Original Research

Use of Fly Ash as Soil Amendment to Offset Anion Exclusion Effect on Nitrate Transport

Ricardo Medina, G.B. Menezes,* C.S. Khachikian, and A. Ellis

This study investigated the direct effect of fly ash used as a soil amendment on anion exclusion in NO_3^- transport in a variably saturated soil. A sandy clay soil was amended with Class F fly ash (FA) at four levels: 0, 2, 10, and 20% FA. The soils were placed in a small soil column and kept at constant saturation using a steady-state centrifugation unsaturated flow apparatus . Three saturation ranges were investigated, 0.75 to 0.9, 0.4 to 0.45, and 0.27 to 0.29, designated as high, medium, and low saturation, respectively. Ammonium nitrate (0.7 mmol L^{-1}) solution was passed through the soil sample, and the leachate was collected at predetermined intervals up to a total volume equivalent to 12 effective pore volumes. The leachate samples were analyzed for NO_3^- concentration using ion chromatography, and breakthrough curves were constructed. Experimental and modeling results showed that the amount of fly ash and saturation level had a significant effect on the hydraulic properties of the soil, reducing the hydraulic conductivity and increasing water retention. Furthermore, it was shown that the fly ash treatment slowed the transport of NO_3^-, especially at low saturation levels, when the effect of anion exclusion is thought to be stronger.

Abbreviations: DI, deionized; FA, fly ash; HFA, high fly ash; LFA, low fly ash; MFA, medium fly ash; NFA, no fly ash; UFA, unsaturated flow apparatus.

Fly ash amendment has the potential to offset anion exclusion effects on the movement of NO_3^- in unsaturated soils. We used a steady-state centrifugation method to control saturation levels and reduce testing time.

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Vadose Zone J.
doi:10.2136/vzj2014.08.0103
Received 1 Aug. 2014.
Accepted 31 Jan. 2015.

Nitrate is one of the most widespread contaminants found in groundwater in the United States. Nitrate-contaminated water has been linked to methemoglobinemia (blue baby syndrome) (Comly, 1945; Downs, 1950; Ward et al., 2005) and is one of the contributing factors in eutrophication of lakes, rivers, and other freshwater bodies. Sources for the NO_3^- found in aquifers can be natural or anthropogenic and include wastewater treatment facilities, septic tanks, mineral dissolution, inorganic fertilizers, urea, nitrifying bacteria, N_2–fixing plants, etc. Among these sources, inorganic fertilizers are of the most concern because of the large volumes and widespread application in irrigated agriculture. A study from the USEPA surveying the integrity of groundwater aquifers throughout the United States determined that volatile organic compounds and NO_3^- are contaminants of greater concern threatening groundwater aquifers (USEPA, 2002). Additionally, the report identified septic tank systems, fertilizer application, animal feedlots, and pesticides as the major sources of contamination in more than half of the total aquifers surveyed.

Current agricultural practices rely on low fallow ratios and heavy use of fertilizers, a practice known as intensive agriculture, to maximize crop yield. Fertilizers provide essential plant nutrients such as K, P, and N (Tucker, 1999). An abundance of N allows the plant to grow faster and larger, thus many agricultural systems use synthetic fertilizers containing high amounts of N. Although plants can take up many different forms of N, including organic and inorganic forms, the ready availability and cheap price tag of nitrogenous inorganic fertilizers have made them the most widely used form of N applied to crops (Mosier et al., 2004). One such fertilizer is NH_4NO_3 because it is readily available, relatively inexpensive, and provides the largest amount of N. When

NH_4NO_3 is dissolved in water, it separates into its two ions, NH_4^+ and NO_3^-; both of these ions contain N and are easily taken up by plants.

Nitrate's high mobility in the subsurface poses additional risks of groundwater contamination. Enhanced NO_3^- mobility has been linked to anion exclusion in the literature (Allred, 2007). A study by Medina et al. (2012) concluded that saturation level alone could affect NO_3^- mobility, accelerating the transport of NO_3^- solution through the soil at low saturation levels. Additionally, Medina et al. (2012) found that the mobility of NO_3^-, relative to water flow, was strongly correlated to the saturation level of the soil; soil samples with lower saturation levels increased NO_3^- mobility, which was attributed to anion exclusion. The results are consistent with the works of others who have found that NO_3^- mobility in soil is influenced by electrostatic interactions between negatively charged NO_3^- ions and either soil minerals or soil organic matter (Allred, 2007; Gvirtzman and Gorelick, 1991). Dissolved anions are repelled by electrostatic forces between negatively charged soil particles and negatively charged molecules, causing anions to move to the center of the pore (i.e., away from the pore walls) where the average transport velocity is higher (Gvirtzman and Gorelick, 1991). Theoretically, the effect of anion exclusion is enhanced in unsaturated media transport due to the NO_3^- molecules' proximity to soil particles.

In the past decade, researchers have demonstrated the ability of recycled materials to reduce NO_3^- leaching into groundwater aquifers. Proposed amendment materials for this purpose include biochar, charcoal, sawdust, and animal manure (Irshad et al., 2014; Angst et al., 2013), and recently others have also included fly ash as a possible amendment. In this study, we investigated the transport of NO_3^- through a sandy loam at different saturation levels to assess the magnitude of anion exclusion on NO_3^- mobility. Also, we hypothesized that fly ash, a ferroaluminosilicate material by nature, will help mitigate NO_3^- transport through a variably saturated soil by the release of cations. We conducted a set of experiments to investigate the effect that different amendment levels of fly ash had on NO_3^- transport through unsaturated media. The first part of the study looked at the effect that fly ash has on the hydraulic properties of the soils. The latter part looked at the effect of fly ash on the transport of NO_3^- at different saturation levels.

