Effect of Wastewater on the Transport and Retention of As(V) on Desert Soils

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Hypothesis

Application of As(V) to desert soils in combination with municipal wastewater effluent will decrease retention and increase diffusivity and percent mass recovery, in comparison to its application with buffer.

Main question

How are the breakthrough curves (BTCs) and sorption isotherms of As(V) altered when applied to arid soils in combination with municipal wastewater effluent relative to application with 0.01 M KNO_3 buffer?

Secondary questions

1. What role do soil properties play in arsenic sorption and transport under these two diverse conditions?

2. Can computer models be used to describe As(V) sorption over time under these two conditions?

Abstract

Chronic low-level exposure to arsenic has been found to increase health risks for cancer, skin lesions, and numerous other illnesses. In January 2006, the Environmental Protection Agency (EPA) lowered the MCL for arsenic from 50 parts per billion (ppb) to 10 ppb. This new standard has affected many communities, requiring them to develop procedures for lowering arsenic concentrations in their drinking water.   Disposal of the arsenic residuals is a problem that must be considered when developing such a procedure. A simple and low cost solution to this problem is to land apply the arsenic concentrates with the municipal wastewater. To insure the usefulness and safety of this disposal method, it is essential to investigate arsenic transport and retention on diverse soils in the presence and absence of wastewater.   In this research, sorption isotherm and breakthrough curve experiments have been performed on three diverse soils taken from a land application facility located in southern New Mexico. Arsenic(V) will be applied with either municipal wastewater or 0.01 M KNO_3 buffer to study the effects of wastewater on As(V) transport through and retention on the soils. Various models will be fit to examine their ability to describe As(V) transport over time under these two conditions. Additionally a Geographic Information System (GIS) will be used to investigate the locations of wells across the continental United States having > 10 ppb arsenic. These well locations will be compared to farmland locations and population values to better understand the potential impact of arsenic contamination across the U.S.

<u>**Introduction**</u>

General Background

The mention of the word arsenic conjures up images of murder mysteries both fact and fiction. The origin of the word arsenic is the Greek word for potent. Arsenic in certain forms can indeed be a potent poison. Recently, however, arsenic has been in the news for its detrimental health effects stemming from chronic low level exposure.

Chronic arsenic exposure places people at higher risk for a wide variety of cancers of both the skin and internal organs. It has also been implicated in disorders such as diabetes, as well as having effects on the respiratory, reproductive and neurological systems (Mead, 2005). Arsenic has also proven to be a potent endocrine disruptor, altering hormone-mediated cell signaling at extremely low concentrations (Bodwell et al., 2004).

At higher risk to arsenic mediated diseases are young and unborn children. The increased susceptibility of children is believed to be due to differences in metabolism between children and adults. Symptoms of low-level arsenic exposure such as skin lesions show up sooner in children and are aggravated by poor nutrition. The effects of arsenic exposure in-uterine are the most detrimental. The first trimester of pregnancy consists of rapid cell division. Exposure to arsenic at this point in fetal development increases cancer rates significantly (Mead, 2005).

In certain regions of the world, including Bangladesh and India, chronic arsenic ingestion occurs due to elevated arsenic in ground water wells. The acquisition of drinking water, over the

past 20 to 30 years, from tube-wells dug into aquifers containing elevated arsenic concentrations in Bangladesh and West Bengal has been described as the greatest mass poisoning in human history (Smith et al., 2000). It is predicted that 200,000-270,000 people will die of cancer from drinking As-contaminated water in Bangladesh alone (WHO, 2001).

The question still remains: How much is too much arsenic? While the debate rages on, the EPA put into effect a new maximum concentration level (MCL) of 10 ppb for drinking water. Many believe that since this level is lower than natural background arsenic levels in many parts of the United States it is an unrealistic and unachievable goal. Others believe standards must be set conservatively as long as there is a possibility that higher levels might be connected to health risk. The events in Bangladesh are a strong case for the argument that naturally occurring background levels cannot be used to set standards.

Arsenic Across the United States

Sources of arsenic in the United States are both natural and anthropogenic. About 60% of the arsenic in the environment is naturally occurring (Chilvers and Peterson, 1987). Weathering of igneous and sedimentary rock, including coal, is a major natural source of arsenic, estimated to release annually 45,000 Mg, while human activities release around 50,000 Mg of arsenic each year (Adriano, 2001). Anthropogenic arsenic sources include: combustion of fossil fuels, leaching from mine tailings and land fills, fertilization practices of the past, and wood staining treatments.

In the United States groundwater arsenic contamination is not a localized occurrence. In figure 1, a map of the continental United States shows the locations of wells containing greater than 10 ppb arsenic, as tested by the United States Geological Survey.   Wells exceeding the

EPA MCL are found in all sections of the U.S., with larger numbers in the northwest, upper mid-

west, eastern seaboard and the desert southwest.
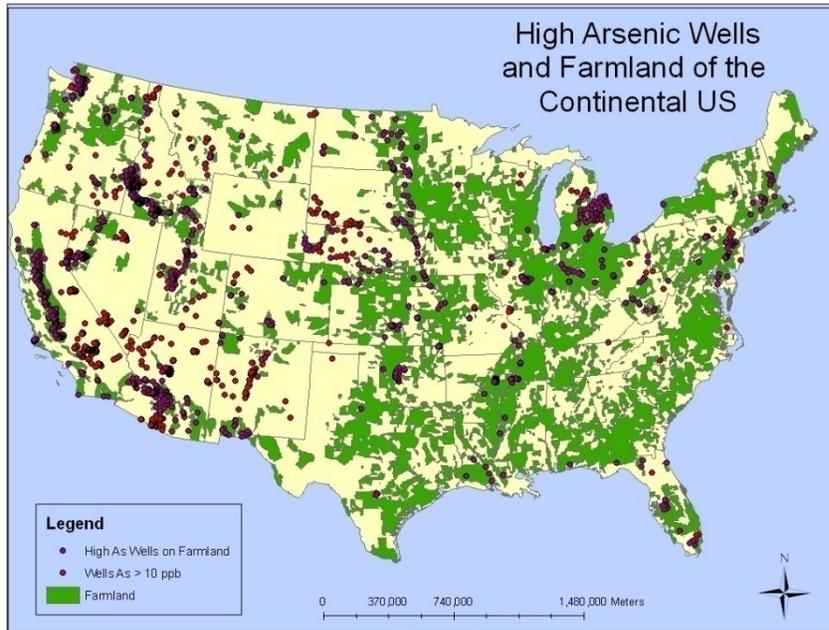
Figure 1 - A map of the continental United States showing the locations of wells, tested

by the United States Geological Survey, containing greater than 10 ppb As, relative to

the position of farmland as designated by Farming on the Edge.

