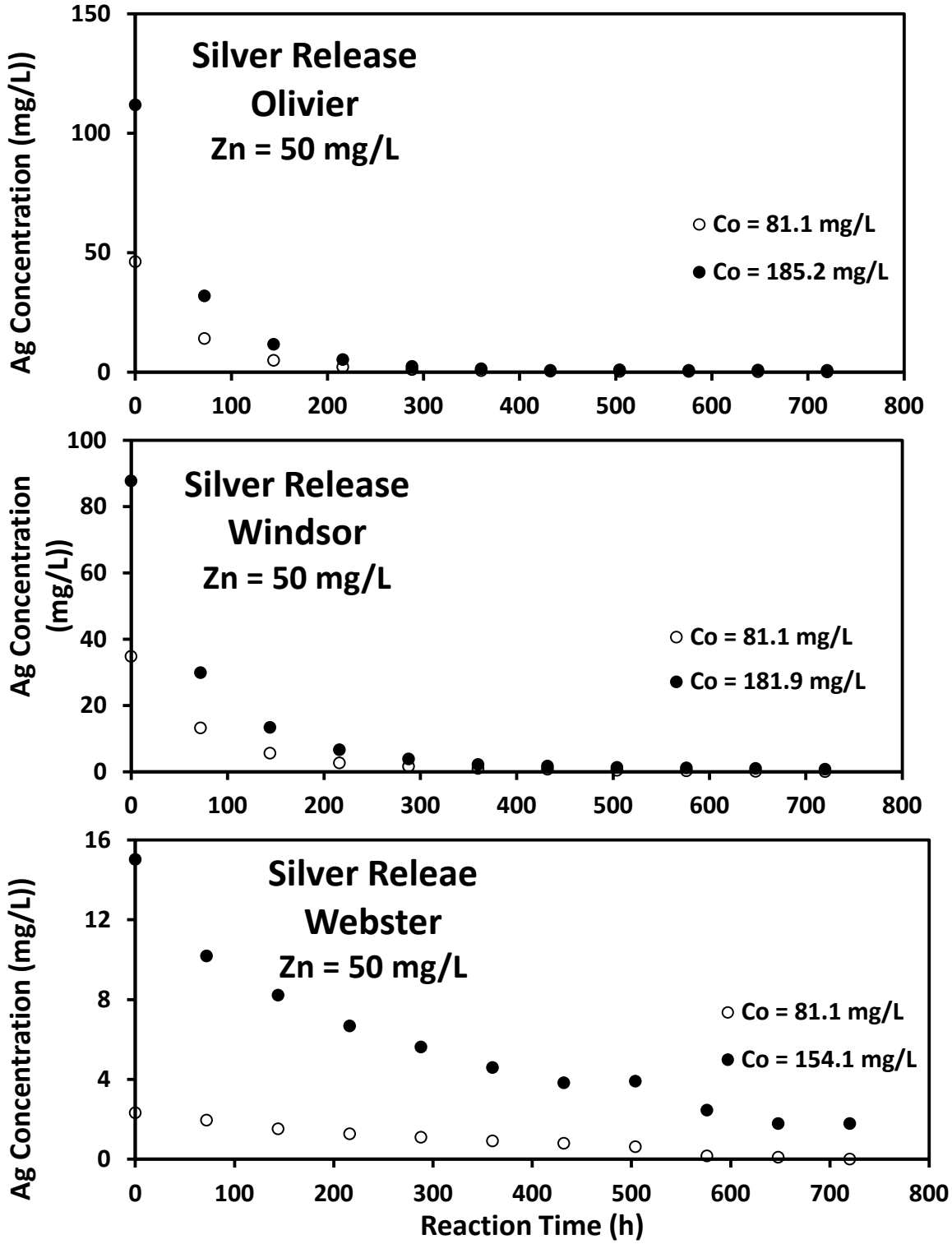

Figure 2.11 Silver concentration in soil solutions vs. time during desorption for various initial Ag concentrations when Zn = 50 mg/L.

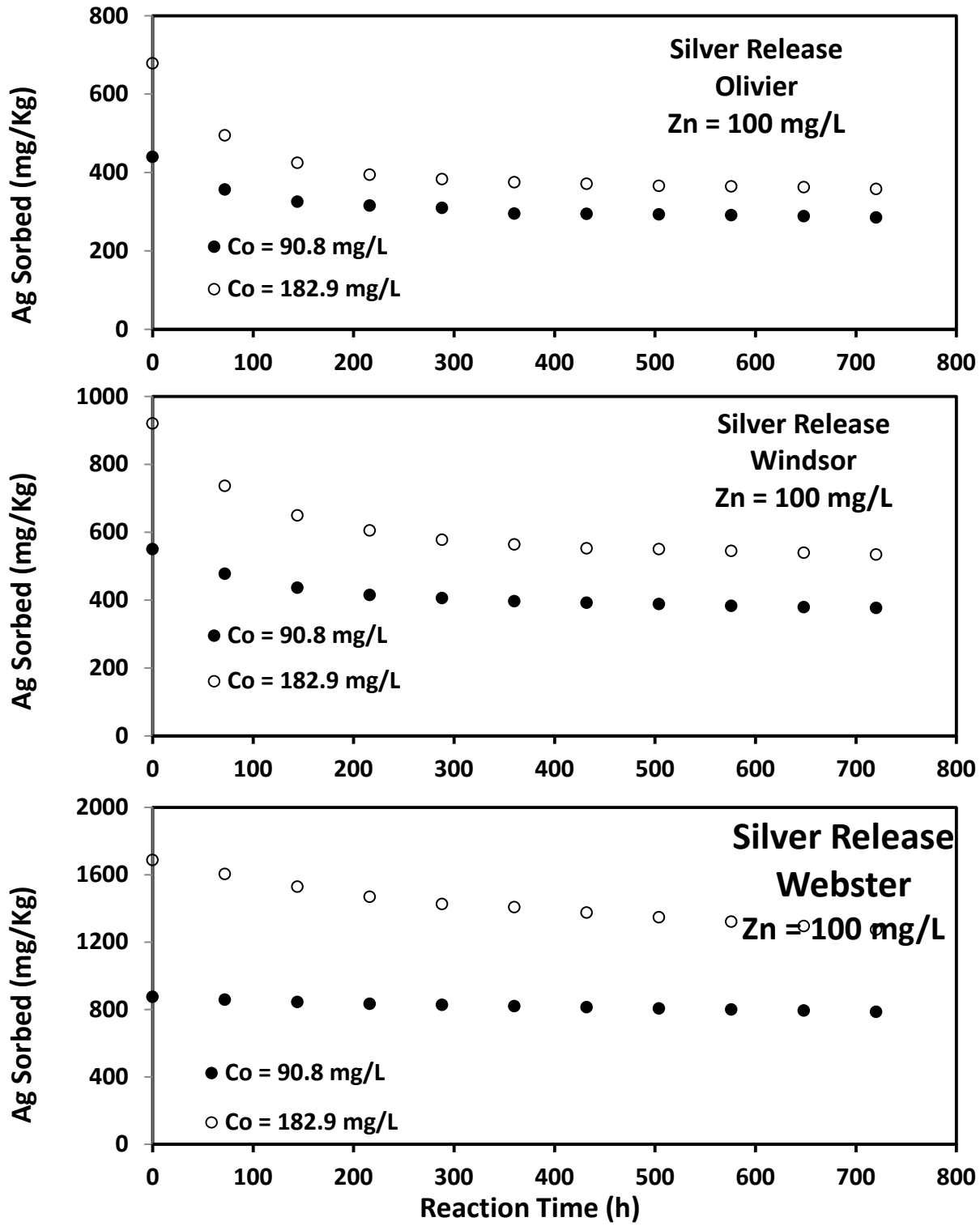

Figure 2.12 Silver sorbed in Olivier, Windsor, and Webster soils vs. time during desorption for various initial Ag concentrations when Zn = 100 mg/L.

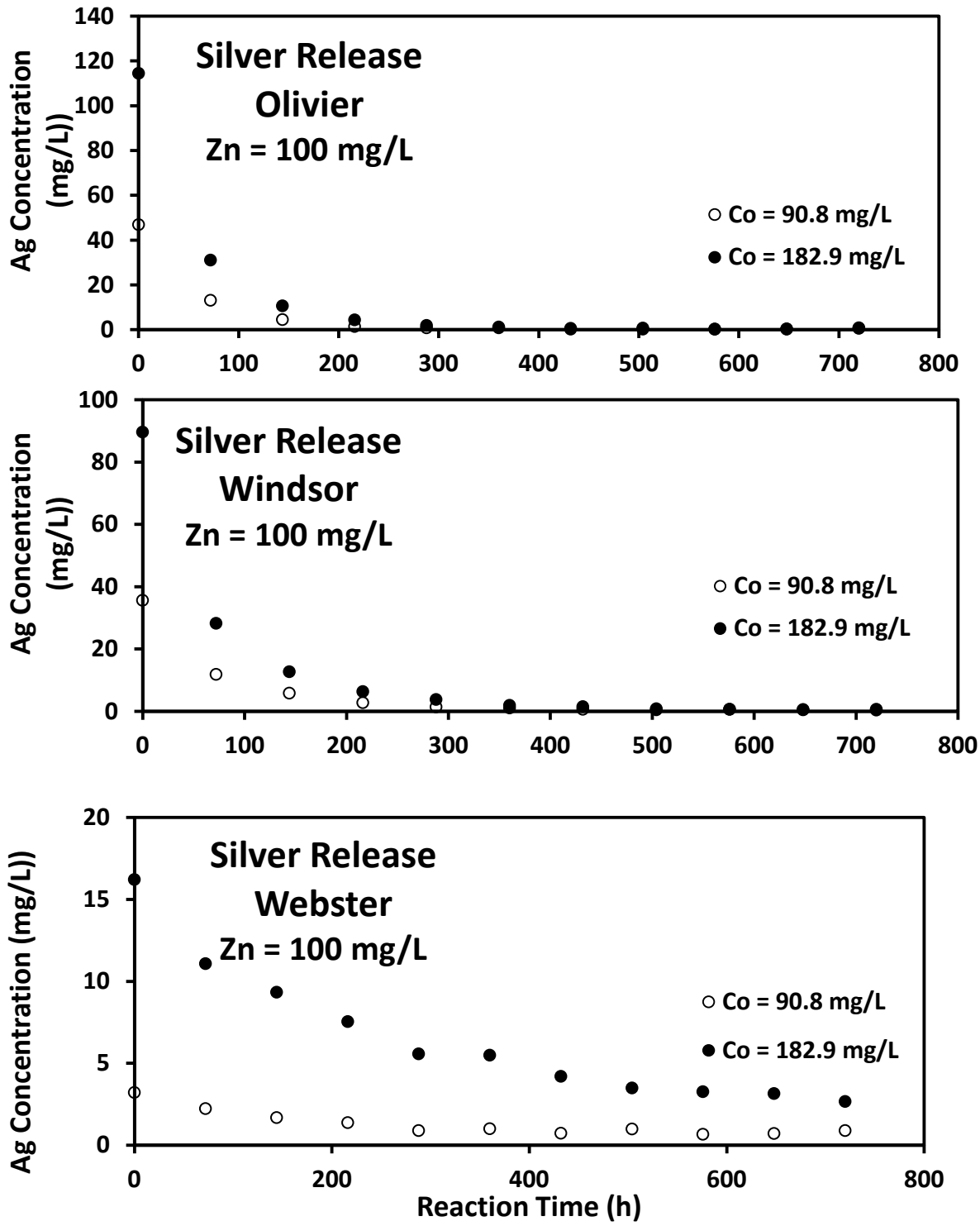

Figure 2.13 Silver concentration in soil solutions vs. time during desorption for various initial Ag concentrations when Zn = 100 mg/L.

