

# Transport of Chloride through Water-Saturated Soil Columns

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## Chlorid-Transport durch wassergesättigte Bodensäulen

### 1. Introduction

Solute transport through soils is a major process involved in leaching of ions from soil profiles, contamination of groundwater, plant nutrient uptake and waste water renovation. When a fluid containing a tracer in solution is displaced by the same fluid without a tracer, this type of miscible displacement results in a tracer concentration distribution which depends upon microscopic flow velocities, tracer diffusion rates and other chemical and physical processes (KIRKHAM and POWERS, 1972).

The concept of holdback is a useful qualitative description whenever interaction between solute, solvent or solid is minimal (NIELSEN and BIGGAR, 1961). Values of holdback for unsaturated conditions are reported to be 3 to 4 times greater than saturated soil conditions (KUTILEK and NIELSEN, 1994). Several miscible displacement experiments have shown that intricate nature of pore structure of media, concentrations of the effluent solutions, pH of the soil matrix and several other soil solute interactions such as

adsorption, exchange, decay, chemical reactions etc influence the manner in which solutes move in the moisture stream (NIELSEN and BIGGAR, 1962; VAN GENUCHTEN et al., 1977; NKEDI-KIZZA et al., 1984; NIELSEN et al., 1986; SARDIN et al., 1991; JURY and FLÜHLER, 1992; DAS and KLUITENBERG, 1996; SHUKLA et al., 1999). All these geometrical, physical, chemical and biological factors influence the shape of the break through curves (BTCs) in different proportions. In this study, two soils, loam and sandy loam were selected and displacement experiments were performed to measure BTCs of chloride and bromide anions. All the displacement experiments through these columns were carried out under constant temperature conditions in the laboratory for several different pore water velocities for continuous and pulse type tracer application. The objectives of this research were the investigation of effect of pore water velocity on solute arrival in the effluent and the influence of pore water velocity, displacement length, texture of soil on the shape of BTCs.

### Zusammenfassung

Es wurden Verlagerungsexperimente mit den Anionen Chlorid und Bromid bei konstanter Temperatur, in mit Lehm- und sandigen Lehmböden gefüllten Bodensäulen unterschiedlicher Länge (10, 20 und 30 cm) durchgeführt. Unvollständige Durchmischung bei niedrigen Porenwassergeschwindigkeiten konnte für beide Anionen festgestellt werden. Die verminderte Durchmischung beweist auch das Fehlen von Verbindungen zwischen den Hauptporenbündeln. Die Durchbruchkurven (BTCs) verlagernten sich bei erhöhter Porenwassergeschwindigkeit, bezogen auf den Punkt der x-Achse mit relativem Porenvolumen eins, nach rechts, was auf vollständigere Durchmischung zwischen leitenden und wenig leitenden Zonen schließen läßt. Diese Experimente zeigen die Dominanz der hydrodynamischen Dispersion bei kleinen bzw. konvektiven Transporten bei höheren Porenwassergeschwindigkeiten. Es konnte durch die Experimente gezeigt werden, daß eine erhöhte Porenwassergeschwindigkeit das Rückhaltevermögen oder den immobilen Wasseranteil vermindert. Fortschreitende Verdünnung der Anfangskonzentration wurde festgestellt, wenn die gleiche Tracer-Menge bei den Bodensäulen unterschiedlicher Länge appliziert wurde. Die Experimente zeigten, daß bei feinerer Bodentextur die gelösten Stoffe relativ zum Porenvolumen eins früher im Ausfluß eintreffen. Die vorliegende Studie beweist, daß während der Verlagerung der Grad der Asymmetrie von BTCs eine Funktion der Bodentextur, der Porenwassergeschwindigkeit, des effektiven Diffusions-Dispersions-Koeffizient und der Länge der Bodensäule ist.

**Schlagnworte:** Durchbruchkurven, Dispersion, Konvektiver Transport, Ausschluß, Verdünnung, Retardationsfaktor, effektiver Diffusions-Dispersions-Koeffizient.

### Summary

Displacement experiments at constant temperature were carried out from loam and sandy loam soil columns of three different lengths i.e. 10, 20 and 30 cm with anions chloride and bromide. Incomplete mixing was clearly demonstrated for both anions for slower pore water velocities. This limited mixing also revealed the lack of interconnections between major pore sequences. The breakthrough curves (BTCs) shifted towards right of one relative displacement volume axis with increasing pore water velocity indicating more complete mixing between conducting and slowly conducting zones. These experiments demonstrated the dominance of hydrodynamic dispersion for low pore water velocities and convective transport for higher pore water velocities. Therefore experiments showed that increasing pore water velocity decreases the hold back or immobile water in the column. The progressive attenuation of the initial concentration was demonstrated when the same amount of tracer was sent through the soil columns of different lengths. The experiments showed that solute arrival in effluent solution is ahead when soil texture was finer. The present study revealed that during miscible displacement the degree of asymmetry in BTCs was a function of soil texture, pore water velocity, apparent diffusion coefficient and length of displacement.

**Key Words:** Breakthrough curves, Dispersion, Convective transport, Exclusion, Attenuation, Hold back, Apparent diffusion coefficient.