Since the EPA MCL of 10 ppb for arsenic applies only to drinking water, it is likely that

the communities surrounding these wells will need to develop arsenic removal plans to deliver

drinking water to their residence. Waste disposal is a critical part of any arsenic treatment plan

and must be taken into consideration. All arsenic treatment technologies, except zero-treatment

options such as alternate source use and blending, create residuals with concentrated arsenic and

other contaminants (New Mexico Environmental Department, 2004).

The new MCL for arsenic will have a significant impact on the water systems and

population of New Mexico. Arsenic in New Mexico is due primarily to geology and other non-

anthropogenic sources. In New Mexico, arsenic-rich sediments are prevalent in many parts of

the state and ground water arsenic in these areas routinely ranges from 10-50 ppb. Over 80% of

the state population is served by public water supply, the vast majority of which utilizes ground

water. In the Albuquerque area, drinking water arsenic levels historically have averaged 10-30

ppb, with maximum detected levels over 50 ppb. In several smaller communities, drinking water

arsenic levels have been measured as high as 200 ppb. The naturally occurring levels of arsenic

will result in a large number of water systems having source water exceeding the new arsenic

MCL. According to the New Mexico Environmental Department (2004), there are 95 water

systems in New Mexico, serving a population of approximately 756,000, or 41% of the state's

population, that will be affected by the new arsenic MCL. The majority of these systems are

very small, serving a population of less than 500. Larger systems are affected as well, including

the cities of Albuquerque, Rio Rancho and Santa Fe.

Although there are several options that can be implemented in order to comply with the

new arsenic standard, many of these options have difficulties that can make them impractical for

the smaller water systems. Specifically, small systems are typically hindered by a lack of

funding, lack of operations staff, and limited water resources. However, these smaller

communities are often located in rural areas with easy access to undeveloped land.

As can be seen in figure 2, wells with greater than 10 ppb arsenic are located throughout

the state, but generally in close proximity to the Rio Grande valley. Many of these wells are

located near small towns in rural areas. These towns are hardest hit by this problem, since they

have limited finances for waste disposal, but undeveloped land is available. For this type of

community land application of wastewater is an inexpensive solution. If reverse osmosis (RO) is

used to remove the arsenic from drinking water, the RO concentrate may be added to the

municipal wastewater effluent for land application. This would provide an easy and inexpensive

solution to this problem. For this reason it is important to ensure that the addition of RO

concentrates, containing arsenic, to land application systems, in a desert environment, is a valid

and safe solution. This issue becomes even more critical when the system design involves

agricultural products grown in the land application area.
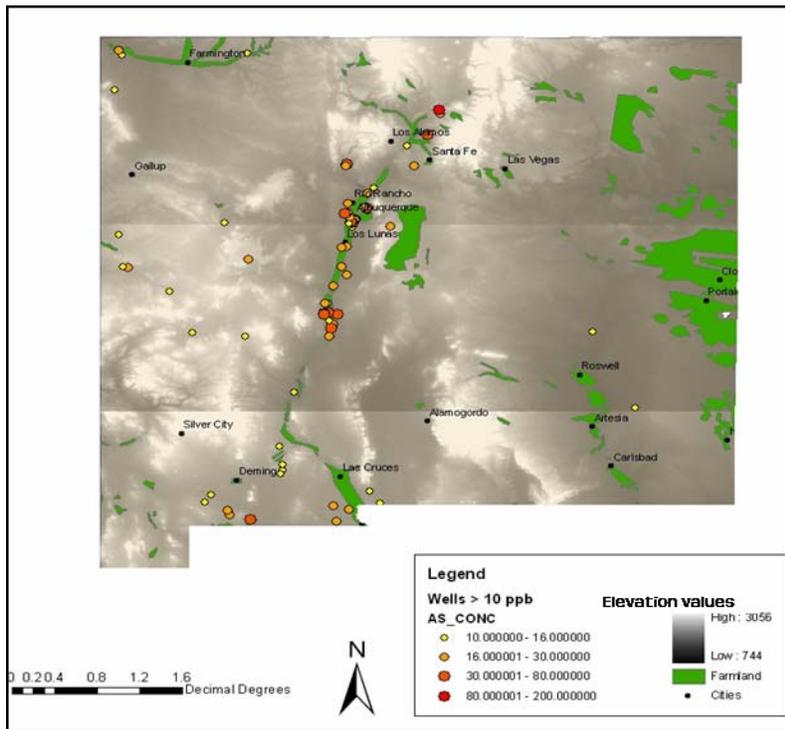
Figure 2 - A map of New Mexico showing locations of wells having greater than 10 ppb

arsenic as tested by the USGS.

Arsenic in the Soil

Although it is impossible to make broad generalities about the behavior of arsenic in soils

due to soil's inherent complexities, numerous studies have demonstrated arsenic sorption onto

soil. Typically, arsenic sorption by soil increases with increased additions of arsenic to the soil,

sorption increasing steeply at low solution concentrations and leveling off at higher

concentrations (Livesey and Huang, 1981). The magnitude of arsenic sorption, however, varies

greatly between different soils, with highly oxidic soils sorbing three times more As(V) than

soils containing small amounts of iron and aluminum oxide minerals (Smith et al., 1999). Soils

may also contain elevated levels of pedogenic arsenic inherited from soil parent material and as a

result of weathering during soil development. Sedimentary rocks, for example, are known to

contain much higher concentrations of arsenic than igneous rocks (Bhumbla and Keefer, 1994).

In soils, arsenic is present as arsenite (As^{III}), arsenate (As^{V}) and organic arsenic (dimethyl As

acid, cacodylic acid). Arsenic species are adsorbed onto Fe, Mn and Al compounds (Smith et

al.,1998). Sorption of arsenic species by organic matter and humic acid is also possible. The

main arsenic species in soils and sediments includes aluminum arsenate, iron arsenate and

calcium arsenate. In aquatic systems, arsenic is predominantly bound to sediments. Arsenate is

the predominant species in aqueous systems. Arsenic oxidation from more toxic As^{III} to less

toxic As^{V} is an important process that helps to alleviate toxicity in aquatic environments, because

As^{V} is readily adsorbed onto the sediments and becomes relatively immobilized (Rubinos et al.,

2003). Arsenic concentration in suspended solids and sediments is many times higher than in

water, indicating that the suspended solids are good scavenging agents and sediments are a sink

for arsenic (Mahimairaja et al., 2005).

