

THE UNIVERSITY OF MANITOBA

THE EFFECT OF SOIL-PHOSPHATE INTERACTION UPON CONVECTIVE  
TRANSPORT OF ORTHOPHOSPHATE IN SOIL COLUMNS

by

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## ABSTRACT

Three Manitoba soils, Wellwood clay loam, Stockton sandy loam, Lakeland silt loam, varying in pH, were chosen for the purpose of investigating the convective transport of orthophosphate in soil.

The technique chosen for this investigation was the miscible displacement experiment. The method consisted of feeding a known solution of orthophosphate continually onto a soil column and collecting the effluent for the analysis of orthophosphate.

Factors affecting the breakthrough curves were studied by choosing various lengths of soil columns and flow velocities. The breakthrough curves of the three soils were quite different with respect to the soils. The breakthrough curve of the Stockton soil appeared earlier than the other two soils. This indicated that the rate of movement of phosphate was the fastest in the Stockton soil. The slowest rate of movement of phosphate was found in the Lakeland soil. The rates of movement of orthophosphate were approximately 4 to 8 times slower than that of water. The Wellwood and Lakeland soils had a higher fixation capacity than the Stockton soil. Increasing the flow rate modified the breakthrough curves. The breakthrough curves of the Wellwood and Lakeland soils were changed more than the breakthrough curve of the Stockton soil. However, the breakthrough curves remained almost unchanged if the contact time between the solution and the soil was kept constant irrespective of the flow rate and soil length. It seemed that the

contact time of the solution with a soil had a great effect upon controlling the breakthrough curve.

The rate of adsorption of orthophosphate by soil was investigated using a soil column of 0.5 cm in length. Two flow rates were applied to observe the effect of the flow rate upon the rate of adsorption of orthophosphate by using thin sections of a soil column. The rates of the adsorption of orthophosphate by the three soils were all linearly expressible on semilog paper. The magnitude of the slope of the three soils at different flow rates showed that the interaction between soils and phosphate in solution was a rather slow process and was dependent upon the soil characteristics and flow rate. The Stockton sandy loam had the lowest phosphate fixation while the Lakeland had the highest phosphate fixation. The Wellwood had an intermediate phosphate fixation.

The rate of desorption of orthophosphate from the soils was studied by leaching the  $^{32}\text{P}$  saturated soils with water. The leaching pattern of phosphate from the Wellwood and Stockton soils showed an initial rapid decrease of phosphate followed by a very slow process. The desorption of phosphate from the Lakeland soil showed only a gradual decrease of phosphate at the slow rate of leaching. The value of the desorption rate was dependent upon the flow rate. The amount of phosphate desorbed seemed independent of the flow velocity and was only the function of the amount adsorbed.

It was concluded that the rate of movement of orthophosphate in soil is the function of the adsorption capacity, flow rate of solution, soil length, and the rate of adsorption of phosphate by soils.

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## CHAPTER I

### INTRODUCTION

Diffusion of orthophosphate in soil or in a soil like system has received considerable investigation. One reason for this extensive investigation was based on the assumption that the rate of supply of orthophosphate to a plant may be controlled by diffusion. Some contradictory explanations are presented. In some cases the diffusion process seems to limit the rate of supply of orthophosphate to the plant while the opposite is true in other cases.

Another reason for the investigation was to estimate the relative magnitude of possible ground water pollution by orthophosphate. A rough calculation based on the diffusion experiment alone showed that orthophosphate did not seem to contribute much to ground water pollution.

Aside from the diffusive transport, orthophosphate applied to a soil can also be transported by convection. Knowledge on convective transport is very limited and little work on this subject has been reported.

The general theory of convective transport of a non-interacting element and of an element which interacts with soil instantaneously is very much advanced. The theory is known to be successful in predicting the rate of movement of the element. However, the theory of transport of an interacting element with finite rate is still in a primitive stage.

Only a few cases were investigated.

Phosphate and soil interaction is known to be relatively slow but the rate law is not yet fully understood. Also the adsorption isotherm which excludes the rate process is known to be non-linear. These two characteristics make theoretical analysis of the phosphate transport in soil very complicated.

The purpose of this investigation is to observe the effects of soil characteristics, solution flow velocity, and the rate of interaction upon the convective transport of orthophosphate in soil. A miscible displacement technique was chosen to study the transport. Three soil samples from Manitoba which were acid, neutral and alkaline in reaction were chosen to represent a varying degree of the magnitude of soil and phosphate interaction.

Various soil column lengths and flow velocity were chosen to observe the effect of flow velocity and the contact time between the soil and solution on the rate of movement of orthophosphate. To determine the relative magnitude of the empirical rate constants, a soil column of 0.5 cm length was chosen. It is assumed that the soil and the solution were more or less uniformly mixed within 0.5 cm length.

An attempt was made to correlate the relative rate of orthophosphate movement in soil with soil characteristics, flow velocities of the orthophosphate solution and the length of soil column.

