Absorption of artificial piggery effluent by soil: A laboratory study

D. E. Smiles\textsuperscript{A,B} and C. J. Smith\textsuperscript{A}

\textsuperscript{A}CSIRO Land and Water, PO Box 1666, Canberra, ACT 2601 Australia.
\textsuperscript{B}Corresponding author. Email: david.smiles@csiro.au

Abstract. Urine, faeces, and waste feed flushed from pens of intensive piggeries produce large volumes of nutrient-rich effluent, which is often most productively used for irrigation. These effluents tend to be similar, with pH values in the range 7.6–8.0 together with high water-soluble ammonium and potassium but lower concentrations of calcium, sodium, and magnesium. There is little experimental information on the behaviour of these mixed ion systems in soils, so the effects of artificial but chemically similar effluents were examined in absorption experiments on columns of ‘natural’ soils. In one series of experiments, NH\textsubscript{4}\textsuperscript{+} was excluded from the artificial effluent to assess the consequences of its presence or absence. Water content and solute concentration data scaled according to distance divided by the square root of time in experiments terminated at different times. This showed that basic flow and reaction equations were valid and that water-soluble and exchangeable cations appeared to be in equilibrium in the ‘time-scale’ of absorption. Systematic patterns of behaviour emerged: chloride, the dominant anion in the absorbed solution, moved with the water and its front coincided with the piston front that would exist if the absorbed water completely displaced the original soil solution; cation exchange was restricted to the inflow end of the columns in an environment of constant Cl\textsuperscript{−} concentration and was retarded relative to the moving water. High concentrations of NH\textsubscript{4}\textsuperscript{+} appeared not materially to affect the exchange isotherms of other cation pairs, although they reduced retardation of other exchangeable cation fronts. The method provides a useful way to define exchange isotherms in an appropriate environment of competing cations.

Additional keywords: adsorption isotherms, effluent irrigation, cation exchange, cation ratios, solute retardation, water-soluble cations.

Introduction

Intensive piggeries often flush urine, faeces, and waste feed from pens, and irrigation is generally the most productive way to use the resulting effluent. Nutrient concentrations are high, however, so care is required to manage the material without environmental damage. Liquid effluents used for irrigation at 5 large piggeries in south-eastern Australia are similar, with pH values between 7.5 and 8, together with high concentrations of water-soluble ammonium-nitrogen (NH\textsubscript{4}\textsuperscript{+}-N) and potassium (K\textsuperscript{+}) but lower concentrations of calcium (Ca\textsuperscript{2+}), magnesium (Mg\textsuperscript{2+}), and sodium (Na\textsuperscript{+}). Smiles and Smith (2004) provide more discussion of the properties of these materials. They also discuss effects of changing cation ratios and concentrations on the structural stability of soils that are irrigated with effluent.

Table 1 identifies salient values. It shows that NH\textsubscript{4}\textsuperscript{+} concentrations average 42 mmolc/L and greatly exceed K\textsuperscript{+} concentrations averaging 13 mmolc/L. Nevertheless, among the cations, K\textsuperscript{+} is seen by the industry as a potential problem because of effects it might have on soil structure, whereas NH\textsubscript{4}\textsuperscript{+} is generally ignored, presumably because common experience is that it disappears from the soil profile relatively soon after irrigation.

The failure of effluent treatment systems to oxidise NH\textsubscript{4}\textsuperscript{+} to NO\textsubscript{3}\textsuperscript{−} to N\textsubscript{2} is common worldwide (Bernal \textit{et al.} 1993; Sloan \textit{et al.} 1999; Pote \textit{et al.} 2001), so NH\textsubscript{4}\textsuperscript{+} must initially participate in cation exchange, whatever its long-term fate in soils. Furthermore, NH\textsubscript{4}\textsuperscript{+} is of similar size to K\textsuperscript{+} and both are strongly adsorbed compared with Na\textsuperscript{+} so the initial effect of NH\textsubscript{4}\textsuperscript{+}, accentuated by its high concentration, should be similar to that of K\textsuperscript{+} and may moderate the effects of high concentrations of K\textsuperscript{+} (Bolt \textit{et al.} 1976).

In principle, the fate of cations such as K\textsuperscript{+} and NH\textsubscript{4}\textsuperscript{+} in solutions absorbed by soils can be predicted using models based on reaction chemistry and chromatographic theory such as LEACHM (Hutson and Wagenet 1992) and UNSATCHEM (Suarez and Simunek 1997; Suarez 2001). In practice, there have been few experiments involving transport and reaction during unsaturated unsteady water flow in natural soils (Mansell \textit{et al.} 1993), although there are studies of competitive exchange of Na\textsuperscript{+}, K\textsuperscript{+}, and Ca\textsuperscript{2+} during absorption by initially homoionic soils (Bond and Phillips...
Artificial rather than actual piggery effluents are used but they illustrate the effects of realistic concentrations of \( K^+ \) in the presence and absence of \( \text{NH}_4^+ \). Initial studies focus on the 'chromatographic' distributions of the major cations observed during unsaturated, unsteady flow and on 'simple' exchange rules used by Hutson and Wagenet (1992) and Suarez (2001).

**Theory**

When a uniform, relatively dry, horizontal column of soil absorbs aqueous solution from a source at constant water potential, the invading solution appears to displace, in its entirety, the soil solution originally present. Simultaneously, hydrodynamic dispersion results in diffusion about the piston front that would separate the absorbed solution from that originally present (Smiles et al. 1978) and adsorption on the soil solid retards individual cation and anion fronts relative to the water and, hence, provide complementary integral estimates of the effects of exchange in response to the exchange isotherms; and (iv) extend Bond's approach using homo-ionic soils to chemically 'natural' soils intended for effluent irrigation.