Much research has focused on the sorption of both arsenate and arsenite species by soils

and individual soil constituents. It is generally agreed that free iron oxides are the dominant soil

constituents responsible for arsenic sorption. For example, arsenic sorption has been positively

correlated with soil free iron oxide content in several studies (Wauchope, 1975; Elkhatib et al.,

1984), and form inner-sphere surface complex via a ligand exchange mechanism (Waychunas et

al., 1998). Although iron oxides appear to dominate arsenic sorption by soils, several other soil constituents are also capable of sorbing various arsenic species. These include phyllosilicate clay minerals, such as kaolinite and montmorillonite (Sieling, 1946; Frost and Griffin, 1977; Goldberg and Glaubig, 1988), aluminum oxides and hydroxides (Anderson et al., 1975; Goldberg, 1986; Xu et al., 1991), manganese oxides (Oscarson et al., 1983a, 1983b) and calcium carbonate (Goldberg & Glaubig, 1988). The relative importance of such materials for arsenic sorption in soils is difficult to establish. Goldberg (2002) investigated the adsorption of As[V] on iron and aluminum oxides, kaolinite, illite and montmorillonite as a function of pH. Arsenic adsorption on oxides and clays was maximal at low pH and decreased with increasing pH; above pH 9 for Al oxide, pH 7 for Fe oxide and pH 5 for phyllosilicate clay minerals.

Equilibrium models of the Freundlich and Langmuir type are commonly used to describe the results of arsenic sorption by soils (Buchter et al., 1989; Manning and Goldberg, 1997). However, the usefulness of the results from short duration studies for predicting the fate and transport of arsenic is questionable since equilibrium conditions are rarely achieved for arsenic transport under field conditions due to a wide variety of biological, chemical and hydrological conditions. In a heterogeneous system such as soil, the occurrence of non-equilibrium conditions can have a great impact on the transport of As. The mechanisms behind the rate-limited sorption and transport of arsenate in soils have not been fully explored. In general, rate-limited processes for reactive solutes are due to both physical (transport) and chemical (sorption) non-equilibrium. Physical non-equilibrium includes processes such as inter- and intra-particle diffusion within soil aggregates and preferential flow through soil macropores (Brusseau, 1993). Non-equilibrium sorption of As[V] is likely a result of different factors acting simultaneously. Zhang and Selim (2005) described these factors as the heterogeneity of arsenic sorption sites on the soil matrix,

three dimensional growth of particular arsenic at the mineral surfaces, and the slow diffusion of arsenic to sites within the soil matrix.

In the long term, it is the ability of sorbed arsenic to desorb back into solution that will control its bioavailability and mobility. However, compared with arsenic sorption, there is relatively little information about its desorption from soils. Desorption of substantial amounts of sorbed As^V has been observed when phosphate has been used as a displacing ion (Woolson et al., 1973; Peryea, 1991). Melamed et al. (1995) performed column experiments using an aggregated Oxisol. They found that at pH 4.5 and 6.5, AsO_4 transport exhibited significant retardation and tailing, while at pH 8.0 the BTC of AsO_4 was nearly symmetrical. This indicates that at the higher pH value of 8.0 there is decreased arsenic sorption. Increase in added PO_4 content resulted in an increase in arsenic recovery, decrease in retardation and a more symmetrical BTC. Increasing the pore volume velocity from 0.2 cm h^{-1} to 90 cm h^{-1} increased arsenic recovery from 7.24 to 74.3%. Much less arsenic desorption occurs in the presence of water alone (Johnston and Barnard, 1979).

Downward movement of arsenic has been reported in the literature in conjunction with contaminated soils. Isensee et al. (1973) investigated residual arsenate in Metapeake silt loam. Arsenic was found to be present 14 years after massive applications of arsenical herbicides. Their results showed that a large amount of arsenic remained in the soil profile and that the concentration decreased with increasing depth. These findings are indicative of slow leaching processes. McLaren et al. (1998) observed considerable downward movement of arsenic through the soils surrounding cattle dips in Australia. They detected arsenic concentrations in the subsurface between 20 and 40 cm ranging from 57 to 2282 mg kg^{-1}. It was their conclusion that the movement of arsenic through the soil was slow and mainly controlled by soil properties.

Laboratory studies have been done to investigate the transport of arsenic in soils. Hiltbold et al. (1974) studied the transport of monosodium methanearsonate (MSMA) in surface and subsurface soils using field profile sampling, batch experiments and soil column experiments. Arsenic distribution in the soil profile after repeated applications of MSMA showed no evidence of leaching. Arsenic K_d values from the batch and column experiments showed large variations which were attributed to the short residence time of arsenic in the soil columns. They concluded that the actual leaching in the field was considerably less than predicted by laboratory adsorption coefficients.

Darland and Inskeep (1997a, 1997b) demonstrated the effect of pore water velocity, pH, and phosphate on the transport of arsenate through packed columns of sand coated with Fe oxides. Their work suggests that the kinetics of AsO_4 adsorption onto the sand were likely limited by physical processes such as film or intraparticle diffusion rather than chemical processes. The results of their column experiments are consistent with *sorption-related non-equilibrium*, and indicate that equilibrium was not reached during transport at pore water volumes (PWVs) of 1 cm h^{-1} or more. Competition between PO_4 and AsO_4 for sorption sites resulted in increased AsO_4 mobility, but did not result in the complete desorption of AsO_4 from the column. Williams et al. (2003) performed column experiments to investigate As^V transport through a heterogeneous soil containing Fe oxides. They concluded that factors affecting arsenic transport increased in the order of pH < pore water velocity < phosphate.

Attempts to model arsenic BTCs from soil columns showed that the use of linear or Freundlich (equilibrium) retention mechanisms describe neither the extent of retardation nor the release (desorption) during leaching. Few studies have focused on the kinetics of As^V retention during transport in soils. Kinetic adsorption data has the advantage of accounting for the non-

equilibrium sorption behavior, which may occur due to heterogeneities of sorption sites and diffusion processes in the interface between the liquid phase and the soil matrix. Zhang and Selim (2006) investigated the transport and retention of As^V on three distinct soils. They conducted BTC experiments and concluded that arsenic sorption was non-linear and highly kinetic. They developed a multi-reaction model to describe As retention over time for all three soils.

Land Application of Wastewater

In this study we will be examining the sorption and transport properties of arsenic in desert soils when applied with effluent from a land application municipal wastewater treatment facility. It is important to be aware of the treatment process in order to better understand the properties of this effluent. For this reason a brief introduction to wastewater treatment (Grady, 1980) and land application will be provided.

One of the most commonly measured constituents of wastewater is the **biochemical oxygen demand,** or **BOD**. Wastewater is composed of a variety of inorganic and organic substances. The organic molecules are easily decomposed into smaller molecules and eventually into carbon dioxide and water by bacteria during wastewater treatment. However, oxygen is required for this process. The amount of oxygen required for this process is known as the biochemical oxygen demand or BOD. The five-day BOD, or BOD_5, is measured by the quantity of oxygen consumed by microorganisms during a five-day period, and is the most common measure of the amount of biodegradable organic material in sewage. Based on criteria for surface water discharge, the secondary treatment standard for BOD has been set at 30 mg

BOD/L, which means that 30 mg of O_2 will be consumed per liter of water over 5 days to break down the organic waste.