Procedure

We conducted a set of flow-through experiments to investigate the effect of saturation and fly ash level, added as an amendment, on NO_3^- mobility. A small soil column (diameter = 3.3 cm, height = 5.0 cm) was placed inside an unsaturated flow apparatus (UFA), and NO_3^- solution was pumped through the sample. The UFA allows control of the saturation level of the sample by adjusting the angular velocity and fluid injection flow rate.

Unsaturated Flow Apparatus

Hydraulic properties of the soil specimen were controlled using the steady-state centrifugation–unsaturated flow apparatus (SSC-UFA) shown in Fig. 1 and a Beckman Coulter JE-6B centrifuge. A soil specimen is placed inside the UFA, a centrifugal force is applied to the soil, and fluid is simultaneously delivered through an external volumetric infusion pump (AVI Micro 210A). The specimen is allowed to rotate for a predetermined amount of time, after which the UFA must be stopped and the specimen weighed and placed back on the UFA until the water content reaches steady state. The time it takes for a soil to reach steady state depends on the physical and hydraulic properties of the soil, the rotation speed of the centrifuge, and the flow rate of the fluid passing through the soil.

The UFA allows the operator to control the variables of fluid flux and driving force in Darcy's law, which states that the flux is equal to the hydraulic conductivity of the material times the driving force. The matric potential gradient and the centrifugal force per unit volume drive the water through the soil. Darcy's law is then given by

$$q = -K(\psi)\left(\frac{d\psi}{dr} - \rho\omega^2 r\right) \qquad [1]$$

where q is the fluid flux density into the sample, K is the hydraulic conductivity, ψ is the matric potential, $d\psi/dr$ is the matric potential gradient, $\rho\omega^2 r$ is the centrifugal force per unit volume, r is the radius from the axis of rotation, ρ is the fluid density, and ω is the rotation speed (rad s^{-1}). If sufficient flux density exists, the matric potential is much less than the acceleration, $d\psi/dr << \rho\omega^2 r$. This is true above speeds of about 300 rpm for the UFA's radius of centrifugation. Hydraulic conductivity is a function of the matric potential, which is a function of the volumetric water content of the soil (Conca and Wright, 1998; Vogel et al., 2000; Singh and Kuriyan, 2002). Rearranging Eq. [1] and representing hydraulic conductivity

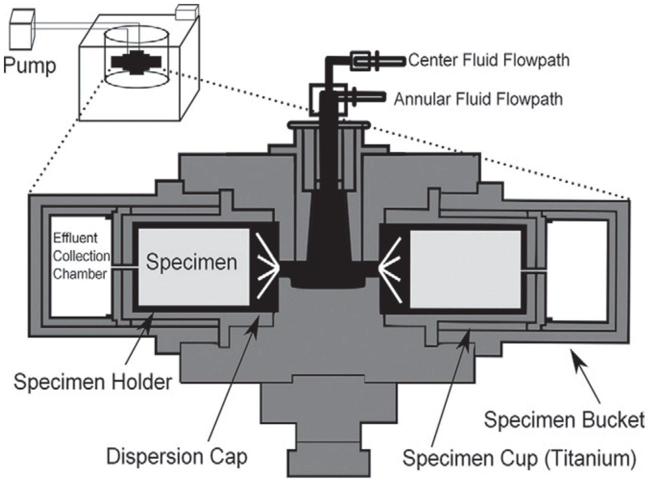

Fig. 1. Schematic of steady-state centrifugation–unsaturated flow apparatus (adapted from Conca and Wright, 1998).

as a function of volumetric water content yields a simplified equation (Menezes et al., 2011; Singh and Kuriyan, 2002):

$$K(\theta)=\frac{q}{\rho\omega^2 r} \qquad [2]$$

where θ is the volumetric water content. The UFA–infusion pump setup used in these experiments allows the user to control the fluid flux and the rotation speed; r and ρ are constant assuming that an incompressible fluid is used. With everything else constant, adjusting q and ω in the UFA setup will impose the hydraulic conductivity of the soil at a given volumetric water content. These parameters are adjusted throughout the experiment to cover a large range, across five orders of magnitude, of hydraulic conductivity values. The result shows how the hydraulic conductivity varies as a function of the volumetric water content of the soil being analyzed.

The experimental setup also allows measurement of the matric potential of a soil. The matric force is a result of interactions between the soil phase, the liquid phase (water), and the gaseous phase (air), and provides a measure of the water retention potential of the soil matrix. The use of centrifugation to measure the matric potential, i.e., fluid retention, must make the assumption that pressure and acceleration are equivalent in their effect, as felt by the soil and water inside the specimen, which only occurs at equilibrium (Conca and Wright, 1998). Using the UFA, the pressure is calculated as (Conca and Wright, 1998)

$$P=\frac{\rho\omega^2 r}{2g}\left(r_1^2-r_2^2\right) \qquad [3]$$

where P is the equivalent pressure difference (cm of H_2O), g is the acceleration due to gravity (981 cm s^{-2}), r_1 is the radial distance to the sample top (cm), r_2 is the radial distance to the sample bottom (cm), and ρ and ω are as previously defined. For a given value of P, which is equivalent to the matric potential in this case, a value of volumetric water content is obtained.