## 2. Material and Methods

### 2.1 Collection of Soil Samples

Based upon the textural classification available at the Institute for Hydraulics and Rural Water Management, University of Agricultural Sciences Vienna (CEPUDER, 1990; KLIK et al., 1997), two locations namely, Pyhra and Gross-En-

zersdorf were identified for soil sample collection. Loam soil from the experimental farm of farmers training center at Pyhra, Lower Austria was collected up to a depth of 15 cm and sandy loam soil was collected from the experimental farm of University of Agricultural Sciences Vienna at Gross-Enzersdorf from a depth of 40 to 70 cm. After removing the gravel, stones and roots, the remaining soil was passed through 2 mm sieve and all the material passing through

Table 1: Physical and chemical properties of loamy soil from Pyhra  
Tabelle 1: Physikalische und chemische Eigenschaften des Pyhra-Lehmbodens

(a)

Depth (m)	Sand	Silt	Clay	Bulk Density kg/m <sup>3</sup>	Humus %	pH nKCl
0-0.3	40	45	15	1420	2.7	6.4
0.3-0.65	39	38	23		1.0	5.7
>0.65	33	39	28		0.9	5.7

(b) From earlier experiments

Depth m	CEC mmol <sub>c</sub> /kg	Ca mmol <sub>c</sub> /kg	Mg mmol <sub>c</sub> /kg	K mmol <sub>c</sub> /kg	Na mmol <sub>c</sub> /kg
0-0.3	84.6	66	9.5	5.3	3.2

(c) Soil properties from representative sample of loam soil (USDA) (0-15 cm)

Texture			Organic Carbon %	Total N %	Electrical Conductivity μS/cm	pH CaCl <sub>2</sub>
Sand %	Silt %	Clay %				
33.7	44.5	21.8	1.23	0.15	67	6.88

was collected separately. This portion of soil was used as porous media in the soil columns. About 600 g of each soil was collected from the sieved portions (< 2mm) for both locations and was used as representative samples for determining physical and chemical properties of soils. Some physical and chemical properties of both sandy loam soil and loam soil were obtained from the earlier experiments conducted by Institute for Hydraulics and Rural Water Management (CEPUDER, 1990; KLIK et al., 1997). The investigated soil properties included particle size analysis, bulk density, particle density, saturated hydraulic conductivity, organic carbon, humus, total nitrogen, pH, electrical conductivity, and cation exchange capacity. All these properties for loam soil are presented in table 1a-c and for sandy loam soil in table 2a-c.

## 2.2 Breakthrough Curves

The Plexiglas columns used in the study were 10 cm in diameter and 10, 20 and 30 cm long. One end of the column was closed and the column was carefully packed by dropping 200 g of soil each time into it. The soil inside the column was spread and tapped uniformly with a very fine rod to remove layers. At each end of the Plexiglas soil col-

umn, fine nylon filter was placed to prevent loss of soil during displacement experiments. Weight of Plexiglas assembly and dry and saturated soil weight were determined gravimetrically for each column in order to calculate porosity, dry bulk density and moisture content of soil. Each soil column was slowly saturated from the bottom with  $\text{CaBr}_2$  solution of 0.1M concentration (figure 1). The steady state flow required for obtaining a given pore water velocity was adjusted by measuring the effluent volume with respect to time. The supply line was switched to 0.1M  $\text{MgCl}_2$  solution for the selected steady state flow. The effluent solutions were collected at fixed time intervals in small plastic bottles. The supply was switched back to  $\text{CaBr}_2$  solution for the step input when no more  $\text{Br}^-$  was detected in the effluent solution and at time  $t_0$  (end of pulse) for pulse input. For Bromide BTCs, the steady state flow was adjusted with  $\text{MgCl}_2$  solution and then the supply was changed to  $\text{CaBr}_2$  solution till no chloride was detected in the effluent solution. All the experiments were conducted at a constant temperature of  $20^\circ \text{C} \pm 2^\circ \text{C}$ . Utmost care has been taken that the soil columns always remain flowing. The concentrations of  $\text{Cl}^-$  and  $\text{Br}^-$  ions present in the solution were measured in the laboratory using SM 902 Titrator. To obtain the effective value of water content of soil, weight of each soil column was determined at the cessation of an experi-

Table 2: Physical and chemical properties of sandy loam soil from Grossenzersdorf  
Tabelle 2: Physikalische und chemische Eigenschaften der sandigen Grossenzersdorf-Lehmböden

(a)

Depth (m)	Sand	Silt	Clay	Saturated Conductivity (m/d)	Dry Bulk Density ( $\text{kg/m}^3$ )	Organic Matter (%)
0-0.2	33.2	45.1	21.7	76.8	1460	4.2
0.2-0.4	34.0	43.0	22.8	2.1	1530	4.0
0.4-0.6	33.1	42.8	23.1	16.7	1380	3.5
0.6-1.2	46.9	38.5	14.6	1.7	1400	1.9

(b) From earlier experiments

Depth (m)	CEC $\text{mmol}_e/\text{kg}$	Ca $\text{mmol}_e/\text{kg}$	Mg $\text{mmol}_e/\text{kg}$	K $\text{mmol}_e/\text{kg}$	Na $\text{mmol}_e/\text{kg}$
0.4-0.6	329.7	286	29.9	3.85	9.95

(c) Soil Properties from representative sample of sandy loam soil

Texture			Organic Carbon %	Total N %	Humus %	Electrical Conductivity $\mu\text{S}/\text{cm}$	pH $\text{CaCl}_2$
Sand %	Silt %	Clay %					
53.3	34.7	12.0	0.264	0.05	0.455	159.75	7.42

ment also. One soil column was used for 3 to 4 different sets of pore water velocities. This number was arbitrarily set assuming that a column may not remain same for a very long time. Therefore, in order to minimize the effects of physical distortion in the soil column, it was replaced with a new column of nearly same bulk density and water content.

