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TRANSPORT OF K+, Br– AND KBr THROUGH SATURATED INERT AND REACTIVE POROUS MEDIA

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ABSTRACT

Anion and cations from applied agrochemicals move differently during their bulk solution flow through sandy and clayey soils. Saturated inert and reactive porous media were generated from solid glass beads and sepiolite clay minerals to mimic sandy and clayey soils. At various flow rates, solutions of potassium bromide (KBr) of various concentrations were separately displaced by deionised water through above media. Concentration of the Br^- and K^+ were determined with ion-specific electrodes and bulk solution by electrical conductivity (EC). Non-linear curve fitting technique, CXTFIT 2.0 was used to parameterize the breakthrough curves (BTCs) of each displacement for the anion, the cation and the bulk solution, separately. Shapes of BTCs and parameters including retardation factor (R) and coefficient of hydrodynamic dispersion (D) were used to interpret the results. For inert media, (a) the matching BTCs of the anion, cation and bulk solution were observed, (b) the values of R did not differ significantly from unity, and (c) the values of D were identical and changed with pore-water velocity, (v). For reactive media, the BTCs of anion appeared before and those of cations appeared after those of bulk solution. The values of R were less than unity for the anion, greater than unity for the cation and close to unity for the bulk solution. However, the values of D were unaffected by nature of solutes or solution. Results of this study show that separation of ions observed during transport through reactive material means that the composition as well as the concentration of a solution change continuously during flow through reactive soils i.e. clay or clay loam. These results have implications for exchange of cations and exclusion of anions from the soils of varying net negative charges and cation exchange capacity.

Keywords: Solute transport, pore-water velocity, retardation, hydrodynamic dispersion, reactive soils, sepiolite.

INTRODUCTION

Surface of the sandy soils is inert whereas those involved clay aggregates are reactive. When nutrients are applied to such soils their fate differs based on net charge on the surface of aggregates. In soils having a net surface charge the individual ions move through the soil matrix at rates which differ from that of the bulk solution. If the net charge is negative, cations are retarded because of adsorption at the surfaces of the soil particles, and anions accelerated because of their exclusion from the diffuse double layer (De Haan and Bolt, 1963). As a result, the composition as well as the concentration of the soil solution changes as the solution moves through the soil. The simultaneous flow of water and solutes through a porous material can be represented with the convection dispersion equation (CDE) as:

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} \qquad (1)$$

Where c is concentration of solute, t is time, v is pore-water velocity, x is linear distance, D is coefficient of hydrodynamic dispersion, and R is retardation factor. Over a small range of concentration, as in experiments of this study, R may be assumed constant so that Equation1 becomes

$$\frac{\partial c}{\partial t} = D^*\frac{\partial^2 c}{\partial x^2} - v^*\frac{\partial c}{\partial x} \qquad (2)$$

With $D^* = D/R$ and $v^* = v/R$.

Transport of solute through reactive media has been the interest for soil scientists in the past. Investigating anion exclusion by leaching calcium chloride solution through three Texan soils, Thomas and Swoboda (1970) reported that Cl^- exclusion increased as the concentration decreased, and also decreased at a given concentration as the cation-exchange capacity of the soil decreased. McMahon and Thomas (1974) reported that the behaviour of Cl^- depended on the net surface charge of soils. James and Rubin (1986) modified the convective-dispersive model of Bresler (1973) to include the effect of anion exclusion. They concluded that lower water contents enhanced the relative effect of anion exclusion, creating a significant increase in anion velocity over that of the average pore-water velocity. Nkedi-Kizza et al., (1983) observed that in their experiments at a given concentration, values of retardation factor for ^{36}Cl and $3H_2O$ were on either side of unity. However, for coefficient of hydrodynamic dispersion, there was no effect of concentration, tracer, but only of speed of displacement. Hills et al., (1991) and Scotter and Tillman (1991) monitored the movement of tritiated water and Br^- and reported that Br^- moved ahead of the tritium due to anion exclusion. Melamed et al., (1994) investigated how adsorbed phosphate affected the mobility of Br^-, at different pore-water velocities, through saturated Oxisol soil columns. They found that the mobility of Br^- increased with phosphorous (P) treatment because of Br^- exclusion induced by the negative surface charge generated by adsorbed P. Iqbal and Krothe (1996)

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observed from temporal changes in cation to anion ratios that anions are more mobile due to anion exclusion.