Materials

Fly ash, used as the soil amendment, is a coal combustion byproduct and is generally treated as a waste or in some occasions reused as a concrete additive for its binding properties. Fly ash is a heterogeneous mixture of amorphous and crystalline phases and is generally a fine, powdered, ferroaluminosilicate material with Al, Ca, Fe, Na, and Si as the predominant elements. In recent years, some researchers have proposed using fly ash as a soil amendment and as a source of additional nutrients for plants. Fly ash contains essential macronutrients including P, K, Ca, Mg, and S and micronutrients like Fe, Mn, Zn, Cu, Co, B, and Mo (Basu et al., 2009). However, the lack of P and N in addition to the potential leaching of trace elements has prevented fly ash from being implemented in an agricultural system. The use of fly ash as a liming agent, replacing lime and gypsum, in acidic soils has been documented by Yunusa et al. (2006). Researchers have also reported a significant increase in crop production of several products such as rice (*Oryza sativa* L.), wheat (*Triticum aestivum* L.), maize (*Zea mays* L.), grasses, mustards, as well as other cereals and grains when fly ash was added as a soil amendment (Basu et al., 2009; Kalra et al., 1998; Sarangi et al., 2001). However, most of these investigations combined fly ash with some form of organic matter and could not conclusively attribute the increased crop yield to the fly ash addition. Nevertheless, concerns about heavy metal leaching persist.

Much research has been done to study the potential for trace element leaching from fly ash. The results of several investigations have indicated that trace element leaching from fly ash is highly dependent on the type and alkalinity of the fly ash, the treatment and storage of the fly ash, the chemical properties and pH of the leaching solution, the distribution of elements, and the chemical composition and source of the parent coal (Ghodrati et al., 1995; Iyer et al., 2001; Iyer, 2002; Kim, 2002). Kim (2002) concluded that cations in fly ash (including trace elements) are only slightly soluble and thus are not too prone to leaching. Kim (2002) also showed that elements tend to be more soluble when an acid solution is passed through the fly ash, with As being the only exception. Ghodrati et al. (1995) demonstrated that heavy metal concentrations in the leachate from fly ash decreased rapidly as the leaching solution was passed through. This indicates that any soluble metals will be leached rapidly out of the fly ash. Therefore, the bulk of the heavy metals can be extracted by allowing the fly ash to be weathered, a process that can occur naturally during storage.

Fly ash has been previously used as a soil amendment in an agricultural environment. Sarangi et al. (2001) showed that fly-ash-amended soil increased the plant biomass and grain yield of rice; however, they also noted that fly ash retarded underground biomass production. Although researchers have shown that fly-ash-amended soils improve crop yield, they have not been able to attribute the increased crop yield entirely to the fly ash; instead it was attributed to various combinations of fly ash, organic matter, and nutrients (via sludge or fertilizers). Previous researchers (Sarangi et al., 2001; van der Hoek and Comans, 1996) demonstrated that Fe can slow down NO_3^- transport; however, it was also shown that the NO_3^- concentration in an Fe-rich soil was much higher at very low saturation levels than at high saturation levels. These findings are of importance because fly ash contains Fe, which may have a significant role in the transport of NO_3^- through the amended soil at different saturation levels. The inconsistencies and conflicting results of fly ash incorporated into an agricultural system indicate that there is much room for further investigation, and a study on the effect of fly ash on NO_3^- movement is lacking.

A sand–clay soil mix, the transport medium, was prepared by mixing bentonite clay with pure sand. The soil mix was prepared with 5% (w/w) bentonite and treated as the base soil. This bentonite–sand mixture is closer to an ideal loam and provides qualities beneficial for an agricultural system, such as improved texture and workability and decreased infiltration rates of fluid though the soil. Class F fly ash was added as an amendment to the base soil mixture at four different levels: 0, 2, 10, and 20% (w/w). The four amendment levels were designated as: no fly ash (NFA), low fly ash (LFA), medium fly ash (MFA), and high fly ash (HFA), respectively. The NFA soil was considered to be the control.

Experimental Setup

Duplicate soil samples were packed into two cylindrical specimen holders (inner diameter = 3.3 cm, height = 5.0 cm) and placed inside the specimen assembly as described by ASTM (2008). Three different experiments were performed for each fly-ash-amended soil: Exp. I, hydraulic conductivity; Exp. II, matric potential; and Exp. III, NO_3^- transport. Experiments I and II were used to characterize the soil hydraulic properties and determine the parameter values (q and ω) that keep the soil at a constant saturation level.

Experiment I: Hydraulic Conductivity vs. Water Content

A fully saturated specimen was placed in the UFA at low rotation speed and high flow rate, ω and q, respectively (imposing high hydraulic conductivity); once the specimen reached steady-state saturation, the flow rate was decreased and the rotation speed increased, leading to reduced hydraulic conductivity until a new equilibrium point was reached. These steps were repeated until the rate of change of the specimen weight was <0.1%; at this point, it was assumed that the specimen was close to reaching its residual water content and the experiment was terminated.

Experiment II: Soil Water Characteristic Curve

The soil specimen in Exp. II also started with a fully saturated soil; however, the specimen holder was capped with a no-flow boundary at the top, while the bottom was free to flow. The experiment started with low rotation speed (low pressure); once the specimen reached steady state, the rotation speed (and pressure) was increased and the volumetric water content was recorded for the different values of pressure (equivalent to matric potential). The saturation level was defined as $S = \theta/\theta_s$, where θ_s is the volumetric water content of the soil when fully saturated. Three different saturation levels obtained in Exp. II were analyzed during Exp. III: high saturation (0.75–0.9), medium saturation (0.4–0.45), and low saturation (0.27–0.29).