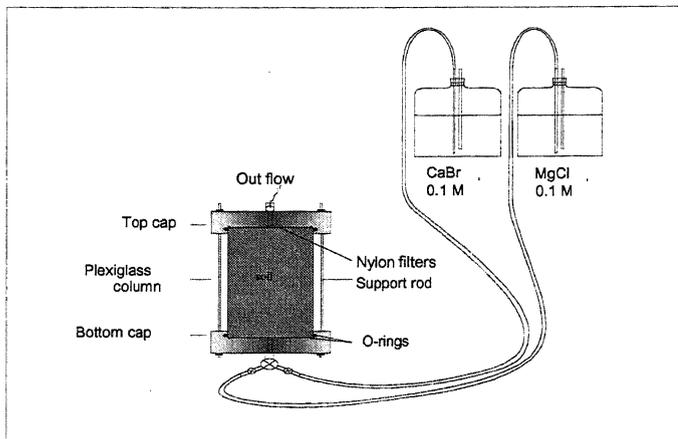


Figure 1: Experimental setup  
Abbildung 1: Experimenteller Aufbau

### 2.3 Miscible Displacement Studies

Breakthrough curves of  $\text{Cl}^-$  were measured for continuous tracer application as well as for pulse application from 10, 20 and 30 cm loam and sandy loam soil columns, whereas BTCs of  $\text{Br}^-$  were measured only from 10 cm loam soil column for step solute application. In case of pulse application, about 300 ml of displacing solution was applied for each of the experiment. The details of the experiments with loam and sandy loam soil columns are presented in tables 3 and 4 respectively (SHUKLA, 1998).

The chloride BTCs were measured from 10 cm loam soil column 1 for 8 different pore water velocities ranging from 0.025 cm/h to 2.6 cm/h for a continuous application of 0.1 M of  $\text{MgCl}_2$ . BTCs from another 10 cm loam soil column 2 for approximately the same pore water velocities were measured for comparison for a continuous application of 0.1 M of  $\text{MgCl}_2$ . The BTCs were also measured for pulse type application of 0.1 M of  $\text{MgCl}_2$  from 10 cm loam soil column 3 for pore water velocities ranging from 0.07–1.0 cm/h, 20 cm loam soil column (0.07–0.9 cm/h) and 30 cm loamy soil column (0.07–0.5 cm/h). The BTCs for bromide were measured from 10 cm loam soil columns for

pore water velocities of 0.036, 0.06, 0.1, 0.2, 0.5, 0.7, 1.1, and 2.53 cm/h when 0.1 M  $\text{MgCl}_2$  solution was displaced by 0.1 M  $\text{CaBr}_2$  solution. The BTCs for chloride were measured from 10, 20 and 30 cm sandy loam soil columns for pore water velocities ranging from 0.1–2.0 cm/h.

## 3. Results and Discussion

### 3.1 Similarity of Soil Columns

The measured saturated hydraulic conductivities from two 20 cm loamy soil columns were 0.022 cm/h and 0.026 cm/h. From 10 cm sandy loam soil columns the saturated conductivities obtained were 1.53 cm/h and 1.36 cm/h and from a 30 cm sandy loam soil column was 1.33 cm/h. These values indicate that columns filled with a given soil have nearly the same saturated hydraulic conductivity. Similarly the water content, bulk density and porosity of soil in each column are also nearly the same (table 3 and 4). Utmost care has been taken that the soil columns always remain flowing. Porosity of soil was obtained by bulk density and particle density data. Comparison between the values of porosities and water contents of both soils in table 3 and 4 indicates that in each of the soil column air was present.

### 3.2 Measured Chloride Breakthrough Curves from Loam Soil Columns

BTCs in figures 2 and 3 show that for slower pore water velocities, chloride is appearing in the effluent solution ahead of the higher pore water velocities. However, it is requiring more relative displacement volumes (ratio of the effluent volume to the volumetric water content of column,  $\text{cm}^3/\text{cm}^3$ ) for attaining a relative concentration of 1. With increasing pore water velocity the  $\text{Cl}^-$  BTCs shift towards the right and require lesser relative displacement volumes of effluent solution to displace  $\text{Br}^-$  completely. The figure 2 and 3 also show that the BTCs of lower pore water velocities are flatter and most of them cross the BTCs of higher pore water velocities before attaining their maximum, whereas BTCs for higher pore water velocities are more abrupt or steep. Similar observations can be made for measured BTCs from other loam soil columns presented in figures 4, 5 and 6.

Table 3: Soil column data for displacement experiments with loamy soil columns (a) 10 cm (b) 20 cm (both continuous input) and (c) 30 cm long (pulse input)

Tabelle 3: Ergebnisse der Säulenexperimente (mit Lehm Böden gefüllt) (a) 10 cm (b) 20 cm (jeweils kontinuierlicher Input) und (c) 30 cm (pulsförmiger Input)

(a)

Column 1			Column 2			Column 3 (pulse)		
$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P	$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P	$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P
0.44	1.433	0.454	0.4469	1.413	0.46	0.4367	1.48	0.44
Pore Water Velocity in cm/h								
Cl		Br	Cl		Br	Cl		Br
0.025		0.036	0.028		0.03	0.068		0.068
0.056		0.05	0.051		0.05	0.098		0.098
0.11		0.1	0.074		0.06	0.294		0.294
0.18		0.32	0.118		0.2	0.508		0.508
0.51		0.77	0.246		0.5	0.7		0.7
0.72		1.13	0.51		0.7	1		1
1.39		2.53	0.765		1.1			
2.6			1.32		2.42			
			2.47					

(b)

Column 4			Column 5			Column 6		
$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P	$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P	$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P
0.4393	1.447	0.45	0.3584	1.461	0.44	0.4246	1.458	0.445
Pore Water Velocity in cm/h								
Cl		Br	Cl		Br	Cl		Br
0.023		0.028	0.04		0.04	0.0716		0.0716
0.038		0.036	0.043		0.044	0.104		0.104
0.041			0.09		0.0925	0.337		0.337
0.078			0.0925			0.5		0.5
						0.7		0.7
						1		1

(c)

