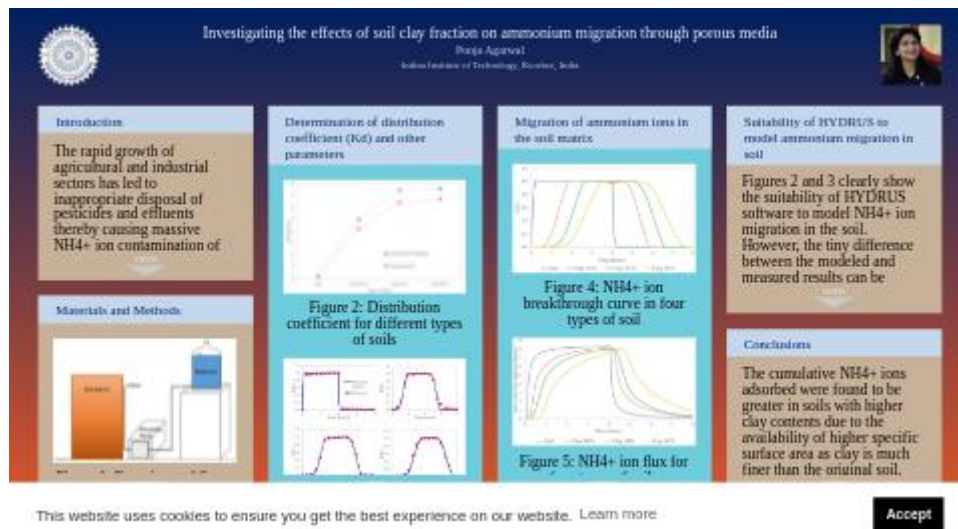


# Investigating the effects of soil clay fraction on ammonium migration through porous media



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## ABSTRACT

Ammonium contamination is one of the most noxious forms of groundwater contamination caused due to the extensive use of nitrogen fertilizers. Contaminant transport is governed by the adsorption mechanism, which varies as the contaminant migrates through different types of soils. It is important to understand the adsorption mechanism of ammonium ions and the factors influencing it to predict and mitigate their contamination. This work attempts at thoroughly investigating the effects of clay content present in the soil on the adsorption and eventually on the retardation of ammonium ions movement in the porous media. Ammonium ions transport was examined for three soil types with different clay proportions, by column and batch experiments. The experimental results were verified by simulating ammonium ion migration by numerical modeling using HYDRUS 2D software. It was observed the ammonium ions adsorption increases with the increase in the clay content of the soil. Therefore, greater content of clay in the soil enhances the retardation of ammonium migration in the soil. Further, it can be construed that the soil clay fraction ensures a reduction in deeper penetration of ammonium ions as a contaminant into the subsurface.

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## INTRODUCTION

The rapid growth of agricultural and industrial sectors has led to inappropriate disposal of pesticides and effluents thereby causing massive  $\text{NH}_4^+$  ion contamination of surface and groundwater resources.

In order to resolve this problem, we must elucidate the migration and adsorption of  $\text{NH}_4^+$  ions in the soil, emphasizing determining the total amount of  $\text{NH}_4^+$  ion absorbed by the soil and the depth of migration of ammonium in the soil.

Ammonium is an inorganic pollutant and being a positively charged ion, has been found to be prone to adsorption by negatively charged clay particles.

For this purpose, the distribution coefficient ( $K_d$ ) of  $\text{NH}_4^+$  ions in soil and water has been found to be the most reliable parameter to describe the  $\text{NH}_4^+$  ion adsorption capacity of the soil.

The distribution coefficient of ammonium differs significantly with the size of soil particles thereby defining the process of adsorption for different types of soils.

In this study, an attempt has been made to establish the effect of increasing clay content in the soil on the distribution coefficient of ammonium to get a better understanding of the overall adsorption of ammonium in a soil matrix and to quantitatively characterize the migration of ammonium ion. The objectives of the present work are (1) to determine the distribution coefficient for soils having different clay contents and explore its behavior to the increasing clay content in the soil and (2) to quantitatively illustrate the effects of clay content present in the soil on the adsorption and eventually on the retardation of ammonium ions movement.