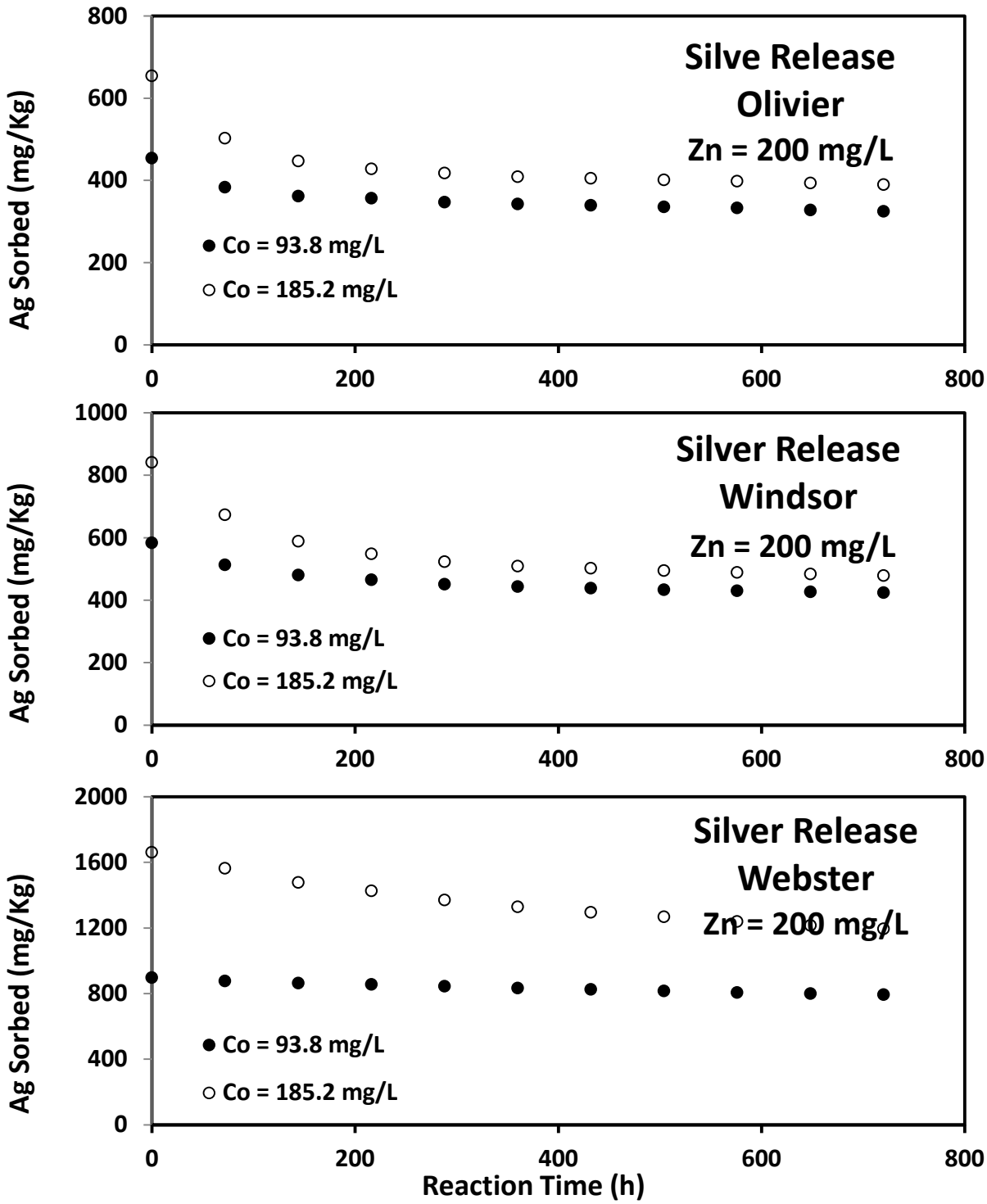

Figure 2.14 Silver sorbed in Olivier, Windsor, and Webster soils vs. time during desorption for various initial Ag concentrations when Zn = 200 mg/L.

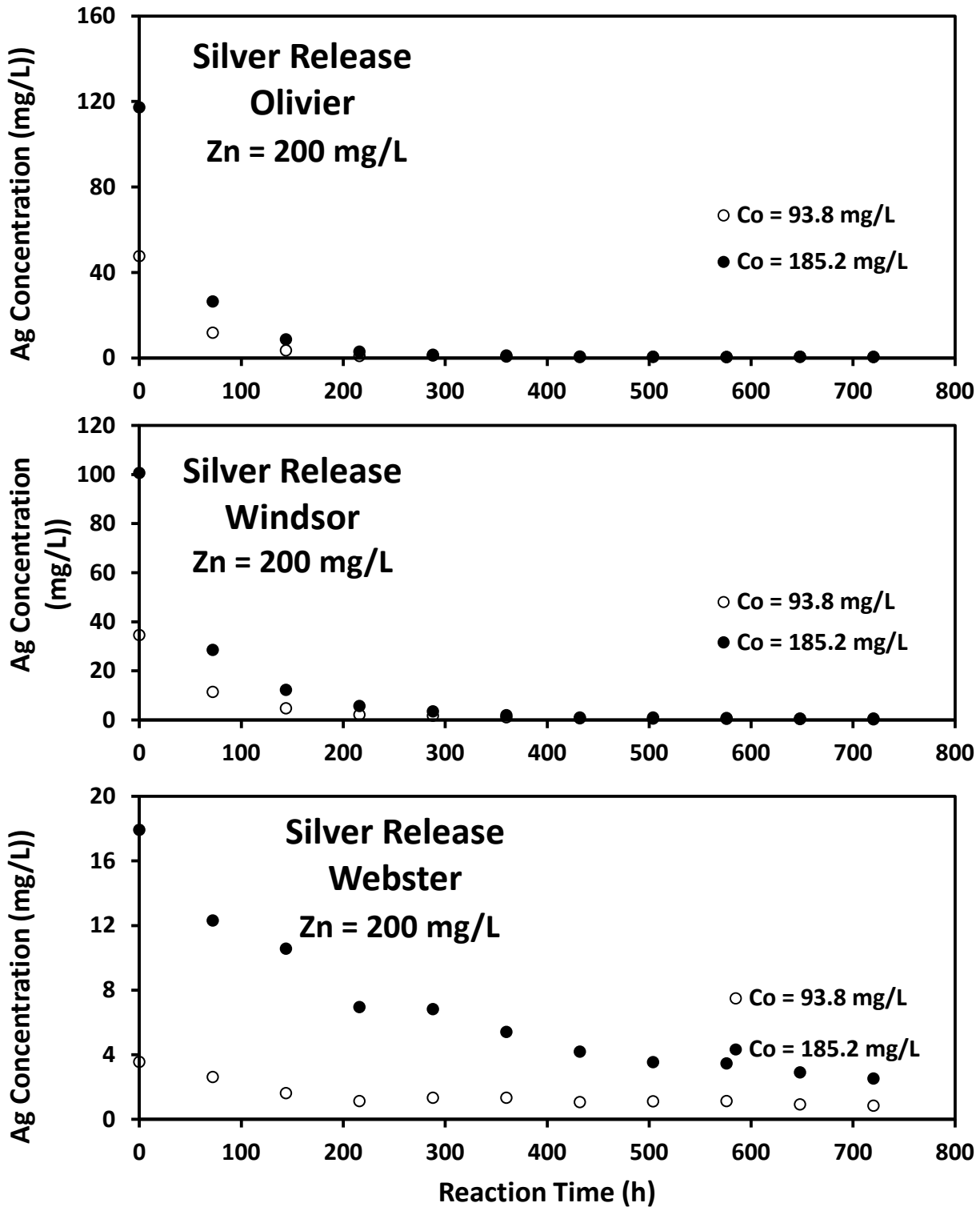

Figure 2.15 Silver concentration in soil solutions vs. time during desorption for various initial Ag concentrations when Zn = 200 mg/L.

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CHAPTER 3: TRANSPORT OF SILVER IN DIFFERENT SOILS: COLUMN EXPERIMENTS AND KINETIC MODELING

3.1 Introduction

Heavy metals in soils pose serious threats to the ecosystem through groundwater contamination, toxicity to plants and accumulation in the food chain. The mobility, bioavailability and toxicity of silver (Ag) in soils is highly dependent on its affinity to bind with different reactive surfaces in the soil matrix and pore water such as particulate and dissolved organic matter, clays or oxide surfaces (Jacobson, 2005). Thus, understanding of the complex transport and mobility of Ag in the environment is a prerequisite in the effort to predict their behavior in the vadose zone.

Several mathematical models were developed to describe heavy metals transport in soils. Earlier scientists proposed linear analytical model to predict solute transport. They assumed that solute transports were due to dispersion alone and local equilibrium occurs instantaneously and reversibly in a homogenous porous medium. Liu et al. (2006) used linear adsorption with the convection-dispersion equation to obtain the retardation factors and dispersion coefficient of Cd, Ni and Zn transport in an acidic soil in China. Their assumptions were acceptable for transport under equilibrium condition or in homogenous porous medium.

Barrow (1989) emphasized that the use of a single reaction and linear equation are not adequate since different reaction sites with different affinities exists for heavy metal and soils. Therefore, the validity of these models for accurately describing non-equilibrium transport phenomena has been questioned (Goltz and Roberts, 1986; Pang and Close, 1999; Hu and Brusseau, 1996; Selim et al., 2001). Transport under conditions where non-equilibrium is dominant is often characterized by retardant and asymmetrical breakthrough curves (BTCs) (van Den Brink and Zaadnoordijk, 1997; Pang and Close, 1999; Goltz and Roberts, 1986; Selim et al.,

1988).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 described the retention and transport of some heavy metal ions in soils (Selim et al., 1992; Zhang and Selim, 2006; Liao et al., 2009).

A literature search revealed little research on the Ag kinetic retention and transport in soils. Such information is a prerequisite in quantifying Ag mobility in the soil environment. In this study, we focused on investigating the mobility of Ag in soils having different properties using miscible displacement column experiments. Our hypothesis was that nonlinear kinetic rather than linear equilibrium reactions are the dominant mechanisms for Ag during transport in soils. To demonstrate the hypothesis, we examined whether the transport of applied Ag in different soil columns can be successfully described based on nonlinear multireaction models which account for kinetic as well as equilibrium retention mechanisms. Furthermore, we also investigated the influence of the presence of Zn in the soil solution on Ag transport in soils.

3.2 Model

3.2.1 Multi-reaction and Transport Model

In this study, a conceptual-type model: multireaction transport model (MRTM) was used to describe kinetic retention behavior and transport of heavy metals in soils. The MRTM accounts for several interaction so heavy metals with soil matrix surfaces soils (Selim, 1992). It is perhaps one of the earliest multisite approaches 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.

