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SOIL COLUMN EXPERIMENTS WITH LEACHATE FROM A WASTE TIP

II. BEHAVIOUR OF LEACHATE COMPONENTS IN SOIL AND GROUNDWATER

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CONTENTS

This report is a sequel to Nota 816, which deals with theoretical considerations about transport in soil columns and with the experimental design of column experiments.

1. INTRODUCTION

Large amounts of municipal and industrial solid waste have been (and still are) dumped in or on the soil. In humid regions the dumped refuse is leached by percolating rain water and the contaminated leachate is discharged into the groundwater and surface waters. As the groundwater flow depends on the geohydrological situation this aspect should receive special attention in selecting locations for waste disposal (HOEKS, 1976).

Several pollutants of the leachate are involved in fysical, chemical and biochemical processes on their way through the soil. In order to predict the mobility of these pollutants in soil information is needed about the rate of these processes.

This study deals with the results of experiments with soil columns, which were percolated with leachate from a waste tip. Column experiments were supposed to be the best way to study the interaction processes in soil.

2. FUNDAMENTALS OF CHROMATOGRAPHIC TRANSPORT

In soil solved components are mainly displaced by the motion of the liquid phase. This type of transport is called convective transport. In addition to convection the solved components move with respect to the mean velocity of the liquid phase due to diffusion and dispersion. The solute flux can be described as the sum of both fluxes:

$$F = vC - D\,\frac{\partial C}{\partial x} \qquad (1)$$

where

F = solute flux ($mg.cm^{-2}.s^{-1}$)

v = mean volume flux of the liquid phase ($cm^3.cm^{-2}.s^{-1}$)

C = concentration of the solute ($mg.cm^{-3}$)

D = dispersion coefficient, which combines the effect of diffusion and dispersion ($cm^2.s^{-1}$)

x = distance (cm)

For the case of one-dimensional, linear flow the equation of continuity is found as:

$$\varepsilon_w \frac{\partial C}{\partial t} = - \frac{\partial F}{\partial x} - S \tag{2}$$

where

ε_w = soil moisture content ($cm^3.cm^{-3}$)

S = 'sink term' resulting from chemical or biochemical reactions by which components are removed (S is positive) from or added (S is negative) to the liquid phase ($mg.cm^{-3}.s^{-1}$)

Combination of eq. (1) and (2) results in:

$$\varepsilon_w \frac{\partial C}{\partial t} = - v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - S \tag{3}$$

If interaction processes can be ignored (e.g. for the Cl-ion), i.e. S = 0, eq. (3) can be solved for different boundary conditions. For a finite soil column BRENNER (1962) has given a solution for the following boundary conditions:

$t = 0$	$0 < x < L$	$C = C_i$
$t > 0$	$x = 0$	$vC - D \frac{\partial C}{\partial x} = vC_f$
$t > 0$	$x = L$	$\frac{\partial C}{\partial x} = 0$

where C_i is the initial concentration in the soil solution, C_f is the concentration in the feed solution and L is the length of the soil column. Brenner introduced the dimensionless variables

$T = vt/\varepsilon_w L$ and $B = vL/D$ ($B = 4P$, where P is the Péclet number). He has tabulated the numerical values of $(1 - C_e/C_f)$ as a function of B and T (C_e is the concentration in the effluent of the column). The calculated Brenner-curves can be compared with experimental 'break-through' curves for a non-interacting ion like chloride. With the B-value of the best fitting Brenner-curve the dispersion coefficient D can be calculated for a particular soil column.