Column 7			Column 8			Column 9		
$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P	$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P	$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P
0.4049	1.482	0.435	0.4142	1.454	0.446	0.407	1.49	0.43
Pore Water Velocity in cm/h								
Cl		Br	Cl		Br	Cl		Br
0.019		0.019	0.068		0.068	0.29		0.29
0.0496		0.0496	0.1012		0.1012	0.5		0.5

Following remarks can be made on the BTCs presented in figures 2 to 6:

Figures 2 and 3 show that the BTCs for pore water velocities less than 0.056 cm/h from column 1 and less than

0.12 cm/h from column 2 are translated towards left from one relative displacement volume axis. Similarly, the BTCs of pore water velocities less than 0.5 cm/h from column 4 (figure 5) and less than 0.5 cm/h from column 5 (figure 6)

Table 4: Soil column data for displacement experiments with (a) 10 cm; (b) 20 cm (both continuous input); and (c) 30 cm sandy loam soil columns for pulse input

Tabelle 4: Ergebnisse der Säulenexperimente (mit sandigen Lehmböden gefüllt) (a) 10 cm (b) 20 cm (jeweils kontinuierlicher Input) und (c) 30 cm (pulsförmiger Input)

(a)

Column 11a			Column 11b		
$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P	$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P
0.429	1.45	0.456	0.42	1.51	0.433
Pore Water Velocity (cm/h)					
Cl		Br		Cl	
0.104		0.104		0.68	
0.32		0.32		1.01	
0.48		0.48		1.503	
				1.99	

(b)

Column 12 a			Column 12 b		
$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P	$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P
0.431	1.433	0.46	0.429	1.46	0.45
Pore Water Velocity (cm/h)					
Cl		Br		Cl	
0.104		0.104		1.0	
0.29		0.29		1.47	
0.529		0.529		1.96	
0.718		0.718			

(c)

Column 13 a			Column 13 b		
$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P	$\theta$ cm <sup>3</sup> /cm <sup>3</sup>	$\rho$ g/cm <sup>3</sup>	P
0.415	1.484	0.44	0.417	1.468	0.449
Pore Water Velocity (cm/h)					
Cl		Br		Cl	
0.11		0.11		1.02	
0.32		0.32		1.5	
0.5		0.5		1.93	
0.7		0.7			

are also translated to the left from one relative displacement volume axis. The translation of Cl<sup>-</sup> curve to the left could be the result of repulsion of negatively charged Cl<sup>-</sup> ions from the negatively charged soil particle surfaces (anion exclusion, KEMPER, 1960). The loam soil has a higher clay content compared to sandy loam soil (table 1) Thus, the early breakthrough of chloride in all these figures (2-6) is, indeed, indicative of a tracer that is repelled from the predominantly negatively charged clay surfaces. All curves which are translating towards the left from one relative displacement

volume axis are for small pore water velocities. All these curves are flatter and chloride is also appearing in the solution ahead and each has a longer tail (KUTILEK and NIELSEN, 1994).

This type of translation could take place either due to the increase in concentration within the soil or due to incomplete mixing throughout the entire soil solution. In these experiments, the first reason is not valid as the total solution concentration was maintained constant throughout the experiment. Therefore, the possible reasons for the translation

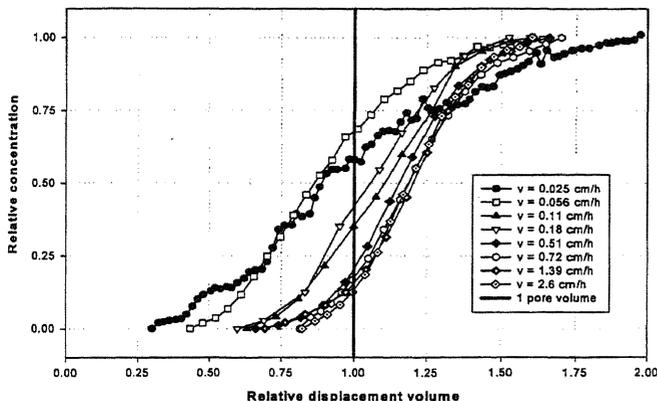


Figure 2: BTCs for chloride from 10 cm loam soil column for continuous application (column 1)  
 Abbildung 2: Chlorid-BTCs der mit Lehmboden gefüllten Bodensäulen (10 cm), bei kontinuierlicher Applikation (Bodensäule 1)

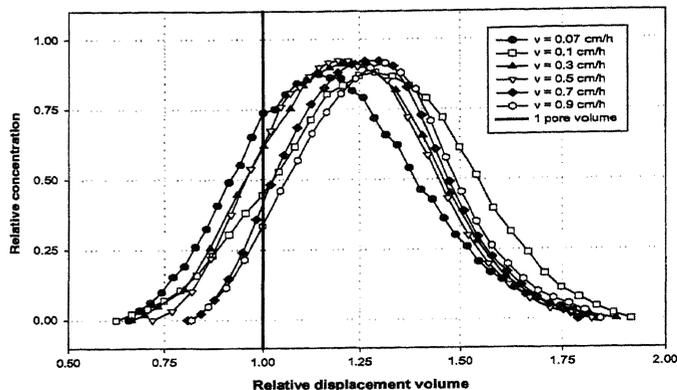


Figure 5: BTCs for chloride from 20 cm loam soil column for pulse application (column 4)  
 Abbildung 5: Chlorid-BTCs der mit Lehmboden gefüllten Bodensäulen (10 cm), bei pulsformiger Applikation (Bodensäule 4)