One of the main objectives of wastewater treatment is to reduce BOD in treated effluent. BOD removal can be especially important where sewage effluent flows to a leaching field in tight soils. Heavy or thight soils are usually composed of silts and clays (particle size < 0.05 mm). These small soil particles are tightly packed and the pore space between them is small. Reducing BOD means that the sewage will support the growth of less bacteria and therefore the effluent will be better able to infiltrate tight soils.

Municipal wastewater also contains large quantities of suspended solids that are organic and inorganic in nature. These solids are measured as Total Suspended Solids or TSS and are expressed as mg TSS/L of water. This suspended material is objectionable primarily because it can be carried with the wastewater to the leachfield. Because most suspended solids are small particles, they have the ability to clog the small pore spaces between soil grains in the leaching facility.

Nitrogen is present in many forms in wastewater. Most nitrogen excreted by humans is in the form of organic nitrogen (dead cell material, proteins, amino acids) and urea. This organic nitrogen is broken down fairly rapidly and completely to ammonia (NH_3) by microorganisms. In the presence of oxygen, bacteria will convert ammonia to nitrate (NO_3), which can have serious health effects when it enters drinking water wells and is consumed. Nitrate and other forms of nitrogen can also have deleterious effects on the environment, especially in coastal areas where excess nitrogen stimulates the process known as eutrophication. For these reasons, many alternative technologies have been designed to remove total nitrogen from wastewater. These

technologies use bacteria to convert ammonia and nitrate to gaseous nitrogen, N_2. In this form

nitrogen is inert and is released to the air.

Biological conversion of ammonia to nitrogen gas is a two step process. Ammonia must

first be oxidized to nitrate; nitrate is then reduced to nitrogen gas. These reactions require

different environments and are often carried out in separate areas in the wastewater treatment

system. The first step in the process, conversion of ammonia to nitrite and then to nitrate, is

called nitrification ($NH_3 \longrightarrow NO_2 \ NO_3$). The process is summarized in the following equations:

$NH_4 + 3/2 \ O_2 \longrightarrow NO_2^- + 2H^+ + H_2O$

$NO_2^- + 1/2 \ O \longrightarrow NO_3^-$
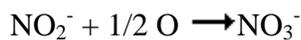
It is important to note that this process requires and consumes oxygen. This contributes to the

BOD or biochemical oxygen demand of the sewage. The process is mediated by the bacteria

Nitrosomonas and *Nitrobacter,* which require an aerobic environment for growth and

metabolism of nitrogen. Thus, the nitrification process must proceed under aerobic conditions.

The second step of the process, the conversion of nitrate to nitrogen gas, is referred to as

denitrification. This process can be summarized as:

$NO_3^- + 5/6 \ CH_3OH \longrightarrow 1/2 \ N_2 + 5/6 \ CO_2 + 7/6 \ H_2O + OH^-$

This process is also mediated by bacteria. For the reduction of nitrate to nitrogen gas to occur,

the dissolved oxygen level must be at or near zero; and the denitrification process must proceed

under anaerobic conditions. The bacteria also require a carbon food source for energy and

conversion of nitrogen. The bacteria metabolize the carbonaceous material or BOD in the

wastewater as this food source, metabolizing it to carbon dioxide. This in turn reduces the BOD

of the sewage, which is desirable. However, if the sewage is already low in BOD, the carbon

food source will be insufficient for bacterial growth and denitrification will not proceed efficiently.

Phosphorus is a constituent of municipal wastewater, averaging around 10 mg L^{-1} in most cases. The principal forms are organically bound phosphorus, polyphosphates, and orthophosphates. Organically bound phosphorus originates from body and food waste and, upon biological decomposition of these solids, is converted to orthophosphate. Most household phosphate inputs come from human waste and automatic dishwasher detergent. Polyphosphates can be hydrolyzed to orthophosphates. Thus, the principal form of phosphorus in wastewater is assumed to be orthophosphate, although the other forms may exist. Orthophosphates consist of the negative ions PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$. These may form chemical combinations with cations and compete with arsenate for soil binding sites.

The wastewater effluent used in this study was obtained from an aquatic system that is discharged to a land application area of about 60 acres. Aquatic systems are large basins filled with wastewater undergoing some combination of physical, chemical, and/or biological treatment processes that render the wastewater more acceptable for discharge to the environment. This type of system has the disadvantage of requiring a large amount of land, but has the advantage of low maintenance costs.

The treatment train for the facility investigated in this study consists of three aerated lagoons followed by a gravel marsh and a polishing pond. Aerated lagoons use mechanical equipment to enhance and intensify the biodegradation rate. They do not produce the intense algal load on downstream processes and have smaller areal requirements than facultative systems. Aerated lagoons require far less land and could theoretically be used in place of aerobic biological treatment, but they cannot be buried and insulated in northern climates, making them

particularly well suited to southern climates. The gravel marsh planted with cattails and reeds, has the ability to perform wastewater treatment by removing BOD_5, suspended solids and nitrogen (Hammer, 1989). The polishing pond is the final stop prior to land application.

Land application of wastewater is a method of reusing treated wastewater. It is a natural way of recycling, by which wastewater is applied to land for irrigation. The wastewater is sorbed by the crop or assimilated into the soil. Land application systems have included application to edible and non-edible crops, rangelands, forests and wood plantations, recreational areas such as parks and golf courses, and to disturbed lands such as mine spoil sites. A variety of land application system designs have been developed. These include application of wastes to the soil surface using Slow Rate (SR), Rapid Infiltration and Overland Flow land treatment systems, or to the subsurface using leaching fields and absorption beds (Pescod, 1992). The suitability of a particular system depends on site characteristics such as soil properties, topography, local hydrology, depth to the water-table, local water quality, land use, climate, evapotranspiration rates and length of the growing season. Land application is generally limited to smaller communities due to land requirements.

Objectives

It is clear that land application of municipal waste is a common and inexpensive means of disposing of wastewater in areas where land is plentiful. It is also clear from the literature that competing ions (such as phosphate) and suspended solids that are certainly present in municipal wastewater effluent are likely to reduce arsenic sorption and increase its mobility through the soil profile. To date there have been no investigations of As(V) sorption in the presence of wastewater effluent. The objectives of this study are to perform BTC and batch sorption

experiments on three desert soils collected from a land-application site in southern New Mexico. Arsenate was dissolved in either 0.01 M KNO_3 buffer or municipal wastewater effluent collected from the same land-application site. Batch sorption and BTC experiments were carried out to determine the dispersion coefficient (D), retardation factor (R), partition coefficient (K) and percent (%) mass recovery values for both treatments. These values were used to investigate the relative adsorption kinetics and transport behavior of As(V) under both conditions. Furthermore, we have fit one and two step models for both treatments, using the program CXTFIT, to investigate the ability of these models to describe As(V) sorption over time.