For components which are involved in interaction processes, i.e. $S \neq 0$, eq. (3) cannot readily be solved except for a few simplified cases. Assuming for instance that adsorption is linearly related to the concentration in the soil solution, i.e. the adsorbed amount $q = kC$ (k = adsorption coefficient), then $S = k\, \partial C/\partial t$ ($= \partial q/\partial t$). In this case eq. (3) can be rewritten as:

$$(\varepsilon_w + k)\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} \qquad (4)$$

This equation can also be solved for the mentioned boundary conditions. The solution is similar as for $S = 0$, except for the factor ε_w which is replaced by $(\varepsilon_w + k)$. The B-value does not change, only the T-value is reduced, i.e. the breakthrough curve for the case of adsorption appears in a later stage. This is also evident from eq. (5), which is derived from eq. (4) ignoring the dispersive flow:

$$v_s = v^*\left(\frac{1}{1 + R}\right) \qquad (5)$$

where

v_s = moving velocity of the solute front (cm.s^{-1})

v^* = mean flow velocity of the liquid phase, in the soil pores, i.e. $v^* = v/\varepsilon_w$ (cm.s^{-1})

R = distribution ratio indicating the amount adsorbed (q) relative to the amount in solution ($\varepsilon_w C$), so $R = q/\varepsilon_w C$ ($= k/\varepsilon_w$)

If a particular component of the feed solution is already present in the soil in the initial situation, then the distribution ratio should be modified as:

$$R = \frac{\Delta q}{\varepsilon_w \; \Delta C} \qquad (6)$$

where $\Delta q = q_f - q_i$ and $C = C_f - C_i$, the subscripts i and f refer to the initial situation before and the final situation after passage of the feed solution.

Eq. (5) shows that the actual velocity of the solute is reduced with respect to the water flow velocity. The distribution ratio R can be easily determined from the breakthrough curves.
In Fig. 1 two breakthrough curves are presented, one for a reference ion without adsorption (R = 0) and one for an ion which is adsorbed in the soil. Area A represents the amount in solution in the soil column (related with $\varepsilon_w C$) and area B represents the amount adsorbed in the soil column (related with q), so R = area B/area A.

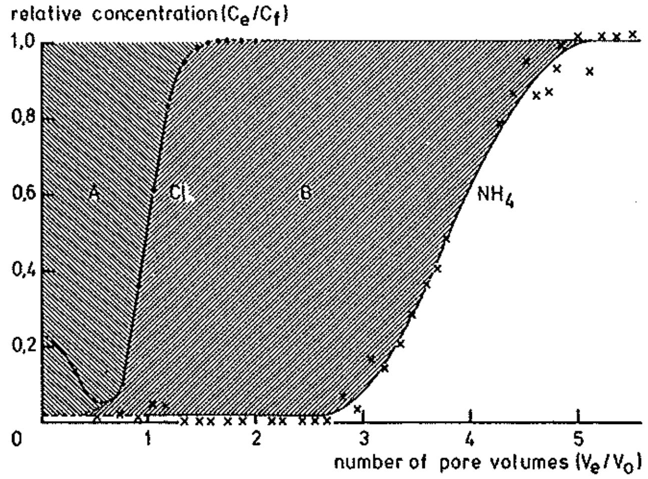


Fig. 1. Breakthrough curves for the reference ion Cl (R = 0) and the NH_4-ion in a sandy loam soil column. Breakthrough of the latter has been delayed by adsorption (V_e = effluent volume, V_o = water volume in the column, V_e/V_o = number of pore volumes passed)

3. EXPERIMENTAL DATA

Soil column experiments were set up to simulate the processes in soil below a waste tip. The soil columns were filled with air-dried soil. Next the soil was wetted by adding oxygen-free distilled water until saturation or in the case of unsaturation until the moisture content of the column remained constant at the chosen percolation rate. After that the soil columns were percolated with (diluted) leachate from a waste tip under anaerobic conditions (N_2/CO_2-atmosphere with 30-35 vol. % CO_2 in the gasmixture). The leachate, which was derived from a waste tip near Delden (Twente, Netherlands), was continuously added to the column by means of a pump at a rate of approximately 5 to 10 mm per day. The effluent of the columns was collected anaerobically (N_2/CO_2-atmosphere) to avoid oxidation. The effluent volume was measured by weighing. In a few columns the redox potential was measured at different depths in the soil column with combined Electrofact-electrodes.

Experiment I was done with sandy soil poor in humus (Veluwe sand, 0.45% humus). In this experiment the soil columns were unsaturated. The degree of saturation was higher at the higher percolation rate. At a rate of 4.6 mm per day the water-filled pore volume was 0.158 $cm^3.cm^{-3}$ (41% of the total pore volume), and at a rate of 13.0 mm per day the water-filled pore volume was 0.240 $cm^3.cm^{-3}$ (63% of the total pore volume). The transport time in the columns varied between 9 and 23 days. The feed solution consisted of leachate, diluted with water (1:2).