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associated with the soil solid (mmol/kg), $C_F$ is the flux of solute advected with the water, and $j$ is the flux of solute that diffuses relative to the water according to Fick’s law in response to $\partial C_i / \partial t$ (Smiles 2001). For horizontal, non-hysteretic soil water flow, substitution of Darcy’s law in Eqn 1 results in the familiar non-linear diffusion equation (Smiles and Rosenthal 1968). Substitution of Fick’s law in Eqn 2 to describe $j$ results in a Fokker–Planck equation (Reiniger and Bolt 1972) that reduces to a diffusion equation when space-like coordinates, based on the distribution of the water, are employed (Smiles 2000, 2001). This manipulation of Eqn 2 also requires that we rewrite its left-hand side in terms of $C_s$ which, in turn, requires we relate $C_s$ to $C_i$ according to some exchange rule (Bond and Phillips 1990b). The simplest of these (Crank 1956; Reiniger and Bolt 1972) assumes a linear ‘isotherm’, so, for $K^+$ (for example):

$$K^+_{ex} = B[K^+]$$  

(3)

where the square braces represent the water-soluble cation, the suffix ‘ex’ its exchangeable form, and $B$ is a constant.

Equation 3 is used systematically in modelling (Robbins et al. 1980, Hutson and Wagenet 1992; Suarez and Simunek 1981; Suarez and ˇSimunek 1992). Cation exchange, illustrated by substitution of Eqn 3 in Eqn 2, displaces the salt front relative to the piston front and also reduces the diffusion coefficient for the salt in question (Crank 1956; Freeze and Cherry 1979). Use of Eqn 3 in systems containing many competing cations requires that it be derived in an appropriate cation environment, and for such cases, it represents but one of a number of ‘isotherms’ that qualify solution of Eqn 2 for each competing cation (Bolt 1976; Robbins et al. 1980; Bond and Phillips 1990a). These issues are discussed in more detail later.

During horizontal absorption of solution, we believe that Eqn 1 and Eqn 2 subject to the experimental conditions of Eqn 4 describe transfer:

$$m = 0; \quad t > 0; \quad \partial \theta / \partial t = 0; \quad C_s = C_s(i)$$

$$m > 0; \quad t = 0; \quad \partial \theta / \partial t = 0; \quad C_s = C_s(i)$$

(4)

For these circumstances, the Boltzmann substitution, $M = m t^{1/2}$, eliminates $m$ and $t$ from both the flow equations for the water and the solute as well as from Eqns 4. It then follows that, if Eqn 1 and Eqn 2 are valid and Eqn 4 is realised, sets of profiles of water content and of solute concentration observed at different times each fall on the same curves if graphed in terms of $M = m t^{1/2}$. Furthermore, the diffusion equation that arises for solute flow when a water-based coordinate, $g t M$, $i$ is used also implies similarity in terms of the corresponding substitution, $G = g t M^{1/2}$ (Smiles 2001), where $g$ is a space-like coordinate based on the distribution of the water (Smiles et al. 1981). Thus, if the approach is valid, then (i) the experiments should yield water and solute profiles that scale in distance/$(time)^{1/2}$, (ii) the cation concentration profiles should reflect the exchange isotherms relevant to the local environment of competing cations, and (iii) the integral consequences of these results should be reflected in retardation of the reactive solutes relative to the water flow.

**Materials and methods**

Topsoil (0–100 mm) from a Deep Red Chromosol that had not previously been irrigated with piggery effluent was used. The soil contains 15–20% clay with a cation capacity (CEC) of approximately 55 mmol/kg. The clay is predominantly kaolinite with about 20% illite. It is identified as CP338 and 339 in the CSIRO National Soils Database (c/- david.jacquier@csiro.au) (Smiles and Smith 2004).

Soil that passed a 2-mm sieve and with initial water content, $\theta_i = 0.05$ g/g, was packed into a sectioned cylindrical column of internal diameter 20 mm. The columns were composed of sections approximately 4, 8, and 10 mm long with the shortest sections close to the inflow end. The soil was added in increments of 2–3 g and packed using a small drop-hammer to ensure uniformity. A solution of similar concentration to piggery effluent but with $Ca$ the sole anion was applied at zero water potential to one end ($m = 0$) of the horizontal column at $t = 0$.

Two experimental sets were performed. In the first, the major cation, $NH_4^+$, and the minor cation, $Mg^{2+}$, were absent from the artificial effluent. The second set contained all cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $NH_4^+$). The experiments were terminated at different times within each set.

**Experiment Set 1**

Sectioning the columns terminated the experiments. Each moist section was weighed, and a water sample was removed by centrifuging in the presence of an organic liquid with a specific gravity of 1.57 (Phillips and Bond 1989). The soil sample was then leached to remove excess water-soluble salts using glycerol-alcohol, exchangeable cations were removed with 1 M $NH_4Cl$, and, after further washing with alcohol, the CEC was estimated by measuring the remaining $NH_4^+$ (Rayment and Higgins 1992). All soil solid was retained through these operations.