Experiment III: Nitrate Transport

In Exp. III, the specimen was prepared in the same manner as for Exp. I. The specimen started from fully saturated, and q and ω were set such that the desired saturation level (using the soil water saturation curve obtained in Exp. II) was obtained for that specific soil–fly ash mixture. Deionized (DI) water was pumped through the soil until the desired saturation level was reached, at which point the pump feed line was changed from DI water to a 7.0 mmol L^{-1} NH_4NO_3 solution. The fluid passing through the soil was collected in the effluent collection chamber; this effluent was subsequently filtered and analyzed using an ion chromatograph (Metrohm 882 Compact IC Plus). The NO_3^- concentration evolution was analyzed from data obtained from the ion chromatograph and plotting the NO_3^- breakthrough curves.

Numerical Approximation

The soil water retention curve and hydraulic conductivity of unsaturated soils can be approximated through the use of numerical methods. Numerous models have been developed in the past decades to estimate these hydraulic properties of soils, even when only limited information about the soil is known such as bulk density, particle size distribution, soil texture, and limited water content measurements. In 1980, van Genuchten introduced a model, derived from the analytical Mualem (1976) model, to estimate the volumetric water content as a function of the matric suction (or matric potential) of the unsaturated soil:

$$\Theta = \frac{\theta - \theta_r}{\theta_{sat} - \theta_r} = \left[\frac{1}{1+(\alpha h)^n}\right]^m \qquad [4]$$

where Θ is the effective (or normalized) water content, θ_r and θ_{sat} are the residual and saturated water contents, respectively, h is the matric suction (cm) assumed positive in this equation, and α (cm^{-1}), n, and m are fitting parameters. In Eq. [4], the θ_{sat} and h are assumed known parameters. The van Genuchten (1980) model prescribes $m = 1 - 1/n$; therefore, the problem reduces to finding three unknown parameters, θ_r, α, and n. Parameter estimation was performed using differential evolution (DE), a derivative-free population-based global optimization algorithm. The method starts by creating an initial population, X of N parents, $X = \{x^1, x^2, ..., x^N\}$, by sampling from the parameters' ranges $x^i \in \chi \in \Re^d$, where d denotes the dimensionality of the search space. The objective function $f(x^i)$ is calculated for each individual parent, $i = \{1, ..., N\}$, and stored in a vector, $\mathbf{F} = \{f(x^1), ..., f(x^N)\}$. The objective function for this specific problem is to minimize the sum of square residuals (SSR) calculated from the measured and estimated volumetric water contents, $SSR = \Sigma(\theta - \hat{\theta})^2$. The offspring population, Z, is created from the parent population, X, using the DE/rand/1/bin variant introduced by Storn and Price (1997), represented by

$$z^i = x^i + \mathbf{F}_{DE}\left(x^a - x^b\right) \qquad [5]$$

where z^i is a d-vector offspring from the ith parent, a and b are selected without replacement from the integers $\{1, 2, i - 1, i + 1, N\}$, and $\mathbf{F}_{DE} \in (0,2]$ is a control parameter that determines offspring diversity. Once the offspring population, $Z = \{z^1, ..., z^N\}$, has been created, their objective function values are calculated and stored in vector $\mathbf{G} = \{f(z^1), ..., f(z^N)\}$. Finally, we pairwise compare each parent with its respective child. If $G^i < F^i$, then $x^i = z^i$ and $F^i = G^i$, otherwise the ith child is rejected; $i = \{1, ..., N\}$. If the maximum number of generations has not been reached, the process returns to Eq. [5]; otherwise it is stopped, and the parent with the lowest objective function value is returned as the solution to the optimization problem.

In an effort to assess the respective effect of NO_3^- adsorption and reduced anion exclusion, the retardation factor of NO_3^- solution passing through the soil was estimated using the analytical solution to the one-dimensional advection–dispersion equation proposed by Ogata and Banks (1961). The retardation factor and dispersivity of NO_3^- were treated as unknowns and were estimated by fitting the function to the experimental breakthrough curves using MATLAB.

Results and Discussion

Soil Hydraulic Properties

The fly ash amendments had a large effect on the soil's bulk density. The greatest change was seen in the HFA samples (21.2%), while the MFA and LFA samples had bulk density increases of 10.6 and 5.3%, respectively. These results are in agreement with those obtained by Salé et al. (1996). Saturated water content increased for the LFA and MFA samples; however, the saturated water content of the HFA samples was lower than the control. The average saturated water content, θ_s, and bulk density for the soil samples used in these experiments are presented in Table 1.

The results from Exp. I indicate that the level of FA has a significant effect on the unsaturated hydraulic conductivity of the soil. The hydraulic conductivity, K, is plotted vs. volumetric water content in a semi-log plot in Fig. 2 and shows that increasing FA levels consistently shift the $K(\theta)$ plot to the right, with a divergence for the HFA amendment at high volumetric water content. The $K(\theta)$ plot of HFA initially remains closer to saturation and decreases quasi-linearly; the reason for this divergence is unknown. Research on fly-ash-amended soil has largely been focused on the crop yield resulting from fly ash applied at different rates. However, there is a lack of consensus in the literature with regard to the optimal amount of fly ash to be added as an amendment. Based on crop yield, reduced bulk density, or nutrient leachability, researchers have proposed using from 10 to 200 Mg of fly ash per hectare of agricultural land (Kalra et al., 1998; Basu et al., 2009) up to 1120 Mg ha^{-1} (Adriano et al., 2002) and 5 to 40% (w/w) (Basu et al., 2009; Ghodrati et al., 1995; Kalra et al., 1998; Pathan et al., 2003), without considering the hydraulic properties of the soil. Hydraulic conductivity can control retention time and, as a consequence, how much of the irrigation water and dissolved nutrients are absorbed by the crops. Some researchers (Ghodrati et al., 1995; Pathan et al., 2003) have proposed 20% (w/w) FA as an optimal amount; however, the results presented in Fig. 2 demonstrate that there is no significant change in hydraulic conductivity when the level of fly ash increases from 10 to 20%.