## MATERIALS AND METHODS

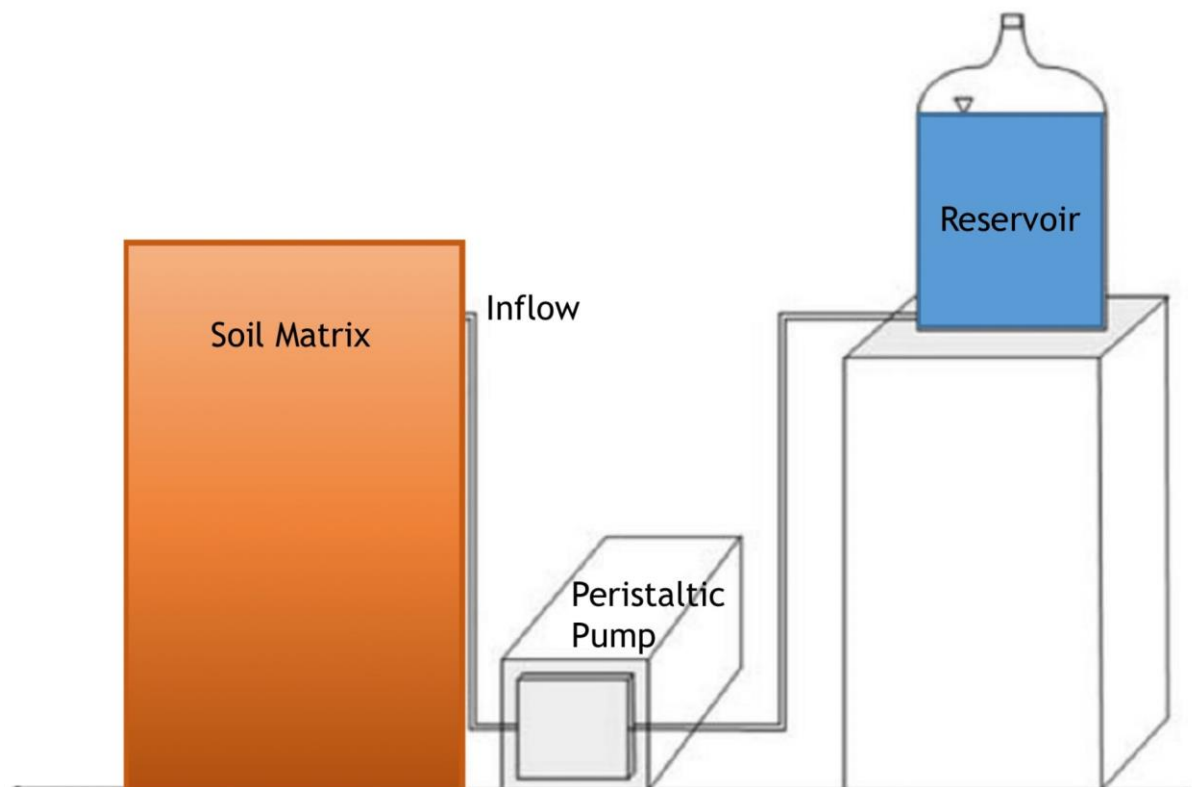


Figure 1: Experimental Setup

Experiments were conducted to analyze the flow of ammonium ions through four types of soil samples. The first soil sample was the natural soil and three other samples were prepared by mixing 10, 30, and 60 percent of clay in the original sample.

The properties of the natural soil and clay are mentioned in the table below:

Type of soil	Bulk density (g/cm <sup>3</sup> )	Porosity (%)	Hydraulic conductivity (10 <sup>-3</sup> cm/s)	Moisture (%)
Soil	1.46	44.93	6.79	13.41
Clay	1.39	47.74	2.55	15.60

The distribution coefficient and relevant parameters were then calculated using the following formulas:

$$K_d = V/M \cdot (C_0 - C_1) / C_1$$

$$R_d = 1 + (\rho) / (n_e) K_d$$

The experimental results were verified by numerical solutions obtained by HYDRUS software. The following equation was used to acquire the numerical solution:

$$\frac{\partial C}{\partial t} = D/R_d \left( \frac{\partial^2 x}{\partial x^2} \right) - V/(n_e R_d) \frac{\partial C}{\partial x}$$