Water-soluble cations were measured using inductively coupled plasma spectroscopy (ICP) on the water sample after diluting the small amount of soil solution (0.2–0.5 cm$^3$) to 10 cm$^3$. Exchangeable cations were measured on the $NH_4Cl$ extract by atomic absorption spectroscopy (AAS), and $NH_4^+$ representing the exchange capacity was measured using an autoanalyser (Rayment and Higginson 1992). Dilutions were tracked gravimetrically and all quantities were referred to the oven-dry weight of soil in each section, which was determined following all extractions, by oven drying. Profile data were graphed in $m$-space, i.e., the cumulative mass of soil per unit area of cross-section of the column, measured by adding the oven-dry weight of the soil in each section from the inflow end of the column and dividing by the column cross section area.

**Experiment Set 2**

The sectioning procedure was the same as that for Set 1 but chemical analysis was complicated by the need to analyse for exchangeable $NH_4^+$. We therefore split the column sections before any extractions because centrifuging tends to separate particle sizes during extraction of water-soluble salts. About two-thirds of the sample was treated as described above with the water-soluble cations (including $NH_4^+$ measured by ICP) and the exchangeable cations displaced by $NH_4^+$ and assayed using...
Table 2. Key details for column experiments

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>( \theta_i ) (kg/kg)</th>
<th>( \theta_o ) (kg/kg)</th>
<th>( S(\theta_i, \theta_o) ) (kg/m² s^1/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>0.048</td>
<td>0.18</td>
<td>0.29</td>
</tr>
<tr>
<td>106</td>
<td>0.051</td>
<td>0.18</td>
<td>0.31</td>
</tr>
<tr>
<td>144</td>
<td>0.051</td>
<td>0.19</td>
<td>0.34</td>
</tr>
<tr>
<td>Set 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>0.055</td>
<td>0.2</td>
<td>0.281</td>
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<tr>
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<td>0.055</td>
<td>0.2</td>
<td>0.291</td>
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<tr>
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<td>0.059</td>
<td>0.2</td>
<td>0.313</td>
</tr>
<tr>
<td>270</td>
<td>NA</td>
<td>0.2</td>
<td>0.290</td>
</tr>
</tbody>
</table>

NA. Not available.

AAS. The remaining third of the column section was washed with alcohol to remove the water-soluble salts and the exchangeable cations were extracted with 1 M KCl. The exchangeable NH_4^+ was assayed using the autoanalyser method.

Initial water contents, times at which the experiments were terminated, and \( \theta_i, \theta_o \), the measured sorptivities (Philip 1957), are found in Table 2 for both experimental sets.

Statistical analysis

Effects of different elapsed times on the C_i and C_o profiles were analysed using the NONLINEAR regression option of FITCURVE in Genstat 5 (Payne 1993). Arbitrary curves were fitted to the variable \( C_i \) and \( C_o \) regressed against the space-like variable, M/S (defined in relation to Eqn 4), so that similarity in the profiles of Fig. 1a, normalised with respect to the measured \( \theta_i, \theta_o \) of each, shown in Table 2. Figure 1c reveals no statistical differences related to the termination time of the experiments and equality of the shaded areas locates the piston-front at M/S = 5.5 kg solid/kg water. Figure 1f shows M/S vs. M/S calculated using Eqn 6 and Fig. 1e.

Solute concentration profile—the exchangeable cations

Experiment Set 1

Figure 1a shows water content profiles observed during these experiments. Within acceptable experimental error arising mainly from packing differences, these profiles preserve similarity when graphed in terms of \( M = m t^{1/2} \), so they are consistent with the flow laws for the water and the initial and boundary conditions. This figure also shows the piston-front at \( M = 1.6–1.8 \) kg solid/m² s¹/² that would exist if the absorbed solution completely displaced the soil water originally present. The piston front is found where the water-based space-like coordinate G(M), defined (Smiles et al. 1981) by:

\[
G(M) = \int_0^M \theta_o dM - S(\theta_i, \theta_o) \quad (5)
\]

is zero. Practically, it amounts to finding the value of \( M \) where the shaded areas of Fig. 1a are equal. Non-reactive solutes diffuse relative to the water about this plane, while chemical reaction with the solid phase results in displacement of the plane of ‘diffusion’ from \( G(M) = 0 \) according to the magnitude of \( B \) of Eqn 3 for each ion species.

To reduce the effects of variations in column packing, the Fig. 1a profiles were normalised in Fig. 1b with respect to the measured \( \theta_i, \theta_o \) of each, shown in Table 2. Subsequent discussion relates to data presented in terms of M/S. Figure 1c graphs the water-based G(M)/S vs. M/S that may be calculated from Fig. 1b using the equation (eqn 20 of Smiles 2001):

\[
G(M)/S = \int_0^M \theta_o d(M/S) - 1 \quad (6)
\]

Figure 1c permits us to present profile data in terms of a water-based space-like coordinate if we wish. It also shows that the scaled piston front (the origin of G(M)/S) is at M/S = 5.5 kg solid/kg water, while M/S = 0 corresponds to G(M)/S = –1.

Experiment Set 2

Figure 1d shows water content profiles of Experiment Set 2. Again, within acceptable scatter arising from packing differences, they preserve similarity, so they are again consistent with the flow laws for the water and the initial and boundary conditions. Sorptivity \( S \) values were a little less than those in Set 1, however, and Fig. 1e presents the profiles of Fig. 1d, normalised with respect to the measured \( \theta_i, \theta_o \) of each, shown in Table 2. Figure 1e reveals no statistical differences related to the termination time of the experiments and equality of the shaded areas locates the piston-front at M/S = 5.4 kg solid/kg water. Figure 1f shows M/S vs. M/S calculated using Eqn 6 and Fig. 1e.

