

# Comparison of bromide and nitrate transport in the Bainsvlei soil of South Africa under natural rainfall

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## Abstract

Bromide is commonly used to simulate the movement of nitrate fertilisers through the soil profile. However, there exists no comparative evaluation of the leaching properties of Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>-N under local soil and rainfall conditions at Bloemfontein. The purpose of this work was to conduct a field experiment to evaluate the leaching behaviour of Br<sup>-</sup> in comparison with NO<sub>3</sub><sup>-</sup>-N on the Bainsvlei soil of South Africa under natural rainfall conditions. For this purpose, KBr and KNO<sub>3</sub> solutions were applied to a 2.45 x 2.45 m<sup>2</sup> plot at rates of 13.5 g Br·m<sup>-2</sup> and 20 g N·m<sup>-2</sup> respectively. The subsequent movement of the solutes through the soil was investigated through studies of the water and mass balances, determined from soil samples taken from a 1600 mm deep soil profile during the period October 2000 to May 2001, the rainy season in Bloemfontein. The results were also analysed with the one-dimensional convective dispersive equation and stream tube models. Two important results were derived from the study: Br<sup>-</sup> can be used with confidence as a substitute for NO<sub>3</sub><sup>-</sup>-N in studies of the movement of the latter through soils, and it is more economical and environmentally friendly to distribute the application of nitrate over the growing season of a crop, instead of applying it as a batch at the time of planting.

**Keywords:** Field observations, bromide, nitrate, transport

## Introduction

In most instances, the leaching of nitrate is the single largest cause of nitrogen loss from the soil-plant system (Cameron and Haynes, 1986). Nitrate leaching from agricultural soils represents an economic loss to the farmer and a pollutant to groundwater resources. Since nitrogen experiences complex biochemical transformations in the soil-plant system, it is often difficult to determine the fate and movement of NO<sub>3</sub><sup>-</sup>-N through the soil profile. Isotopically labelled fertiliser (using <sup>15</sup>N) can be used to distinguish between fertiliser N and N from other sources with a high degree of accuracy. However, the use of these techniques is very costly (Silvertooth et al., 1992). Anions that are biologically and chemically conserved and similarly charged, with low background concentrations in the field, such as Cl<sup>-</sup> and Br<sup>-</sup>, are therefore often used to simulate the movement of NO<sub>3</sub><sup>-</sup>-N through natural soil profiles. Since bromide usually has very low background concentrations in the field and bears no known adverse effects to human health, provided it is applied in small quantities (Flury and Papritz, 1993), bromide is usually preferred in such studies (Nachabe et al., 1999; Silvertooth et al., 1992; Jardin et al., 1990; Jaynes et al., 1988; Rice et al., 1986; Smith and Davis, 1974).

The nitrate leaching behaviour of Bainsvlei soil of South Africa, which represents most of the South African land mass (Soil Classification Working Group, 1991), has not been studied before. The purpose of this investigation was to evaluate the leaching behaviour of Br<sup>-</sup> in comparison with NO<sub>3</sub><sup>-</sup>-N in this soil under natural conditions through a field experiment at the experimental

station of the Department of Soil, Crop, and Climate Sciences of the University of the Free State, South Africa, from October 2000 to May 2001, the rainy season of the region. The computer package CXTFIT of Toride et al. (1995) was used to determine solute transport parameters with cumulative drainage (instead of time) as independent variable and to compare the movement of Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>-N in the soil.

## Materials and methods

### Field experiment and laboratory analysis

The experimental site, located at 26.1°S and 29.0°E with an altitude of 1 372 m, is underlain by a cultivated Bainsvlei Amalia sandy loam soil. It is characterised by orthic topsoil and red apedal/soft plinthic subsoil. The area is semi-arid with a mean annual rainfall of 510 mm.

A square plot (2.45 x 2.45 m<sup>2</sup>) of bare soil was prepared for the experiment. The plot was kept bare and weed-free throughout the experiment. The plot was levelled to prevent runoff and erosion from one part of the plot to another and isolated from the surrounding area by a sheet of galvanised iron to prevent surface and shallow subsurface flows into and out of the plot. The sheet of iron was driven into the soil to a depth of 200 mm, with a 200 mm section protruding above ground level.

An access tube for a neutron probe was installed at the centre of the plot to a depth of 2 000 mm to determine the soil water content at various depths. Rainfall was measured with two rain gauges near the experimental plot.

A water sample was taken from a borehole used at the experimental farm to determine the NO<sub>3</sub><sup>-</sup>-N concentration of the groundwater. The soil was analysed for its textural properties. The results of the soil particle analysis, the textural group and bulk densities of each soil layer are presented in Table 1.