Experiment II was done with sandy loam soil, Winsum clay and humic Sinderhoeve sand. The feed solutions consisted of leachate, in the case of the sandy loam soil diluted with distilled water (1:0; 1:3; 1:8). In view of biological processes the percolation rate was low resulting in transport times of 17 to 40 days.

Experiment III was done with the Veluwe sand (0.45 % humus) and a humic sandy soil (Sinderhoeve sand, 6.5% humus). In this experiment the percolation rate was much higher with transport times of 1 to 7 days. Biological processes can hardly be important at such high flow velocities. The main purpose of this experiment was to study the adsorption and mobility of heavy metals in the soil columns. Because of the low contents of Ni, Cd, Cu and Pb in the leachate, these elements were added to the feed solution in a concentration of 5 mg per liter.

The feed solutions were stored at 2 to 3°C in a cooling box and from there they were pumped to the columns. Both the feed solutions and the column effluents were analyzed for the following constituents: pH, electrical conductivity, Cl, SO_4, Na, K, Ca, Mg, NH_4, Fe, Zn, Ni, Cd, Cu, Pb. The organic load was determined by measuring the Chemical Oxygen Demand (COD) and analyzing the free volatile fatty acids by gaschromatography. The chemical characteristics of the feed solutions are summarized in Table 1.

The adsorption of leachate components in soil was also studied with help of batch shaking experiments. In this experiment three soil types were used: Veluwe sand, humic Sinderhoeve sand and sandy loam. These soils were shaken during one hour with leachate (shaking ratio 1:5). After centrifuging the supernatans was analyzed for cations including heavy metals. These batch shaking experiments were also done with synthetic solutions of heavy metals with or without free volatile fatty acids. The pH-correction of these solutions was performed with NaOH and HCl.

4. RESULTS

4.1. Dispersion

As discussed before (Section 2) the dispersion coefficient (including diffusion) can be determined by comparing the experimental breakthrough curve for a noninteracting ion (e.g. Cl, if anion exclusion may be ignored) with the theoretical Brenner curves. The B-value of the best fitting curve is then used for the calculation of the dispersion coefficient.

The shape of the breakthrough curve for chloride under unsaturated conditions was not well predicted with the sigmoid Brenner-curve (cf. Fig. 2). The concave shape of the Cl-curve suggests that a part of the water volume in the soil column is immobile, i.e. it is not

Table 1. Chemical characteristics of the feed solutions used for the column experiments. In experiment I and II leachate was diluted with destilled water, in experiment III the pure leachate was used but heavy metals (except Zn) were added here (- not determined; [1] estimated; concentrations in $mg.l^{-1}$)

Component	Experiment I columns 2-6	Experiment II columns 4-6	Experiment II column 7 columns 10-12	Experiment II column 8	Experiment II column 9	Experiment III columns 1-4
pH	5.7	5.6	5.8	5.7	5.6	5.9
EC ($25^{o}C$; $\mu S.cm^{-1}$)	10,600	4,680	37,200	13,800	7,000	21,300
COD (mg $O_2.l^{-1}$)	21,600	6,640	60,600	16,000	7,750	68,300
Cl	1,314	506	9,280	-	-	7,120
SO_4	580	150	1,580	-	-	-
HCO_3	6	-	-	-	-	-
PO_4-total	8.0	-	-	-	-	-
PO_4-ortho	1.3	-	-	-	-	-
Kjeldahl-N	600	-	-	-	-	-
NH_4-N	470	135	1,942	-	-	-
Na	998	363	5,650	-	-	4,335
K	601	193	2,070	-	-	2,190
Ca	875	395	3,080	-	-	3,677
Mg	150	53	840	-	-	729
Fe	565	302	1,110	260	117	2,080
Zn	-	2.06	47.0	11.9	6.54	53
Ni	-	0.19	0.99	0.25	0.23	7.0
Cd	-	-	-	-	-	5.0
Cu	-	-	-	-	-	5.0
Pb	-	-	-	-	-	5.0
Acetic acid	-	-	10,800	2,630	1,230	10,200
Propionic acid	-	-	4,390	950	470	4,230
i-butyric acid	-	-	670	160	61	680
Butyric acid	-	-	9,810	2,510	1,210	9,160
2-methyl butyric acid	-	-	560	100	52	260
i-valeric acid	-	-	540	120	52	310
Valeric acid	-	-	2,590	630	290	2,260
Caproic acid	-	-	5,700	1,450	650	5,000
Total acids (as CH_3COOH)	8,900[1]	2,740[1]	26,624	6,471	3,046	24,590