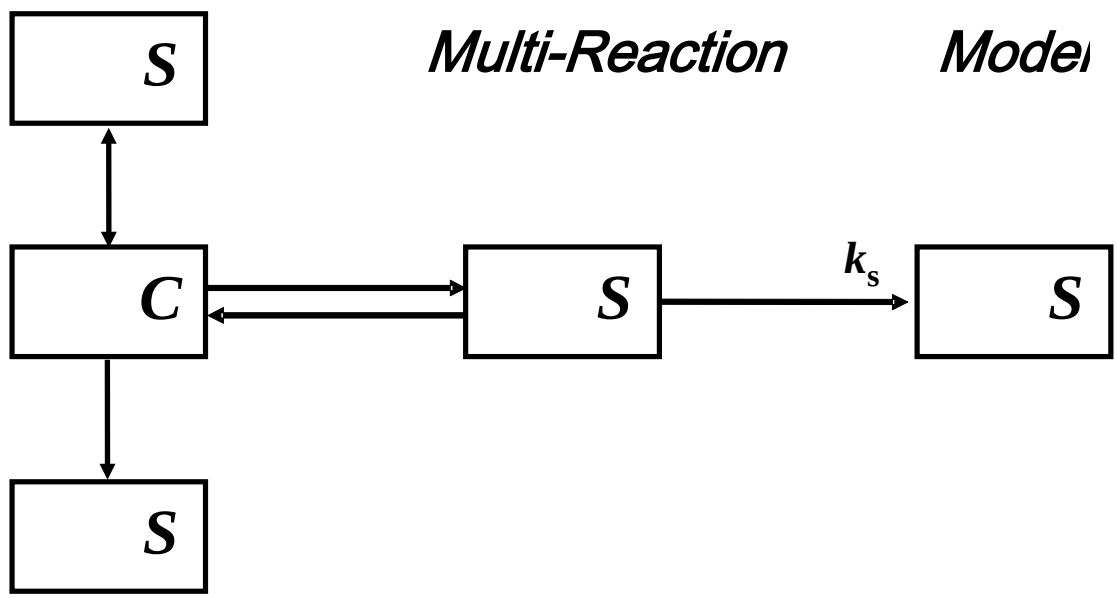

Figure 3.1. A schematic diagram of the multireaction and transport model, where *C* is concentration in solution, *S*e represents the amount retained on equilibrium sites, *S*1 and *S*2 represent the amount retained on reversible kinetic sites, S_{irr} and S_s represent the amounts irreversibly retained, 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,

$$S_e = K_e \frac{\theta}{\rho} C^n \qquad [1]$$

$$\frac{\partial S_k}{\partial t} = k_1 \frac{\theta}{\rho} C^m - (k_2 + k_s) S_k \qquad [2]$$

$$\frac{\partial S_s}{\partial t} = k_s S_1 \qquad [3]$$

$$\frac{\partial S_{kirr}}{\partial t} = k_{kirr} \frac{\theta}{\rho} C \qquad [4]$$

where S_e is the amount retained on equilibrium sites (mg kg^{-1}), S_k is the amount retained on kinetic sites (mg kg^{-1}), S_s is the amount retained irreversibly by consecutive reaction (mg kg^{-1}), S_{irr} is the amount retained irreversibly by concurrent type of reaction (mg kg^{-1}), C is concentration in solution (mg L^{-1}), ρ is the soil bulk density (g cm^{-3}), θ is the water content (m3 m^{-3}), n and m are dimensionless reaction order commonly less than 1, K_e is a dimensionless equilibrium constant, k_1 and k_2 (h^{-1}) are the forward and backward reaction rates associated with kinetic sites, respectively, k_{irr} (h^{-1}) is the irreversible rate coefficient associated with the kinetic sites, and k_s (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:

$$S = S_e + S_1 + S_2 + S_s \qquad [5]$$

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] to [4] were incorporated into the one-dimensional reactive convective-dispersive transport equation (CDE) under steady water flow

$$\rho \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t} = \theta \frac{\partial^2 C}{\partial z^2} - q \frac{\partial C}{\partial z} \qquad [6]$$

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

3.2.2 Linear Modeling

We also utilized a linear model to describe transport results from the miscible displacement column experiments. Specifically we used the linear model CXTFIT as described by Toride et al. (1999). This analytical model was utilized to solve the inverse problem based upon the CDE where linear equilibrium sorption was assumed. To account for irreversible reactions, the CXTFIT version selected here 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,

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - \mu C \qquad [7]$$

where R is a dimensionless retardation factor ($R = 1 + \rho K_d/\theta$), and K_d is a partitioning coefficient (mL g^{-1}). In Eq. [14] the term R accounts for linear equilibrium sorption. The rate coefficient μ (h^{-1}) associated with the sink term (μC) captures irreversible retention (or removal) of a chemical directly from the soil solution based on first-order decay. Since heavy metals do not undergo decay or degradation, we consider this term as that for irreversible retention equivalent to that associated with k_{irr} (Eq. 7) of the MRTM model of Fig. 1. Analytical solution of the linear model subject to the above boundary and initial conditions is given in Selim and Amacher (1997).

3.2.3 Optimization and Curve Fitting

The MRTM and linear models described above were utilized in an inverse mode to describe Ag as well as Zn transport results from the column miscible displacement experiments. Specifically, each model was fit to the transport data using a nonlinear, least-squares curve-fitting method. The curve-fitting method is basically the maximum neighborhood method of Marquardt (1963) and is based on an optimum interpolation between the Taylor series method

and the method of steepest descent (Daniel and Wood, 1973). Criteria used for estimating goodness-of-fit of the model to the data were the coefficient of determination (r^2) and the root mean square error (RMSE) statistics,

$$RMSE = \sqrt{\frac{rss}{N_d - P}} \qquad [8]$$

where *rss* is the residual sum of squares, N_d is the number of data points and P is the number of fitted parameters.

3.3 Materials and Methods

3.3.1 Soils

Three surface soils having different properties were used in this study. Olivier loam is a fine-silty alluvial soil occurring in the lower Mississippi River basin in Louisiana and southern Mississippi. 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. All 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 Column Transport

To quantify the mobility of Ag in the above soils, a series of miscible displacement column experiment as described by Zhang and Selim (2006) were carried out. The column experiments were conducted in saturated soil for the three soils: Olivier, Windsor, and Webster. Air-dry soils was uniformly packed into acrylic columns (5-cm in length and 6.4-cm of inner diameter) and then the columns were slowly water-saturated with 0.005 M $Ca(NO_3)_2$ as a background solution where upward flow was maintained. Before and after soil packing, each

column with and without the soil was weighed. From the weight and volume of the column, soil bulk density and water content were calculated. A piston pump (FMI lab pump, Model QG 6, Fluid Metering Inc., Oyster Bay, NY) was used to ensure a constant flux of the solution in the soil column. To ensure saturation, each column received 10 to 20 pore volumes of 0.005 M $Ca(NO_3)_2$ background solution prior to the introduction of silver solution.

Following saturation a pulse of 200 mg L^{-1} $AgNO_3$ in 0.005 M $Ca(NO_3)_2$ was introduced into each column. Olivier and Windsor columns received a Ag pulse of 40-45 pore volume. Since low Ag recovery in the effluent solution from out miscible displacement column experiment of Webster soil, a larger pulse (90-95 pore volume) was applied to the Webster soil. The Ag pulses were followed by several pore volumes of the background solution. Column effluent was collected using an ISCO fraction collector (model Retriever II, Teledyne Isco Inc., Lincoln, NE). During pulse application, column flow was completely stopped for 2 day duration to evaluate the influence of flow interruption on Ag retention and transport. The samples collected were analyzed by ICP-AES (Spectro CItros CCD, model CCD; Spectro Analytical Instruments, Kleve, Germany).

During pulse application, column flow was completely stopped for 2 day duration to evaluate the influence of flow interruption on Ag retention and transport. Moreover, the pH and Eh of the effluent solution was monitored frequently during the miscible displacement experiments.

To investigate the influence of the presence of Zn on Ag reactivity and mobility in the three soils, another set of miscible displacement column experiments was performed where a mixed pulse of Ag and Zn was introduced. Here the pulse solution contained a mixture of 200 mg L^{-1} Ag as $AgNO_3$ and 200 mg L^{-1} Zn as $Zn(NO_3)_2$ in 0.005 M $Ca(NO_3)_2$ background solution.

The volume of each applied pulse, along with associated soil parameters for each column, is presented in Table 3.1.

The volume of each Ag pulse, along with the associated soil parameters for each column, is presented in Table 3.1.

Table 3.1 Physical parameters for all three soils.

Soil	**Ion**	**Bulk density**	**Water content**	**Darcy flux**	**Pore volume**	**Pulse**
		g cm^{-3}	m^3 m^{-3}	cm h^{-1}	cm^3	pore volumes
Olivier	Ag	1.240	0.532	10.59	85.601	42.45
Olivier	Ag+Zn	1.258	0.546	11.27	84.484	44.07
Windsor	Ag	1.169	0.509	11.86	89.906	38.36
Windsor	Ag+Zn	1.156	0.487	10.00	90.661	35.31
Webster	Ag	1.150	0.517	13.08	91.038	95.63
Webster	Ag+Zn	1.100	0.508	12.00	94.057	93.21

3.3.3 Distribution in Soil versus Depth

Due to the strong affinity of Ag and Zn to soils, complete recovery of applied heavy metals in the soil columns was not expected. Therefore, the distribution of heavy metals retained by the soil matrix vs. soil depth provides essential information on the extent of their mobility in the soil profile. Following the termination of each column experiment, the column was sectioned into 5 equal sections of 1 cm in length. The soil was then dried and the amount of Ag sorbed or retained by the soil in different depth was determined using an Innov-X Delta Premium PXRF as a screening method (USEPA, 2007).

3.4 Results and Discussion

3.4.1 Silver Transport

Silver breakthrough results (BTCs) for all three soil columns are shown in Figure 3.2 to 3.4. These BTCs, which exhibit the extent of Ag mobility, indicate extensive transport of Ag in Olivier and Windsor soils, whereas less mobility was observed in Webster. Olivier soil exhibited

highest recovery in the effluent 84.20%, whereas Windsor soil showed a lower recovery of 64.75%. Webster soil showed lowest recovery 75.83% among all soils.

For Olivier soil, the BTC in Fig. 3.2 reached the highest concentration of some 80% of that applied (C/C_0 = 0.794) after 16 pore volumes. During the pulse time, we had a 2-day flow interruption at 25.92 pore volumes a small decrease of Ag concentration was observed. After 9 pore volumes, Ag was detected in the effluent solution. This is indicative Ag sorption due to physical or chemical nonequilibrium in this soil. During leaching, the Ag concentration exhibited a gradual decrease with time and reached low concentration (C/C_0 = 0.053) after 70 pore volumes. Slow release or tailing of the Ag BTCs is probably due to kinetic reactive with soil matrix surfaces (Selim and Amacher, 1997). Based on the area under the BTCs, 84.20% of the applied Ag was recovered in the effluent solution. It's a strong indication of the high mobility of Ag in Olivier soil.

For the Windsor soil, the BTC shown in Fig. 3.3 shows less Ag mobility than that for Olivier soil, as indicated by the late arrival of Ag in the effluent. The BTC reached a peak concentration C/C_0 = 0.805 after 33 pore volumes. Moreover, a significant decrease in concentration occurred due to flow interruption. After about 20 pore volumes of leaching, the decrease rate of Ag concentration slowed down and reach a gently drop. The recovery of applied Ag in Windsor soil was 64.75% which is significantly lower than Olivier.

For the Webster soil, the BTC shown in Fig. 3.4 indicates strong sorption and limited mobility of Ag. This is manifested by the lower recovery of Ag in the effluent solution (75.83%) compared to the other two soils maximum considered the double pulse (95.63 pore volumes). The Ag concentration did not reach a stable phase like Olivier, the BTC kept going up until leaching started. We can notice that there are two drops in the BTC, they was a flow interruption for half an hour. Considered the short interruption time compared with 2 days for Olivier and

Windsor soils, the decrease was significant. After leaching started, the Ag concentration started going down gently. Such strong Ag retention is consistent with the isotherm results, where the amount of Ag sorbed by Webster soil is much more than Olivier and Windsor soils. This is primarily due to the higher percentage of clay, organic matter, and amorphous Fe and Al and the presence of carbonates compared with Olivier and Windsor soils.

3.4.2 Model Fit

The solid and dashed curves shown in Figure 3.2 to 3.4 are simulations based on the MRTM and linear model for the three soils. Associated model parameters that provided the simulations shown along with their goodness-of-fit statistics are given in Table 3.2. A comparison of simulated BTCs and measured Ag effluent results presented in Figure 3.2 to 3.4 illustrates better overall predictions using MRTM when compared to the linear.

The MRTM accounts for several possible interactions of Ag within the soil system. As a result, different versions of the model shown in Fig. 3.2 represent different reactions from which Ag retention mechanisms can be deduced. Several versions were attempted to get the best prediction. A version with a three-parameter model with k_1, k_2, and k_s (V_1), a four-parameter model with k_1, k_2, k_s, and k_e (V_2), and another three-parameter model with k_1, k_2, and k_{irr} (V_3) were examined. These versions assumed the presence of at least a fraction a fraction of retention sites that interacted reversibly (kinetic) and others that were kinetic but irreversible or slowly reversible. The linear model with only k_e and k_{irr} which means only equilibrium and irreversible mechanisms were considered.