Table 1. Average saturated volumetric water content (θ_{sat}) and soil bulk density (ρ_b) of the investigated soil with no, low, medium, and high additions of fly ash.

Parameter	No fly ash	Low fly ash	Medium fly ash	High fly ash
θ_{sat}, %	31.22 (0.86)†	34.97 (0.59)	34.04 (0.55)	29.54 (1.20)
ρ_b, g cm^{-3}	1.51 (0.02)	1.59 (0.01)	1.67 (0.02)	1.83 (0.03)

† Standard deviation shown in parentheses.

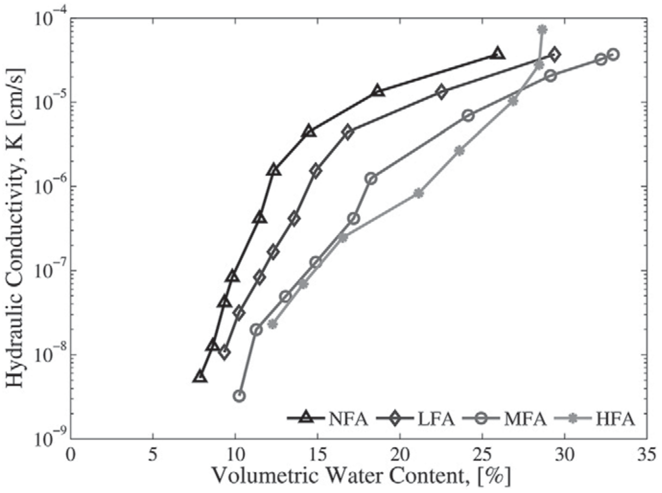

Fig. 2. Hydraulic conductivity of soils amended with low (LFA) , medium (MFA), and high (HFA) additions of fly ash or no amendment (NFA) as a function of volumetric water content.

The results from Exp. II show that water retention is also highly affected by the level of fly ash; these results are shown in Fig. 3. It can be observed that there was little difference between the control (NFA) and the LFA application at θ >10%, i.e., a soil amended with 2% FA will hold about the same amount of water as that same soil without the FA amendment. Experiment II for the NFA and MFA samples was terminated 36 h before completion due to mechanical failure; however, the general trend indicates that the residual water content (the water content that will be retained by the soil

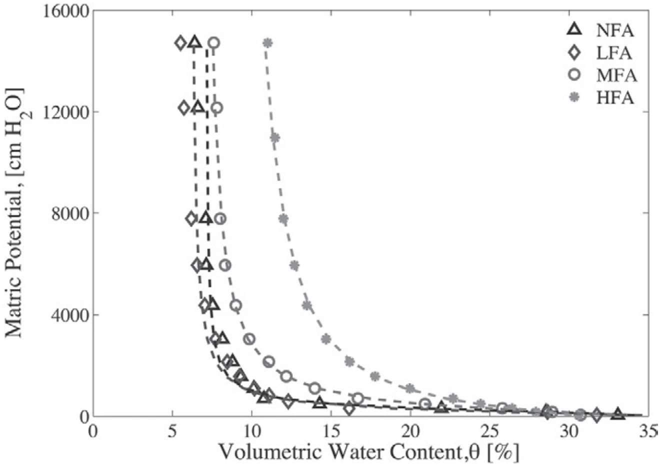

Fig. 3. Measured (symbols) and estimated (dashed lines) soil water retention curve for samples amended with low (LFA) , medium (MFA), and high (HFA) additions of fly ash or no amendment (NFA).

regardless of the pressure applied) clearly correlates with the level of FA added to the soil. The increased water retention property of a FA-amended soil has been attributed to the small particle size of the fly ash (Ghodrati et al., 1995; Kalra et al., 1998), which changes the soil texture and classification, depending on the amount of FA. In contrast with the unsaturated hydraulic conductivity, it can be seen that soil amended with 20% FA has significantly different water retention properties than a soil amended with 10% FA.

When considering fly ash as a soil amendment in an agricultural system, the impact it will have on soil hydraulic properties, such as hydraulic conductivity and water retention, should be an integral part in the decision. In terms of reducing the unsaturated hydraulic conductivity, a fly ash addition of 20% offers little advantage over that of 10% FA, and thus doubling the amount of fly ash would not be justified. However, an amendment level of 20% offers a major improvement to moisture retention compared with 10, 2, and 0% amendment levels.

Experimental data show that the field capacity increases with the level of fly ash; however, the curve did not reach its asymptote and, as such, the assumption that the last measured water content is the residual water content cannot be made. The residual water content was therefore treated as an unknown parameter and was estimated via differential evolution, along with the n and α parameters. The modeling results presented in Table 2 (and graphically in Fig. 3), indicate that the fly ash content did not have a significant effect on the residual water content. From the results obtained from differential evolution, it is clear that the fly ash content is inversely proportional to the n and m parameters; that is to say that, for a given soil, the n and m values will decrease with increasing fly ash content. The physical implication here is that the decreased n and m values increase the soil's water retention capacity; thus, for a given matric potential, the water content will be higher for the same soil with increasing fly ash content.