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**TABLE 1**  
**Particle size distribution and bulk density of the soil profile**

Soil depth (mm)	Sand (%)				Silt (%)	Clay (%)	Soil texture	Bulk density (g·cm <sup>-3</sup> )*
	Coarse	Medium	Fine	Total				
0-200	0.4	6.8	83.8	91	4	5	Sand	1.64±0.05
200-400	0.4	7.7	78.9	87	2	11	Loamy sand	1.72±0.07
400-600	0.3	5.5	70.2	76	6	20	Sandy loam	1.62±0.04
600-800	0.4	5.5	72.1	78	6	18	Sandy loam	1.58±0.05
800-1000	0.2	4.8	73.0	78	4	20	Sandy loam	1.64±0.06
1000-1200	0.3	4.8	73.9	79	4	18	Sandy loam	1.67±0.08
1200-1400	0.3	5.4	71.3	77	4	20	Sandy loam	1.68±0.08
1400-1600	0.2	2.8	73.0	76	4	20	Sandy loam	1.71±0.04

\* Mean of 8 values ± standard deviation

At the beginning of the experiment, KBr and KNO<sub>3</sub> were applied at intensities of 200 kg KBr·ha<sup>-1</sup> (13.5 g Br·m<sup>-2</sup>) and 1450 kg KNO<sub>3</sub>·ha<sup>-1</sup> (20 g N·m<sup>-2</sup> or 200 kg N·m<sup>-2</sup>). Similar rates for Br have been used in other studies (Nachabe et al., 1999; Bicki and Guo, 1991; Owens et al., 1985; Baker and Laftlen, 1982), while the KNO<sub>3</sub> intensity was chosen to use the N application rate commonly used by the farmers in the area. To make the solute application easier, the plot was divided into 6 subplots each with an area of 1 m<sup>2</sup>. For each subplot 20 g KBr and 145 g KNO<sub>3</sub> were mixed in 500 mL distilled deionised water. The solution was applied uniformly with a hand held sprayer on 13 October 2000.

Soil samples were taken five times during the season using an auger type coring tube 200 mm long and 42 mm in diameter. The samples were taken from two locations at depth intervals of 200 mm from 0 mm to 1 600 mm. The core sampler was cleaned with tap water and rinsed with distilled water before reinsertion for the next depth of sampling. The plot was accessed through wooden planks put on concrete blocks around the plot to avoid soil disturbance and compaction. The resultant holes were all backfilled with soil from outside the plot immediately after retrieval of the cores.

Two samples taken from the same depths were mixed and a subsample of each was put in paper bags to determine its water content. The rest of the soil sample was sealed in polyethylene bags for Br and NO<sub>3</sub><sup>-</sup>-N analysis. The soil water content analysis was done gravimetrically by drying about 100 g of soil for 24 h at 105°C.

The soil samples for Br and NO<sub>3</sub><sup>-</sup>-N analysis were oven dried and ground to pass a 2 mm sieve. A sample of 50 g of the dried soil was then mixed with 50 ml of distilled deionised water (1:1 ratio) and the mixture shaken for one hour with a laboratory shaker. The solution was filtrated and the filtrates stored in a refrigerator at 4 °C until the Br and NO<sub>3</sub><sup>-</sup>-N concentrations were determined by ion chromatography (Dionex 2200I, Dionex Corp., Sunnyvale, CA) at the Institute for Groundwater Studies of the University of the Free State, South Africa. The Br and NO<sub>3</sub><sup>-</sup>-N concentrations in the soil were calculated from the filtrate concentration based on the mass of soil and volume of water used for extracting the filtrate and the gravimetric water content of the soil sample.

### Data analysis

Rainfall, evaporation, deep percolation, and change in water content of the soil profile constitute the major components of water balance for the experimental plot. Of particular interest to this study is the deep percolation,  $D_p$ , the quantity of water that percolated below the potential rooting depth of plants, equated here with the

sampling depth (1 600 mm), over a given period. This quantity is defined as:

$$D_p = R - E_v - \Delta S \quad (1)$$

where:

$R$  = the rainfall,

$E_v$  = evaporation,

$\Delta S$  = change in storage over the given period.

The change in storage,  $\Delta S$ , was calculated from the water contents measured with the neutron probe. Evaporation from the bare soil has been determined using the equation of Ritchie (1972):

$$E_v = C t^V \quad (2)$$

where:

$t$  = is the time.

The applicability of this equation in the study area has been investigated by Bennie et al. (1998). The results of this study indicated that  $E_v$  is limited more by soil properties than climatic factors and that the coefficient,  $C$ , can be expressed as

$$C = 26.35(\theta_i - \theta_a) \quad (3)$$

where:

$\theta_i$  and  $\theta_a$  are the initial and air-dry volumetric water contents of the topsoil respectively.

The mass balance of the applied solute was checked by computing the mass recovered from the core samples as:

$$m_{i,j} = c(z_i, t_j) \theta(z_i, t_j) A \Delta z_i \quad (4)$$

where:

$c(z_i, t_j)$  = the solute concentration,

$\theta(z_i, t_j)$  = volumetric soil water content at depth  $z_i$  and sampling time  $t_j$ ,

$A$  = cross-sectional area of the core sampler, and

$\Delta z_i$  = thickness of the sample (200 mm).

The total mass,  $m_k$ , of solute recovered from the soil profile over a depth  $Z$  at a given horizontal position ( $x_k, y_k$ ) is then simply the sum of the  $m_{i,j}$  at ( $x_k, y_k$ ):

$$m_k = \sum_i m_{ij} \quad (z_i \leq Z) \quad (5)$$

The average downward motion of a solute front is theoretically determined by the average seepage velocity of the water:



$$v_w = q/\theta \quad (6)$$

where:

- $q$  = the Darcian flux, and
- $\theta$  = the average volumetric water content from the soil surface to the maximum depth at a given sampling date.

The Darcian flux was estimated as the ratio of the amount of deep percolating water to its duration.

