Transport of fertilizer-derived chemicals through unsaturated soil

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Abstract

An experimental approach using the steady state centrifugation method to study the transport of nutrients derived from agriculture related activities, under different soil saturation conditions, is presented. The level of saturation in a sand-clay mixed soil is controlled in the laboratory using steady-state centrifugation. A 7.0 mM NH_4NO_3 solution was used to study the transport of nitrate through the soil mixture. The solution was pumped into the soil with the volumetric flow rate controlled by an external pump which is connected to a steady-state centrifugation-unsaturated flow apparatus (UFA). Three target saturation levels (S_H=0.95, S_M=0.50, and S_L=0.25) were chosen to represent high, medium and low saturations of the soil, respectively. Nitrate breakthrough curves were plotted and adsorption coefficients, K_d, were then calculated for the high, medium, and low saturation level; they were 13.5 µl/mg, 2.9 µl/mg, and -8.8 µl/mg, respectively. The data shows a relationship exists between the saturation level and adsorption coefficient for the given soil; suggesting that saturation does play a role in the distribution coefficient and consequently in the retardation factor.

Keywords: nitrate, saturation level, transport, centrifuge, adsorption.

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Introduction

Agriculture in semi-arid regions relies on the use of fertilizers to provide essential nutrients such as nitrogen, phosphorous, and potassium. The desire and/or necessity for high crop yield in these regions may lead to the irresponsible application of fertilizers (Young et al, 2009). Application of nitrate based fertilizer leads to increased percolation into the subsurface and into groundwater. High levels of nitrate in the groundwater pose a serious health hazard if it reaches the drinking water supply. The U.S. EPA has established the MCL for NO_3 to be 10mg/L (measured as NO_3-N). Therefore, the investigation of the effect of saturation level on the mobility of a nitrate-based fertilizer in a clay-sand mix soil is pertinent**.** This study presents nitrate mobility in a bentonite-sand soil mix (5% clay by weight) analyzing the mass transport parameters of hydraulic conductivity and nitrate adsorption coefficient as they are affected by the saturation level of the soil receiving the solution.

Methodology

A sand-clay soil mix (soil) was prepared by mixing bentonite (montmorillonite K-10, Acros Organics) clay, five percent by weight, with sand (pure sand, 40-100 mesh, Acros Organics). An unsaturated flow apparatus (UFA) was used to control variables under unsaturated conditions for the analysis of the fate and transport parameters. The soil was compacted into two separate specimen holders and saturated with deionized water (DI water) following specifications set forth in ASTM-D6527. The saturated soil in the specimen holder was then placed into the specimen assembly of the UFA. The specimen assembly was attached to the UFA (as seen in Fig. 1); rotation speed and pump flowrate was set according to the target saturation level desired. A 7.0 mM NH_4NO_3 (100.0 mg L^{-1} NO_3-N) solution was used to represent an intensive application of nitrate fertilizer which had a pH ranging from 4.68-6.18.

The experiment was run in the UFA using DI water until steady-state was reached; here steady-state is defined as the condition when there is no change in weight of the specimen, which means that the amount of fluid going in is equal to the amount of fluid going out. After reaching steady-state the DI water line, was replaced by the NH_4NO_3 solution, nitrate solution herein. Using the UFA to the hydraulic conductivity can then be computed using a modified version of Darcy's equation, Eq. 1. (Menezes et al, 2011, Singh et al. 2002).

$$K = \frac{q}{(\rho\omega^2 r)} \qquad \text{(Eq. 1)}$$

where K is hydraulic conductivity, q is flowrate, ρ is the density of the fluid, ω is the rotation speed, and r is the radius from the axis of rotation to the center of the soil sample. The hydraulic conductivity is a function of the volumetric water content (Vogel et al. 2000, Singh et al. 2002, Conca et al. 1998), using Eq. 1 and running a continuous UFA desaturation experiment the water retention curve is developed. From the water retention curve, the appropriate flowrate and rotation speed were chosen for the desired saturation level, which is directly related to the water content in the soil. Thus, the proper flowrate and rotation speeds to get three distinct saturation levels are determined.