Solute concentration profile—the exchangeable cations

Experiment Set 1

Figure 2a–d shows the concentrations (mmol/kg solid) of exchangeable Na⁺, K⁺, Ca²⁺, and Mg²⁺ in M/S-space. Analyses of arbitrary curve fits using GENSTAT 5 (Payne 1993) give no reason to discriminate between data from columns sampled after different elapsed times \( T > 0.3 \). Thus, the data preserve similarity and we conclude that Eqn 4 are realised and that diffusion-like equations describe transfer and chemical reaction of the solute in both coordinate systems. We also presume that we can compare the total datasets shown in Fig. 2a–d, later, with data from Experiment Set 2 shown as Fig. 2e–h.

Figure 1c and f shows that there is a 1:1 relation between M/S and G/S, so similarity in M/S implies similarity in G/S. In this regard:

\[
\int C_o dM/S = \int (C_i/\theta_o) dG/S \quad (7)
\]

over intervals of M/S and G/S that correspond according to Fig. 1c.
We now focus on the data in $M/S$-space in Fig. 2a–d and we neglect units of variables but refer the reader to the nomenclature table (Table 3) for their definition.

To facilitate comparison of solute profiles, we also introduce the notion of a centre of mass of a solute 'front', $(M/S)^*$, calculated from the equation:

$$(M/S)^* = \left( \int_{0}^{M/S} (C - C_i) \, d(M/S) \right) / (C_0 - C_i) \quad (8)$$

$(M/S)^*$ is the leading edge of a rectangle of the same area and height $(C_0 - C_i)$ as the actual profile. It applies both to the displacing and displaced exchangeable cation profiles. Values of $(M/S)^*$ are presented in Table 4.

In Fig. 2a–d:

(i) Cation exchange is confined to $0 < M/S < 2$ where the $K^+$ in the absorbed solution displaces the exchangeable $Ca^{2+}$ and $Mg^{2+}$ originally present. In it, $Ca^{2+}$ decreases from approximately 32 to about 22 mmolc/kg; $Mg^{2+}$ decreases from $\approx$8 to $\approx$1 mmolc/kg because there was no $Mg^{2+}$ in the absorbed solution in the Set 1 experiments; and $K^+$ increases from about 6 to about 22 mmolc/kg. Exchangeable $Na^+$ increases slightly but represents $\approx$5% of the CEC (CEC $\approx$ 55 mmolc/kg).

(ii) The leading edge of region of chemical reaction, where $(M/S)^* = 0.9$, lies well behind the piston front for the water where $M/S \approx 5.5$. 

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**Fig. 1.** Water content profiles observed, at the times shown, during absorption of solutions by uniform, relatively dry soil for both experimental sets. The times at which the profiles were observed are shown for each experimental set above the graphs. The space-like coordinate, $M \text{kg}_{solid}/m^2\sqrt{s}$, is the cumulative mass of soil per unit area per unit square root of time of observation. (a, d) Original data; (b, e) data normalised according to the sorptivity, $S(\theta_i, \theta_o) \text{kg}_{water}/m^2\sqrt{s}$, of each set; (c, f) relation between the mass-based coordinate, $M/S \text{kg}_{solid}/\text{kg}_{water}$, and the dimensionless, water-based coordinate, $G/S$, defined by Eqn 6. $G/S = 0$ when $M/S \approx 5.5 \text{kg}_{solid}/\text{kg}_{water}$. The vertical lines in a, b, d, and e represent the interface that would separate absorbed solution from that originally present if displacement of the latter by the former were complete. The hatched areas either side of these lines are equal.
Fig. 2. Exchangeable cation profiles observed in M/S-space (kg solid/kg liquid) for both experimental sets. Dimensional consistency is maintained when concentration is expressed as mmol c/kg solid. (a, e) Na⁺; (b, f) K⁺; (c, g) Ca²⁺; (d, h) Mg²⁺; (i) NH₄⁺.
Table 3. Nomenclature used in this paper

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Unit</th>
<th>Meaning</th>
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</thead>
<tbody>
<tr>
<td>( C_{i0} )</td>
<td>mmol/L</td>
<td>Initial solution solute concentration</td>
</tr>
<tr>
<td>( C_{i0} )</td>
<td>mmol/L</td>
<td>Absorbed solution solute concentration</td>
</tr>
<tr>
<td>( C_s )</td>
<td>mmol/L</td>
<td>Solute associated with the soil solid</td>
</tr>
<tr>
<td>( C_s )</td>
<td>mmol/kg</td>
<td>Solute associated with the soil solution</td>
</tr>
<tr>
<td>( F )</td>
<td>kg/m²/s</td>
<td>Darcy (mass) flux</td>
</tr>
<tr>
<td>( f )</td>
<td>mmol/m²s</td>
<td>Diffusive flux of solute</td>
</tr>
<tr>
<td>( F_s )</td>
<td>mmol/m²s</td>
<td>Total flux of solute</td>
</tr>
<tr>
<td>( g )</td>
<td>kg/kgsolid/m²</td>
<td>Space-like coordinate based on solid distribution</td>
</tr>
</tbody>
</table>
| \( G \) | kg/kgsolid/m²a² | Slope of ‘adsorption’ isotherm (using Eqn 11 and data of Figs 1 and 2, with that estimated from retardation)
| \( m \) | kg/kgsolid/m²a² | Space-like coordinate based on solid distribution |
| \( M \) | kg/kgsolid/m²a² | Slope of ‘adsorption’ isotherm (using Eqn 11 and data of Figs 1 and 2, with that estimated from retardation)
| \( \beta \) | m⁻¹; g/kgwater | Selectivity coefficient |
| \( \lambda \) | m²/s⁻¹ | Sorptivity |

(iii) For \( M/S > 2 \), the exchangeable cations are constant with values that existed originally in the soil at its initial water content. \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) dominate the exchange capacity to, and beyond, the piston front at \( M/S \approx 5.5 \).