As illustrated in Figure 3.2 to 3.4, the linear model overpredicted the mobility of Ag in all soils. During leaching, the linear model did not predict the slow release of Ag (right side of the BTCs) in all soils. Linear model simulations indicated earlier arrival of Ag in the effluent solution than observed for the three soils. Parameter values that provided the simulations using

the linear model are given in Table 3.3. A comparison of the goodness-of-fit statistics from the linear and MRTM models illustrates the shortcoming of the linear model (see Table 3.3). Nevertheless, the linear model is adequate for predicted maximum concentration and to lesser extent the arrival of Ag in the effluent in leaching.

In an effort to describe the behavior of Ag and to achieve the MRTM predictions shown in Figure 3.2 to 3.4, several model versions were attempted; only simulations using the best predictions are shown. The model versions that provided best predictions of the three soils (V1) with kinetic reactions dominantly (S_k and Ss phases with k_1, k_2, and k_s). Four-parameter model version did not improve the model predictions much, which suggests overfitting of the model (Ma and Selim, 1997). Based on the four-parameter model (V3), k_1 was an order of magnitude larger than k_2 (see Table 3.2). Since adding S_e did not have a significantly improvement in the prediction, model version (V_1) is preferred. For Webster soil, several model versions equally produced good predictions of the Ag BTCs, as shown in Table 3.2. Nevertheless, best prediction was obtained using model version (V1).

The extent of heterogeneity of Ag retention reactions in Olivier and Windsor soils are manifested by the sharp decrease in the Ag concentration in the effluent solution during the early stages of leaching, as shown in Fig. 3.2 and 3.3. A sharp decrease in concentration was not observed for Webster soil. We observe that a decrease in concentration maxima and a shift of the BTCs to the left (or right) resulted as the value for $k_2$decreased. Such a shift of the BTCs signifies an increase in solute retention due to the influence of the kinetic mechanism associated with S_1. As the rate of backward reaction (k_2) decreases or k_1/k_2 increases, the amount of S_1 retained increases and solute mobility in the soil becomes more retarded.

From Fig. 3.2, 3.3, and 3.4, there were concentration decrease during the pulse, for Olivier and Windsor, they were caused by flow interruption of two days, while for Webster soil,

it was a flow interruption of half an hour. During the time, the decreases of Ag concentration were caused by the kinetic reaction between Ag and soil particles. Since the short interruption time in Webster soil compared with Olivier and Windsor soils, the concentration decrease in Webster is significant; this indicates that there were more kinetic in Webster soil than Olivier and Windsor soils.

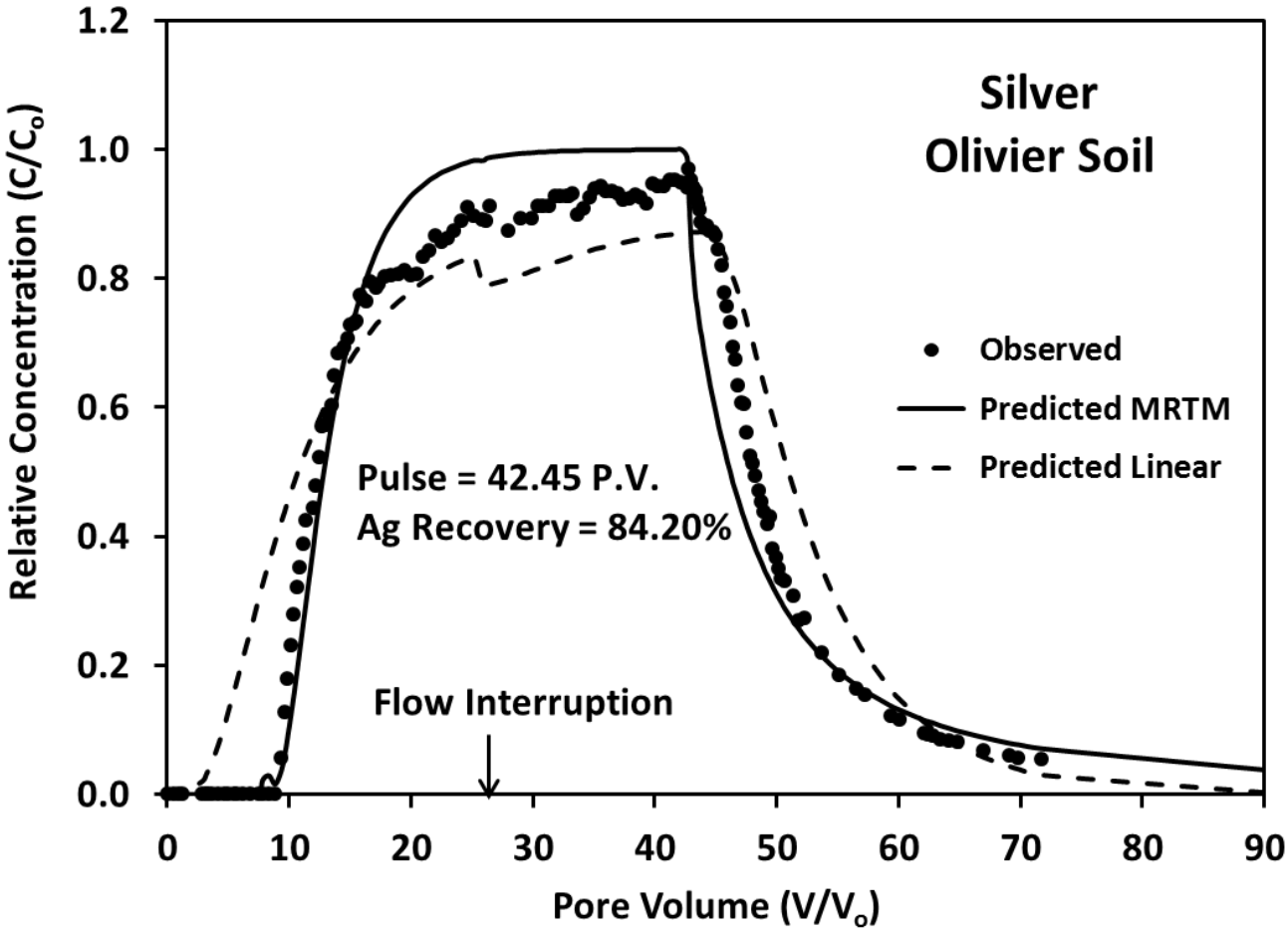

Figure. 3.2 Breakthrough results for Ag from the Olivier soil column. Solid and dashed curves are simulations using a multireaction and transport model (MRTM) and CXTFIT model.

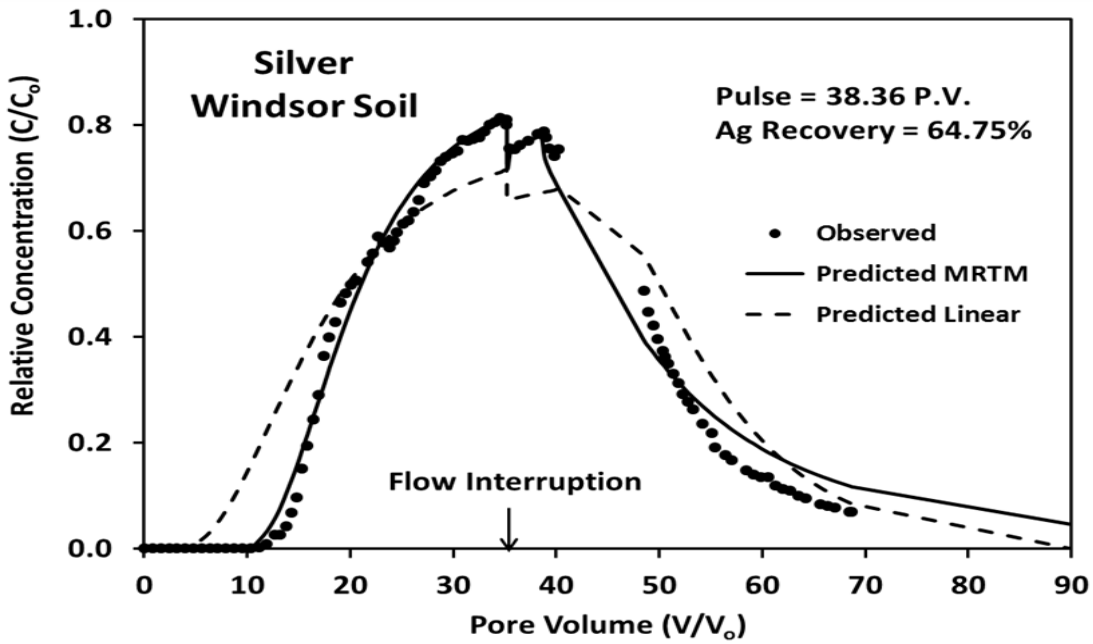

Figure. 3.3 Breakthrough results for Ag from the Windsor soil column. Solid and dashed curves are simulations using a multireaction and transport model (MRTM) and CXTFIT model.

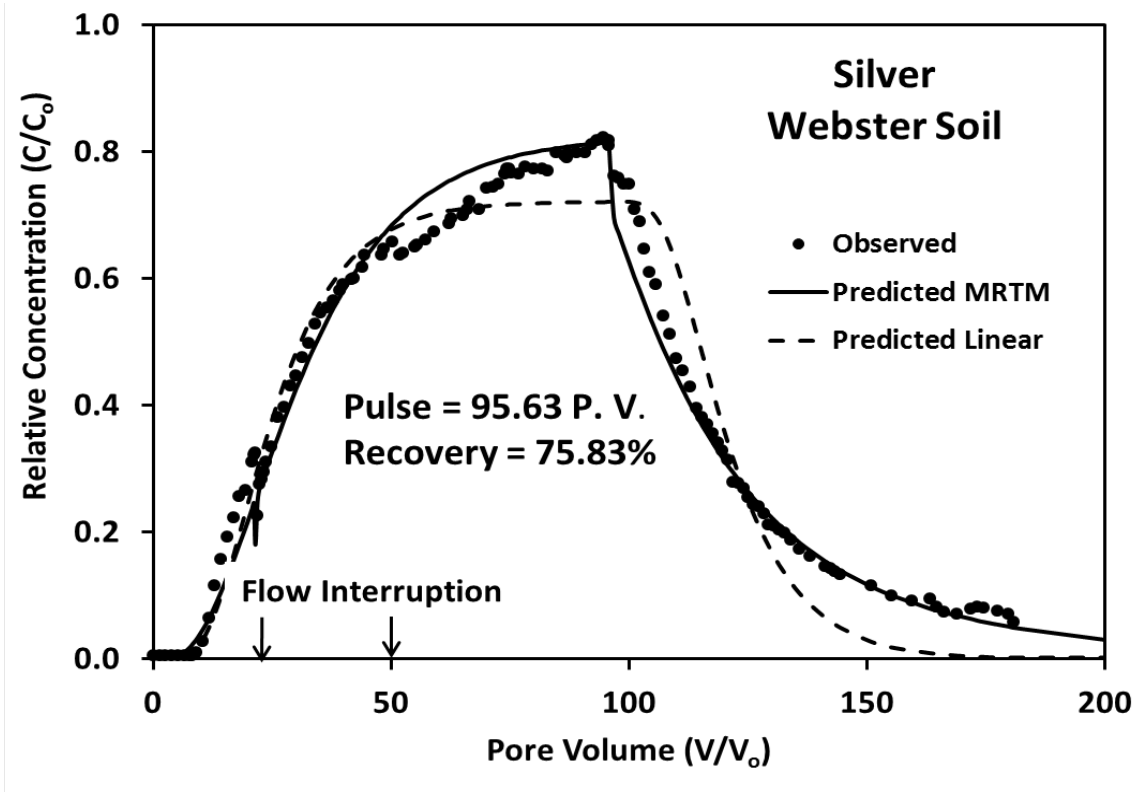

Figure. 3.4 Breakthrough results for Ag from the Webster soil column. Solid and dashed curves are simulations using a multireaction and transport model (MRTM) and CXTFIT model.