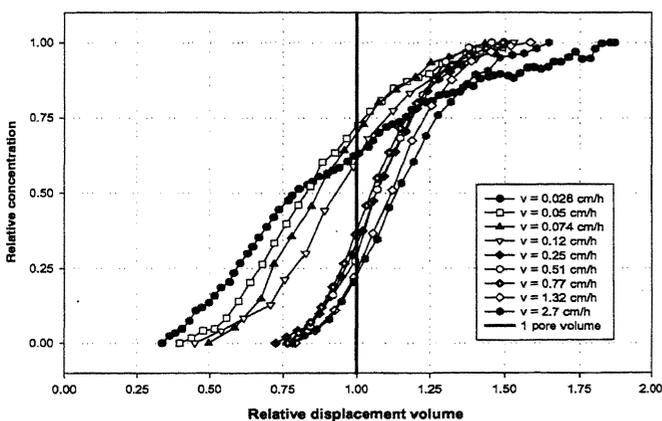


Figure 3: BTCs for chloride from 10 cm loam soil column for continuous application (column 2)  
 Abbildung 3: Chlorid-BTCs der mit Lehmboden gefüllten Bodensäulen (10 cm), bei kontinuierlicher Applikation (Bodensäule 2)

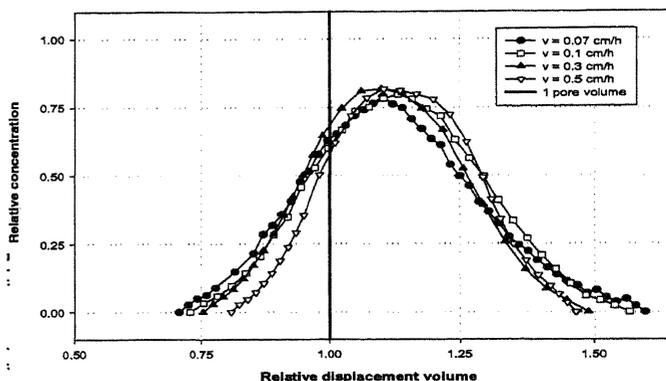


Figure 6: BTCs for chloride from 30 cm loam soil column for pulse application (column 5)  
 Abbildung 6: Chlorid-BTCs der mit Lehmboden gefüllten Bodensäulen (10 cm), bei pulsformiger Applikation (Bodensäule 5)

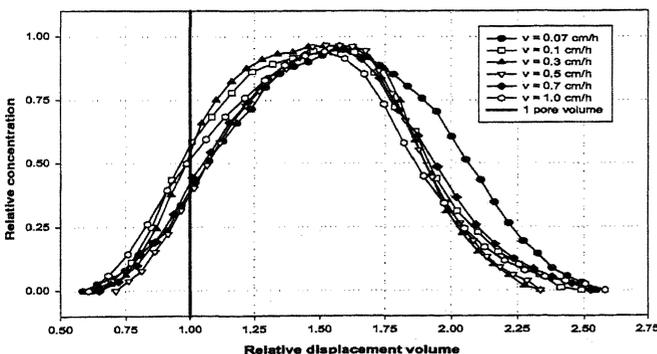


Figure 4: BTCs for chloride from 10 cm loam soil column for pulse application (column 3)  
 Abbildung 4: Chlorid-BTCs der mit Lehmboden gefüllten Bodensäulen (10 cm), bei pulsformiger Applikation (Bodensäule 3)

tion of BTCs could be the presence of the negatively charged surfaces and the incomplete mixing owing to the stagnant pores.

With increasing pore water velocity chloride BTCs shift towards right (Figures 2 to 6). This indicates that as apparent diffusion coefficient (sum of hydrodynamic dispersion and convective flow) increases the displacing solute mixes more completely with the solute in stagnant and slowly conducting zones, thus delaying the appearance of displacing solute in the effluent solution. The appearance of Cl<sup>-</sup> in the effluent solution requiring lesser relative displacement volume and the flatter curves at smaller fluxes illustrate the important contribution of hydrodynamic dispersion to the transport of solute.

Figures 2 to 4 also indicate that delay in appearance of chloride in effluent solution with increasing pore water velocity is not always valid for example  $\text{Cl}^-$  BTC for pore water velocity of 1.39 cm/h in figure 2, 0.77 cm/h in figure 3 and 1.0 cm/h in figure 4. In some cases specially in higher pore water velocity ranges chloride appeared ahead in the effluent solution for a higher pore water velocity than for a lower pore water velocity. This could be due to the fact that at higher pore water velocities the solute has much higher apparent diffusion coefficient. The mass transfer or convective mixing also become significant at these higher flow velocities. The combined diffusion, dispersion and convection transport make it possible for the solute to invade the slowly conducting pores and move faster inside the soil column, thus, appearing ahead in the effluent solution. The BTCs at higher fluxes break sharply in contrast to the smaller fluxes. The BTCs of  $\text{Cl}^-$  in figures 2 to 6 are not crossing each other at relative displacement volume of 1. This indicates that not only diffusion and dispersion but adsorption, exclusion or ionic exchange processes are taking place during the transport which are affecting the shape of BTCs.

The left handed displacement of the  $\text{Cl}^-$  curves with increasing pore water velocities mentioned in the above paragraph also indicates the presence of transport related nonequilibrium. Similar observations are given by GABER et al. (1995). The transport related nonequilibrium is dealt with in more details elsewhere (for field conditions - WHITE et al., 1986; SEYFRIED and RAO, 1987; SINGH and KANWAR, 1991; GABER et al., 1995; and in repacked soil columns - BIGGAR and NIELSEN, 1962; RAO et al., 1980; NKEDI-KIZZA et al., 1982, 1984) and VALOCCHI A. J. (1985).

The amount of solute not easily displaced during miscible displacement has been described as hold back (H). The area under BTC up to 1 relative displacement volume was defined as hold back by DANCKWERTS (1953). H varies from 0 for piston flow to values less than 1 for other cases for non reacting solutes. H calculated for the BTCs of figure 2 and 3 are given in table 5 which shows that H decreases with increasing pore water velocity. In other words immobile water decreases with increasing pore water velocity. This can be due to the higher pore water velocity which makes possible for the solute to invade more dead or slowly conducting liquid zones. The chloride BTCs in figures 2 and 3 shift towards right as pore water velocity increases or holdback decreases. This should happen as more and more wetted pore spaces are included actively in transport.