Study site description

The study site is located at a wastewater treatment facility in southern New Mexico which serves about 1700 people. Figure 3 is an aerial photograph that shows the site as it looked in 2005. In 2007 the entire site was leveled, and everything was removed, except the engineered wetlands which are located near the center of the site. New aeration ponds and a gravel marsh were installed to the east of the wetlands. The yellow lines overlaid on this photo indicate soil sampling units.

The site consists of three major soil units. To the west is the Soniota soil series, which is a Coarse-loamy, mixed, superactive, thermic Typic Haplargid. The eastern side of the site is primarily covered by the Hondale soil which is a Fine, mixed, superactive, thermic Typic Natrargid. The south-east corner consists of the Verhalen series which is a Fine, smectitic, thermic Typic Haplotorrert. These diverse soils provide an interesting case study for arsenic sorption.

Figure 3 – An aerial photograph of the location of the Columbus New Mexico land application site taken in 2005.

Methodology

Sample collection

The Soniota and Hondale soils were collected from the A_p horizon (0–10 cm) on the land application site in summer 2007 just after leveling and before becoming operational. The Verhalen soil was collected from the B_t horizon (30-50 cm) located in a field just east of the land application site. The soils were air-dried and passed through a 2-mm sieve. Composite soil samples were produced by combining soil samples from individual application fields in the south-west and in the north-east quadrants, in addition to the soil collected from the field to the east of the land application site. These composite samples were analyzed for percent sand, silt and clay, pH, organic matter content, total iron, aluminum and arsenic, cation exchange capacity and elemental composition using standard soil analytical methods by an accredited commercial

laboratory at New Mexico State University. Iron oxides were also measured on the composite samples using citrate-bicarbonate-dithionite extraction and analysis with inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Wastewater effluent samples were collected from the polishing pond at the municipal wastewater treatment facility. Effluent was collected via the pump used for land application into clean 10 L plastic jugs which were transported to NMSU and stored at 4 °C until needed. The wastewater effluent was analyzed for pH, electrical conductivity (EC) which was used to calculate total dissolved solids (TDS), and elemental composition with ICP-OES.

Batch Sorption

Solution preparation: Two arsenic solutions were prepared, one using a control buffer and the other using wastewater effluent. The control buffer was a 0.01 M $NaNO_3$ solution. The effluent collected from the wastewater treatment facility was used unaltered for the wastewater effluent solution. Arsenic solutions were prepared using arsenic in the form of As(V) as sodium arsenate (Na_2HAsO_4 $7H_2O$).

Kinetic retention of As(V) was studied using a modified version of the batch method described by Selim et al. (1992). Triplicate 1-g samples of the three soils were placed in polypropylene tubes and mixed with 10-mL of either buffer or effluent solution of known As(V) concentrations. Six initial As(V) concentrations (C_o) were used, namely 5, 10, 20, 40, 80, and 100 mg L^{-1}. The samples were shaken at 150 rpm for 1 hour on a reciprocal shaker, then left for 24 hours, and subsequently centrifuged for 10 min at 4000 rpm. A 2-mL aliquot was sampled from the supernatant. The collected samples were analyzed for total As concentration using ICP–OES. The amount of arsenate adsorbed by each soil was calculated from the difference

between concentrations of the supernatant and that of the initial solutions. Sorption isotherms were plotted for each of the soils to determine differences due to solution composition and soil properties.

Breakthrough curve experiments

Transport of As(V) through the three soils was investigated using the miscible displacement technique as described by Selim et al. (1987). Acrylic columns (10 cm x 7 cm) were uniformly packed with air-dry soil sieved to 2-mm and slowly saturated with either a 0.01 M KNO_3 buffer or wastewater effluent at a low Darcy flux. Input solutions of 0.01 M KNO_3 or effluent were applied for several pore volumes using a variable speed peristaltic pump, and the fluxes were adjusted to the desired flow rate of near 0.7 cm h^{-1}. Between 10 and 20 pore volumes of the respective solutions were applied to each column before introduction of an As(V) pulse solution. Pulses of 100 mg L^{-1} As(V) solution (as KH_2AsO_4) in either 0.01M KNO_3 or wastewater effluent as the background solution, were introduced to each soil column. Each As(V) pulse was approximately 1 pore volume, and was subsequently eluted by the background solution of either 0.01 M KNO_3 buffer or wastewater effluent. Column effluent was collected and analyzed for total As using ICP-OES. Equilibrium and non-equilibrium models were fit using XFITIM to examine there ability to describe As transport over time. Also solute transport parameters including retardation (R), diffusivity (D), partition coefficients (Kd) and % mass recovery were calculated.

To obtain independent estimates for the dispersion coefficient (*D*), separate pulses of a tracer solution were applied to each soil column before As(V) pulse applications. The tracer was chloride, prepared as a 0.1 M $MgCl_2$ solution, and the collected samples were analyzed using a

chloride titrater. The chloride data were described using the classical convection dispersion

equation. The best-fit parameters for D and the retardation factor were obtained from nonlinear

least square optimization using XFITIM.

Results

Selected properties of the Soniota, Hondale and Verhalen soils are presented in Table 1.

The three soils were texturally diverse, Soniota being a sandy loam, Hondale a sandy clay loam,

and Verhalen a clay. All three soils had alkaline pH values ranging from 8.19 to 8.67. The three

soils also had low organic matter content ranging from 0.01 to 0.55. It is also worth noting that

all three soils contained between 3 to 4 mg kg^{-1} of background arsenic.

Table 2 contains some of the properties of the wastewater effluent collected from the

study site. Similar to the soils, the pH value of the effluent is alkaline, having a value of 8.65.

The sodium adsorption ratio (34.5) and the total dissolved solids (1420 mg L^{-1}) suggest that the

soils are likely to suffer from a loss of structure over time, due to increased sodium applied in the

effluent. The effluent also contains 71 ppb total arsenic. The effluent was collected prior to any

introduction of arsenic concentrates from the RO facility, so this value is likely to increase

significantly once the facility is operational.

Soil	Soniota	Hondale	Verhalen
Percent saturation	24.2	34.5	43.8
pH in saturated paste	8.19	8.36	8.67
ECe (dS m^{-1})	2.47	3.69	1.26
Sodium Adsorption Ratio (SAR)	24.23	38.77	30.12
Organic matter (%)	0.55	0.09	0.01
CEC (cmol$_+$/kg soil)	10.52	13.64	23.60
Texture (by hydrometer)	Sandy loam	Sandy clay loam	Clay
Sand (%)	66.2	50.2	19.2
Silt (%)	18.8	25.4	35.8
Clay (%)	15.0	24.4	45.0
HCO$_3$-Extractable P (mg kg^{-1})	3.8	4.63	2.6
Total Fe; *Fe oxides* (mg kg^{-1})	6963; *4691*	7069; *5331*	15830; *6455*
Total Al (mg kg^{-1})	7490	7721	17780
Total As (mg kg^{-1})	3	4	3