The actual solute velocity,  $v_s$ , was estimated from the depth and time it takes the concentration peak to reach the depth (Butters et al., 1989), and the motion of the centre of mass of the solute plume (Ellsworth et al., 1991). The velocity of the concentration peak of the solute can be expressed as:

$$v_s = \frac{(z_p)_i - (z_p)_{i-1}}{t_i - t_{i-1}} = \frac{\Delta z_p}{\Delta t} \quad (7)$$

and the depth to the centre of mass of the profile as:

$$\bar{z}_i = \frac{1}{m_i} \sum_{z=0}^z z\theta(z,t)c(z,t_i)\Delta z \quad (8)$$

where:

- $z_p$  = the position of the concentration peak at the sampling time  $t_p$ ,
- $Z$  = total sample depth and the other symbols have the same meanings defined above.

This yields the following expression for the velocity of the centre of mass of the solute between two sampling times:

$$v_s = \frac{\bar{z}_i - \bar{z}_{i-1}}{t_i - t_{i-1}} = \frac{DZ}{Dt} \quad (9)$$

The one-dimensional longitudinal dispersion coefficient can be expressed as (Bear, 1979):

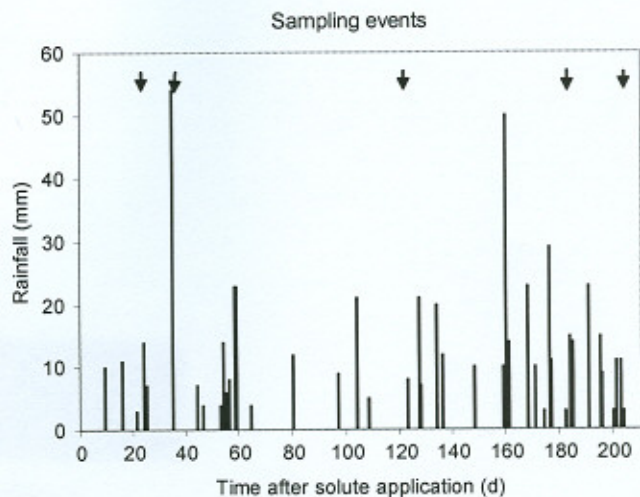
$$D = \lambda |v| \quad (10)$$

where:

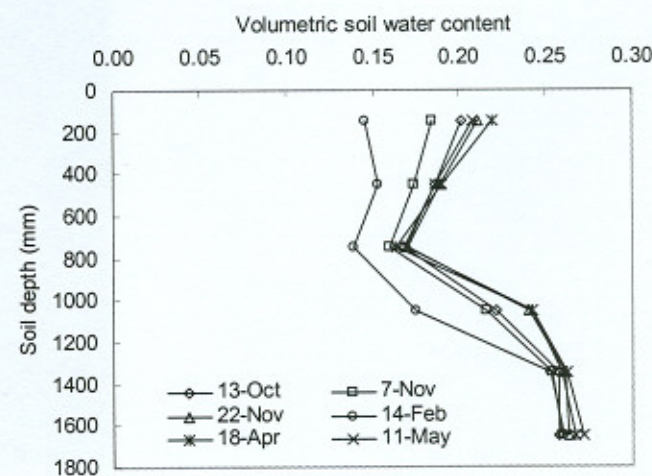
- $\lambda$  = longitudinal dispersivity and
- $v$  = seepage velocity of the water.

The solute transport parameters ( $v$  and  $D$ ) in these equations were all determined by fitting the observed concentrations at the various depths with the computer package CXTFIT of Toride et al. (1995). This package allows one to fit the observed data to analytical solutions of the conventional convection-dispersion equation (CDE) and the stochastic stream tube model (STM) described by Toride and Leij (1996a and b). The main difference between the CDE and STM is that the CDE model assumes that the concentration of the solute is uniform and perfectly mixed across both the vertical and horizontal planes (Jury and Fluhler, 1992), while the STM considers the field as a series of independent vertical soil columns with no horizontal mixing (Jury and Roth, 1990; Dagan, 1993; Toride and Leij, 1996a).

The CDE and STM in CXTFIT are both continuous source models and therefore do not apply to intermittent sources, such as natural rainfall. However, several authors (Meyer-Windel et al., 1999; Sharma and Taniguchi, 1991; Jury et al., 1982; Wierenga, 1977) have shown that models in CXTFIT can handle intermittent rainfall conditions if cumulative drainage is used as the independent variable instead of time. This approach was therefore also used in this study.



**Figure 1**  
Daily rainfall after the application of bromide and nitrate to the experimental plot



**Figure 2**  
Water content of the soil profile at the dates soil samples were taken

## Results and discussion

### Water balance

Soil sampling times and the daily rainfall during the experimental period are presented in Fig. 1. The total precipitation of 574 mm from October 2000 to May 2001 was higher than the average of 463 mm at the experimental site.

As shown in Fig. 2, the average water content in the soil profile decreased from the surface up to a depth of 750 mm and then increased steadily before it stabilised at depths  $\geq 1200$  mm. This behaviour seems to be largely determined by the soil bulk density, which reaches a minimum at the same depth as the water content, Table 1, and the clay contents of the soil in Table 1 displays similar behaviour.