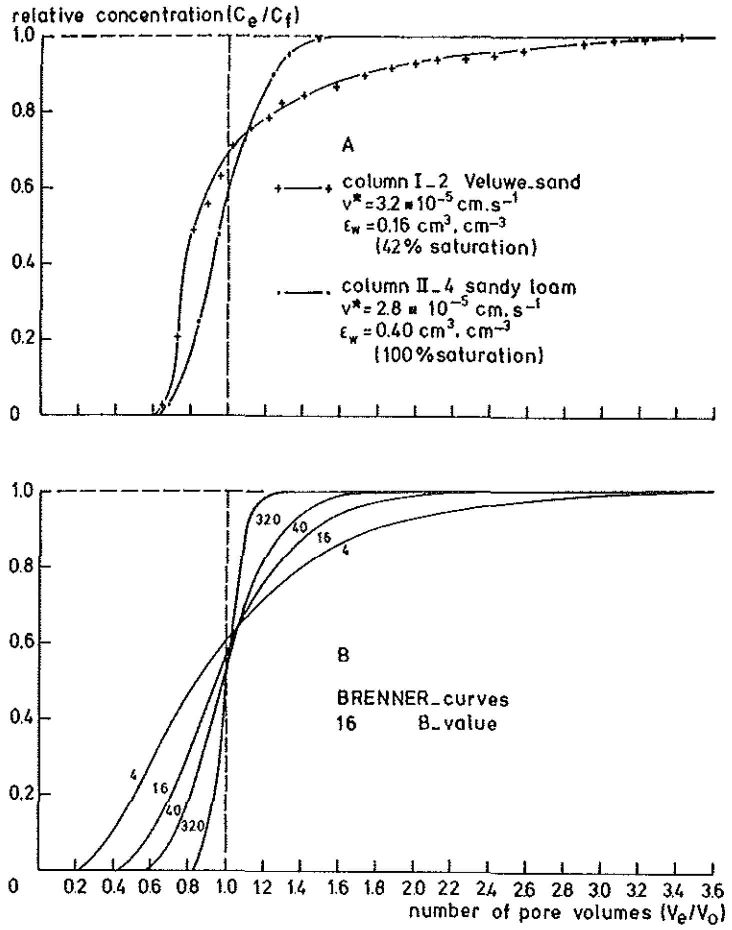


Fig. 2. Experimental breakthrough curves for chloride in two soil columns (A) compared with theoretical breakthrough curves after Brenner (B)

involved in the water flow. In such cases the breakthrough curve shifts to the left, while at the right hand side a 'tailing' effect is observed, i.e. it takes much time (volume) before the effluent concentration equals the influent concentration. This 'tailing' effect is caused by diffusion of chloride from the mobile water phase into the immobile phase, and it becomes more pronounced the more the moisture content deviates from saturation (NIELSEN and BIGGAR, 1961, 1962).