Table 3.2. Goodness-of-fit of the multireaction and transport model for the simulation of Ag breakthrough curves for Olivier, Windsor, and Webster soils columns. Estimated model parameters (equilibrium constant, k_e, forward and backward reaction rates associated with kinetics sites, k_1 and k_2, respectively, and the irreversible rate coefficient, k_s and k_{irr}) and their standard errors for all miscible displacement column experiments.

Ion	Model Version $$	r^2	RMSE	k_e	k_1	k_2	ks	k_{irr}
					----------h^{-1}----------			
					Olivier Soil			
Ag	V1	0.932	0.102	------	1.750±0.041	0.080±0.002	0	------
	V2	0.944	0.091	0.072±0.001	2.472±0.043	0.1094±0.0022	0	------
	V3	0.914	0.111	------	1.212±0.027	0.0544±0.0013	------	0.0000
Ag+Zn	V1	0.945	0.116	------	1.000±0.041	0.209±0.005	0	------
	V2	0.958	0.099	0.129±0.0005	5.664±0.023	0.335±0.004	0	------
	V3	0.942	0.118	------	2.806±0.050	0.183±0.003	------	0.0000
Windsor Soil								
Ag	V1	0.986	0.037	------	27.7626±0.2981	0.0605±0.0008	0.0008±0.00044	------
	V2	0.987	0.036	0.0011±0.0003	30.9232±0.3080	0.0678±0.0007	0.0008±0.00004	------
	V3	0.984	0.042	------	30.9081±0.0011	0.0686±0.0005	------	0.0211±0.0011
Ag+Zn	V1	0.983	0.039	------	6.136±0.275	0.0292±0.0017	0.0014±0.00009	------
	V2	0.990	0.031	19.706±1.557	3.6399±0.195	0.0191±0.0012	0.00155±0.00009	------
	V3	0.984	0.038	------	6.1830±0.292	0.0328±0.0019	------	0.0164±0.0008
Webster Soil								
Ag	V1	0.980	0.041	------	6.4968±0.3793	0.0186±0.0013	0.0008±0.00004	------
	V2	0.980	0.041	28.3654±6.0302	3.8499±0.4771	0.0131±0.0014	0.0010±0.00006	------
	V3	0.983	0.036	------	7.0210±0.4189	0.0224±0.0015	------	0.0351±0.0013
Ag+Zn	V1	0.982	0.038	------	4.220±0.187	0.0139±0.0008	0.0009+0.00004	------
	V2	0.983	0.038	0	4.229±0.190	0.0139±0.0008	0.0009±0.00004	------
	V3	0.984	0.035	------	4.305±0.197	0.0163±0.0008	------	0.0317±0.0011

$$ V1 = S_1 and S_s (k_1, k_2, and k_s); V2 = S_e, S_1, and S_s (k_e, k_1, k_2, and k_s); V3 = S_1 and S_{irr} (k_1, k_2, and k_{irr}).

Table 3.3 Parameter estimetes from the Linear Model along with r^2 and RMSE

Soil	R	μ	r^2	RMSE
Olivier	12.7288	0.0185	0.9025	0.1246
Windsor	22.7755	0.0415	0.9174	0.1047
Webster	33.3125	0.0558	0.9584	0.0597

3.4.3 Ag transport in the presence of Zn

Silver BTCs from columns that received a mixed pulse of Ag and Zn are presented in Fig. 3.11, 3.12, and 3.13 are BTCs for Ag and Zn of the three soils.

For Olivier soil, the result in Fig. 3.14 shows the BTC for Ag from the Olivier soil column with Ag single pulse and Ag and Zn mixed pulse. The BTC indicates a gradual increase of the effluent Ag front, with the highest concentration of 98% of the applied pulse concentration. Based on the area under the curve 95.80% of the applied Ag was recovered in the effluent in the presence of Zn. In contrast, 84.20% of the applied Ag was recovered from the Olivier column when Zn was not added in the applied Ag pulse. For Zn, the BTC associated shown in Fig. 3.11, illustrates the extent of Zn retention and mobility in the Olivier soil. The highest concentration of Zn was 98% of the applied pulse concentration. Fig. 3.11 indicates early arrival of Ag than Zn. It took less time for Ag to reach a maximum in the presence of Zn in the applied pulse. Furthermore, Zn was more retarded than Ag as indicated by the delay shown by the BTCs. During leaching, silver concentration decreased faster than that for zinc. These observations indicate the enhanced the mobility of silver, which is consistent with kinetic batch results presented in Chapter 2.

For Windsor soil, the BTC shows Ag came out after 10 pore volumes in the column with single silver solution applied, while the BTC shows silver was detected after just 1.5 pore volumes (see Figure 3.15) in the column with Ag and Zn mixed solution. Measured results also

indicate early arrival and higher recovery (77.04%) in the presence of Zn when compared to 64.75% of Windsor soil where no Zn was applied. Zinc BTC associated with the mixed pulse show similar trends with higher Zn concentration maximums (Fig. 3.12).

For Webster soil, Ag BTC results in the presence of Zn are shown in Figure 3.9, 3.13, and 3.16 and indicate strong Ag sorption in this neutral soil. The breakthrough front exhibited a gradual increase. The BTC results also indicate that in the presence Zn, 79.49% of applied Ag was recovered from the Webster soil. A comparison of the BTC results shown in Figure 3.16 indicates decreased retention of Ag during transport in the Webster soil column in the presence of Zn. Similar with Olivier and Windsor soils, the presence of Zn resulted in an earlier arrival of Ag in the effluent and an enhanced decrease in leaching.

Breakthrough curves for Ag and Zn presented in Fig. 3.5-3.16 were described using the MRTM described above and are given by the solid and dashed curves shown in Fig 3.11-13 for Ag and Zn, respectively. The model parameters associated with these predictions are given in Table 3.2, 3.3 and 3.4 along with parameter standard errors and RMSE and r^2. Best model versions in describing Ag and Zn transport (mixed pulse) in the columns of Olivier, Windsor, and Webster are the same as the single pulse columns. These predictions were obtained using model version (V1) with S_k and Ss phases with k_1, k_2, and k_s as the dominant kinetic reactions.

Table 3.4. Goodness-of-fit of the multireaction and transport model for the simulation of Zn breakthrough curves for Olivier, Windsor, and Webster soils columns. Estimated model parameters (equilibrium constant, k_e, forward and backward reaction rates associated with kinetics sites, k_1 and k_2, respectively, and the irreversible rate coefficient, k_s and k_{irr}) and their standard errors for all miscible displacement column experiments.

Soil	r^2	RMSE	k_e	k_1	k_2	ks	k_{irr}
			----------	----------h^{-1}----------			----------
Olivier	0.958	0.088	------	2.584±0.041	0.1431±0.0013	0	------
Windsor	0.994	0.025	------	4.239±0.115	0.0297±0.0010	0.00095±0.00004	------
Webster	0.972	0.042	------	5.067±0.170	0.0065±0.0003	0.00031±0.00004	------

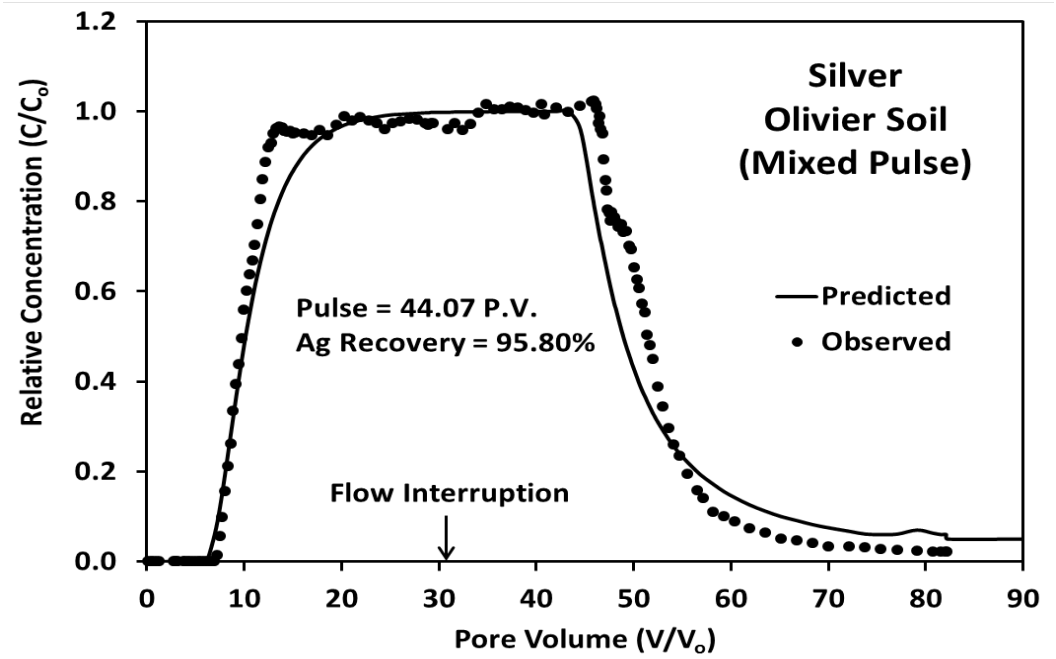

Figure 3.5 Breakthrough results for Ag from the Olivier soil column with Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

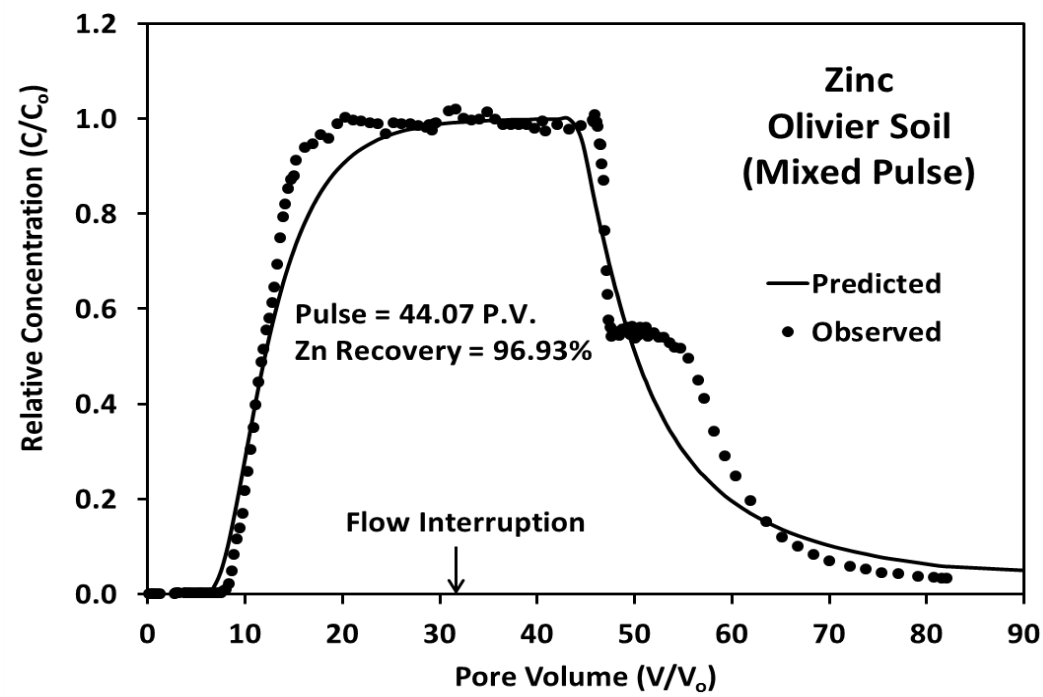

Figure. 3.6 Breakthrough results for Zn from the Olivier soil column with Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