Despite high variation in daily rainfall, which varied from 1 mm for light showers to more than 50 mm for heavy showers, the

No of days	Date (interval)	R	$E_v$	$\Delta S$	$D_p$	$q$ ( $\text{mm}\cdot\text{d}^{-1}$ )
		(mm)				
29	13/10-11/11	45	37	-13	21	0.72
39	12/11-22/11	54	9	26	19	1.90
124	23/11-14/02	148	75	-62	135	1.59
187	15/02-18/04	252	83	65	104	1.65
210	19/04-11/05	75	32	-1	44	1.92
	Total/Average	574	236	15	323	1.56

results in Fig. 2 indicate that the rainfall did not have a significant effect on the form of soil water content profile. This behaviour of the profile suggests that the ability of the soil to store water at a given depth is not only determined by the rainfall rate, but also by the physical properties of the soil.

The components of the water balance, computed from Eqs. (1) and (2), are presented in Table 2. These results indicate that the deep percolation always exceeded the evaporation except for the first sampling period. The reason for this behaviour is that the rainfall during the first sampling period consisted mainly of light showers (see Fig. 1) with the result that evaporation dominated the water balance. The heavier showers, including one of more than  $50 \text{ mm}\cdot\text{d}^{-1}$ , that occurred during the second sampling interval resulted in a substantial deep percolation rate (high  $q$ ). It can be stated that only major rainfall events resulted in deep percolation and small showers resulted only in wetting of the topsoil from where water easily evaporated.

Despite the high rainfall during the third sampling interval (Table 2), the average deep percolation ( $q$ ) was low and the soil had lost much water. This was due to the high evaporation that resulted from the dry and windy climatic conditions of the period (Table 2). During the fourth sampling interval (15 February to 18 April) rainfall was very high (Table 2) which resulted in an increase in deep percolation rate and soil water storage. In the final sampling interval (19 April to 11 May), evaporation was low and the average deep percolation ( $q$ ) was at its highest.

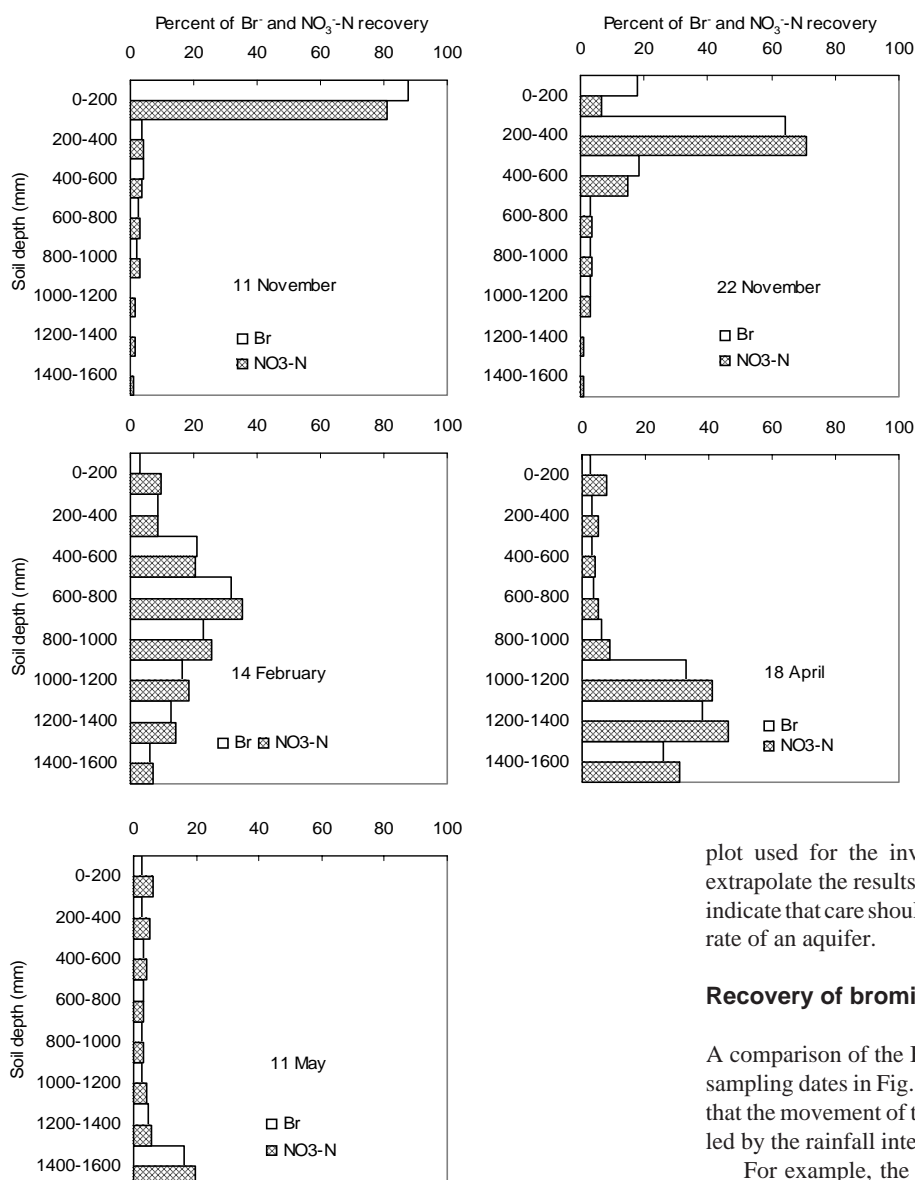
The water balance for the entire season shows that about 41% of the rainfall was lost through evaporation, 56% percolated below the potential root zone and that only 3% was stored in the soil profile. However, the plot was already wet when the experiment commenced. These results suggest that the direct recharge of the aquifer that underlies the site may be considerably higher than the  $15$  to  $25 \text{ mm}\cdot\text{yr}^{-1}$  given by Vegter and Seymour (1995) for the area. It could, however, be argued that since the

plot used for the investigation was bare and too small to extrapolate the results to large areas. Nevertheless, the results indicate that care should be exercised in estimating the recharge rate of an aquifer.