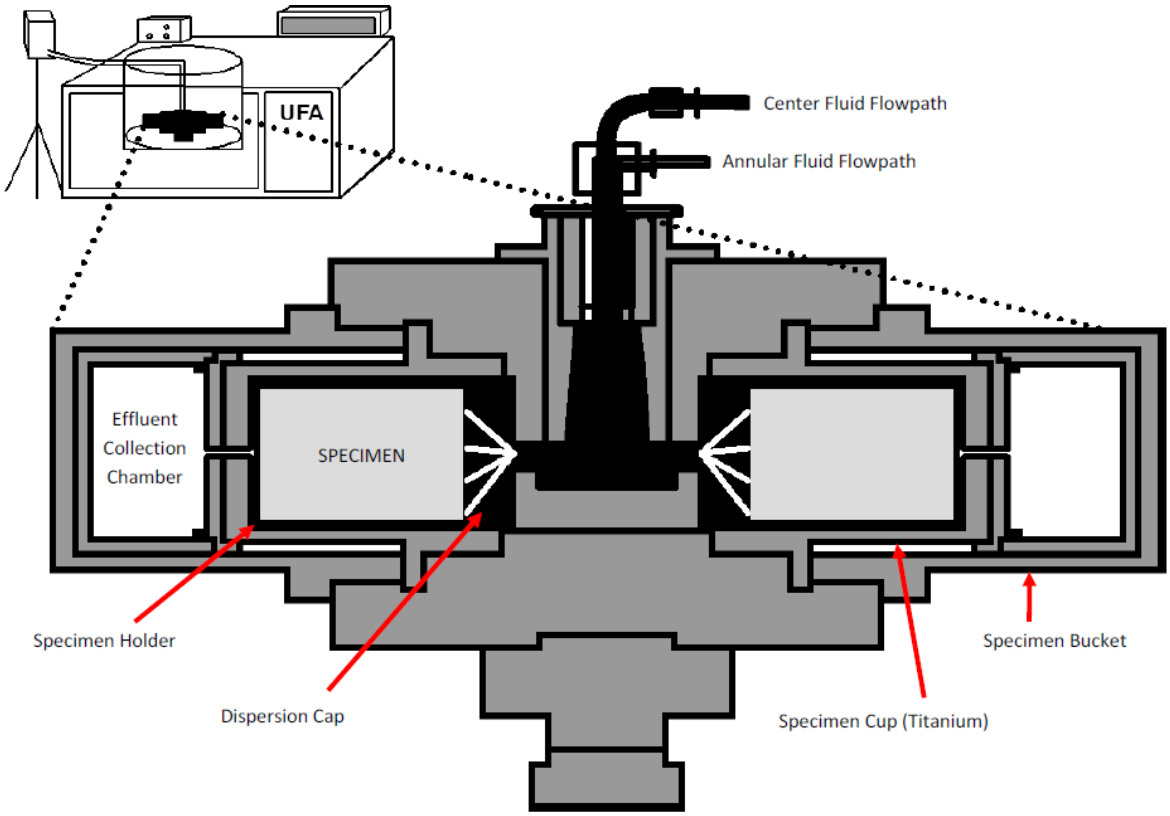

Figure 1. Schematic of SSC-UFA rotor. (Adapted from Conca and Wright, 1998)