Solute behaviour in soils has usually been determined using TDR. The data from TDR has been used to estimate the dispersion parameters (D and R) of bulk $CaCl_2$ solution in uniform and relatively, unreactive soils (Mojid *et al.,* 2004, 2006). Using complicated procedure to trace the movement of bromide and nitrate in a reactive, variable-charge ferrasol, Vogeler *et al.,* (2000) found anion retardation factors ranging from 1.2 to 1.7 but the concentrations of both anions were measured in effluent using unspecified methods. Misselbrook *et al.,* (2005) recommended that such techniques could be used to study the behaviour of bulk solution, e.g. during the infiltration of animal slurry into soil.

The transport of solutes is also affected by the characteristics of the porous medium. For example, in the micro-pores of the aggregates, transport depends on diffusion, since convection in these smaller pores is usually negligible. This results in slow and incomplete mixing and hence tailing in the BTC, even under saturated conditions. In large aggregates the amount of immobile water increases while the diffusion pathway becomes longer, resulting in BTCs with more and longer tailing (van Genuchten and Wierenga, 1976; Al Sibai *et al.,* 1997). No work in the literature reports any systematic study involving the effects of different factors responsible for anion, cation, and bulk solution transport of solutes. An effort has been made to do this by conducting a series of displacement experiments in the laboratory.

MATERIALS AND METHODS

Solid glass beads and sepiolite clay minerals were used as inert and reactive materials, respectively. The sepiolite was from Vallescas in Spain, supplied as porous aggregates (Berk Mineral Products, Worksop, S81 7QQ, UK). This sepiolite has a cation exchange capacity of 0.26 mol_c/kg and a total (internal plus external) surface area of 330 m^2/g giving a density of surface charge of 0.79 mol_c/m^2 (Robertson 1957). The aggregates retained their geometry and physical structure as the composition and concentration of the saturating solutions changed.
A 50 mm diameter laboratory column (XK50 gel-filtration columns; Amersham Pharmacia Biotech, Little Chalfont, Bucks HP7 9AA, UK) was packed separately with these material sieved into aggregate size ranging from 1.7 to 2.0mm average diameter (Table-1). Pistons (flow adaptors) of these columns are designed to provide uniform flow at the entrance and exit of the bed of porous material and a minimal dead volume (less than 1% of the total column volume). The columns were saturated under vacuum with deionised water, and remained saturated with liquid throughout the experiments. The solutions used were KBr (0.01, 0.003, 0.001 and 0.0006 M).

Table-1. Properties of the experimental columns.

Material	L	θ_m	θ_a	θ_t
Beads	0.318	0.381	–	0.381
Sepiolite	0.322	0.400	0.396	0.796

L, length (m); θ_m, porosity in micropores (m^3/m^3); θ_a, porosity in aggregates (m^3/m^3); θ_t, total porosity ($\theta_m + \theta_a$)

Miscible displacement experiments involved an ionic solution displacing deionised water resident in a vertical column of porous material, and vice versa. Miscible displacements were conducted at 6 pore-water velocities, ranging from 1.04 to 174 cm/h through the beads and 7, between 0.98 and 64 cm/h, through the sepiolite. The flows were controlled at the lower velocities by a cartridge pump (Model 7553-85, Cole Parmer Instruments, Chicago, IL 60648, USA) and at the higher velocities by a standard peristaltic pump (type MHRE, Watson-Marlow Bredel Pumps, Falmouth, TR11 4RU, UK). The effluents were collected using a fraction collector (type FC203B, Gilson, 3000 West Beltane Highway, Middleton, WI 53562, USA) modified to accept volumes of up to 30 cm^3 per aliquot. Displacements were continued until 3 pore volumes of liquid had been collected. All experiments and chemical analyses were done at a temperature of 20 ± 1°C. Sequence of the experiments was as follows: (i) displacements at the highest solution concentration were completed before starting those at the intermediate concentration, and so on; (ii) for a given solution and concentration, displacements proceded from slowest to fastest, though some were repeated; (iii) alternate experiments involved solution displacing water resident in the porous material and *vice versa*, irrespective of the speed of displacement. A schematic and a photograph of the experimental setup are given in Figure-1a and b.
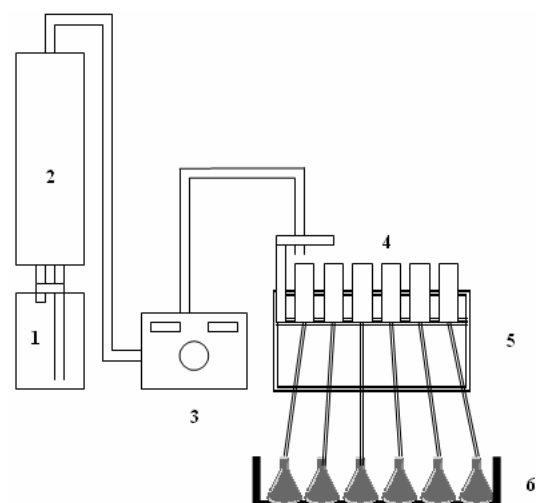