Nitrate Transport

The fly-ash-amended soils were subjected to three different levels of saturation—low, medium, and high—using the UFA. Based on the results from Exp. I and II, the flow rate and rotation speed were adjusted to maintain the soil at the corresponding saturation level. The soils were initially saturated with DI water; the UFA was operated using DI water until the samples reached steady state for the desired saturation level, at which point the NO_3^- flow-through experiment began. Nitrate injection was performed in a plug-flow fashion and the effluent was collected and analyzed. Analytic concentrations were used to plot the NO_3^- breakthrough curves at each of the three different saturation levels shown in Fig. 4. Two main parameters can be extracted from these plots: the breakthrough and exhaustion points. The breakthrough point defines the point at which the invading solute starts displacing the inner solute and begins to be detected at the outlet. The exhaustion point is the point at which equilibrium is reached in the sample and the inlet and outlet concentrations begin to equilibrate around a value of $C/C_0 = 1$, where C_0 is the NO_3^- concentration of the invading fluid and C is the effluent concentration.

Table 2. Estimated parameters including residual soil water content (θ_r) and shape parameters α, n, and m and the respective sum of square residuals (SSR) from differential evolution parameter estimation for soil with no, low, medium, and high additions of fly ash (NFA, LFA, MFA, and HFA, respectively).

Parameter	NFA	LFA	MFA	HFA
θ_r, %	0.0713	0.0618	0.0690	0.0801
α, cm^{-1}	0.0042	0.0059	0.0035	0.0025
n	2.5758	2.1604	1.9353	1.5733
m	0.6118	0.5371	0.4833	0.3644
SSR	7.124×10^{-4}	2.703×10^{-3}	6.280×10^{-4}	9.305×10^{-5}

Nitrate breakthrough curves for the control samples (NFA, open triangles in Fig. 4) show that the level of saturation has an effect on the way NO_3^- is transported: the low- (LS) and medium-saturation (MS) samples reached breakthrough faster (relative to water flow) than the high-saturation (HS) sample; however, the exhaustion points are the same for LS and HS, with the MS sample reaching the exhaustion point at a later time. The output NO_3^- concentrations of the sample subjected to low saturation were greater than the input concentration, i.e., $C/C_0 > 1.0$. The fact that $C > C_0$ and breakthrough was reached faster under low conductivity is partially attributed to anion exclusion, where the negatively charged NO_3^- ions are repelled from the negatively charged soil particles; this repelling action causes the NO_3^- ions to travel through the pores faster than the bulk soil solution, as discussed above.

Breakthrough curves for the soil samples subjected to high saturation are shown in Fig. 4a; the plotted curves show that all four samples reached the breakthrough point after 0.7 effective pore volumes (EPVs). After the samples reached the breakthrough point, their respective concentrations rose rapidly until they reached the exhaustion point. After the samples reached the exhaustion point, the concentrations remained semi-constant around $C/C_0 = 1$, with very little variation among samples. The results for soil samples subjected to medium saturation are presented in Fig. 4b. The samples reached the breakthrough points after only 0.2, 0.4, 0.6, and 0.8 EPVs for the LFA, NFA, MFA, and HFA amended samples, respectively. All samples then reached the exhaustion point at around 1.9 EPVs. After this, the concentrations rose at a slower rate and reached $C/C_0 = 1$ after 3 EPVs and remained close to this concentration for the rest of the experiment. At medium saturation, the level of FA started to have a more noticeable role in the transport of NO_3^-. It can be observed that at medium saturation, the retardation of NO_3^- increased with an increase of fly ash, expressed by the breakthrough curves being shifted to the right as the level of FA was increased. The behavior of the MFA breakthrough could be due to the reduced anion exclusion induced by the FA addition.

The results for the soil samples subjected to low saturation are presented in Fig. 4c. It can be seen that the level of FA had a direct impact on the retardation of the NO_3^- breakthrough curve, evidenced by the curves shifted to the right (while C/C_0 is increasing) with an increase in FA. The NFA samples reached the breakthrough point at 0.3 EPV, while the LFA, MFA, and HFA samples all reached the breakthrough point at 0.6 EPV. The exhaustion point was reached at approximately 1.4, 1.4, 1.7, and 2.2 EPVs for the NFA, LFA, MFA, and HFA amended samples, respectively. Thus comparing the control vs, the fly-ash-amended soils reinforces the hypothesis that the addition of fly ash can potentially reduce anion exclusion effects between NO_3^- and the soil when the soil is at a low enough saturation level. The addition of 2% FA effectively counteracted the repelling forces, which may be attributed to the ferroaluminosilicate nature of the fly ash matrix and its positively charged adsorption sites. Increasing the level of fly ash to 10 and 20% seems to have had a slight effect in reducing anion exclusion; however, its effects are difficult to distinguish from those effects exerted by the soil without fly ash (NFA).