For the 3 levels of saturation, the effluent solution exiting the soil sample was collected in the effluent collection chamber and analyzed for anion concentration using an ion chromatograph. Specimen holder was weighed every time the UFA was stopped, to verify the saturation level at every step. The samples were run in the UFA and at every 2.0 ml of solution (about 15% of pore volume) pumped through, the UFA was stopped, effluent was collected and the specimen holder was weighed. The concentration of nitrate in the effluent and the original solution were determined using an ion chromatograph. The ratio of nitrate concentration in the effluent, C, to the nitrate concentration of the original solution being pumped, C_0, were plotted versus the number of *effective pore volumes*. Here, one *effective pore volume* is defined as the pore volume occupied by the water in the void space at the given saturation level, it is not the total porosity of the soil. The *effective pore volume* is used because it is assumed any space which is not saturated does not contribute to the transport and are considered inactive and therefore lowers the pore volume that contributes in the transport of the fluid. Plotting the ratio of nitrate concentrations versus the pore volumes that have passed through the soil specimen gives the breakthrough curves shown in Figure 3. From the breakthrough curves the retardation factor of nitrate can be calculated using Eq. 2 (Site, 2001 and Dudukovic, 2005); once the retardation factor is determined for a given saturation level, the adsorption coefficient can be derived using Eq. 3 (Site, 2001):

$$R_f = \int_0^{p_{max}} \left(1 - \frac{C}{C_0}\right) dp \qquad \text{(Eq.2)}$$

$$R_f = 1 + \left(\frac{\rho_b}{\theta}\right) K_d \qquad \text{(Eq. 3)}$$

where R_f is the retardation factor, p is the 'effective' pore volume, ρ_b is the bulk density of the soil (g/ml), θ is the volumetric water content, K_d is the adsorption coefficient (ml/g), and C and C_0 as previously defined (mg/l). Equation 2 above represents the area above the breakthrough curves. The adsorption coefficient, K_d, has units of (ml/g) which is the volume of contaminant being sorbed onto the surface of the soil per gram of soil.

Results and Discussion

The UFA is best suited to study fluid movement in low conductivity materials under unsaturated conditions. Figure 2 shows a plot of the aimed measured saturation level for the 3 levels investigated. While some variation was observed in the high saturation samples, minimal variation was observed for the medium and low saturation samples. It is possible that the deviation of saturation levels observed (from 0.93 to 0.76) was caused by soil loss due to the high pumping flowrate and the relatively low rotation speed.