Table 1 – Soil properties for Soniota, Hondale and Verhalen soils

pH	**8.65**
EC (dS m^{-1})	**2.16**
Sodium Adsorption Ratio	**34.51**
Total Dissolved Solids TDS (mg L^{-1})	**1420**
Carbonate (meq L^{-1})	**0.40**
Total Suspended Solids TSS (mg L^{-1})	**21**
Arsenic (ug L^{-1} or ppb)	**71**

Figure 2 – Wastewater effluent properties

A 24 hour batch isotherm study was performed to investigate the sorption of arsenic on the

soils collected from the study site. These experiments were performed using either 0.01 M

KNO$_3$ buffer or wastewater effluent. In general, the Hondale and Verhalen soils sorbed arsenic

better than the Soniota soils in both treatments (figure 5 and 6). This agrees with the literature,

since the Hondale and Verhalen soils have much higher clay contents. All of the soils sorbed

more arsenic when applied in buffer than when applied with wastewater effluent. The

application of arsenic with effluent decreased the retardation values (R) greatly compared to R

values for arsenic in buffer (table 3). The R values for arsenic in buffer ranged from 6.73 to

11.14, while the R values for arsenic in effluent were much lower and ranged from 1.23 to 2.35.

It was these preliminary observations that confirm the need for further investigations in the

sorption, desorption and transport of arsenic in the soil when applied with wastewater effluent.

As Sorption in Buffer
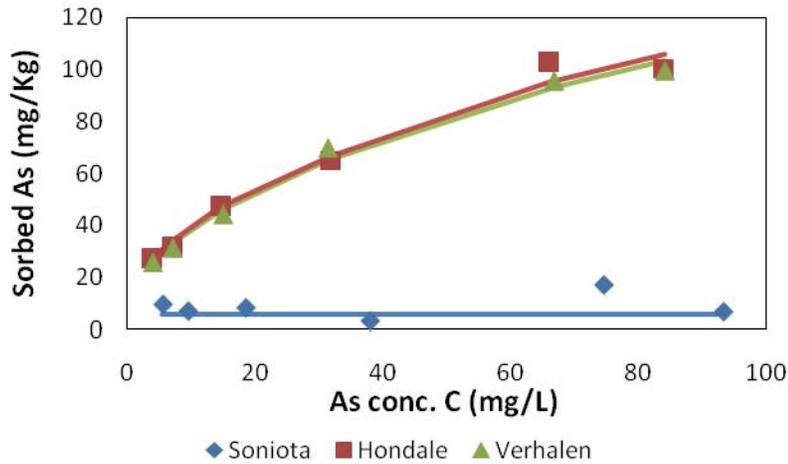
Figure 5. 24-h sorption isotherm data for the Soniota, Hondale and Verhalen soils when

As was applied at the initial concentrations of 5, 10, 20, 40, 80 and 100 mg L^{-1} with 0.01

M KNO$_3$ buffer.

As Sorption in Wastewater
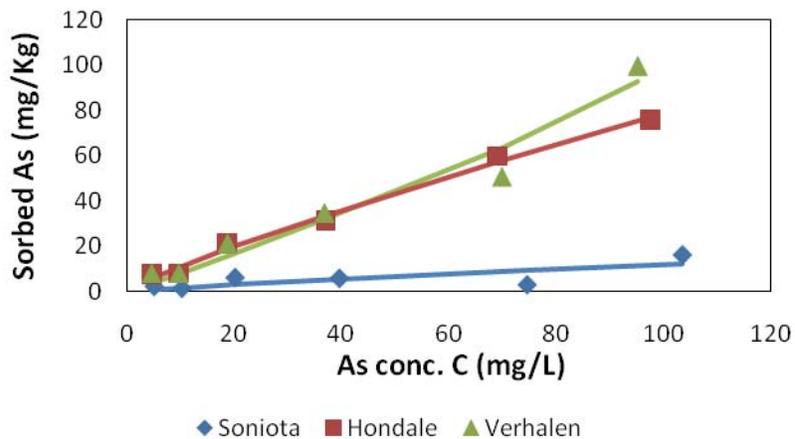
Figure 6. 24-h sorption isotherm data for the Soniota, Hondale and Verhalen soils when

As was applied at the initial concentrations of 5, 10, 20, 40, 80 and 100 mg L^{-1} in

wastewater effluent.

Soil	Solution	K	n	R
Soniota	Buffer	5.74	0.10	6.73
Hondale	Buffer	10.14	0.52	11.14
Verhalen	Buffer	10.03	0.51	11.03
Soniota	Effluent	0.23	0.85	1.23
Hondale	Effluent	1.35	0.87	2.35
Verhalen	Effluent	0.51	1.12	1.51

Table 3. Partition coefficients (K) and retardation values (R) for As^V when applied to the three soils with either buffer or wastewater effluent.

Breakthrough curve experiments were performed on all three soils using the conserved solute chloride (Figure 7). All three soils had R values near 1 and K_d values of zero (Table 4). These values are in good agreement with the expected values for conserved solutes. All three breakthrough curves were well described by a one-site equilibrium model.

Breakthrough curves were also performed on the three soils using As(V) in 0.01 M KNO_3 buffer (Figure 8). The maximum C/C_0 values were between 0.03 and 0.2 and the arsenic peaks took between 10 and 20 pore volumes to return to near-initial levels. Retardation values ranged from 4.5 to 11.9, while K_d values were between 1.4 and 4.5. The % mass recovery of arsenic for these columns ranged from 40 to 67%. All of these breakthrough curves were well modeled by a two-site non-equilibrium model.

The last set of break through curves were obtained by applying As(V) in wastewater effluent to the three different soils (Figure 9). In contrast to the BTCs for As(V) in buffer, the C/C_0 values were much higher ranging from around 0.2 to 0.8, and were eluted in less than 10