### Recovery of bromide and nitrate

A comparison of the  $\text{Br}^-$  and  $\text{NO}_3^-$ -N recovered at the various sampling dates in Fig. 3 and the rainfall data in Table 2, shows that the movement of these anions in the soil is largely controlled by the rainfall intensity.

For example, the data from the first sample taken on 11 November (about a month after  $\text{KBr}$  and  $\text{KNO}_3$  application) show that although some of the  $\text{Br}^-$  and  $\text{NO}_3^-$ -N moved down to a depth of 1 000 mm, more than 80% of the anions remained in the top 200 mm layer of the profile. However, at the second



**Figure 3**

The mass of  $\text{Br}^-$  and  $\text{NO}_3^-$ -N recovered at the various sampling dates, expressed as a percentage of the mass originally applied, as functions of the sampling depth

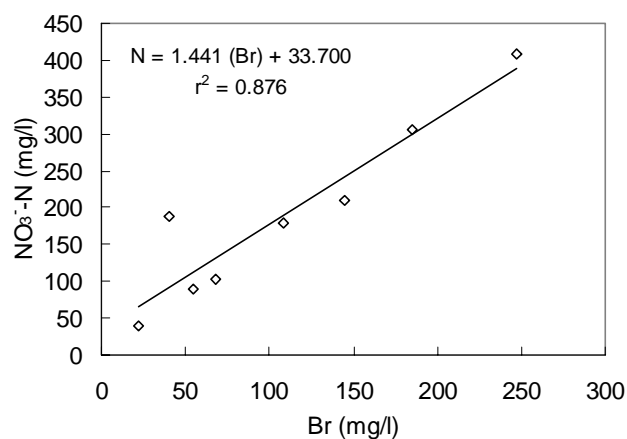


Time (d)		29	39	124	187	210
Recovery (%)	Br <sup>-</sup>	99.8	109.0	123.4	114.7	37.6
	NO <sub>3</sub> <sup>-</sup> -N	99.5	104.2	140.7	149.5	52.1

No of days	Time interval	<i>q</i> (mm·d <sup>-1</sup> )	$\theta$	<i>v<sub>w</sub></i> (mm·d <sup>-1</sup> )
29	13/10-11/11	0.72	0.212	3.4
39	12/11-22/11	1.90	0.215	8.8
124	23/11-14/02	1.59	0.205	7.8
187	15/02-18/04	1.65	0.206	8.0
210	19/04-11/05	1.92	0.223	8.6
	Average	1.56	0.212	7.3

sampling date (only 12 d later) 65% of Br<sup>-</sup> and 70% of NO<sub>3</sub><sup>-</sup>-N had moved to the second layer (200 to 400 mm) and 17% of NO<sub>3</sub><sup>-</sup>-N and 20% of Br<sup>-</sup> was to the third layer (400 to 600 mm). As mentioned above, 45 mm rainfall was recorded during the first sampling period, but most of it was in the form of light showers and therefore evaporated rapidly. The 54 mm of rain recorded during the second sampling period fell in one day. This allowed a significant volume of the rainwater to infiltrate the soil and displace the anions deeper into the soil profile. By the third sampling date, 14 February, the 247 mm rain moved the concentration peaks of Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>-N to halfway between the soil surface and the maximum sampling depth. On 18 April, almost all of the applied Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>-N were leached to below the top 1 000 mm soil layer and a significant quantity below the maximum sampling depth. However, the mass of Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>-N recovered was still high (Table 3). On the last sampling date, 5 May, only 38% of Br<sup>-</sup> and 52% of NO<sub>3</sub><sup>-</sup>-N remained within the sampling depth, of which 20% resided in the bottom layer (1 400 to 1 600), with the concentration peak at the maximum sampling depth. These results indicate that an intense rainfall event induces a higher infiltration rate and the deeper transport of solutes than intermittent moderate to light showers. Patra and Rego (1996) made similar observations which showed a strong influence of heavy rainfall events on the leaching of bromide in an Alfisol of the Indian semi-arid tropics.

The preceding observations are very significant for the application of fertilisers, as it shows that a single rainfall event can swiftly leach fertilisers deeper into the soil profile, thereby reducing the availability of fertilisers to plants. Fertilisers, leached below the rooting depth, not only represent an economic loss to farmers, but also pose an environmental threat to the groundwater resources in fertilised areas. Since the area in which the experiment was performed is an agricultural area, fertilisers might be the primary source of the high concentration of NO<sub>3</sub><sup>-</sup>-N (27.96 mg·L<sup>-1</sup>) observed in groundwater samples taken from a borehole near the experi-



**Figure 4**  
Relation between the Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>-N concentrations recovered from the soil profile 124 days after beginning of the experiment

mental plot. This value is more than twice the concentration of 10 mg·L<sup>-1</sup> recommended by the World Health Organisation for drinking water. One approach to limit the adverse effects of applied fertilisers would be to distribute the application of fertilisers over the growing season of the crop, instead of applying it in batch mode at the beginning of the season.