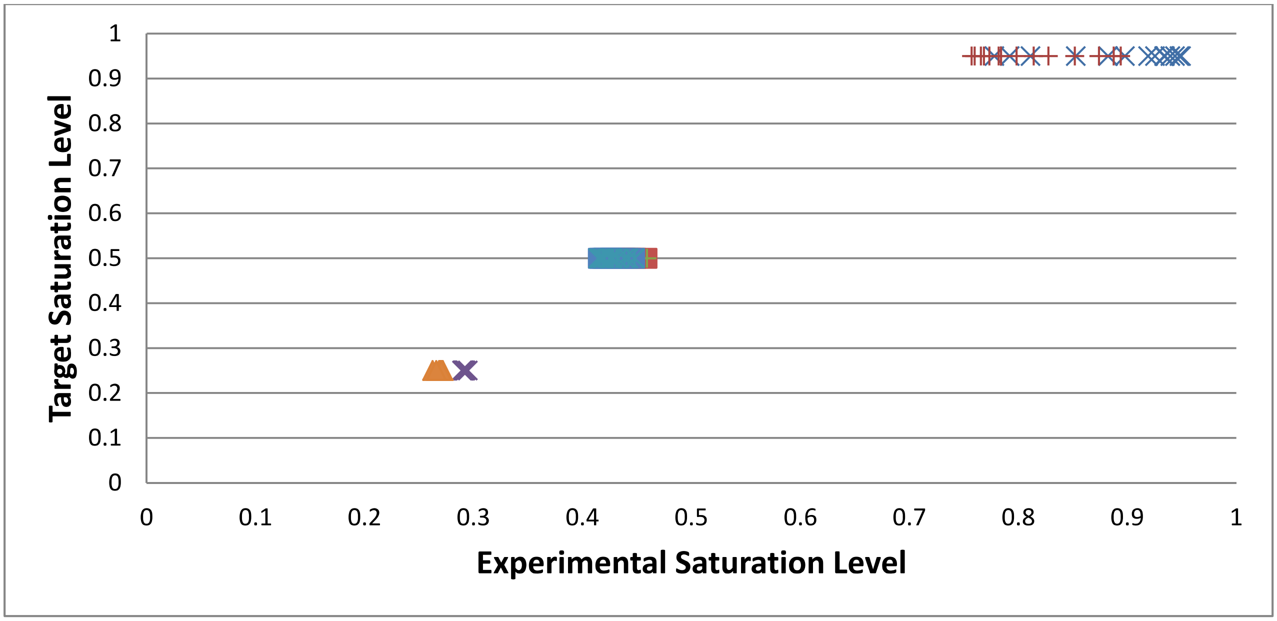

Figure 2. Experimental versus target saturation levels (Target saturation levels: S_L=0.25, S_M=0.5, S_H=0.95).

Though the high saturation samples presented some deviation from steady state conditions, based on the weight of the sample and the calculated saturation level at each step, it can be assumed that the chemical interactions are not affected by this fact, because the hydraulic properties under centrifugation were shown to hold true for steady-state (Conca and Wright, 1998) and transient conditions (Nimmo, 1990).

The nitrate breakthrough curves (BTC's) follow the same pattern, as expected, however there are some interesting differences that can be observed. The BTC's in Fig. 3 show that the high and low saturation samples reach the breakthrough value of 1 faster than the medium saturation; the high saturation curve has a steeper slope at the beginning compared to that of the low and medium saturations; and both medium and high saturation samples level out, while the low saturation samples fluctuate and deviate from the expected maximum level of 1.

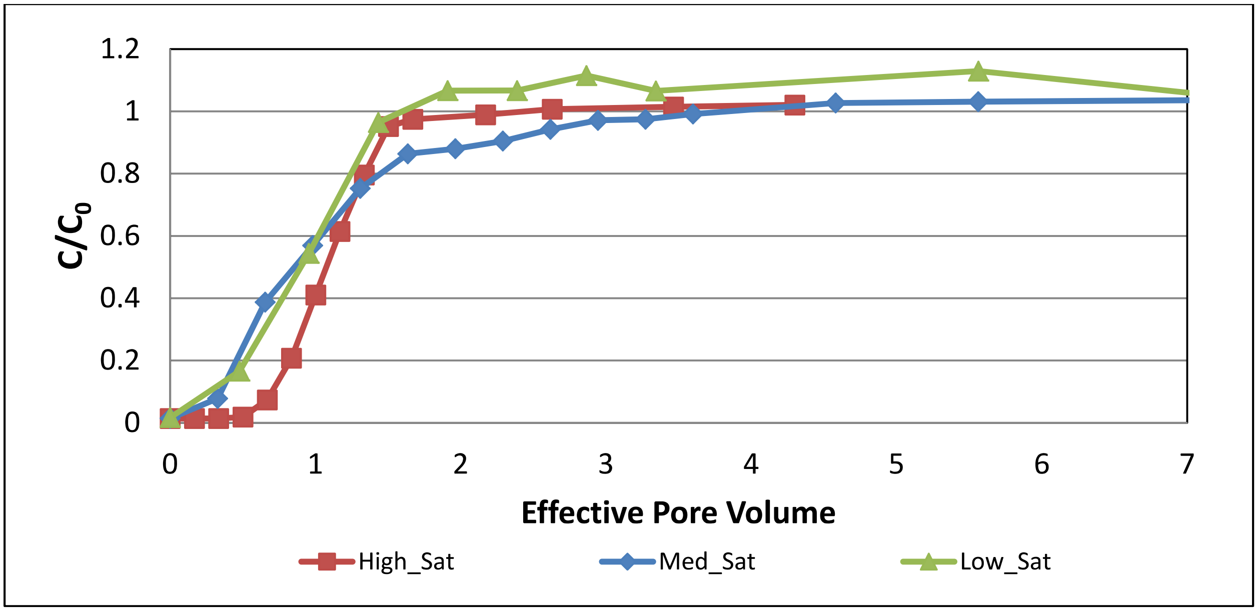

Figure 3. Nitrate breakthrough curves (BTC) at different saturation levels.