## DETERMINATION OF DISTRIBUTION COEFFICIENT (KD) AND OTHER PARAMETERS

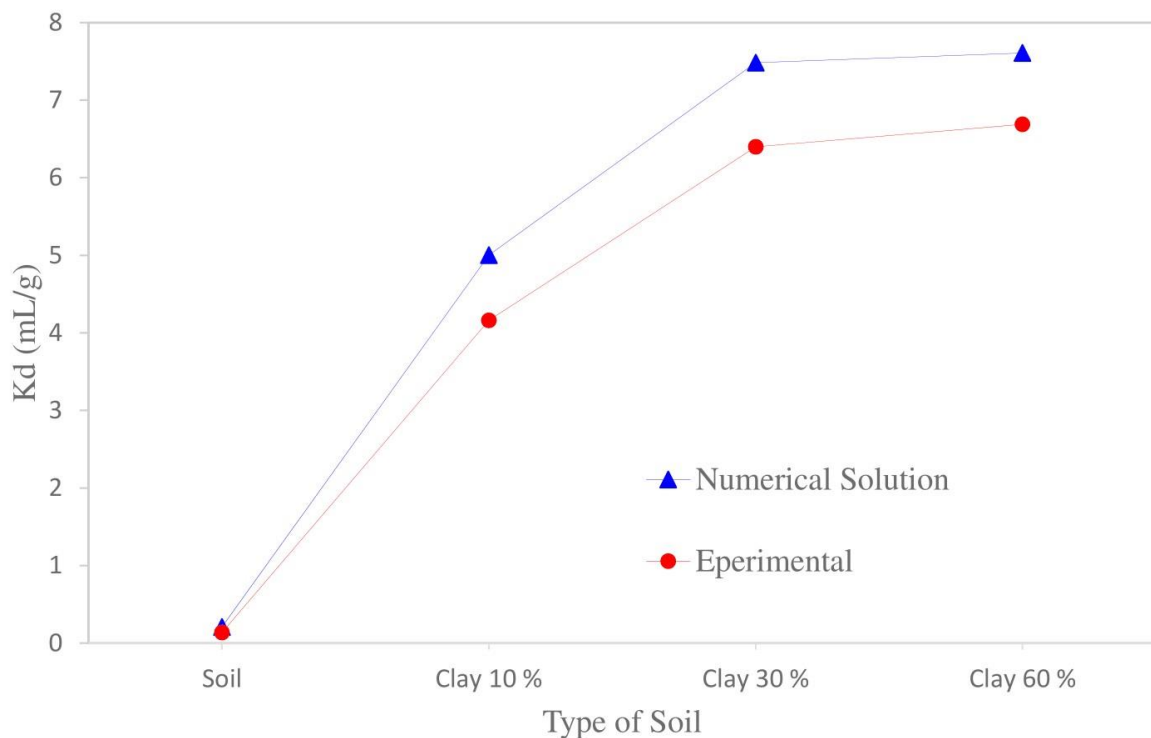


Figure 2: Distribution coefficient for different types of soils

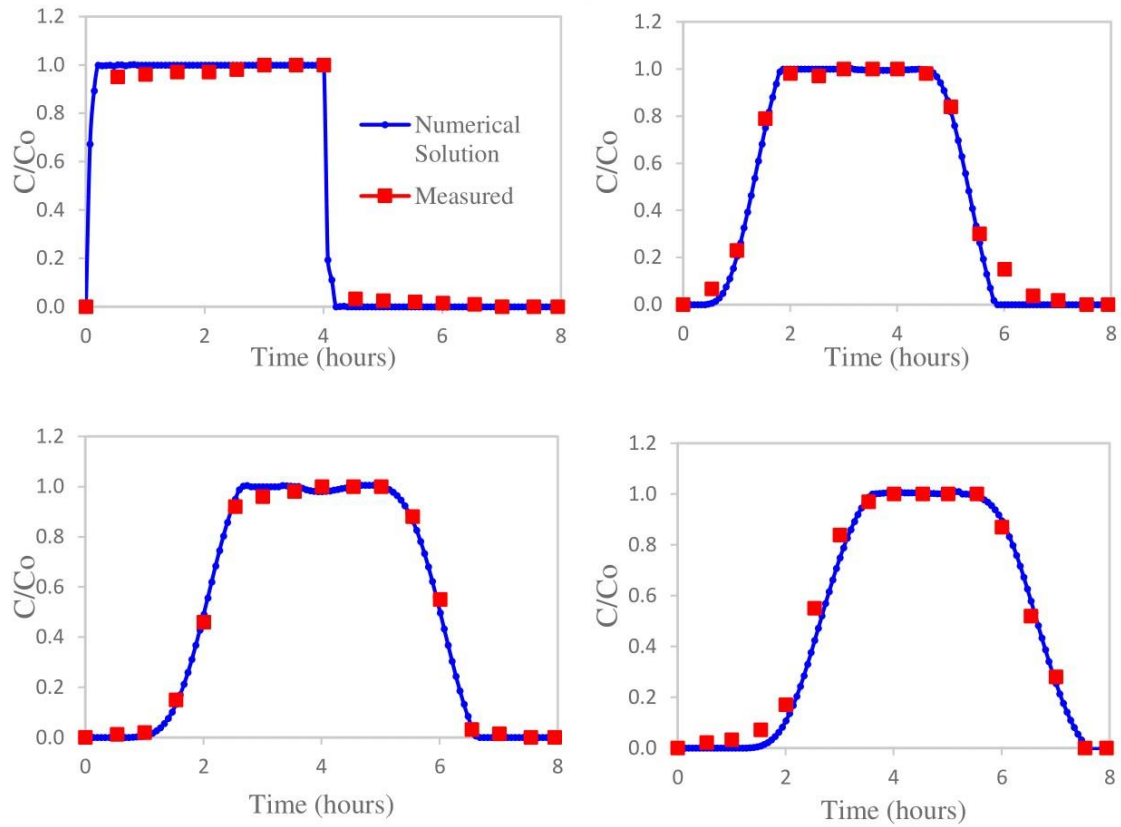


Figure 3: The breakthrough curve of  $\text{NH}_4^+$  ion in (a) Soil, (b) Soil with 10% clay, (c) Soil with 30% clay, and (d) Soil with 60% clay

Table 2: Distribution coefficient and relevant parameters of  $\text{NH}_4^+$  ion in the soil matrix

Types of Soils	Kd		Rd		Migration time (min)	Rate of migration (cm/min)
	Experimental Solution	Numerical Solution	Experimental Solution	Numerical Solution		
Soil	0.135	0.206	1.439	1.671	264.492	35.417
Clay 10%	4.159	5.001	14.369	17.073	352.596	1.059
Clay 30%	6.398	7.483	21.117	24.526	400.656	0.684
Clay 60%	6.688	7.608	21.344	24.140	456.726	0.530

The average size of the soil mixed with clay was smaller than that of the original soil, so the distribution coefficient of ammonium in the mixed soil increased with the increase in the proportion of clay in the soil.

At the beginning of the experiment, the  $\text{NH}_4^+$  adsorption rate was relatively high, and it became nearly zero after some time when sorption-desorption equilibrium is reached before the concentration of ions eventually decreases to zero.