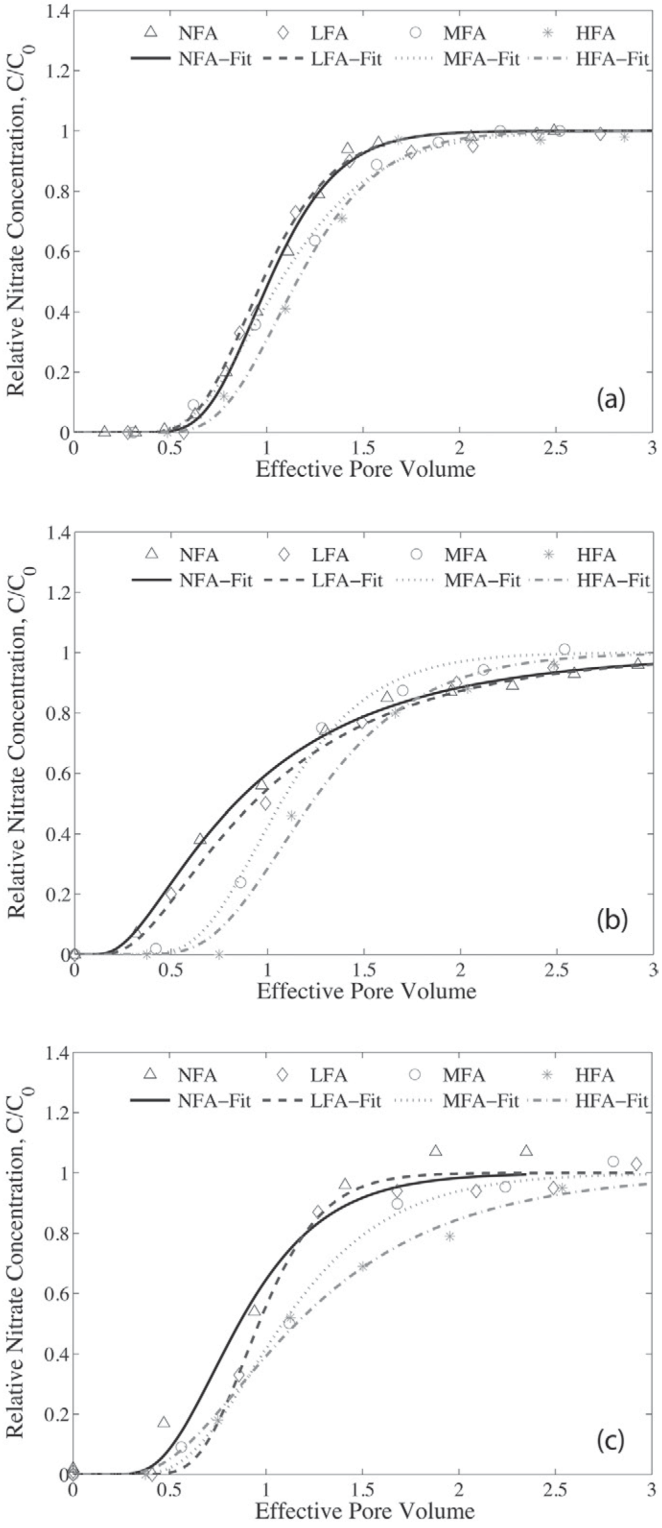

Fig. 4. Experimental and fitted NO_3 breakthrough curves for soils amended with low (LFA), medium (MFA), and high (HFA) additions of fly ash or no amendment (NFA) and subjected to (a) high saturation, (b) medium saturation, and (c) low saturation.

Although the results shown in Fig. 4c seem to indicate that FA addition to the soil mitigates anion exclusion of NO_3^-, it is difficult to distinguish between possible adsorption of NO_3^- onto the FA particles and reduced anion exclusion effects. The estimated retardation factors are plotted in Fig. 5 (and shown in Table 3) as a function of the fly ash content and level of saturation. The results show that there is a clear correlation between the levels of fly ash added to the soil and the retardation factor; however, the relationship between fly ash level and saturation is not as clear. The retardation for all saturation levels increased as the level of fly ash increased; this indicates that the fly ash was indeed slowing down NO_3^- transport through the soil sample. The effect of fly ash on the retardation factor for samples subjected to high saturation was the lowest compared with the control sample. A retardation factor <1 has been thought to be associated with anion exclusion and is clearly observable in the estimated values.

The results show similar trends of increasing retardation factor with increasing fly ash content. One possible explanation for why the retardation factor of the soil amended with 20% fly ash is higher when it is at low saturation than at higher saturation is related to the attracting and repelling van der Waals forces. When the soil is at low saturation, the fluid travels through a thin layer adjacent to the walls of the solid matrix. The reduced proximity to the wall, when the soil is at low saturation, increases the repelling forces between the soil matrix and the NO_3^- ions. This repelling force can be observed for the control case, where the retardation factor is <1 and the solution is said to be experiencing anion exclusion. Replacing 20% of the soil with fly ash changes the soil texture and increases the surface area through which the solution can pass. This increase in the surface area of the solid matrix increases the number of adsorption sites, thus reducing NO_3^- movement through the soil. Additionally, when the soil is at low saturation, the NO_3^- ions are closer to the solid matrix and thus closer to the adsorption sites, which may explain why the retardation factor for low saturation is higher than that of the same soil sample at higher saturations.

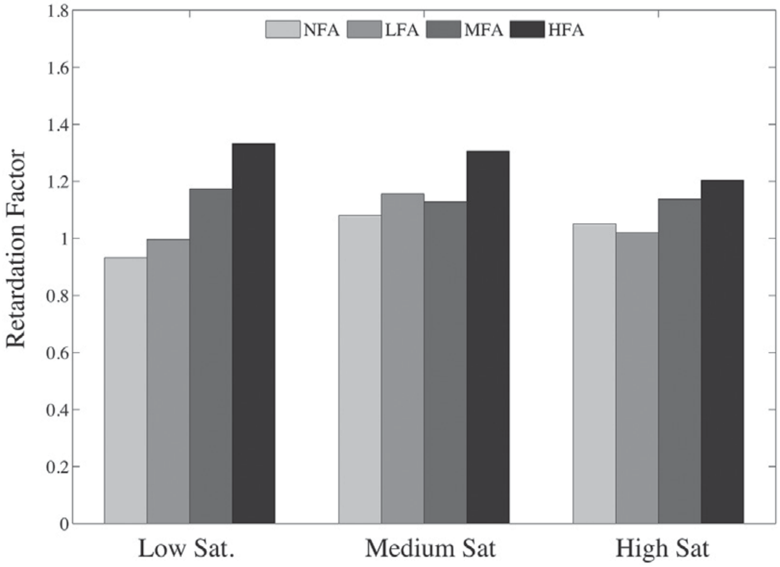

Fig. 5. Estimated retardation factors plotted as a function of no (NFA), low (LFA) , medium (MFA), or high (HFA) fly ash amendment for low, medium, and high saturation.