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 MISCIBLE DISPLACEMENT

Transport phenomena of an element through porous material like soil can be grouped depending upon the mode of input. If a solution of different composition is introduced into one end of a soil column continuously, it is generally called miscible displacement. If, however, a finite quantity of some material is introduced into a porous material and it is eluted with another solution, it is called elution development (15). The plot of the solution concentration coming out from a finite length of soil or porous material against the volume of solution passed is called a breakthrough curve for miscible displacement, and an elution curve for elution development.

The subject of miscible displacement in soil research was reviewed by Nielsen and Biggar (26). They have presented five possible types of breakthrough curves for miscible displacement depending upon the following effects.

These are (1) piston flow, (2) longitudinal dispersion, (3) extremely wide range in velocity distribution, (4) chemical reaction, (5) exclusion of solute by solute-solid interaction or velocity distribution with velocity near zero.

Piston flow would rarely occur in soil because of the diffusion and dispersion due to variation in velocity

within the soil pore.

Longitudinal dispersion occurs in soil because of the radial variation in the velocity within a soil pore as well as the variation in pore sizes. The problem for the simplest capillary tube was researched by Taylor (34) and presented by Scheidegger (33). According to Taylor (34), the dispersion coefficient is directly proportional to the velocity and inversely proportional to the diffusion coefficient. Scheidegger (33) presented the velocity dependence of the dispersion coefficient to be  $v^n$  where the value of  $n$  lies between 1 and 2, and  $v$  is the velocity. An extremely wide range in velocity distribution will occur in a soil which is composed of unequal-sized aggregates with a large variation in pore radius.

Chemical reactions in soil can be classified as adsorption, exchange, precipitation and transformation. These affect the breakthrough curve considerably.

Exclusion of solute is caused by electrostatic repulsion by charged soil particles and incomplete mixing throughout the entire soil. For example, anions are repelled from the negatively charged clay surfaces and incomplete mixing occurs due to the nearly stagnant pore solution.

In practice, all effects except piston flow may contribute to the pattern of breakthrough curve. The effect of longitudinal dispersion and variation in velocity distribution tend to cause a general broadening of the breakthrough curve. Separation of these two effects is very

difficult. In practice both effects are grouped into one, the dispersion effect.

Any interaction of the solute with a medium directly or indirectly will modify the shape and position of the breakthrough curve. If the displacing fluid or its solutes are retained within the column by any chemical or physical process, such as adsorption and/or exchange, the breakthrough curve will be translated to the right of one pore volume. The breakthrough curve translates to the left of one pore volume when there are increasing effects of solute concentration, the repulsion of anions away from the negatively charged clay surfaces and solution of slightly soluble salts in the soil. At each flow rate, the breakthrough curves are changed, indicating different mixing behavior, when the roles of displaced and displacing liquid are reversed. The contribution of diffusion to the dispersion of the moving front might be expected to increase as the velocity is decreased. As the velocity decreases, the front becomes sharper when the dispersion by velocity distribution decreases.

## 2.2 FACTORS AFFECTING THE BREAKTHROUGH CURVE.

### 2.2.1. DENSITY AND VISCOSITY EFFECT

Krupp and Elrick (20) reported that the density difference between the liquids was a much more significant factor than the velocity difference in altering the displacement pattern. Initially the dispersion coefficient decreased when



the flow rate was decreased and then greatly increased in a density unstable configuration. Biggar and Nielsen (3) also used the values of density and viscosity of any two solutions in a simple equation to determine whether a displacement will be stable in a vertical column.

### 2.2.2 VELOCITY EFFECT

Nielsen and Biggar (27) conducted a considerable amount of miscible displacement research by using glass beads to investigate the contribution of diffusion and variations in pore-water velocity to mixing. Sodium chloride and sodium sulphate solution of the same density were allowed to displace each other from the saturated glass beads. Tritium was added to the NaCl at several flow velocities. At the velocity of 56.7 cm per hour, the chloride breakthrough curve was abrupt and  $C/C_0 = .5$  corresponded to one pore volume. At the velocity of 0.122 cm per hour, the chloride breakthrough curve was shifted to the left at 0.2 pore volume. The chloride breakthrough curve at this low velocity was quite skewed and required 3 pore volumes of the solution before  $C/C_0$  reached 1. At the intermediate velocity of 0.395 cm per hour, the breakthrough curve appeared between the previous two curves. The values for the diffusion coefficient of chloride were  $1.74 \times 10^{-4}$ ,  $6.21 \times 10^{-5}$  and  $2.82 \times 10^{-5}$   $\text{cm}^2$  per sec, respectively, for the above experimental velocities. The breakthrough curves of tritium for the three velocities were clearly separated and similar to the chloride breakthrough curves.