The migration time of ammonium solution in mixed soil gradually increases with the increasing clay content of the soil.

## SUITABILITY OF HYDRUS TO MODEL AMMONIUM MIGRATION IN SOIL

[VIDEO] [https://res.cloudinary.com/amuze-interactive/image/upload/v1638363370/agu-fm2021/8B-5D-6B-9C-AF-C5-31-85-21-84-48-E4-90-02-52-26/Image/ezgif.com-gif-maker\\_2\\_oo7m5x.mp4](https://res.cloudinary.com/amuze-interactive/image/upload/v1638363370/agu-fm2021/8B-5D-6B-9C-AF-C5-31-85-21-84-48-E4-90-02-52-26/Image/ezgif.com-gif-maker_2_oo7m5x.mp4)

Figures 2 and 3 clearly show the suitability of HYDRUS software to m

odel  $\text{NH}_4^+$  ion migration in the soil. However, the tiny difference between the modeled and measured results can be attributed to the fact that the parameters optimized by the empirical formula are average parameters, which are slightly different from the actual situation. In general, the distribution coefficient of ammonium in a soil matrix calculated by model fitting is a good validation of the measured results. Therefore, the model could simulate the  $\text{NH}_4^+$  adsorption process although predicting a slightly faster  $\text{NH}_4^+$  transport than the actual transport that occurred in the experiments.