Figure-1a. Schematic of experimental set-up including 1: Displacing solution in the reservoir, 2: Vertical column, 3: Pump, 4: Glass tubes, 5: Fraction collector, 6: Leachate collection in the round–neck plastic bottles.
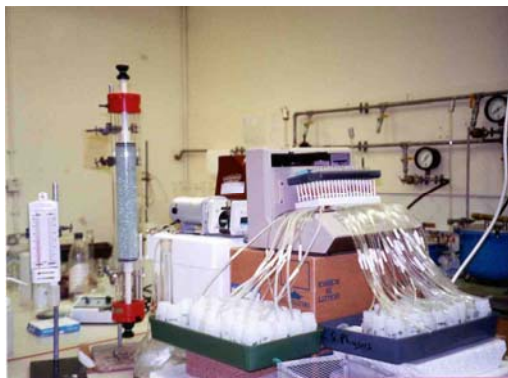
Figure-1b. A photograph of the experimental setup. Glass bead are packed in column.

Leachate cconcentrations for Br^- and K^+ were measured using calibrated ion-specific electrodes. All electrodes and sensors were calibrated frequently using 4 or 5 standard solutions over the range of concentration used in the displacements. Bulk solution concentration was measured using standard electrical conductivity cell and a 4320 conductivity meter (Jenway Ltd., Felsted, Dunmow, Essex CM6 3LB, UK).

Non-dimensional breakthrough curves (BTCs) were produced for the EC of the leachate, representing the bulk solution, and for the concentrations of the individual ions for each displacement. The relevant program of CXTFIT 2.1 (Toride *et al.,* 1995) was then used to optimise the values of R and K for each BTC, specifying the value of $v = q/\theta_t$ as that delivered by the calibrated pump to control flow, where q is the Darcy velocity. The non-linear least-square curve-fitting computer programme CXTFIT version 2.1 is one of the most popular, widely used and flexible techniques available. It is a modified and updated code of CXTFIT of Parker and van Genuchten (1984). It uses the one-dimensional CDE of solute transport. The programme uses the analytical solution of the CDE for appropriate initial and boundary conditions. The programme also uses various statistics to evaluate goodness-of-fit to the data, including R^2, root-mean-square error (RMSE), 95% confidence intervals for computed parameters, and the correlation matrix of the parameters.

RESULTS AND DISCUSSION

Breakthrough curves ($R^2 = 0.95$-0.98) at two extreme velocities for glass beads ($v = 1.04$ and 174 cm/h) and for sepiolite ($v = 0.98$ and 64.4 cm/h) are shown in Figure-2. In every displacement through beads the BTCs for Br^- and K^+ concentrations and for EC were matching within experimental error. In every displacement with sepiolite the anion eluted faster than the bulk solution, the cation slower. At lower pore water velocities the BTCs were steep whereas the same were shifted towards left at the beginning and ended with tailings more profound in case of sepiolite due to the reasons explained by Thomas and Swoboda (1970), James and Rubin (1986), and Melamed *et al.,* (1994). Ttailing of BTCs for non-reactive tracers may result from the media heterogeneities, kinetic