Table 5: Values of Holdback from chloride BTCs  
Tabelle 5: Rückhaltevermögen – Chlorid-BTCs

BTCs in Figure 2					
v	H	v	H	v	H
0.025	0.17	0.18	0.055	1.39	0.022
0.06	0.164	0.51	0.022	2.6	0.012
0.11	0.05	0.72	0.018		
BTCs in Figure 3					
0.028	0.214	0.12	0.116	0.77	0.38
0.05	0.189	0.25	0.35	1.32	0.02
0.074	0.159	0.51	0.35	2.7	0.02

### 3.3 Comparison of Measured Bromide and Chloride BTCs from Loam Soil Columns

Figure 1 and 2 for anion  $\text{Cl}^-$  and figure 7 for anion  $\text{Br}^-$  show that BTCs for both these anions shift towards right as pore water velocities increased. The bromide BTCs for lower pore water velocities are also flatter, translated towards left from 1 relative displacement volume axis and many of them are crossing the BTCs of higher pore water velocities before reaching a unit relative concentration. For a given pore water velocity chloride BTCs are appearing ahead of bromide BTCs in the effluent solution (figure 1, 2 and 7). Both chloride and bromide anions produce similar response during transport through soil columns.

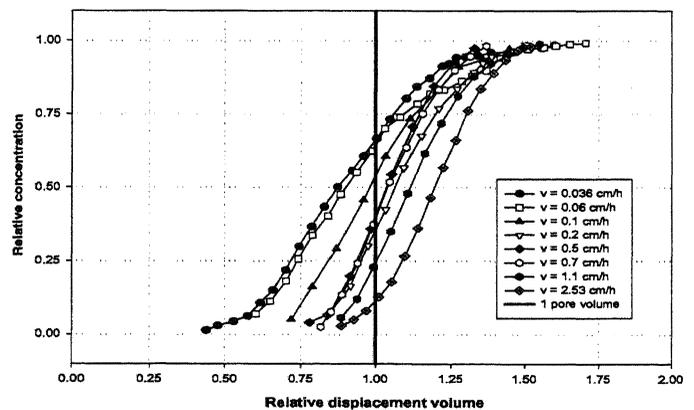


Figure 7: BTCs for bromide from 10 cm loam soil column  
Abbildung 7: Bromid-BTCs der mit Lehmboden gefüllten Bodensäulen (10 cm)

### 3.4 Measured Breakthrough Curves of Chloride from Sandy Loam Soil Columns

Figure 8 shows that chloride BTCs of 0.1 cm/h, 0.5 cm/h and 0.7 cm/h are appearing ahead in effluent solution as compared to the BTCs of pore water velocities greater than

0.7 cm/h. The BTCs for higher pore water velocities also break steeply initially in contrast to BTCs of smaller pore water velocities. The BTCs for smaller pore water velocities are approaching the maximum relative concentration slowly and are also flatter on the recession side of chloride hydrograph (figure 8). The hydrograph bases are broader for smaller pore water velocities than for higher velocities. The BTCs for chloride for similar pore water velocities from 20 cm sandy loam soil columns and from 30 cm sandy loam soil columns show the same responses.

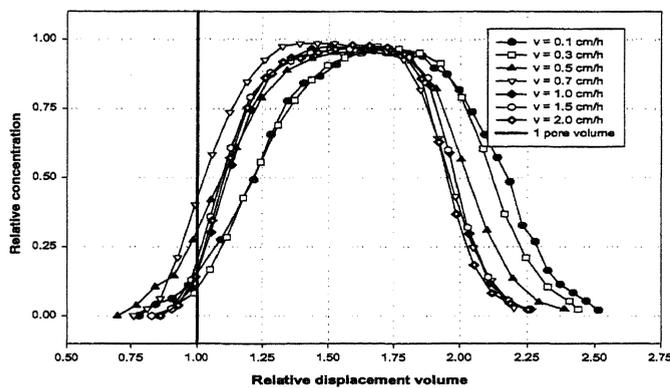


Figure 8: BTCs for chloride from 10 cm sandy loam soil column  
Abbildung 8: Chlorid-BTCs der mit sandigem Lehmboden gefüllten Bodensäulen (10 cm), bei pulsformiger Applikation

### 3.5 Influence of Displacement Length on BTCs

It is well known that mixing and attenuation of a solute by convection is dependent upon the pore size distribution and the number of bifurcations experienced by the soil solute as it flows through the system of microscopic pores (KUTILEK and NIELSEN, 1994). The number of bifurcations in the system and the time for molecular diffusion increases with increasing macroscopic displacement length (KUTILEK and NIELSEN, 1994). Therefore, opportunity for both convective and diffusive mixing in the pore system also increases. The concentration versus volume BTC hydrographs (figure 11) illustrate the progressive attenuation of the initial concentration as solute is displaced through greater macroscopic length.

The figure 11 presents the BTCs for a pore water velocity of 0.07 cm/h when 300 ml pulse of  $MgCl_2$  solution was sent through three loamy soil columns 10 cm, 20 cm and 30 cm long. It is evident from figure 11 and table 6, that for  $v = 0.07$  cm/h, the relative concentration of 0.95 for the 10 cm long

column reduces to about 0.88 when the displacement length increases from 10 to 20 cm. For the 30 cm soil column the relative concentration reduces further to about 0.79. This means that doubling the column length reduces the peak by about 8 % whereas, tripling of column length results in about 17 % reduction in the relative concentration peak. The time bases of hydrographs (table 6) increase from nearly 288 hours for 10 cm column to nearly 328 hours for 20 cm column (approximately 1.2 times). They increase further to about 392 hours (about 1.4 times) for the 30 cm long column for the same pore water velocity. Similarly, volume bases of hydrographs also increase from about 652 ml for 10 cm column to about 781 ml for 20 cm column (1.2 times) and further to about 894 ml (1.4 times) for 30 cm column. Similar lowering of relative concentration and subsequent increase in time and volume bases of BTC hydrographs with corresponding increase in displacement lengths from loamy soil columns and sandy loam soil columns (figure 12) were observed for all pore water velocities (SHUKLA, 1998).