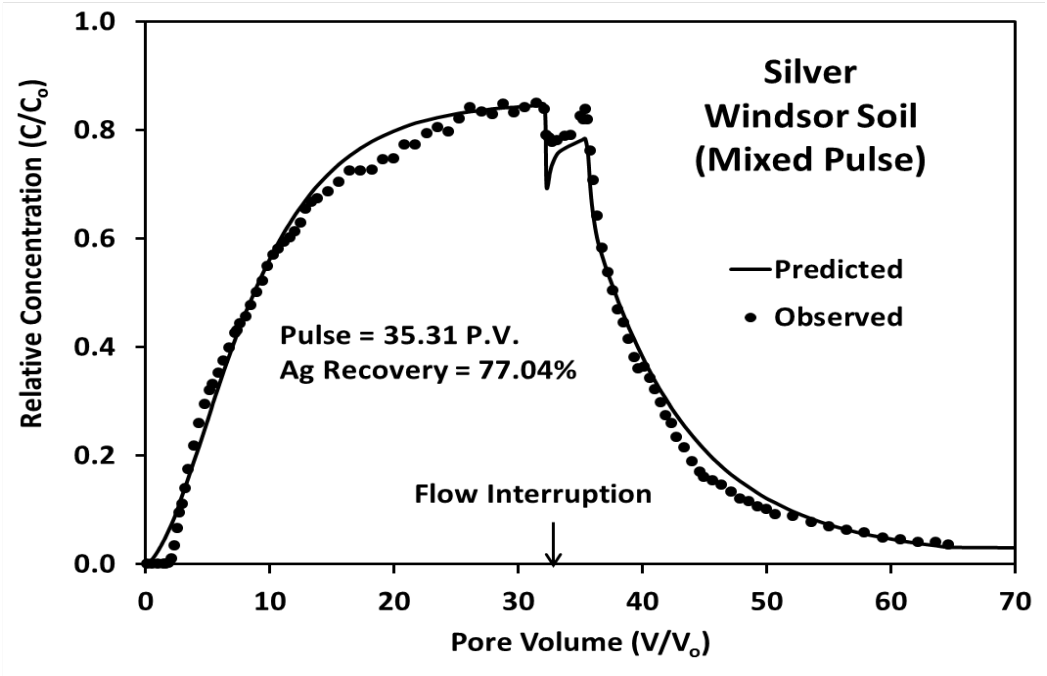

Figure. 3.7 Breakthrough results for Ag from the Windsor soil column with Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

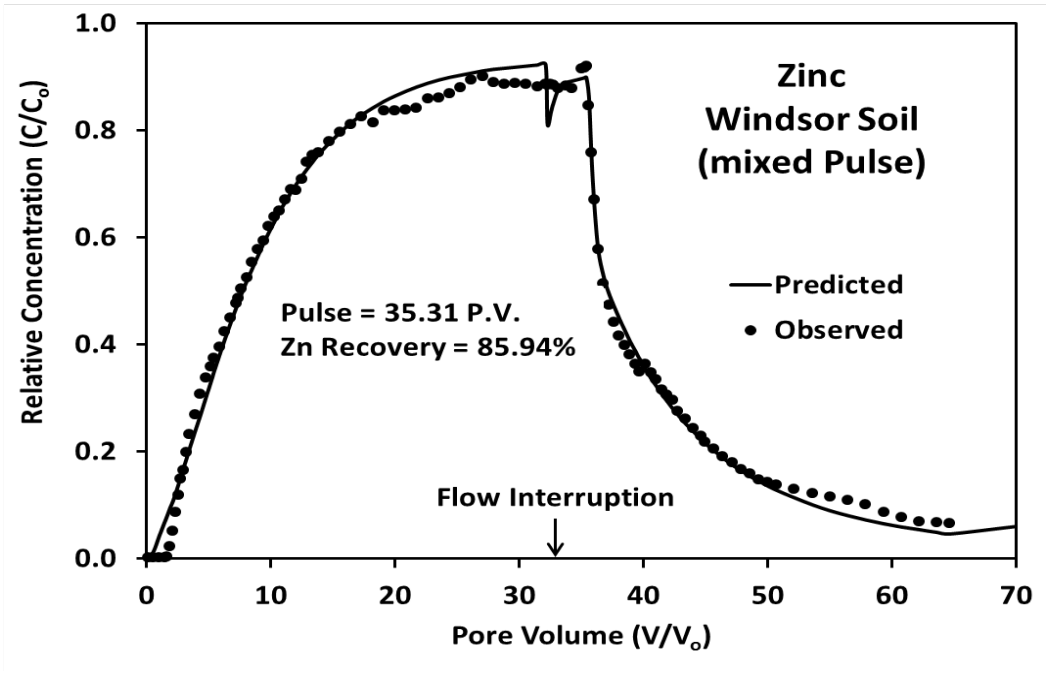

Figure. 3.8 Breakthrough results for Zn from the Windsor soil column with Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

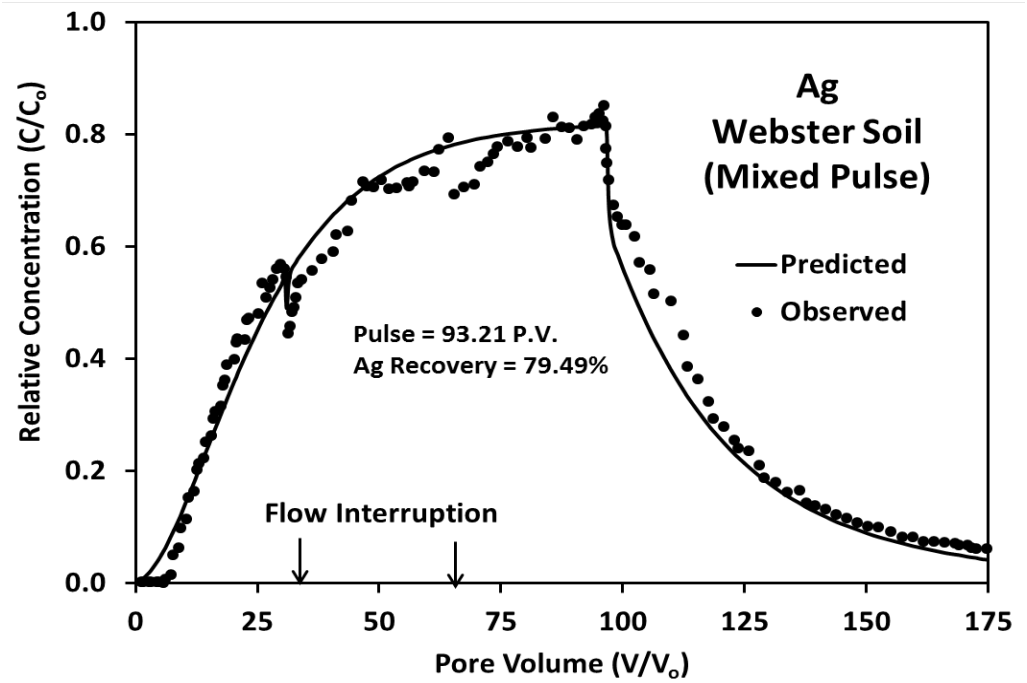

Figure. 3.9 Breakthrough results for Ag from the Webster soil column with Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

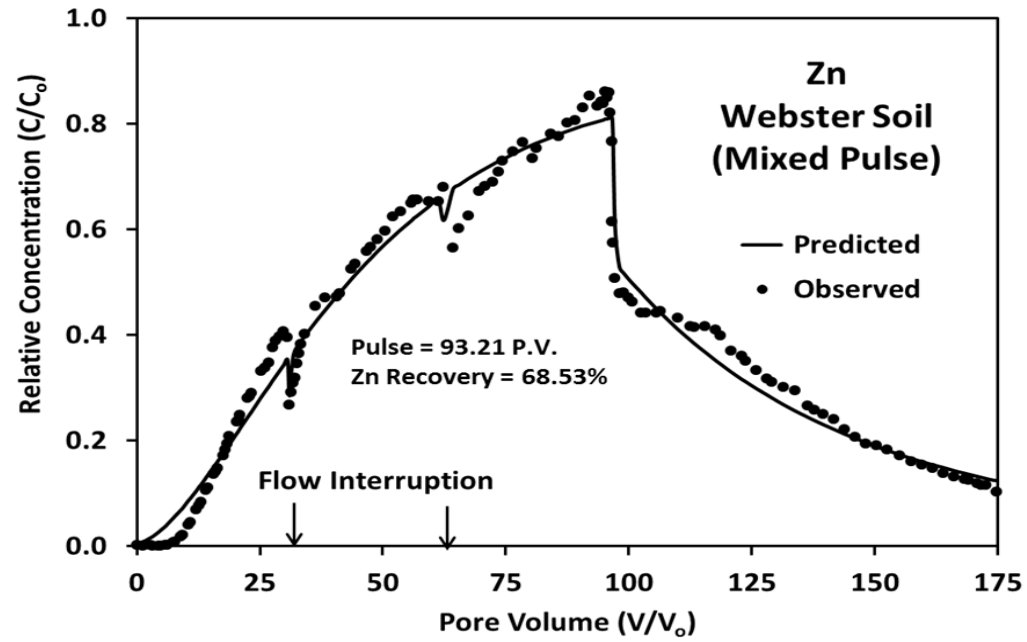

Figure. 3.10 Breakthrough results for Zn from the Webster soil column with Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

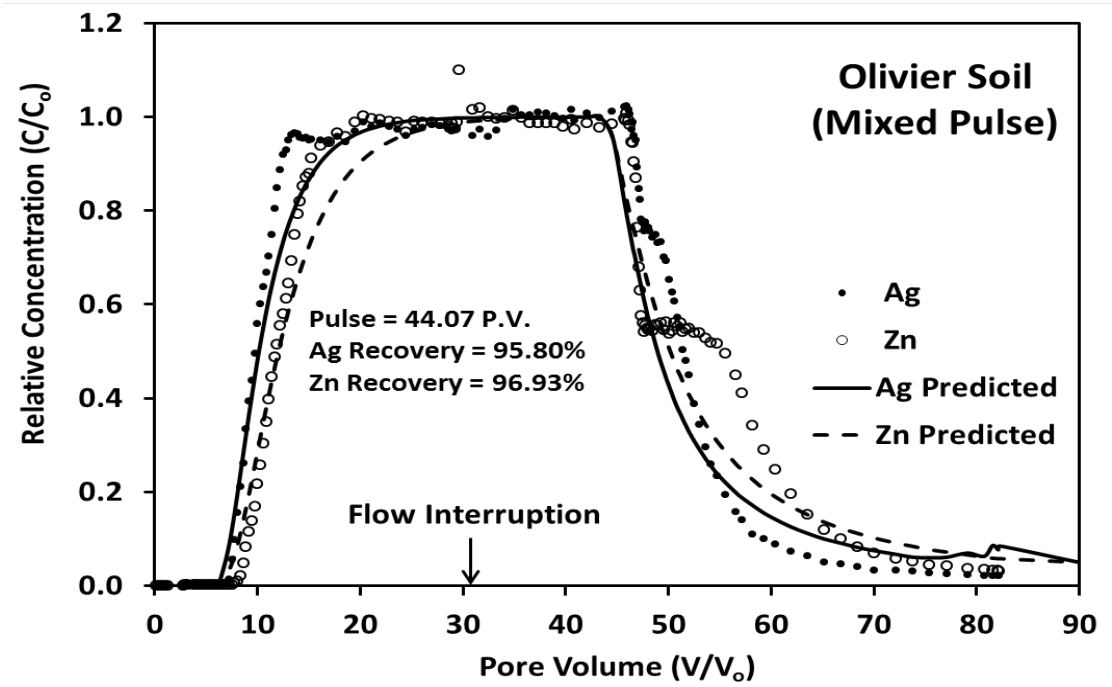

Figure 3.11 Breakthrough results for Ag and Zn from the Olivier soil column with Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