pore volumes. Retardation values for the As(V) in effluent were much lower, ranging from 0.4 to 4.4, and the K_d values were between -0.2 and 1.4. The % mass recovery increased in all cases with values of between 93 and 107%.
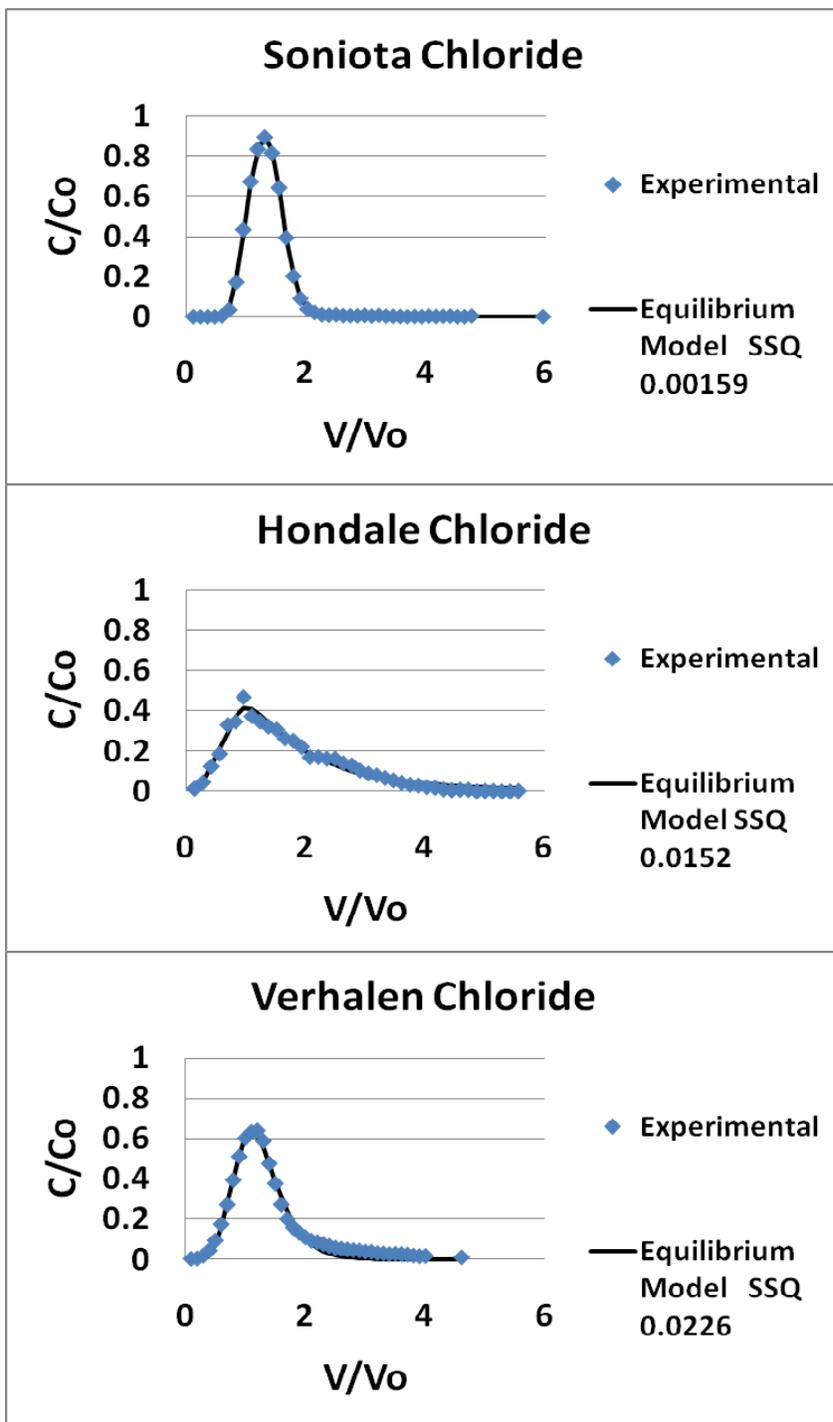
Figure 7. Chloride breakthrough curves for the Soniota, Hondale and Verhalen soils.