Experiment Set 2

Figure 2e–h shows the concentrations of exchangeable \( \text{Na}^+ \), \( \text{K}^+ \), \( \text{Ca}^{2+} \), and \( \text{Mg}^{2+} \), and Fig. 2i shows \( \text{NH}_4^+ \), in \( M/S \)-space. As with Fig. 2a–d, GENSTAT 5 analyses do not discriminate between data from columns sampled after different elapsed times, so data preserve similarity, flow equations appear valid and we again presume that the datasets shown in Fig. 2e–h represent common populations to compare with Set 1 data (Fig. 2a–d).

In Fig. 2e–i:

(i) Cation exchange is now confined to \( 0 < M/S < 2.5 \) where both \( \text{NH}_4^+ \) and \( \text{K}^+ \) displace the exchangeable \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) originally present. Explicitly, \( \text{Ca}^{2+} \) decreases from approximately 32 mmol/kg now to about 15 mmol/kg; \( \text{Mg}^{2+} \) decreases from 8 to about 2 mmol/kg; \( \text{K}^+ \) increases from its original value of about 6 to approximately 12 mmolc/kg; and \( \text{NH}_4^+ \) increases from zero to 15 mmolc/kg. Exchangeable \( \text{Na}^+ \) again increases but remains <5\% of the CEC. Table 4 shows that \( (M/S)^* \) values defined by Eqn 8 in this region are almost double those for the Set 1 data because of the presence of \( \text{NH}_4^+ \) and \( \text{Mg}^{2+} \).

(ii) The leading edge of the region of chemical reaction (identified by \( (M/S)^* \approx 1.5 \) again lies well behind the piston front for the water \( (M/S \approx 5.4) \) although retardation is less than that for Set 1.

(iii) For \( M/S > 2.5 \), the exchangeable cations again assume the values that existed in the soil at its initial water content.

We attribute the anomalously high values of exchangeable \( \text{Ca}^{2+} \) in Fig. 2g for the 270-min experiment to analytical error.

Solute concentration profiles—the water-soluble cations

Experiment Set 1

Figure 3a–d shows the distributions of water-soluble \( \text{Na}^+ \), \( \text{K}^+ \), \( \text{Ca}^{2+} \), and \( \text{Mg}^{2+} \) in \( M/S \)-space. In Fig. 3a–d (and in Fig. 3e–i), the solution concentration is expressed

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Table 4. Comparison of \( B \) (kg/L) estimated from retardation of the centre of mass of the solute front \( (B \text{ (retard'}/a)) \) calculated using Eqn 11 and data of Figs 1 and 2, with that estimated from the appropriate slope of ‘adsorption’ isotherm \( (B \text{ (iso/slope)}) \) shown in Fig. 6

<table>
<thead>
<tr>
<th>Figure numbers</th>
<th>Cation</th>
<th>( (M/S)^* )</th>
<th>( (G/S)^* )</th>
<th>( (B \text{ (retard'}/a)) )</th>
<th>( (B \text{ (iso/slope)}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a, 6a</td>
<td>( \text{Na}^+ )</td>
<td>0.90</td>
<td>-0.84</td>
<td>1.075</td>
<td>1.125</td>
</tr>
<tr>
<td>2b, 6b</td>
<td>( \text{K}^+ )</td>
<td>0.80</td>
<td>-0.86</td>
<td>0.935</td>
<td>1.211</td>
</tr>
<tr>
<td>2c, 6c</td>
<td>( \text{Ca}^{2+} )</td>
<td>0.75</td>
<td>-0.86</td>
<td>0.870</td>
<td>0.80</td>
</tr>
<tr>
<td>2d, 6d</td>
<td>( \text{Mg}^{2+} )</td>
<td>1.65</td>
<td>-0.69</td>
<td>2.38</td>
<td>2.10</td>
</tr>
<tr>
<td>2e, 6e</td>
<td>( \text{Na}^+ )</td>
<td>1.35</td>
<td>-0.70</td>
<td>1.79</td>
<td>1.40</td>
</tr>
<tr>
<td>2f, 6f</td>
<td>( \text{K}^+ )</td>
<td>1.60</td>
<td>-0.72</td>
<td>2.22</td>
<td>2.27</td>
</tr>
<tr>
<td>2g, 6g</td>
<td>( \text{Ca}^{2+} )</td>
<td>1.45</td>
<td>-0.72</td>
<td>2.80</td>
<td>2.50</td>
</tr>
</tbody>
</table>
Fig. 3. Water-soluble cation profiles observed in M/S-space for both experimental sets. (a, e) Na⁺; (b, f) K⁺; (c, g) Ca²⁺; (d, h) Mg²⁺; (i) NH₄⁺.
as mmol/L, so again care must be taken with the integrals in M/S- and G/S-spaces, which, in this case, are related according to:

\[
\int (0_t dM)/S = \int C_0 dG/S
\]

over intervals of M/S (and G/S) that correspond according to Fig. 1c.