Allred (2008) proposes an explanation, citing that in dry soils, anion exclusion makes NO_3^- more mobile and can potentially produce high-concentration NO_3^- "pulses" that move through the soil. This is an interesting point because in this experiment, there are no other anions competing for the adsorption sites, as is the case in Allred's experiment, which might be an indication of anion exclusion caused by the diffusion double layer.

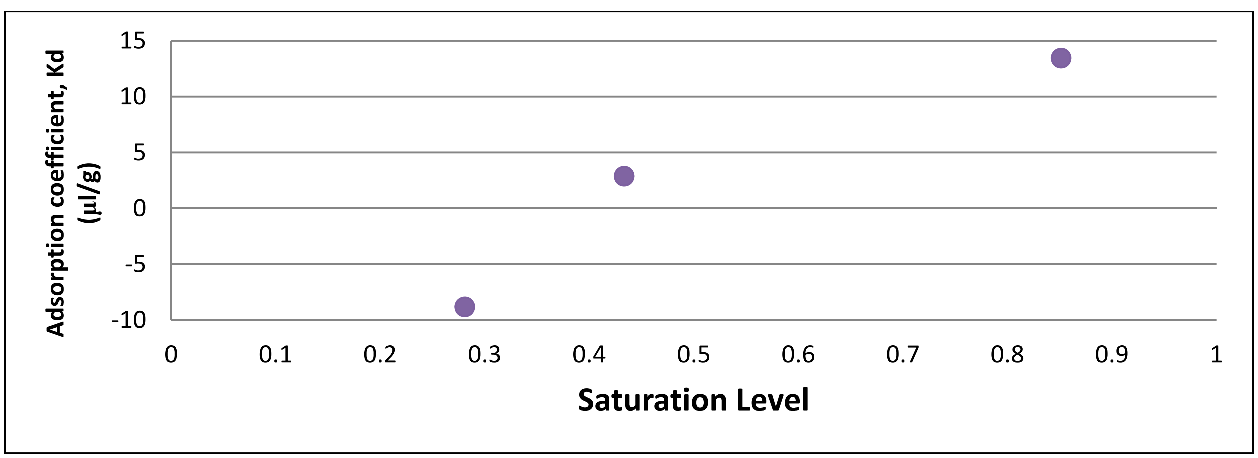

Figure 4. Adsorption coefficient vs. saturation levels.

The calculated values of K_d are plotted versus the saturation level and shown in Figure 4. As can be observed from the figures, the BTC follow the same trend, which is also confirmed by the relatively similar retardation factors. However, the calculation of the adsorption coefficient shows that the saturation level plays a significant role in the removal of nitrate via adsorption under high saturation levels, while it seems to accelerate "pulse" concentrations under low saturation levels. The negative K_d, obtained because nitrate is actually moving faster than the average water velocity, is an indication that equation (3), which is commonly used in modeling fate and transport of contaminants in groundwater should not be applied under low saturation conditions. Further research should focus on better understanding the magnitude of anion exclusion under low saturation conditions. The results are summarized in Table 1. all values derived or calculated shown are the average values of two samples for that particular parameter.

Table 1. Summary of results for the different saturation levels.