mass transfer or diffusion between mobile and stagnant zones (Luo *et al.,* 2007). There were 12 displacements through beads, 0.01 M KBr displacing deionised water and vice versa at each of 6 flow rates. The retardation factor did not vary with velocity; mean values and standard deviations ($n = 12$) were 0.998 ± 0.003 for Br^-, 0.999 ± 0.002 for K^+ and 1.004 ± 0.003 for bulk solution (Figure-3). For sepiolites, the values of R differed between the anion, cation and bulk solution, but did not vary with velocity (Figure-3). The mean values of R and their standard deviations are summarized in Table-2 for anion (R_a), the cation (R_c) and the bulk solution (R_s). For anions the values of R were always less than unity, for cations the values were always greater than unity, and became more extreme as the solute concentration decreased. For bulk solution, R_s was intermediate between the values for the cation and the anion, but always less than R_{avg} and less than unity, and decreased as the solute concentration decreased.
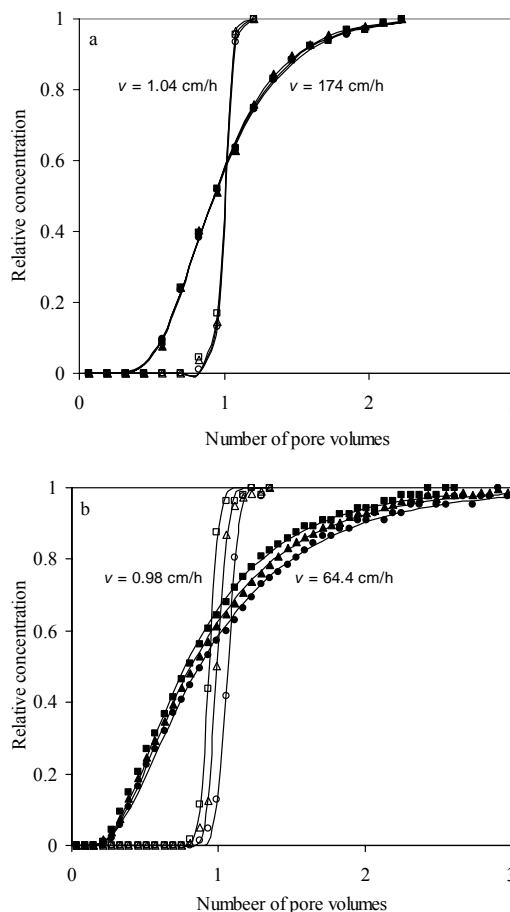

Figure-2. Representative breakthrough curves of Br^- (■), K^+ (●), and of bulk solution (▲) when the solution of 0.01 M KBr was displaced by deionised water through (a) glass beads at 1.04 and 174 cm/h and (b) sepiolite at 0.98 and 64.4 cm/h.
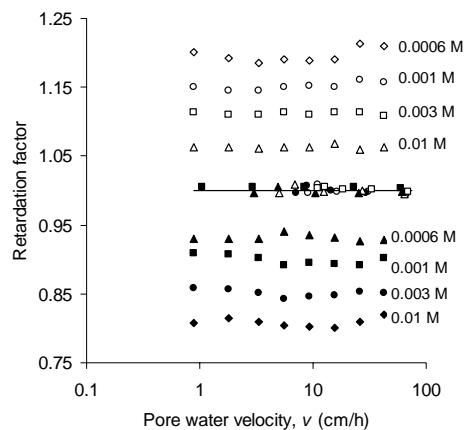
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Figure-3. Retardation factors, R, as functions of pore-water velocity, v, when deionised water displaced 0.01 M ($\blacktriangle$, $\triangle$), 0.003 M ($\blacksquare$, $\square$), 0.001 M ($\bullet$, $\circ$), and 0.0006 M ($\blacklozenge$, $\lozenge$) KBr through sepiolite. The solid line represents $R = 1$ and the data points touching the solid line represent the data for leaching (open symbols) and uptake (solid symbols) of K^+ ($\triangle$, $\blacktriangle$), Br^- ($\circ$, $\bullet$) and bulk solution ($\square$, $\blacksquare$) through glass beads. Note that the x-axis is log scale and for glass beads data has been shifted by addition of 2 to the value of v to avoid overlap.

Table-2. Retardation factors for displacements of KBr through sepiolite.

c range	R_a	R_c	R_s	n
0 – 0.01	0.934	1.064	0.995	7
0 – 0.003	0.900	1.113	0.973	7
0 – 0.001	0.851	1.151	0.961	7
0 – 0.0006	0.807	1.199	0.952	7

c, concentration (M); n, number of displacements

The coefficient of hydrodynamic dispersion did not statistically differ for Br^-, K^+ and EC flow through glass beads at a given pore water velocity. Over the range of flow rates used, D increased by more than 4 orders of magnitude, approximately as $D \propto v^{1.8}$. For sepiolite, D was function of v as for each combination of solute, concentration range and ion or EC, the data fitted equations of the form $D = a + bv + cv^2$ applicable to aggregated materials (Passioura and Rose 1971). There were no statistically significant differences in the regression coefficients between different solutes, different ranges of concentration or between anion, cation or EC. This was confirmed by an analysis using a generalised linear model that showed the only statistically significant factor affecting D was v. Therefore, all estimates of D at a given velocity were averaged.