The scatter in the exchangeable cation data of Fig. 2 is small. In contrast, the scatter in the water-soluble results is greater because extraction of measurable volumes of soil water from relatively small samples, even using the Phillips and Bond (1989) method, is difficult and the dilution (>50-fold) required for analysis of extracts as small as 0.2 cm³ leads to error. Nevertheless, GENSTAT 5 analyses offer no grounds to discriminate between experiments (elapsed time \( t > 0.3 \)), so water-soluble cation profiles also preserve similarity when graphed in terms of M/S in Fig. 3. Thus:

(i) 'diffusion'-like flow equations for the solute are valid;

(ii) initial and boundary conditions (Eqs 4) are realised;

(iii) chemical equilibrium exists among water-soluble and exchangeable cations throughout the column (Smiles and Philip 1978), so the time-scale for chemical reaction is short relative to that characterising movement of the water; and

(iv) the datasets shown in Fig. 3a–d represent a common population when we compare them with those of Fig. 3e–h (discussed below).

The increase in water-soluble Ca²⁺ (Fig. 3c) and Mg²⁺ (Fig. 3d) across the piston front at \( M/S = 5.5 \) represents the diffused interface between the absorbed solution and that of the original soil. The effect is not evident with K⁺ or NH₄⁺ because their initial cation concentrations are small and Na⁺ is also relatively inconsequential.

Experiment Set 2

Figure 3e–h shows the distributions of water-soluble Na⁺, K⁺, Ca²⁺, and Mg²⁺, and Fig. 3i shows NH₄⁺ (mmol/L) in M/S-space. The error in these data is greater than for the corresponding measurements in Fig. 3a–d of Set 1 because of the need to split the original samples to measure exchangeable NH₄⁺. Nevertheless, these data also preserve similarity as do their fellows in Fig. 3a–d and they are consistent with the observation that relatively high concentrations of NH₄⁺ result in greater penetration of the reaction front and greater depression of Ca²⁺. The relatively clear increase in concentration of Ca²⁺ and Mg²⁺ at the piston front (\( M/S = 5.5 \)) in Fig. 3c and d is not as evident in Fig. 3g and h because the total charge concentrations of the absorbed and original solutions were, fortuitously, nearly equal.

Relations between water-soluble and exchangeable cations

Experiment Set 1

In \( 0 < M/S < 2 \), water-soluble (Fig. 3) and exchangeable cation (Fig. 2) profiles correspond in M/S-space and are delayed relative to the piston front (at \( M/S = 5.5 \)). In the absence of Mg²⁺ in the absorbed solution, both water-soluble and exchangeable Mg²⁺ tend to zero at \( M/S = 0 \). Notice that, whereas the solution concentration of Na⁺ is about half of that for K⁺, the latter dominates the CEC at \( M/S = 0 \) while the effect on exchangeable Na⁺ is minor. This is consistent with the relative affinities of K⁺ and Na⁺ for exchange positions shown in fig. 9 of Richards (1954), where the exchangeable sodium ratio is graphed as a function of the sodium adsorption ratio (SAR) of the saturation extract, and in his fig. 10 where the exchangeable potassium ratio is graphed against the potassium adsorption ratio.

In \( 2 < M/S < 5.5 \), the relatively constant water-soluble concentrations represent equilibrium with the constant values of exchangeable cations in the original soil, and in the whole of \( 0 < M/S < 5.5 \), the water-soluble cation sum approximates 35 mmol/L.

For \( M/S > 5.5 \), however, water-soluble cation concentrations increase and their sum tends to approximately 60 mmol/L. We reiterate that this increase in the vicinity of the piston front represents the difference in concentration between the absorbed solution and that originally present at the initial water content. It is not accompanied by change in the exchangeable cation concentrations or their ratios.

Experiment Set 2

In the region \( 0 < M/S < 2.5 \), water-soluble and exchangeable cation ‘fronts’ shown in Fig. 2 and Fig. 3 correspond. In the interval \( 2.5 < M/S < 5.4 \), the relatively constant water-soluble concentrations match constant values of exchangeable cations in the original soil and, throughout the whole region, \( 0 < M/S < 5.4 \), the sum of water-soluble cations (≏65 mmol/L) approximates that of the original soil solution. The greater affinity of K⁺ than Na⁺ for exchange positions is evident, and the influence of high concentrations of NH₄⁺ is clear.

For \( M/S > 5.5 \), water-soluble cation concentrations increase only slightly and their sum tends to ≏65 mmol/L. This increase again represents the (fortuitous) difference in concentration between the absorbed solution and that originally present at the initial water content, and again, it is not accompanied by any change in the exchangeable cation concentrations or ratios associated with the original soil solution.

Total solute concentration profiles

These profiles complement those of the individual cations with some anion detail.
Experiment Set 1

Figure 4a shows the Cl\(^{-}\) profiles and Fig. 4b the water-soluble cation sums corresponding to the data of Fig. 3a–d. GENSTAT 5 criteria applied to arbitrary curve fits again provide no basis for discriminating between experiments, so the Cl\(^{-}\) profiles preserve similarity, and in 0 < M/S < 5, the concentration is effectively constant at 35 mmol/L, which corresponds to the sum of soluble cations (Fig. 4b). The Cl\(^{-}\) front coincides with the piston front at M/S = 5.5, and setting aside diffusion round the piston front, there is no chloride in M/S > 5.5. Cation exchange therefore occurs in an environment of constant anionic charge, with the anion species that of the absorbed solution. Regrettably, we were unable to measure the anion compensating for the charge of the water-soluble cation sum in M/S ≥ 5.5 in this experimental set. In Experiment Set 2, however, it emerges that the anion, which represents the original soil solution, was predominantly NO\(_3\)\(^{-}\).

Experimental Set 2

Figure 4c and d shows total water-soluble anion and cation data for Set 2 experiments. Analytical difficulties of measuring anion concentrations in the very small volumes of solution that could be extracted are mentioned above, but the predominant anion ahead of the piston front appears to be NO\(_3\)\(^{-}\) while that behind is Cl\(^{-}\). Total soluble cation concentrations, on the other hand, appear robust and constant and confirm that cation exchange takes place in an environment of constant solution charge. We reiterate that the almost constant solution charge across the piston front is fortuitous.