## MIGRATION OF AMMONIUM IONS IN THE SOIL MATRIX

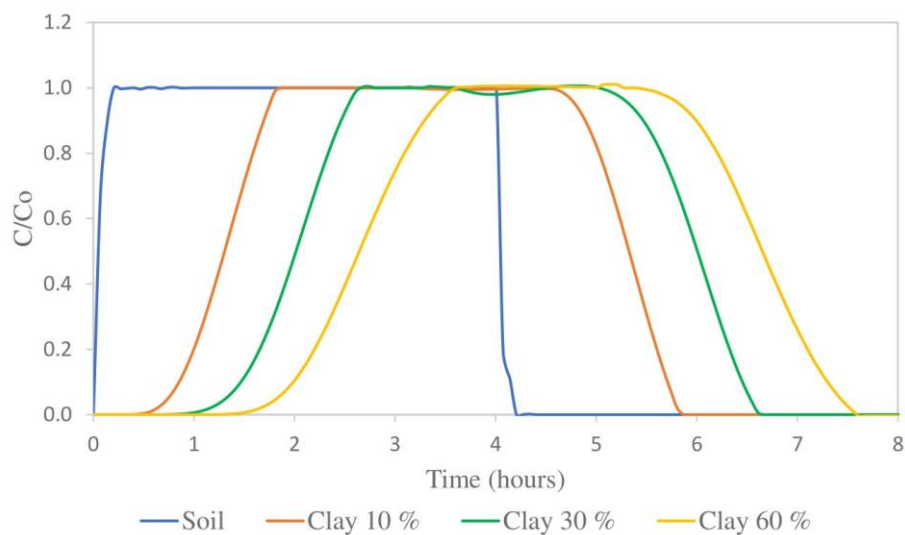


Figure 4:  $\text{NH}_4^+$  ion breakthrough curve in four types of soil

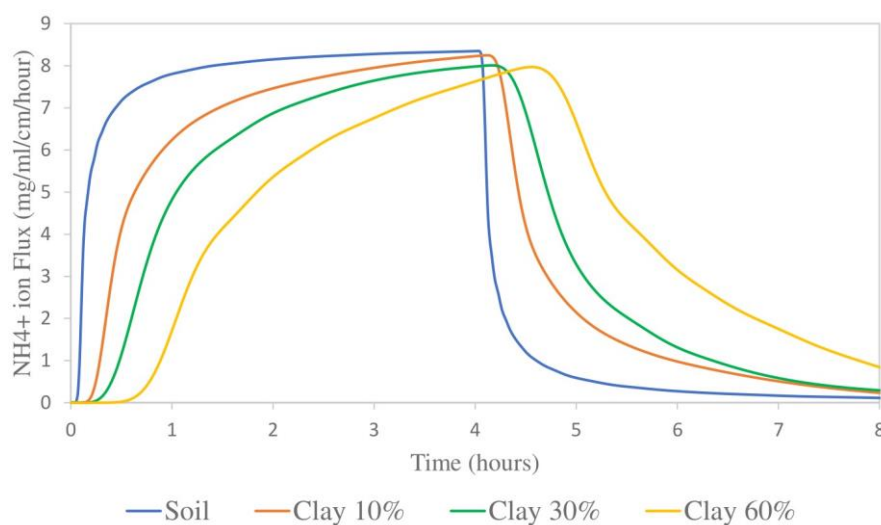


Figure 5:  $\text{NH}_4^+$  ion flux for four types of soils

The increase in the sorption capacity of the porous medium caused the shifting of the breakthrough to the right (greater pore volume) signifying that the BTCs for the higher clay content get slightly retarded as compared to that of the original soil medium. Hence, the soil and clay breakthrough were proved to be affected by the particle size and its sorption capacity.

The  $\text{NH}_4^+$  ions flux peak for soil has been found to be higher and obtained earlier in this study as compared to soil with higher clay content. This implies adsorption kinetics in soil occurred later than in clayey soil. This shows that fast adsorption kinetics play a key role in determining the  $\text{NH}_4^+$  ions adsorption efficiency of the adsorbents. The availability of a larger surface area in clayey soil is also favorable for  $\text{NH}_4^+$  ions adsorption. It can be stated that even a minimal fraction of small grain sizes might have a major impact on  $\text{NH}_4^+$  ions retention in the soil matrix. Hence, retention of  $\text{NH}_4^+$  ions by soil media is lesser than clayey soil media.

## CONCLUSIONS

The cumulative  $\text{NH}_4^+$  ions adsorbed were found to be greater in soils with higher clay contents due to the availability of higher specific surface area as clay is much finer than the original soil. Therefore, depending on geo-environmental conditions, the various type of soils considered in this study facilitates the  $\text{NH}_4^+$  ions transport as well as aid in its adsorption in saturated subsurface flows. Hence, evaluation of clayey soils  $\text{NH}_4^+$  ion transport under different environmental conditions is helpful in prevention and regulation of  $\text{NH}_4^+$  ion concentration in soil, for proposal of waste disposals sites or estimating the degree of contamination of polluted areas, and in checking groundwater contamination.