The effect of the degree of saturation and the flow velocity upon the rate of movement of chloride was investigated by Corey et al. (11). They used saturated and unsaturated sandstone columns of 30 cm length. It was found that under saturated and unsaturated conditions, different average velocities have entirely different shape and position of breakthrough curves. In a saturated condition, and at a velocity of 5.64 cm per hour, the maximum relative chloride concentration of the elution curve was 0.9 and this occurred at 200 ml of effluent volume. The chloride distribution curve had a smaller dispersion in the saturated condition than in the unsaturated condition, as evidenced from the sharper normal distribution curve. The maximum relative concentration of chloride under the unsaturated condition with velocity of 0.534 cm per hour, was close to one and this occurred at 140 ml effluent volume.

### 2.2.3 TORTUOSITY EFFECT

Tortuous pathway of a substance in closely packed spheres, which is one of the simplest, is about 1.22 times longer than a linear path (15). Also the average cross-sectional area of a pathway is not constant throughout the path. These effects undoubtedly cause a substance to travel through a soil column in a more tortuous manner than a corresponding capillary tube. Olsen et al. (29) suggest that the tortuous effect is one of the most important factors affecting diffusion in soil. Tortuosity factor has meaning only if an observer

chooses the external coordinate as a reference.

#### 2.2.4 MOISTURE CONTENT EFFECT

Lowering the moisture content below water saturation decreased the measured diffusion of Rb (14). A reduction in moisture content of 5-10% gave a 1,000 fold decrease in the measured diffusion of Rb. Some of the effect of lowering the moisture content is due to increased tortuosity. Some effects may be due to net decrease in the quantity of ion in solution as compared to adsorbed ion.

Corey et al. (11) found the dispersion coefficient of chloride and tritium had average values of 0.652 and 0.754 cm<sup>2</sup> per hour for saturated systems, respectively. However, under unsaturated conditions, the dispersion coefficient of the chloride and tritium were 0.135 and 0.282 cm<sup>2</sup> per hour, respectively.

Lai and Mortland (21) studied the diffusion of ions in clay minerals under extremely low moisture content where most of the diffusion was assumed to be due to surface diffusion. The diffusion of sodium in expanded Na-vermiculite, which has both internal and external surfaces available for cationic diffusion, decreased with increasing diffusion time. The diffusion coefficient of Na ion for external surface was found to be  $3.01 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$  which was 5 times that of the internal surface ( $0.61 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ ). The diffusion coefficient of Na and Cs ions in collapsed K-vermiculite which

has only external surface available for diffusion remained unchanged with diffusion time.

### 2.2.5 CHEMICAL EFFECT

Chemical reaction is one of the most important factors controlling the position of the breakthrough curve. The previous factors affect mainly the shape of the breakthrough curve. In the case of the diffusion experiment, the chemical reaction contributes variable effects as compared to the above factors. Instead of spreading the diffusion front, the chemical reaction term sometimes contracts and sometimes spreads the diffusion front.

Evans and Barber (13) investigated the factors influencing the diffusion of  $^{86}\text{Rb}$  in soil. They found that the rate of diffusion of  $^{86}\text{Rb}$  was slower when the  $^{86}\text{Rb}$  was more strongly absorbed by soils. In leached dry soils, the correlation coefficient between  $D_p/b$  and percent  $^{86}\text{Rb}$  fixed gave the value of  $r$  of 0.9. When the soil was moist, the correlation coefficient,  $r$ , was found to be 0.42. They found the following relationship for the leached dry soil.

$$\frac{D_p}{b} = K_1 F + K_2$$

where  $D_p$  is the diffusion coefficient,  $b$  is the chemical reaction factor,  $F$  is the percent fixation of  $^{86}\text{Rb}$  against  $\text{NH}_4\text{OAc}$  extraction.  $K_1$  and  $K_2$  are the constants.

Hodgson et al. (16) studied the diffusion of zinc from a  $ZnCO_3$  precipitate through an agar-agar to a stream of continuously flowing water. In one treatment, part of the agar-agar was replaced by Ca-polygalacturonate to incorporate a fixed negative charge in the gel in the form of carboxyl groups. In a second treatment, Ca-citrate was introduced into the following stream of water. All phases of these two systems were kept in equilibrium with  $CaCO_3$ . They found that both Ca-PGA treatment and the mobile complexing agent increased the transport of Zn in the system, but the second treatment was more effective than the first.

Biggar and Nielsen (1) found that the distribution of a tracer some distance from its source, depends upon the geometry of the porous material and the physical and chemical interaction of the tracer solution and media during flow. At flow velocity of 2.11 cm per hour, there was no separation of breakthrough curve between tritium and chloride in saturated glass beads of 200  $\mu$  in diameter. The approach of the curves to  $C/C_0 = 1$  was more gradual. The separation of the tracers occurred in sandstone at a velocity of 0.20 cm per hour and a water content of 0.482  $cm^2$  per  $cm^2$ . The initial breakthrough curves of the tritium was translated to the right of the chloride. As displacement continued the two curves crossed and approached sharply to  $C/C_0 = 1$ . When the water content was decreased by 0.01, both breakthrough curves of tritium and chloride translated to the left of one pore volume and approached  $C/C_0 = 1$  more gradually than at the higher water content.