Variations in NO_3^- transport can be attributed to a combination of anion exclusion and NO_3^- adsorption to the fly ash; it is difficult to attribute it to one or the other, as they might not be mutually exclusive processes. The retardation of NO_3^- solution through the soil increases with increasing fly ash levels, as hypothesized. From the current analysis, it is not possible to separate the effect of sorption from the hypothesized mitigation of anion exclusion by cations released from the fly ash. Nevertheless, the addition of fly ash as an amendment increased retardation, decreasing NO_3^- mobility through unsaturated soils. The reduced or retarded transport of NO_3^- by fly ash amendment is a promising alternative to reduce NO_3^- leaching and increase the time NO_3^- is available for uptake by the plant roots.

Table 3. Results of Ogata–Banks fit of experimental breakthrough curves for samples with no, low, medium, and high additions of fly ash (NFA, LFA, MFA, and HFA, respectively).

Saturation	Sample	Retardation factor	Dispersivity	r^2
			cm	
Low	NFA	0.93199	0.42252	0.97871
	LFA	0.99658	0.17747	0.99551
	MFA	1.1738	0.40852	0.9942
	HFA	1.3326	0.77543	0.99433
Medium	NFA	1.0807	1.5445	0.99725
	LFA	1.1559	1.3056	0.99039
	MFA	1.1291	0.29302	0.99145
	HFA	1.3066	0.33434	0.98974
High	NFA	1.0509	0.19089	0.99797
	LFA	1.0197	0.21869	0.99638
	MFA	1.1379	0.32456	0.99709
	HFA	1.2048	0.21116	0.99568

Conclusion

The experimental results presented here show that the percentage of fly ash added as an amendment to a loamy sand and the saturation level have a significant impact on NO_3^- transport through the soil. Under steady-state conditions, the relative effect of anion exclusion on NO_3^- increases with a decrease in the level of saturation. These results are similar to those found in the literature for experiments under transient conditions. As expected, soil hydraulic properties are affected by the fly ash amendment level as follows: (i) the soil bulk density increased with increasing fly ash content, (ii) the saturated volumetric water content decreased with increased fly ash, (iii) the hydraulic conductivity decreased with increased fly ash, and (iv) moisture retention was increased as the fly ash content was increased. In assessing the optimum amount of fly ash to be added, two additional properties should be considered. If the goal of the amendment is to reduce the hydraulic conductivity, adding 10% fly ash is recommended as the optimum level; however, for moisture retention, adding 20% fly ash to the soil is optimum. It can also be expected that the improved hydraulic properties of the soil amended with fly ash contribute to the soil structure, porosity, and workability of the soil. Furthermore, the reduced hydraulic conductivity and increased moisture retention offer the potential to retain nitrogenous fertilizers for a longer period of time, allowing a longer contact time between the plant roots and NO_3^-, leading to NO_3^- savings through improved N use efficiency and reduced mobility.

The saturation level has a significant effect on the NO_3^- concentrations of the leachate from soils not amended with FA, as seen in Fig. 4. The leachate concentrations from samples at lower FA concentrations tended to be slightly higher than the concentration of the invading fluid. The calculated retardation factors for the control samples decreased with decreasing saturation, reaching a value <1 at the lowest saturation. A retardation factor <1 is indicative of enhanced transport of any solute; in the case of NO_3^- passing through a clayey soil, it is generally attributed to anion exclusion. This decreasing trend in retardation factor with decreasing soil saturation reinforces the role that the saturation level has on anion exclusion, especially for clayey soils. However, NO_3^- retardation factors increased with increasing fly ash amendment level compared with the control sample at each saturation level. It must be noted here that the effect of fly ash was much less when the sample was close to saturation compared with the samples at low saturation. The breakthrough curves obtained from the leaching experiments revealed that FA can offset anion exclusion, leading to reduced NO_3^- losses or increased NO_3^- availability for plant uptake.

The present study has demonstrated that the addition of FA can, indeed, reduce NO_3^- mobility due to a combination of sorption and possibly reducing anion exclusion of NO_3^-. Additionally, it was shown that the optimum fly ash amendment level is between 10 and 20% (w/w). When deciding the amount of fly ash to be used as a soil amendment, several factors should be considered: the possibility of trace element contamination (not considered in this experiment), decreased saturated volumetric water content, increased soil bulk density, decreased unsaturated hydraulic conductivity, increased moisture retention, decreased NO_3^- losses, and increased sulfate release (not presented here). These are all characteristics that may be beneficial to an agricultural system if FA is applied in conjunction with additional organic matter, while mitigating groundwater contamination by NO_3^-. The characteristics mentioned above should be considered when making the decision to add fly ash as a soil amendment. Finally, although the direct effect on anion exclusion is not clear, fly ash amendment does offset anion exclusion of NO_3^- solution; therefore, fly ash offers the possibility of increased retention time, reduced NO_3^- losses, and reduced groundwater contamination.

Acknowledgments

The work presented here was partially supported by the NSF, Center for Energy and Sustainability at CSULA (HRD-0932421) and NSF Research Grants CMMI 1126892 and ARA-R2-0963539. The findings presented here are the sole opinions of the authors and do not represent the views of the National Science Foundation or CSULA.

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