The total recovered mass of the solutes in Fig. 3 does not add up to 100% of the mass applied, as one would expect. Indeed, the values vary from 37.6 to 149.5, as shown in Table 3. There are essentially three factors responsible for this behaviour: the spatial variability of the soil properties, leaching beyond the maximum sampling depth and the background concentrations, which are difficult to determine in practice. The excessive recovery of solute mass obtained for the second to fourth sampling dates were most probably caused by the last factor, although the first factor could also have contributed to the observed values, while the low mass recovery for the last sampling date was caused by leaching beyond the sample depth. Sampling errors and analytical uncertainties might have also caused some discrepancy.

As mentioned in the introduction, a major objective of the present study was to determine to what extent Br<sup>-</sup> could be used as a substitute for NO<sub>3</sub><sup>-</sup>-N in studies of the motion of NO<sub>3</sub><sup>-</sup>-N through soils. It is therefore interesting to observe that the results in Fig. 3 and the graph of the concentrations of NO<sub>3</sub><sup>-</sup>-N as a function of the Br<sup>-</sup> concentrations in Fig. 4, show that the two anions exhibit very similar transport properties in this soil profile. From similar plots as in Fig. 4 for the other sampling dates, correlation coefficients of 1.000, 0.955, 0.995 and 0.931 were obtained; which implies that it is obvious that Br<sup>-</sup> can be used as a substitute for NO<sub>3</sub><sup>-</sup>-N in studies of the motion of NO<sub>3</sub><sup>-</sup>-N through soils.

### Hydrodynamic dispersion

It is interesting to note that the deep percolation values in Table 2 over time can be equated with the average Darcy velocities, *q*, of the water, below the root zone and used to derive values for the seepage velocities below the root zone, as shown in Table 4.

The rate at which Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>-N were moving in the soil profile was determined from the positions of the concentration peak and the centre of mass of the moving plume. The velocities of the concentration peaks of Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>-N computed from Eq. (7), which were the same for Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>-N, are given in Table 5, while Table 6 lists the centre of mass velocities of the solutes, computed

Soil depth (mm)	Time (d)	Difference		Velocity, v <sub>s</sub> (mm·d <sup>-1</sup> )	v <sub>s</sub> /v <sub>w</sub>
		Depth (mm)	Time (d)		
0	0				
100	29	100	29	3.4	0.47
300	39	200	10	20.0	2.74
700	124	400	85	4.7	0.64
1300	187	600	63	9.5	1.30
1500	210	200	23	8.7	1.19
Average				9.3	1.27

Time (d)	t (d)	$\bar{z}$ (mm)		$\Delta\bar{z}$ (mm)		v <sub>s</sub> (mm·d <sup>-1</sup> )	
		Br	NO <sub>3</sub> -N	Br	NO <sub>3</sub> -N	Br	NO <sub>3</sub> -N
29		160	220				
39	10	320	400	160	180	16.5	18.0
124	85	820	800	500	400	5.8	4.7
187	63	1170	1120	350	320	5.6	5.1
210	23	1070	980	-100	-140	-4.5	-5.9

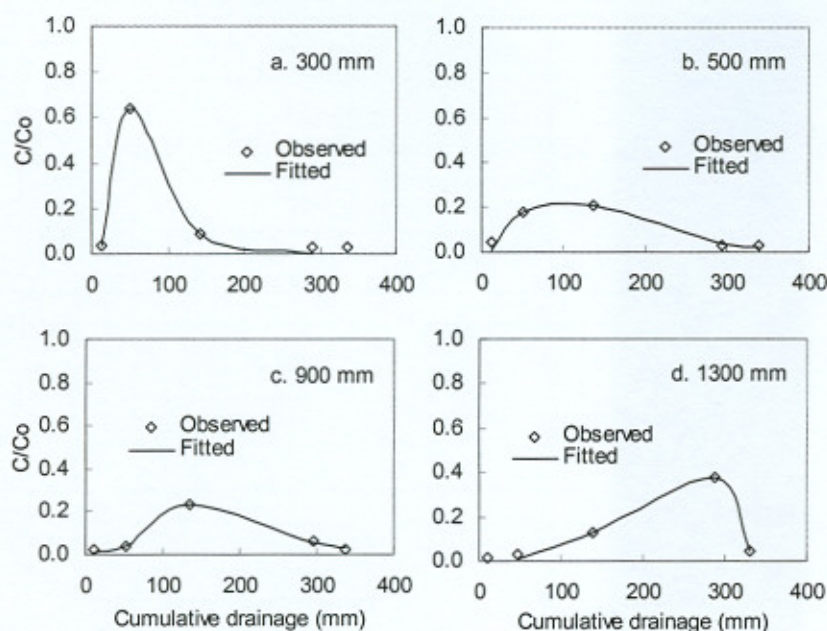


Figure 5  
Observed and CDE fitted breakthrough curves as a function of the cumulative drainage at different depths of the soil profile

from Eq. (9). The high velocity of the concentration peaks for the second sampling interval can probably be attributed to the single high rainfall event that occurred during this sampling interval. The average  $v_s/v_w$  ratio in Table 5 was greater than 1, indicating some preferential flow. The negative centre of mass velocities indicate that the solute had moved beyond the maximum sampling depth and were not included in the calculation of the average centre of mass velocities in Table 6.