Summary of observations

The piston model of solute flow applies insofar as the advancing front for the non-reactive species (Cl\(^{-}\)) coincides with the piston front that would exist if displacement of the original soil solution by that absorbed were perfect (see Saffman 1959).

Specifically, artificial effluents with an original concentration of about 35 and 60 mmol/L displace soil solution of about 65 mmol/L, creating a concentration and anion species change at the piston front near M/S = 5.5. In this soil, there is no anion exchange or exclusion, so the invading anion (Cl\(^{-}\)) in the artificial effluent is effectively constant to, and then diminishes rapidly at, the piston front where another anion set (in this case predominantly NO\(_3\)\(^{-}\)) at a concentration of about 65 mmol/L, representing the initial soil solution concentration, appears. The anions inter-diffuse across the piston front to ‘smear’ the concentration step change, as is revealed with the Cl\(^{-}\) in Fig. 4a. This diffusion appears not to perturb the cation ratios, which are ‘buffered’ by the exchangeable cations either side of the piston front so the total concentration adjusts while the exchangeable and water-soluble cation ratios appear to stay constant.

In the region of cation exchange (approximated by 0 < M/S < (M/S)*), chemical equilibrium is established.
quickly relative to the water flow rate and occurs in an environment of constant negative charge associated with the anions (Cl−) in the absorbed solution (cf. Bond and Phillips 1990b). These provide close to a 1 : 1 match with the sum of soluble cations. In this region, Ca2+ and Mg2+ are displaced by invading K+ (Set 1) and NH4+ as well in Set 2, and the region is finite because there is a finite amount of invading cation (=C1 × S). Between the region of cation exchange and the piston front, no cation exchange appears to occur in the column and exchangeable cations retain their original ratios. The water-soluble cation species change because of cation exchange in the reaction region and the displaced Ca2+ and Mg2+ compensate for the adsorption of the K+ and NH4+, and the charge concentrations adjust to match the Cl−, which remains the constant, sole anion up to the piston front. This is particularly evident in Set 2 data.

Ahead of the piston front, water-soluble cations and anions tend to the constitution and concentrations of the original soil solution despite the local increase in water content and corresponding local increase in the amount of solute. This solution concentration change is an ‘accident’ of the initial water content, which established the initial water-soluble and exchangeable cation ratios. As we noted above, no cation exchange appears to take place across the piston front although diffusion leads to concentration changes.

### General discussion

Three complementary ‘criteria’ reflect chemical reaction among competing cation pairs during unsteady unsaturated flow in soils. They are:

- (i) isotherms (such as the Gapon equation) that relate water-soluble and exchangeable cation pairs in an environment of 4 and 5 competing cations;
- (ii) equations such as Eqn 3 that relate the exchangeable cation to its water soluble form in a relevant environment of cation competition;
- (iii) retardation of the reacting cation ‘front’ relative to the rest frame of the water.

#### Exchange isotherms

Scaling in M/S or G/S implies local chemical equilibrium, so the concentration distributions of Fig 2 and Fig 3 permit examinations of cation exchange relations and their consequences. Eqn 10 represents some particular function that relates exchangeable and water-soluble cation pairs. For the K+/Ca2+ pair, it takes the form:

\[
Kex/Caex = f([K+]\sqrt{[Ca^2+]/2}) \tag{10}
\]

Equation 10, in the form of the Gapon equation (Bolt et al. 1976, Spinson 1989, Bond 1995), yields a straight line with a slope \(K_{k/caf}\).

Figure 5a–j shows how the parameters of Eqn 10 apply to each of the 10 combinations of the 5 cations Na+, K+, Ca2+, Mg2+, and NH4+ involved in these experiments. Corresponding data from Fig. 2 and Fig. 3 within each set are combined, but the 2 sets are distinguished using different symbols. These relations, together with the exchangeable cation sum (the CEC) and the water-soluble cation sum (which is constant in each set for M/S < 5.5), permit us, in principle, to determine functions of the form of Eqn 3 in the appropriate environment of competing cations and, hence, to solve Eqn 2 for each cation (e.g. Bond 1997).

The greatest difficulty with the use of Eqn 10 is that it is based on ratios of often small numbers. Thus, the error associated with the ratios of the water-soluble cation concentrations on the right-hand side complicates comparisons as do the small concentrations, particularly of Na+. Nevertheless, over the ranges of concentration we observe, and consistent with difficulties of measurement and the consequent errors, these relations appear to be reasonably well defined. Furthermore, for the major cations K+ and NH4+ relative to Ca2+, they appear linear to a good approximation although the K+/Ca2+ function has a significant intercept. This intercept is an artifact of the linear approximation and would need to be identified if the Gapon form of Eqn 10 were used over these concentration ranges.

Data involving Mg2+ also appear well behaved though curvilinear. The data of Fig. 5a–j do not reveal any effects associated with the presence or absence of NH4+. Ratios involving Na+ with the other cations, however, are untidy. We reiterate that this presumably arises from errors associated with relatively low concentration of Na+ and small volumes of analysable solution, particularly in the Set 2 experiments, leading to unreliable water-soluble values.