Sample	Pump Flowrate, q (ml/hr)	Rotation Speed (rpm)	Avg. Saturation Level	Avg. Retardation factor, R_f	Avg. Adsorption Coefficient, K_d (µl/mg)
High_Sat	30	400	0.85	1.08	13.46
Med_Sat	20	1600	0.43	1.03	2.89
Low_Sat	1	3500	0.28	0.86	-8.81

Conclusion

Nitrate is a very mobile contaminant that can reach drinking water aquifers very easily. The work presented here demonstrates that the saturation level of the soil plays a significant role in the adsorption and/or "pulse" acceleration of this contaminant. A soil with high saturation level (~0.85) may be able to adsorb up to 13.5 µl of nitrate per gram of soil, medium saturation level (~0.43) may adsorb 2.9 µl of nitrate per gram of soil, while a soil with a low saturation level (~0.28) might actually speed up the transport of nitrate, indicated by the negative sign of the adsorption coefficient, -8.8 μl of nitrate per gram of soil mixture. The negative K_d, is an indication that approaches for modeling retardation in unsaturated soils needs to take into account the effect of anion exclusion. The effect the saturation level of the soil has on the transport of a mobile contaminant such as nitrate should be regarded with priority when considering remediation techniques for the removal of this and other contaminants that may have similar properties as that of nitrate.

Future work should examine the effect of saturation level for a soil mixture with different clay percentage; furthermore, the effect observed for low saturation level should be further investigated.

Acknowledgements

The authors would like to thank Dr. Andre Ellis for his kind support and advice and the CSU-Council on Ocean Affairs, Science and Technology (COAST) Federal Work-Study Pilot Program and the NSF-funded CREST center (HRD-0932421) for partially funding the work presented here. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

Manufacturers and/or product names are provided for information purposes only and do not imply endorsement by the authors, CEAS, or COAST.

References

Allred, B.J. (2008). "Cation effects on nitrate mobility in an unsaturated soil." In transactions of the American Society of Agricultural and Biological Engineers, Soil and Water Division. 51: pp. 1997-2012

ASTM Standard D6527,(2000) "Determining unsaturated and saturated hydraulic conductivity in porous media by steady-state centrifugation" ASTM International, West Conshohocken, PA, 2000, DOI: 10.1520/D6527-00R08, www.astm.org.

Conca, J.L., Wright, J. (1998). "The UFA method for rapid, direct measurement of unsaturated transport properties in soil, sediment, and rock." Australian Journal of Soil Research, 36: pp. 291-315.

Dudukovic, M. (2005). "Adsorption" St. Louis, MO: Chemical Reaction Engineering Laboratory, Washington University.

Menezes, G. B., Ward, A., Moo-Young, H. K. (2011). "Unsaturated flow in anisotropic heterogeneous media: a centrifuge study". International Journal of Hydrology Science and Technology 1(3/4):147 - 163

Nimmo, J.R. (1990). "Experimental testing of transient unsaturated flow theory at low water content in a centrifugal field." Water Resources Journal, 26: pp. 1951-1960

Prado, B., Duwig, C., Etchevers, J., Gaudet, J., & Vauclin, M. (2010). "Nitrate fate in Mexican Andosol: Is it affected by preferential flow?" Agricultural Water Management, 98: pp. 1441-1450.

Singh D.N., Kuriyan, S.J. (2002). "Estimation of hydraulic conductivity of unsaturated soils using a geotechnical centrifuge." Canadian Geotechnical Journal, 39: pp. 684-694.

Site, D.A. (2001). "Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants: a review." Journal of Physical and Chemical Reference Data, 30: pp. 187-439

Vogel, T., van Genuchten, M.Th., Cislerova, M. (2000). "Effect of the shape of the soil hydraulic functions near saturation on variably-saturated flow predictions." Advances in Water

Resources, 24: pp. 133-144.

Young, S.M., Pitawala, A., Gunatilake, J. (2009). “Fate of phosphate and nitrate in waters of an intensive agricultural area in the dry zone of Sri Lanka.” Paddy Water Environment Journal, 8: pp. 71-79.