The observed Br concentrations were fitted to the convection-dispersion equation (CDE) and stream tube model (STM) with CXTFIT and the cumulative deep percolation, derived from Table 2, was used as independent parameter instead of the time. Since there was not much difference between the two sets of fits, only the fitted curves of the convection-dispersion model are given in Fig. 5. If it is kept in mind that the experiment was conducted in the field under natural soil and climatic conditions and that the cumulative drainage was calculated from the water balance of the soil profile, the agreement between the observed and simulated values is excellent.

The transport parameters determined with the CDE and STM are presented in Table 7. It is interesting to note that the seepage velocities ( $v = 8.3 \text{ mm}\cdot\text{d}^{-1}$  and  $\langle v \rangle = 8.1 \text{ mm}\cdot\text{d}^{-1}$ ) in Table 7 are slightly larger than the average seepage velocity of  $7.3 \text{ mm}\cdot\text{d}^{-1}$  in

Table 4. This indicates that the seepage velocity calculated from deep percolation underestimated the average seepage velocity across the soil profile. This difference could be due to water and solutes preferential flow. Preferential flow is not very common in sandy soils, such as the Bainsvlei soil, but cannot be ruled out in the present experiment. Different values of the ratio  $v_s/v_w$  were found under different conditions even for the same soil textural class (sandy loam). Jaynes et al. (1988) using water application rate of  $35 \text{ cm}\cdot\text{d}^{-1}$  on a sandy loam soil found the ratios  $v_s/v_w = 0.6$  and  $1.0$  in the soil depth ranges of 0 to 0.6 and 1.0 to 3.0 m respectively. Star et al. (1978) on a layered sandy loam soil with water application rate of  $47 \text{ cm}\cdot\text{d}^{-1}$  calculated  $v_s/v_w$  of 2.1. However, most studies showed this ratio to be unity (Ellsworth et al., 1991; Van der Pol et al., 1977; Biggar and Nielsen, 1976; Wild and Babiker, 1976).

## Conclusions

The preceding discussion shows that Br and NO<sub>3</sub>-N exhibit similar transport behaviours and thus that Br can be used as a substitute for NO<sub>3</sub>-N to estimate the loss of nitrate by leaching under bare soil conditions. The average solute velocity was found to be about 18% higher than the seepage velocity indicating some preferential flow. This indicates that, during this long duration



Depth (mm)	Convection-dispersion				Stochastic stream tube				
	$v$ (mm·d <sup>-1</sup> )	$D$ (mm <sup>2</sup> ·d <sup>-1</sup> )	$\lambda$ (mm)	$r^2$ (-)	$\langle v \rangle$ (mm·d <sup>-1</sup> )	$\langle D \rangle$ (mm <sup>2</sup> ·d <sup>-1</sup> )	$\lambda$ (mm)	$\sigma_v$ (-)	$r^2$ (-)
300	7.9	455	57.6	0.995	8.0	324	40.5	2.6	0.995
500	6.5	686	105.5	0.954	6.2	662	106.7	2.8	0.953
900	8.9	1048	117.7	0.987	8.5	1067	125.5	4.6	0.987
1300	9.8	1790	183.0	0.994	9.5	1620	170.5	3.4	0.994
Average	8.3	995	116.0	0.983	8.1	918	110.8	3.4	0.982

seasonal experiment, where drying and wetting of the soil occurred, even this weakly structured soil can exhibit slight preferential flow.

Under the assumption of no biochemical processes, which could add or remove nitrogen to or from the soil, the experimental results indicate that by the end of a rainy season, much of the Br and NO<sub>3</sub>-N could have leached to below the potential rooting depth, as evidenced by the low mass recovery at the last sampling event. There is a substantial potential for NO<sub>3</sub>-N leaching below crop rooting depth in the area. Therefore, leaching of fertiliser-N could be a serious crop production and environmental constraint in this and similar soils of the area. Shallow rooted crops grown in these soils could be more at risk of facing nutrient deficiency than deep-rooted crops. Moreover, NO<sub>3</sub>-N concentration in a nearby borehole that exceeds World Health Organisation standards, may indicate NO<sub>3</sub>-N contamination of groundwater from leached fertiliser-N. Split application of fertiliser-N could help increase plant availability of fertiliser-N and minimise nutrient deficit during critical growth stages of the crop, thereby minimising excessive nutrient loss and potential pollution of the groundwater.