These relations are characteristics of the clay mineral but not of its concentration in the soil, so for this soil and experimental conditions, isotherms other than those for Na+ seem to represent robust properties that apply across the whole range of data found in Fig. 2 and 3. Together with the water-soluble and exchangeable cation sums, they represent a necessary and sufficient characteristic set (e.g. Robbins et al. 1980), using a convention based on Eqn 10, that is needed to model cation exchange accompanying absorption of solutions or reactions that might accompany desiccation or dilution in this soil.

#### Exchange relations based on Eqn 3

Figure 6 also derives from Fig. 2 and Fig. 3. It shows exchangeable cation concentrations as functions of their solution concentration, according to Eqn 3, for Na+ (Fig. 6a, c), K+ (Fig. 6b, j), Ca2+ (Fig. 6c, g), Mg2+ (Fig. 6d, h), and NH4+ (Fig. 6i).

Common relations between cation pairs revealed by Eqn 10 for Sets 1 and 2 do not imply common cation exchange fractions revealed in Eqn 3 between sets. This is because the high concentrations of NH4+ in Set 2 perturb exchangeable and solution concentrations of the other cations up to the piston front, so we do not expect Sets 1 and 2 relations based on Eqn 3, to correspond.
The Na\(^+\) data again scatter substantially, but, within the other sets, to reasonable approximations, the data are linear until they approach values near the piston front. In the case of Ca\(^{2+}\) and Mg\(^{2+}\) (Fig. 6c, d) water-soluble concentrations then increase without change in exchangeable values. The effect is less evident in Set 2 because of the approximate correspondence between the total charge concentrations in the absorbed and original solutions, together with the fact that, beyond the region of exchange reaction where the invading NH\(_4^+\) and K\(^+\) are adsorbed, the cations balancing the absorbed but non-reacting Cl\(^-\) must be represented by enhanced values of the displaced Ca\(^{2+}\) and Mg\(^{2+}\). The monovalent invading cations do not reveal the effect because their initial solution concentrations are small (K\(^+\)) or zero (NH\(_4^+\)). It is important to recall that these data remain consistent with the isotherm data of Fig. 5.

Comparisons between Eqn 3 and reaction front retardation
In M/S < 5.5, and particularly in the region of cation exchange (0 < M/S < 2), a linear relation between the water-soluble and exchangeable cation concentrations (Eqn 5) appears to describe cation exchange for each set reasonably well. Table 4 compares estimates of B using Eqn 3 and Fig. 6 data, with B-values calculated using retardation of exchangeable cation profiles of Fig. 2. In this calculation, B is defined according to Eqn (27) of Smiles (2001), normalised according to S, viz:

\[
(M/S)^* = -B(G/S)^* \quad (11)
\]

In Eqn 11, (M/S)* is calculated from Fig. 2 using Eqn 8 and (G/S)* is found from Fig. 1c and f. These comparisons test estimates of material continuity rather than basic theory, so the comparisons must be regarded as acceptable within the accuracy of measurement. We reiterate that 'step changes' in soluble salt concentration at the piston front, which are not accompanied by cation exchange, prejudice uncritical calculation of B using Eqn 3 and profile data.

Coordinate systems
We do not dwell on the opportunities for using water-based, rather than solid-based or other coordinates here beyond noting that Fig. 1c and f shows the unique relation that exists in these experiments between the solid- and water-based approaches and subsequent discussion presumes the consequences of this are evident. More detail, however, is available in Smiles (2001).
Fig. 6. Graphs, based on Figs 3 and 4, testing the Eqn 3 relation between water-soluble cations and their exchangeable counterparts for each cation. The vertical lines in (particularly) c, d, g, and h relate to conditions on the piston front; the remaining lines refer to conditions within the region of exchange.
Conclusions

The experiments described here are the simplest in a series to illustrate the fate of the cations, particularly that of Ca$^{2+}$, Mg$^{2+}$, and the invading K$^+$ and NH$_4^+$ applied to relatively dry soil at solution concentrations that approximate those in pigman's effluents. The physical chemistry of these processes is complex; nevertheless, well-defined patterns of behaviour emerge despite difficulties of analysis of water-soluble salts. Thus:

(i) Hydrodynamic dispersion and chemical reaction are distinguished well during unsteady, unsaturated, 1-dimensional water flow using solid- and water-based space-like coordinates. These coordinates are discussed in detail elsewhere (Smiles et al. 1981, Smiles 2001). It suffices to observe that their use ensures that material balances of all elements are correctly estimated and separates analyses of the flows of water and solute so that equations of flow of the water and of the solute are reduced to second-order partial differential equations in space and time whose solutions are well known.

(ii) While the anions appear not to interact with the soil solid matrix, they move with, and relative to, the water as a non-reactive solute, regardless of cation exchange undergone by the accompanying cations (Wilson and Gelhar 1981; Smiles et al. 1981).

(iii) The distributions of the water-soluble cations appear to be constrained by the charge distribution of the anions and chemical equilibrium appears to be achieved within the time scale of water flow driven by 'natural' gradients of water potential (Smiles and Philip 1978).

(iv) Within this framework, cation exchange occurs according to accepted 'laws', and retardation of the reaction front relative to the water flow is consistent with the simplest of them (Eqn 3) provided we distinguish between areas where concentration changes are associated with cation exchange and regions where concentration change is associated with displacement of the original solution and where exchange equilibrium is undisturbed.

(v) These experiments show that the presence of NH$_4^+$--N appears not to affect the exchange isotherms of the other major pairs of cations by soil. In terms of the parameters of the Gapon equation. At the same time, its presence reduces the initial impact of K$^+$ in the effluent but later fairly rapid removal of the exchangeable NH$_4^+$ appears to negate this initial moderating effect. These issues require further study.

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References


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