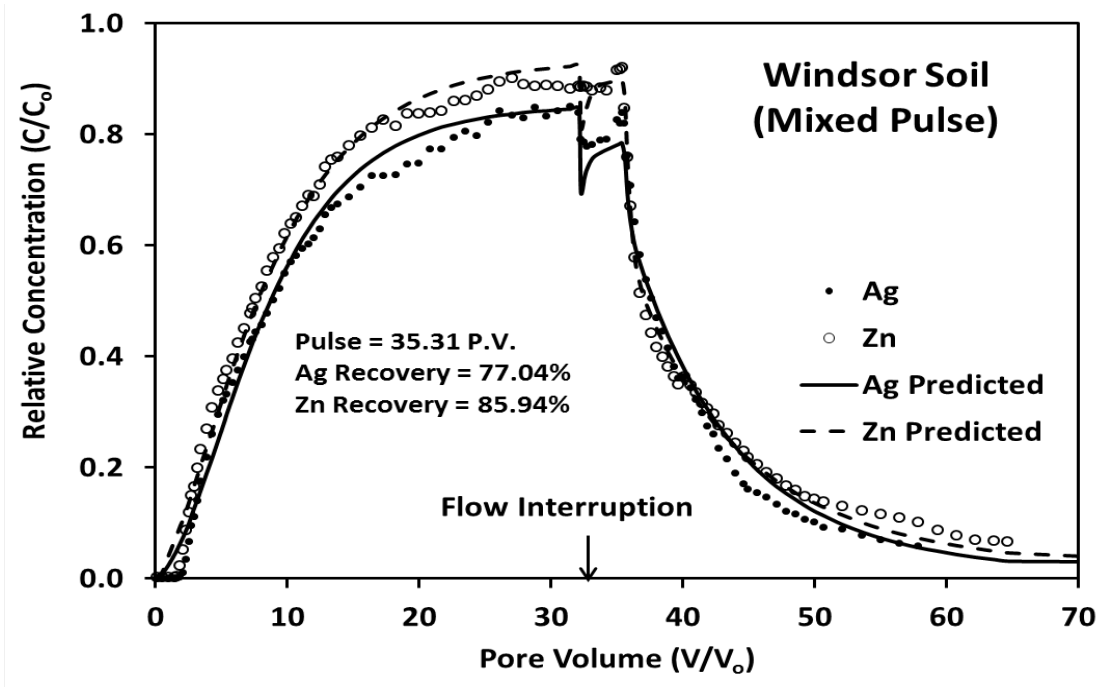

Figure 3.12 Breakthrough results for Ag and Zn from the Windsor soil column with Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

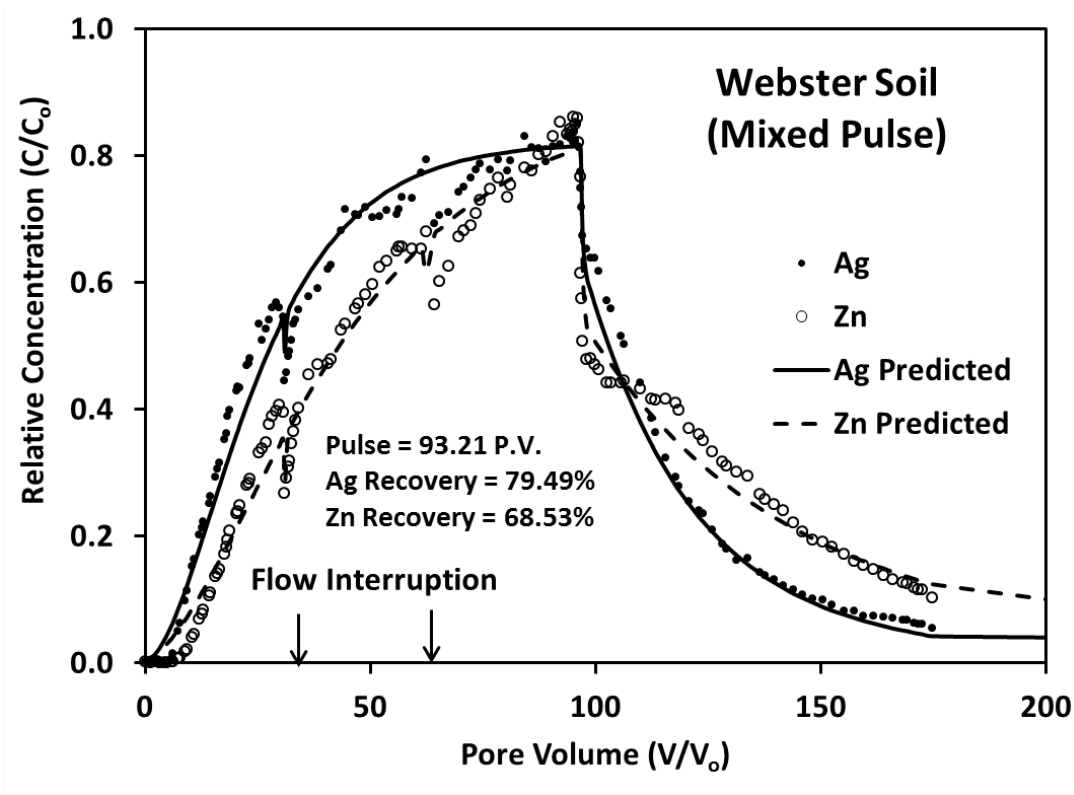

Figure 3.13 Breakthrough results for Ag and Zn from the Webster soil column with Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

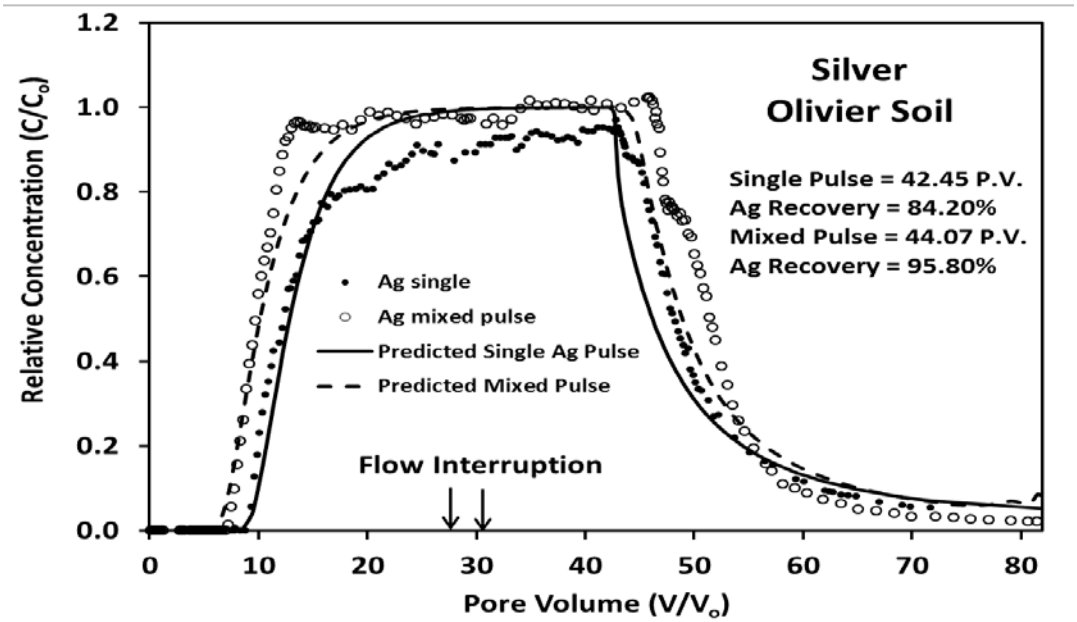

Figure 3.14 Breakthrough results for Ag from the Olivier soil column with Ag single pulse and Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

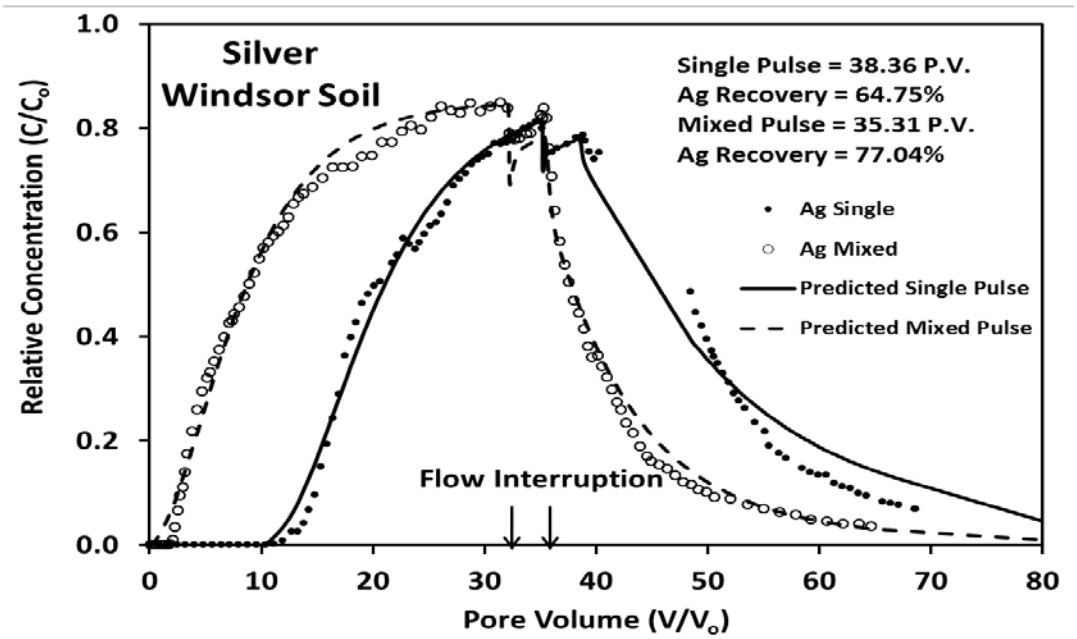

Figure 3.15 Breakthrough results for Ag from the Windsor soil column with Ag single pulse and Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

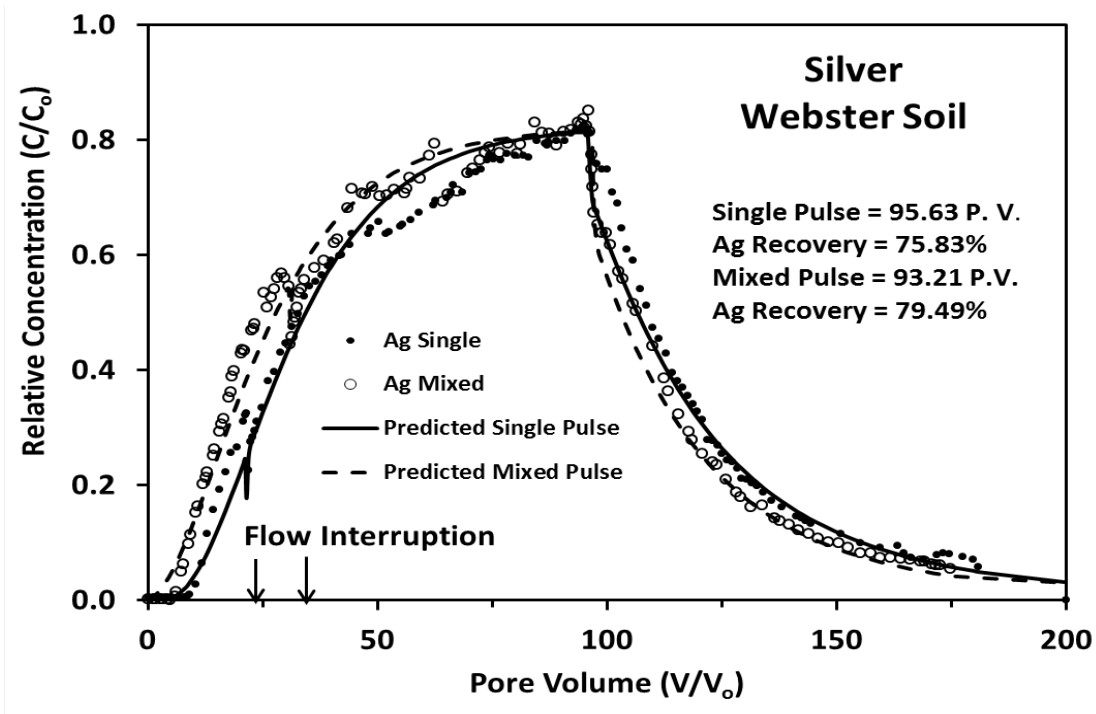

Figure 3.16 Breakthrough results for Ag from the Webster soil column with Ag single pulse and Ag and Zn mixed pulse. Solid curve is simulation using a multireaction and transport model (MRTM).