## References

- BAKER JL and LAFTLEN JM (1982) Effects of corn residue and fertiliser management on soluble nutrient runoff losses. *Trans ASAE* **25** 344-348.
- BEAR J (1979) *Hydraulics of Groundwater*. Water Resources and Environmental Engineering. McGraw-Hill, Book Co., New York.
- BENNIE ATP, STRYDOM MG and VERY HS (1998) The Application of Computer Models For Agricultural Water Management On Ecotope Level (Afrikaans). Report No 625/1/98. Water Research Commission, Pretoria, South Africa. 42-45.
- BICKI TJ and GUOL (1991) Tillage and simulated rainfall intensity effect on bromide movement in an argudoll. *Soil Sci. Soc. Am. J.* **55** 794-799.
- BIGGAR JW and NIELSEN DR (1976) Spatial variability of leaching characteristics of a field soil. *Water Resour. Res.* **12** 78-84.
- BUTTERS GL, JURY WA and ERNST FF (1989) Field scale transport of bromide in an unsaturated soil. 1. Experimental methodology and results. *Water Resour. Res.* **25** 1575-1581.
- CAMERON KC and HAYNES RJ (1986) Retention and movement of nitrogen in soils. Haynes, R.J. (ed.). *Mineral Nitrogen in the Plant/Soil System*, New York, Academic Press. 166-241.
- DAGAN G (1993) The Bresler-Dagan model of flow and transport: Recent theoretical developments. In: Russo D and Dagan G (eds.) *Water Flow and Solute Transport in Soils*. Springer-Verlag, Berlin, Heidelberg.
- ELLSWORTH TE, JURY WA, ERNST FE and SHOUSE PJ (1991) A three dimensional field study of solute leaching through unsaturated soil. I. Methodology, mass balance, and mean transport. *Water Resour. Res.* **27** 951-966.
- FLURY M and PAPRITZ A (1993) Bromide in the natural environment: Occurrence and Toxicity. *J. Environ. Qual.* **22** 747-758.
- JARDIN PM, WILSON GV and LUXMOORE RJ (1990) Unsaturated solute transport through a forest soil during rain storm events. *Geoderma* **46** 103-118.
- JAYNES DB, BOWMAN RS and RICE RC (1988) Transport of conservative tracer in the field under continuous flood irrigation. *Soil Sci. Soc. Am. J.* **52** 618-624.
- JURY WA and FLUHLER H (1992) Transport of chemicals through soils: Mechanisms, models and field applications. *Adv. Agron.* **47** 141-201.
- JURY WA and ROTH K (1990) *Transfer Functions and Solute Movement Through Soils: Theory and Applications*. Birkhauser, Basel, Switzerland.
- JURY WA, STOLZY LH and SHOUSE P (1982) A field test of the transfer function model for predicting solute transport. *Water Resour. Res.* **18** 369-375.
- MEYER-WINDELS, LENNARTZ B and WIDMOSER P (1999) Bromide and herbicide transport under steady-state and transient flow conditions. *Eur. J. Soil Sci.* **50** 23-33.
- NACHABE MH, AHUJA LR and BUTTERS G (1999) Bromide transport under sprinkler and flood irrigation for no-till soil condition. *J. Hydrol.* **214** 8-17.
- OWENS LB, VAN KEUREN RW and EDWARDS WM (1985) Groundwater quality changes resulting from a surface bromide application to a pasture. *J. Environ. Qual.* **14** 543-548.
- PATRA AK and REGO TJ (1996) Movement of bromide as a tracer for nitrate in an Alfisol of the Indian Semi-Arid Tropics under rainfed condition. *Fertilizer Res.* **45** 111-116.
- RICE RC, BOWMAN RS and JAYNES DB (1986) Percolation of water below an irrigated field. *Soil Sci. Soc. Am. J.* **50** 855-859.
- RITCHIE JT (1972) Model for predicting evaporation from a row crop with incomplete cover. *Water Resour. Res.* **8** 1204-1213.
- SHARMA ML and TANIGUCHI M (1991) Movement of a non-reactive solute tracer during steady and intermittent leaching. *J. Hydrol.* **128** 323-334.
- SILVERTOOTH JC, WATSON JE, MALCUIT JE and DOERGE TA (1992) Bromide and nitrate movement in an irrigated cotton production system. *Soil Sci. Soc. Am. J.* **56** 548-555.
- SMITH SJ and DAVIS RJ (1974) Relative movement of bromide and nitrate through soils. *J. Environ. Qual.* **3** 152-155.
- SOIL CLASSIFICATION WORKING GROUP (1991) *Soil Classification. A Taxonomic System for South Africa*. Dept. of Agricultural Development, Pretoria, South Africa. 262 pp.
- STARR JL, DEROO HC, FRINK CR and PARLANGE JY (1978) Leaching characteristics of a layered field soil. *Soil Sci. Soc. Am. J.* **42** 386-391.
- TORIDE N and LEIJ FJ (1996a) Convective-dispersive stream tube model for field-scale solute transport: I. Moment analysis. *Soil Sci. Soc. Am. J.* **60** 342-352.
- TORIDE N and LEIJ FJ (1996b) Convective-dispersive stream tube model for field-scale solute transport: II. Examples and calibration. *Soil Sci. Soc. Am. J.* **60** 352-361.

- TORIDE N, LEIJ FJ and VAN GENUCHTEN M TH (1995) The CXTFIT Code For Estimating Transport Parameters From Laboratory And Field Tracer Experiments. U.S. Salinity Lab. Research Rep. 138. Riverside, CA.
- VAN DER POL RMP, WIERENGA PJ and NIELSEN DR (1977) Solute movement in a field soil. *Soil Sci. Soc. Am. J.* **41** 10-13.
- VEGTER JR and SEYMOUR A J (1995) Groundwater Resources of the Republic of South Africa. Water Research Commission, Private Bag X03, Gezina 0031, Pretoria, South Africa.
- WIERENGA PJ (1977) Solute distribution profiles computed with steady state and transient water movement models. *Soil Sci. Soc. Am. J.* **41** 1050-1055.
- WILD A and BABIKER LA (1976) The asymmetric leaching pattern of nitrate and chloride in a loamy sand under field conditions. *J. Soil Sci.* **27** 460-466.
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