At a given pore-water velocity, the dispersion coefficient was greater in the aggregated material than in the solid particles (Figure-4a). However, when pore-water velocity was converted into Darcy velocity ($q = v\theta_t$), this behaviour is reversed, with D greater in the beads than in the sepiolite below $q = 25$ cm/h (Figure-4b). It is

conventional to relate D to v; however, it is often preferable to use the q rather than v in the studies of solute transport in the environment.

Standard deviations were relatively, large for sepiolite (average s.d./mean = 14.4 %) compared to beads (6.7%), the standard errors are more comparable (average s.e./mean = 3.4% for sepiolite, 2.7% for beads) because of the larger number of individual estimates of D for sepiolite. For both materials, effects of solute and concentration on D are negligible compared to that of velocity.
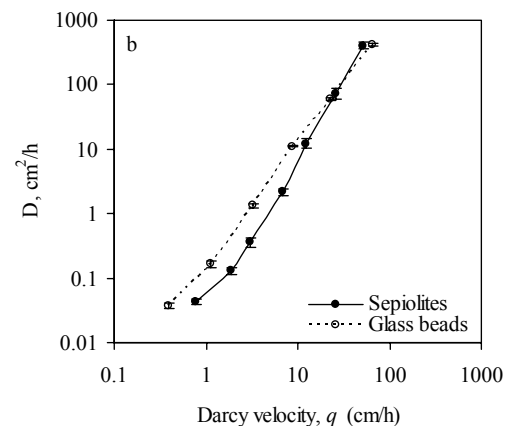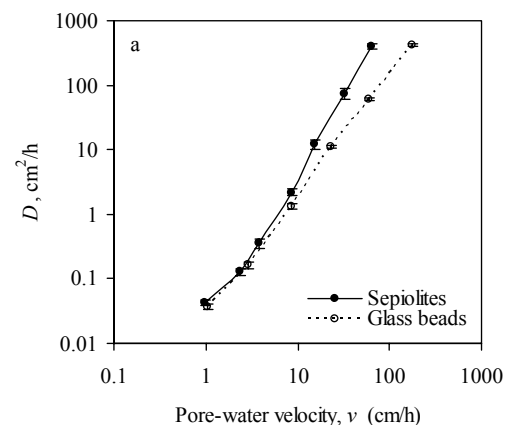

Figure-4. The Coefficients of hydrodynamic dispersion, D, along with standard deviation, as function of (a) Darcy velocity, q and (b) pore-water velocity, v.

CONCLUSIONS

The work reported in this paper is simpler but more extensive and focused than that already reported in literature. For example, Risler *et al.,* (1996) used complex experimental and mathematical techniques to study solute transport in 4 soils under transient flow during cyclic wetting and drying. They measured the EC of Br^- concentration in the effluent following a pulse input of Br^- and also estimated the EC of solution in the soil from measurements of TDR. The BTCs were generally congruent, irrespective of method of measurement, when expressed in terms of relative concentration. They also

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found generally good agreement between estimates of D derived from the various BTCs by time-moment analysis, but they used only one flow rate for each soil, and they did not estimate retardation factors.

Since the absolute values of the D, in reactive materials i.e. sepiolites depend only on the flow rate, the solution and its ionic components actually disperse at rates $D^* = D/R$ with dispersing fronts moving with velocities $v^* = v/R$. Therefore, D and v are increased when $R < 1$ and retarded when $R > 1$. This leaves D (v) as invariant and R appears to be the controlling factor in the behaviour of both the bulk solution and its component ions. The values of R depict the separation of anions from cations during saturated flow through reactive materials. The results illustrate that the composition as well as the concentration of a solution change during flow through reactive materials. This has implications for the interpretation of any leachate monitoring, e.g. TDR, in reactive soils based on the measurement of bulk solution concentration. Therefore, salinity level or concentration of a solution passed through a soil involving clay particles or aggregates must be determined using the techniques specific to the ion of interest. And that the leaching risks of fertilizers in clayey soils must be quantified with a suitable technique.

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