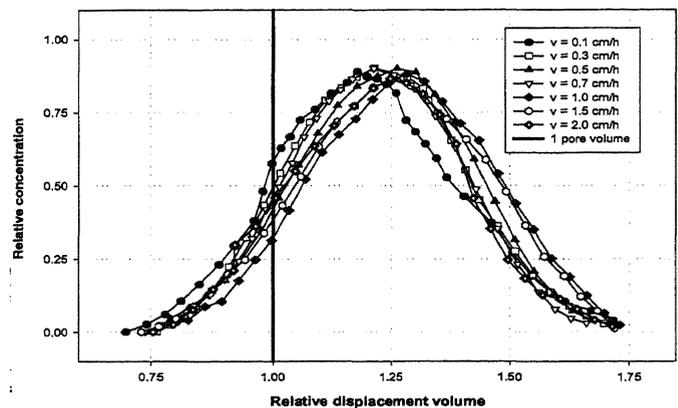


Figure 9: BTCs for chloride from 20 cm sandy loam soil column  
Abbildung 9: Chlorid-BTCs der mit sandigem Lehmboden gefüllten Bodensäulen (20 cm), bei pulsformiger Applikation

The attenuation of relative concentration presented in table 6 and figures 11–12 for both loam and sandy loam soils can be explained as the process of dilution which is taking place along the displacement length. Due to the dilution, the solute applied as a pulse is not able to carry its total mass beyond a certain length. However, the time bases and volume bases decrease with increase in pore water velocity and the hydrographs are getting steeper. Table 6 and figures 11–12 show that the total volume of effluent solution required to completely displace the tracer from the column as well as total time required are increasing with length. However, effluent volumes are not increasing proportional to the length.

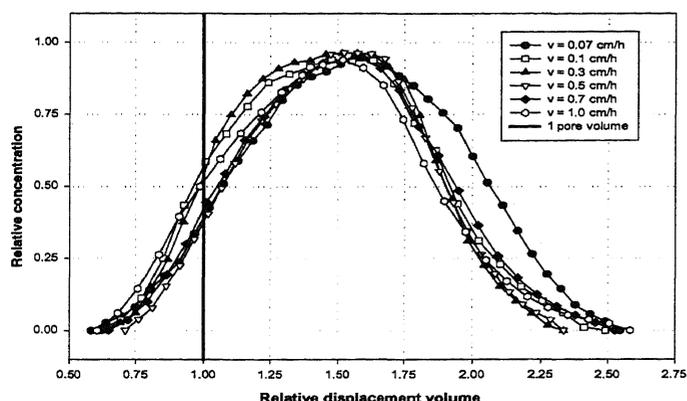


Figure 10: BTCs for chloride from 30 cm sandy loam soil column  
 Abbildung 10: Chlorid-BTCs der mit sandigem Lehmboden gefüllten Bodensäulen (30 cm), bei pulsformiger Applikation

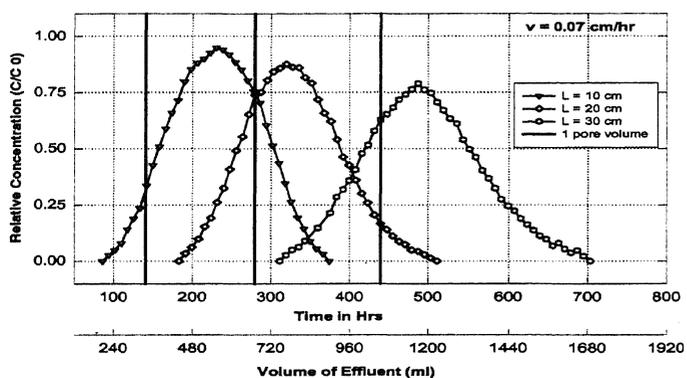


Figure 11: BTCs for chloride from 10 cm, 20 cm and 30 cm loam soil columns for a pore water velocity of 0.07 cm/h  
 Abbildung 11: Chlorid-BTCs der mit Lehmboden gefüllten Bodensäulen (10 cm, 20cm, 30 cm) für eine Porenwassergeschwindigkeit von 0,07 cm/h

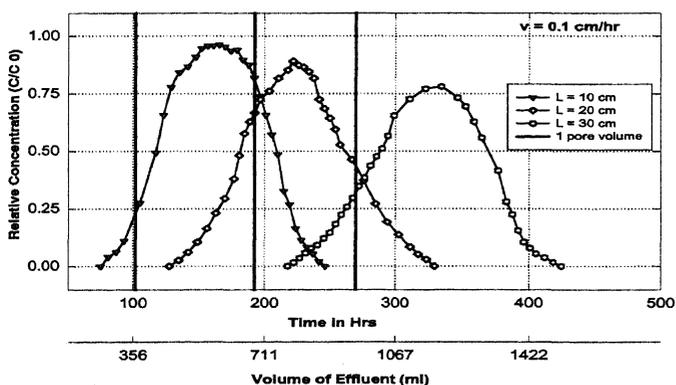


Figure 12: BTCs for chloride from 10 cm, 20 cm and 30 cm sandy loam soil columns for a porewater velocity of 0.1 cm/h  
 Abbildung 12: Chlorid-BTCs der mit sandigem Lehmboden gefüllten Bodensäulen (10 cm, 20cm, 30 cm) für eine Porenwassergeschwindigkeit von 0,1 cm/h

### 3.6 Comparison of Results Between Loam and Sandy Loam Soil Columns

The texture data for loam and sandy loam soil used as porous media in the soil columns are presented in tables 1 and 2 respectively. The loam soil contains large amounts of silt (45 %) and clay (22 %) whereas sandy loam soil has large amount of sand particles (53 %).