Blue points are observed values, solid lines are fitted using XFITIM equilibrium model.
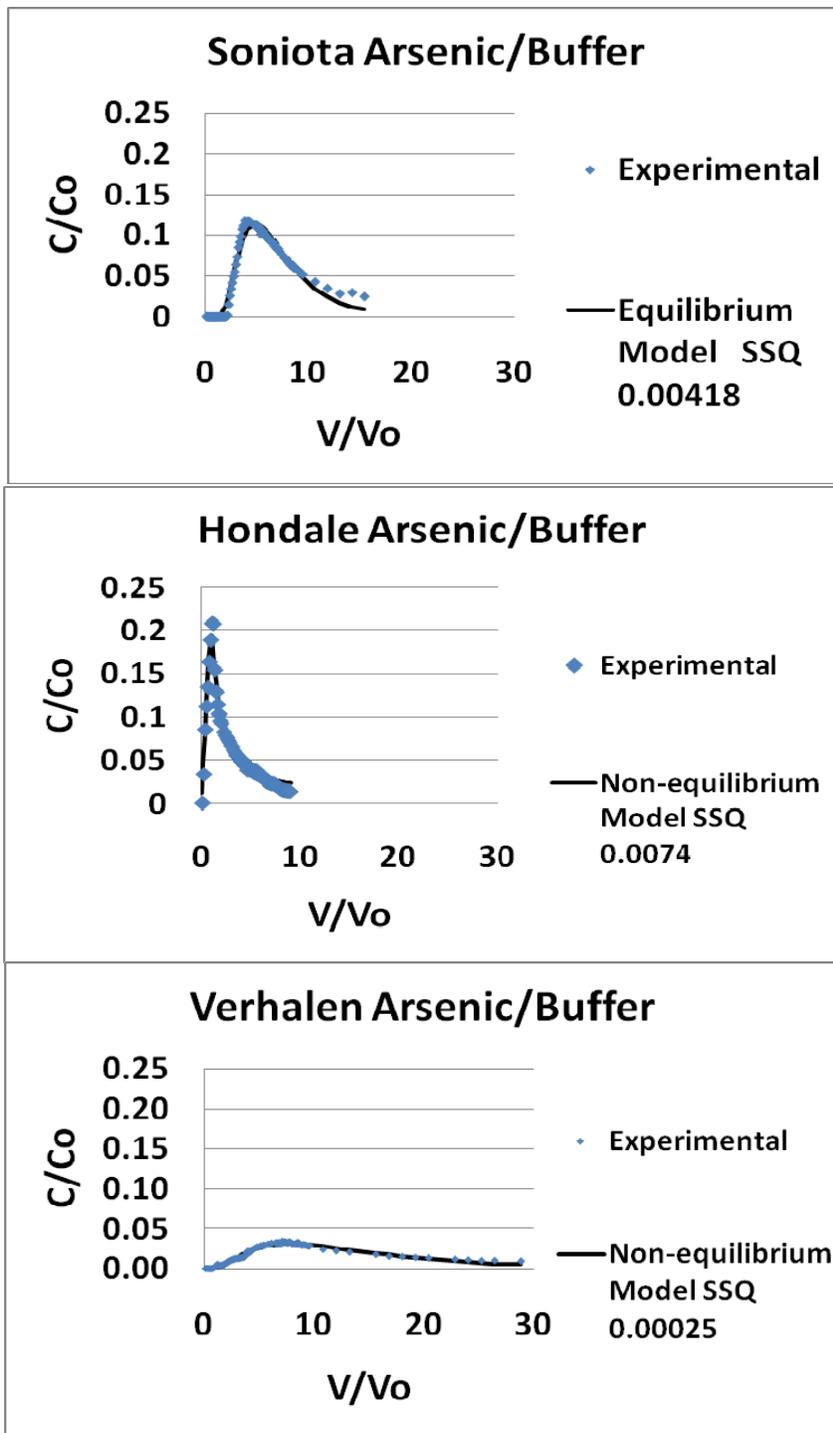
Figure 8. Breakthrough curves for arsenic in buffer on the Soniota, Hondale and
Verhalen soils. Blue points are observed values, solid lines are fitted using XFITIM non-
equilibrium model.
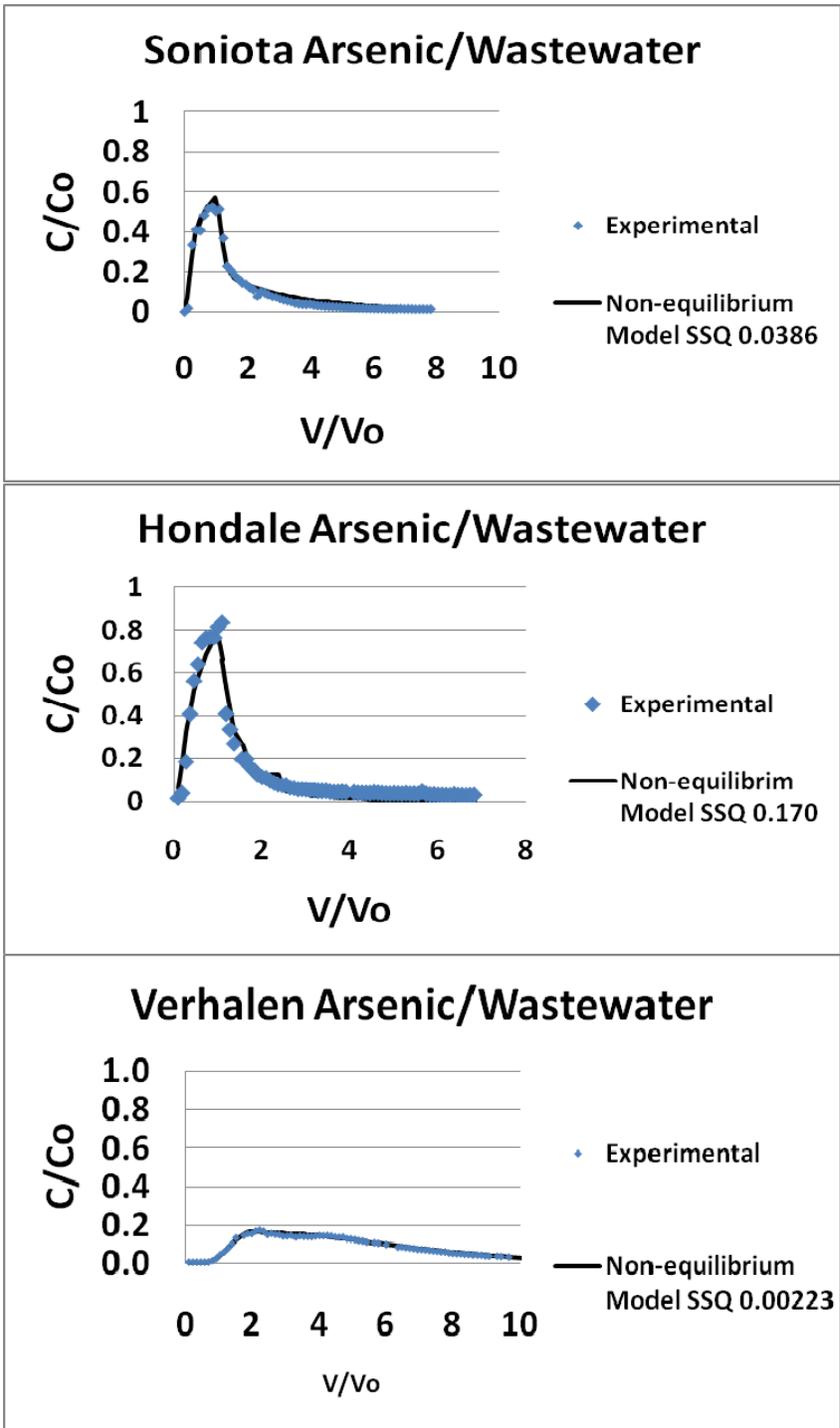
Figure 9. Breakthrough curves for arsenic in wastewater effluent on the Soniota, Hondale and Verhalen soils. Blue points are observed values, solid lines are fitted using XFITIM non-equilibrium model.

	Chloride			Arsenic in Buffer			Arsenic in effluent		
	Son.	Hon.	Ver.	Son.	Hon.	Ver.	Son.	Hon.	Ver.
R	0.99	1.01	0.88	5.87	4.54	11.91	1.29	0.40	4.45
D_m	0.09	2.82	0.43	0.85	360.66	73.09	1.59	4.21	0.28
K_d	0.00	0.00	0.00	1.41	1.35	4.52	0.09	-0.21	1.43
D_b	1.59	1.41	1.28	1.59	1.41	1.28	1.42	1.40	1.21
V_p	0.70	0.81	0.71	0.70	0.81	0.71	0.84	0.64	0.83
% mass return				67.4	53.9	40.2	92.9	107.5	100.7

Table 4. Solute transport data for the three soils with chloride, arsenic/buffer and arsenic/effluent

Discussion

While the three soils studied in this research were collected within the space of a few kilometers, their physical and chemical properties varied greatly. These properties did impact As(V) sorption both when applied with buffer and when applied with wastewater effluent. The sorption isotherms showed that the Hondale and Verhalen soils sorbed much larger amounts of arsenic than the Soniota soil. From the BTCs it can bee seen that the Verhalen clay had a lower breakthrough curve relative to the other two soils in both treatments. This is in good agreement with the literature which has established that increased clay content increases As(V) sorption.

It is also apparent from this work that the presence of wastewater effluent decreases the retardation of As(V) and increases the % mass recovery for all three soils. This finding establishes that the decrease in retardation and increase recovery are not dependent on soil properties. It is far more likely that these differences are due to the alkali pH of the wastewater and the presence of competing ions such as phosphorus in the effluent.

The two-site non-equilibrium model assumes that there are two types of binding sites. One group of sites are available instantaneously, and the other are kinetic, being available after some period of time. This two-site model successfully modeled the mobility of As(V) over time for all three soils under both treatments. While the exact mechanism for arsenic sorption, or decrease there of, has not yet been established, it has been effectively modeled by a two-site model. It is clear that the application of arsenic to soils in wastewater effluent does affect its mobility by decreasing its retardation and increasing its mass recovery values.

Future work is needed in this area to confidently establish the effect of wastewater effluent on As(V) mobility. Batch isotherm experiments must be perform at a variety of time intervals ranging from 2 hours to 3 weeks to examine how K and R vary with time. All columns must be rerun at a slower pore water velocity to investigate any effects pore velocity may have

on sorption parameters. Finally, other sorption models, such as the multi-reaction model, should be fit to the observed data to investigate their ability to better describe the sorption process over time.

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