3.4.4 Silver Distribution with Depth

Results of the distribution of Ag retained by the soil vs. depth, following termination of the miscible displacement experiments, are presented in Fig. 3.17 to Fig. 3.18 for the columns with single Ag pulse of Olivier, Windsor, and Webster soils, respectively. Extensive heterogeneity is manifested for all the three soils, as demonstrated by the confidence interval of measured replications. Nonuniformity in soil column packing may also have contributed to the observed variability.

For Olivier and Windsor soils, the amount retained increased with depth, which indicated downward Ag movement. This pattern indicates downward movement of silver from the soil surface to lower depths, i.e., a leaching pattern. In contrast, for Webster soil, the amount of Ag retained increased a little from 0 to 3 cm, while decreased from 3 to 5 cm, indicative of strong sorption.

Compared the three soil, sorbed amount of Ag has the following sequence: Olivier < Windsor < Webster. These findings were consistent for batch and column experiments. Silver distributions vs. depth also illustrate the high affinity of Webster soil for Ag compared with Olivier and Windsor soils.

Such accumulation patterns were observed by Sukkariyah et al. (2005) for some heavy metals in a clay loam soil. Based on their results, they concluded that the movement of trace metals through the soil profile is negligible and there is little risk of contamination of the ground water at their experimental site.

Figure 3.17 to 3.19 shows results of the distribution of Ag and Zn retained by the soil vs. depth of the columns with mixed pulse of Ag and Zn for the three soils. Sorbed amount of Ag was more than Zn in Olivier, Windsor, and Webster. While compare Fig. 3.14 and 3.17, Fig. 3.15 and 3.18, Fig. 3.16 and 3.19 separately, we can find that retained amount of Ag in the mixed

pulse columns were less than single pulse columns. This indicates that the presence of Zn decreased the sorption of Ag in Olivier, Windsor, and Webster. This results is consistent with what we found in batch and column experiments.

The movement and distribution of Ag in the soil profile is of considerable interest due the potential contamination of land and water resources. Two patterns for the movement of Ag in soils have been observed: a leaching pattern (downward movement) and accumulation pattern (heavy metal retained near the surface soils). In our experiment, Olivier and Windsor soils were observed as a leaching pattern while Webster soil has a high sorption and observed as a accumulation pattern.

3.5 Summary

In summary, we evaluated the nonlinear MRTM for its prediction capability of Ag retention as well as transport in three soils having different soil properties. Column transport experiments indicated extensive Ag retardation followed by slow release of the BTCs. The extent of Ag retardation during the solute transport followed the sequence of Olivier < Windsor < Webster. In the presence of Zn, Ag sorption decreased and had a lower mobility. The MRTM provided a good prediction of Ag transport in soils.

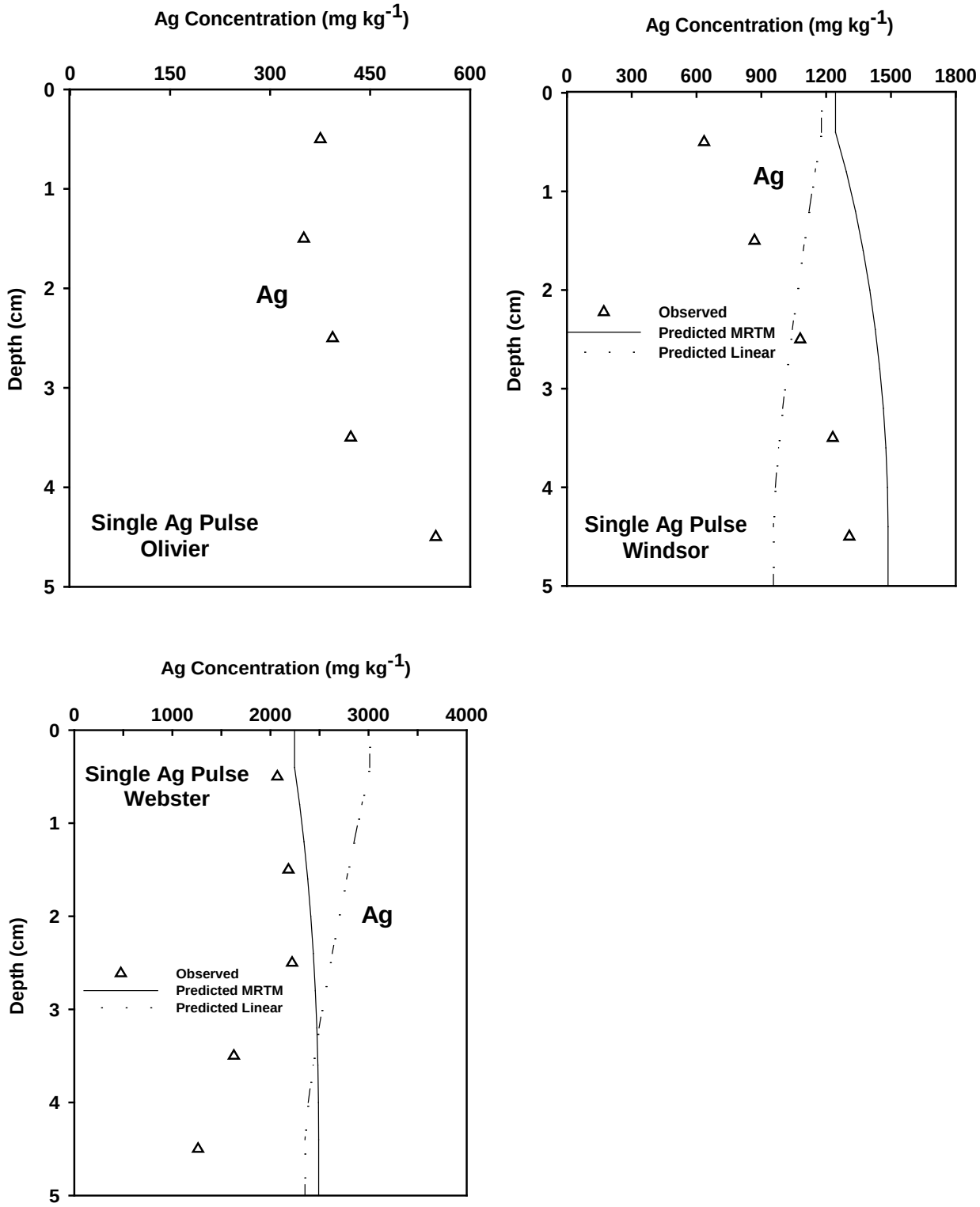

Figure 3.17. Measured sorbed Ag vs. column depth based on soil extractions for the Olivier, Windsor, and Webster soils. Solid and dashed curves represent the multireaction and transport model (MRTM) and CXTFIT model predictions, respectively

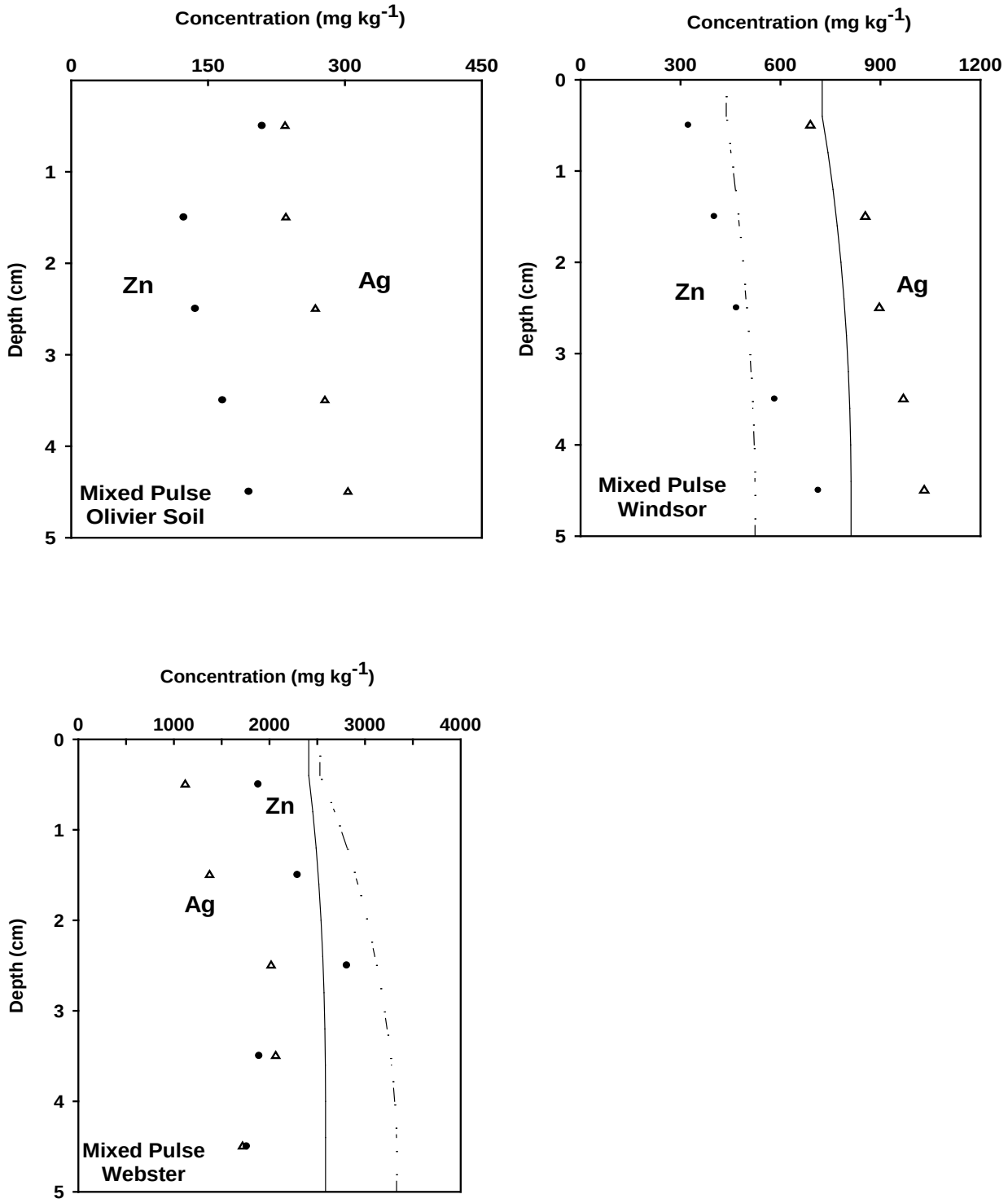

Figure 3.18. Measured sorbed Ag and Zn vs. column depth based on soil extractions for the Olivier, Windsor, and Webster soils. Solid and dashed curves represent simulations based on MRTM model calculations for Ag and Zn, respectively.

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CHAPTER 4: CONCLUSIONS

Batch experiments demonstrated that adsorption-desorption of silver (Ag) is the primary factor that impacts the bioavailability and mobility of Ag in soils. Adsorption of Ag was highly nonlinear with a Freundlich reaction order N much less than 1 for Olivier loam, Windsor sand and Webster loam. Adsorption of Ag by all the three soils was strongly kinetic. Freundlich distribution coefficients exhibited continued increase with reaction time for all soils. Desorption of Ag was retarded in the soils which is an indication of lack of equiliburim retention or irreversible or slowly reversible processes.

Miscible displacement experiments were performed to quantify Ag transport in soil columns. Silver BTCs indicated extensive mobility in the Olivier and Windsor soils, whereas in Webster soil, Ag mobility was strongly retarded, with slow Ag release during leaching.

The presence of zinc decreased the adsorption of Ag and increases the mobility of it.

We tested the capabilities of a nonlinear MRTM in describing the Ag BTCs. Based on our findings, the transport of applied Ag in soils can be successfully described based on the MRTM.

VITA

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