Figures 4 to 6 present the BTCs of chloride for different pore water velocities from 10, 20 and 30 cm long loamy soil columns and figures 8 to 10 present the similar curves from sandy loam soil columns for pulse type application of tracer. These figures indicate that for nearly same pore water velocities from loamy soil columns (figure 4 to 6), chloride appears in the effluent solution ahead irrespective of column length. This could be due to the incomplete mixing inside the loamy soil columns which causes early breakthrough of chloride in effluent solution. The sandy loam soil has large amounts of bigger soil particles and therefore mixing is more complete inside these columns which delays the arrival of chloride in the effluent solution. Since the dispersion path lengths in loamy soil columns are less compared to sandy loam soil columns, probably that is also a reason for the quicker breakthrough of chloride from loamy soil columns. However, the BTCs from sandy loam soils are more steep for a given pore water velocity. This is probably due to the convective flow taking place through the bigger soil particles. The peaks of chloride BTC from sandy loam soil columns (figure 12) are slightly higher than the corresponding chloride peaks from loam soil column (figure 11).

### 4. Conclusions

In the present study displacement experiments were carried out from loam and sandy loam soil columns of three different lengths i.e. 10, 20 and 30 cm with chloride and bromide anions. The BTCs for both anions were generated for several different pore water velocities. The bromide BTCs were measured from only 10 cm columns for continuous tracer application whereas chloride BTCs were measured from all the three columns for continuous as well as pulse tracer application. It was observed that both chloride and bromide tracers are providing a similar response.

In general for slower pore water velocities both chloride and bromide appeared in the effluent solution ahead and the BTCs shifted slightly towards right with increasing pore water velocities. A quicker arrival of tracer in the effluent

Table 6: Effect of displacement length on BTCs hydrographs from loamy and sandy loam soil columns  
 Tabelle 6: Einfluß der Verlagerungslänge auf die BTCs für mit Lehm- und sandigen Lehmböden gefüllte Säulen

BTCs – Hydrograph (loam soil )	v = 0.07 cm/h			v = 0.1 cm/h					
	10cm	20 cm	30 cm	10cm	20 cm	30 cm			
Time Base (hr)	288	328	392	192	248	249			
Vol. Base (ml)	652	781	894	661	822	831			
C/C0 (peak)	0.95	0.88	0.79	0.94	0.88	0.8			
BTCs - Hydrograph (loam soil)	v = 0.3 cm/h			v = 0.5 cm/h					
	10cm	20 cm	30 cm	10cm	20 cm	30 cm			
Time Base (hr)	58	72	76	32	44	42			
Volume Base (ml)	565	740	712	562	690	655			
C/C0 (peak)	0.96	0.91	0.82	0.964	0.92	0.82			
BTCs - Hydrograph (sandy loam soil)	v = 0.1 cm/h			v = 0.3 cm/h					
	10cm	20 cm	30 cm	10cm	20 cm	30 cm			
Time Base (hr)	165	195	207	50.5	58	70.5			
Volume Base (ml)	574	689	739	559	657	769			
C/C0 (peak)	0.96	0.89	0.78	0.97	0.9	0.8			
BTCs - Hydrograph (sandy loam soil)	v = 0.5 cm/h			v = 0.7 cm/h					
	10cm	20 cm	30 cm	10cm	20 cm	30 cm			
Time Base (hr)	35.5	37.5	49.6	21.75	28	29.8			
Volume Base (ml)	547	673	760	487	643	729			
C/C0 (peak)	0.95	0.9	0.8	0.97	0.9	0.8			
BTCs - Hydrograph (sandy loam soil)	v = 1.0 cm/h			v = 1.5 cm/h			v = 2.0 cm/h		
	10cm	20 cm	30 cm	10cm	20 cm	30 cm	10cm	20 cm	30 cm
Time Base (hr)	14.3	21	24	9.5	14.1	16.33	7.3	10.4	14
Volume Base (ml)	494	683	804	480	692	796	492	674	847
C/C0 (peak)	0.97	0.88	0.79	0.97	0.86	0.78	0.98	0.87	0.8

solution for low pore water velocities indicated that mixing inside the column was less complete probably due to the lower solute apparent diffusion coefficient, anion exclusion and the presence of dead water zones inside the soil columns. This limited mixing also revealed the lack of interconnections between major pore sequences. The shift of BTCs towards right with increase in pore water velocity could be due to more complete mixing between conducting and slowly conducting zones causing delay in solute arrival in the effluent solution. In displacement experiments with both loam and sandy loam soils for very high pore water velocities solute arrived in effluent solution ahead for higher pore water velocities. This could be explained by the fact that for these high flow velocities both convective and dispersive transport take place in the soil system and the solute has a higher apparent diffusion coefficient which probably makes possible for the solute to invade the stagnant pores more throughly.

The experiments also showed that as pore water velocity increases the hold back (immobile water) in the column decreases. The progressive attenuation of the initial concentration was demonstrated when same amount of tracer

was sent through the soil columns of different lengths. For a given pore water velocity chloride appeared in the effluent solution ahead from loamy soil columns as compared to sandy loam columns, irrespective of column length. The present study revealed that during miscible displacement the degree of asymmetry in BTCs was a function of pore water velocity, apparent diffusion coefficient, length of displacement and texture.

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Eingelangt am 13. Dezember 1999

Angenommen am 22. Juli 2000