The dispersion coefficients D^* (= D/ε_W) and the dispersion factors L_D(= D^*/v^*), which have been calculated from the B-value of the best fitting Brenner-curve, are summarized in Table 2. From these

Table 2. Dispersion coefficients D* and dispersion factors L_D in soil columns in relation with the degree of water saturation and the flow velocity v*

Column	Soil	Saturation %	v* $cm.s^{-1}$	B-value	D* $cm^2.s^{-1}$	$L_D (= \frac{D^*}{v^*})$ cm
I - 2	Veluwe sand	42	3.2×10^{-5}	8	26×10^{-5}	8.1
- 6	Veluwe sand	63	6.3×10^{-5}	8	35×10^{-5}	5.6
II - 4	Sandy loam	100	2.8×10^{-5}	80	1.4×10^{-5}	0.5
- 5	Sandy loam	100	1.2×10^{-5}	40	1.3×10^{-5}	1.1
- 6	Sandy loam	100	2.8×10^{-5}	80	1.5×10^{-5}	0.5
III - 1	Humic sand	100	2.9×10^{-5}	32	1.6×10^{-5}	0.6
- 2	Veluwe sand	100	4.2×10^{-5}	40	2.2×10^{-5}	0.5
- 3	Humic sand	100	8.8×10^{-5}	32	3.0×10^{-5}	0.3
- 4	Veluwe sand	100	9.0×10^{-5}	40	2.5×10^{-5}	0.3

data it is clear that the dispersion effect is much stronger in unsaturated soil than it is in saturated soil. Under unsaturated conditions the larger pores in the soil are empty and the water is supposed to follow a more complex way to find a continuous flowpath. Several water-filled pores cannot be used for water flow because empty pores are hindering a continuous water flow. Thus the water flow proceeds via a few continuous pore channels. The real flow velocity in these pores is therefore higher than the calculated velocity in Table 2. This means that chloride appears rather early in the effluent, but it takes a lot of leaching before C_e/C_f equals 1.

4.2. Biochemical decomposition

Leachate of waste tips contains a lot of solved organic substances. The Chemical Oxygen Demand (COD) of the leachate is especially high, when the fermentation process in the waste has got stuck in the acid formation stage and for some reason the methane fermentation has not started. In that case about 80-95% of the COD-value (about 60 000 mg $O_2.1^{-1}$) is attributable to the presence of free volatile fatty acids as acetic acid, propionic acid, isobutyric acid, butyric acid, isovaleric acid, valeric acid and caproic acid (HARMSEN, 1979).

Methane fermentation is an effective process in reducing the COD-value of the leachate, both in the dumped refuse and in the soil below the waste tip. The effect of the methane fermentation process in a soil column is illustrated in Fig. 3 as a decrease of the COD in the effluent. In the Veluwe sand (Fig. 3A) with a retention time of 23 days the COD-decrease was slight, probably because of the rather low pH (about 5.7 in the effluent). In the sandy loam soil a strong COD-reduction was observed. Initially during breakthrough the methane fermentation had not yet started and apparently the organic acids are as mobile as chloride. After a certain lag period, however, the methane fermentation started to reduce the COD of the effluent. Ultimately the COD reached an equilibrium value of about 500 to 600 mg $O_2.l^{-1}$, i.e. the purification efficiency was more than 90% both at a retention time of 17 days (Fig. 3B)and 40 days (Fig. 3C). The buffering capacity in the sandy loam soil is larger than it is in the Veluwe sand, which can be derived from the higher pH in the effluent (about 6.5 to 7.0). Probably the fertility of the sandy loam is also higher, which may be favourable for bacterial activity.

The decomposition rate can be calculated as the COD-decrease per unit volume of soil and per unit of time. For column II - 6 thus a decomposition rate is found of 16.6 x 10^{-7} mg $O_2.cm^{-3}.s^{-1}$ and for column II - 5 the rate is 7.0 x 10^{-7} mg $O_2.cm^{-3}.s^{-1}$. In the Veluwe sand the decomposition rate is very low, about 0.87 x 10^{-7} mg $O_2.cm^{-3}.s^{-1}$.

The finally reached COD-value in the effluent amounts to about 8% of the influent COD both in column II - 5 and II - 6, this in spite of the higher percolation rate in column II - 6. This leads to the conclusion that the decomposition rate is dependent here on the rate of supply with organic acids. This means that the decomposition rate will be still higher at a higher rate of supply, i.e. at a higher percolation rate.

According to FARQUHAR and ROVERS (1973) the methane fermentation process may be disturbed at high organic acid concentrations. They

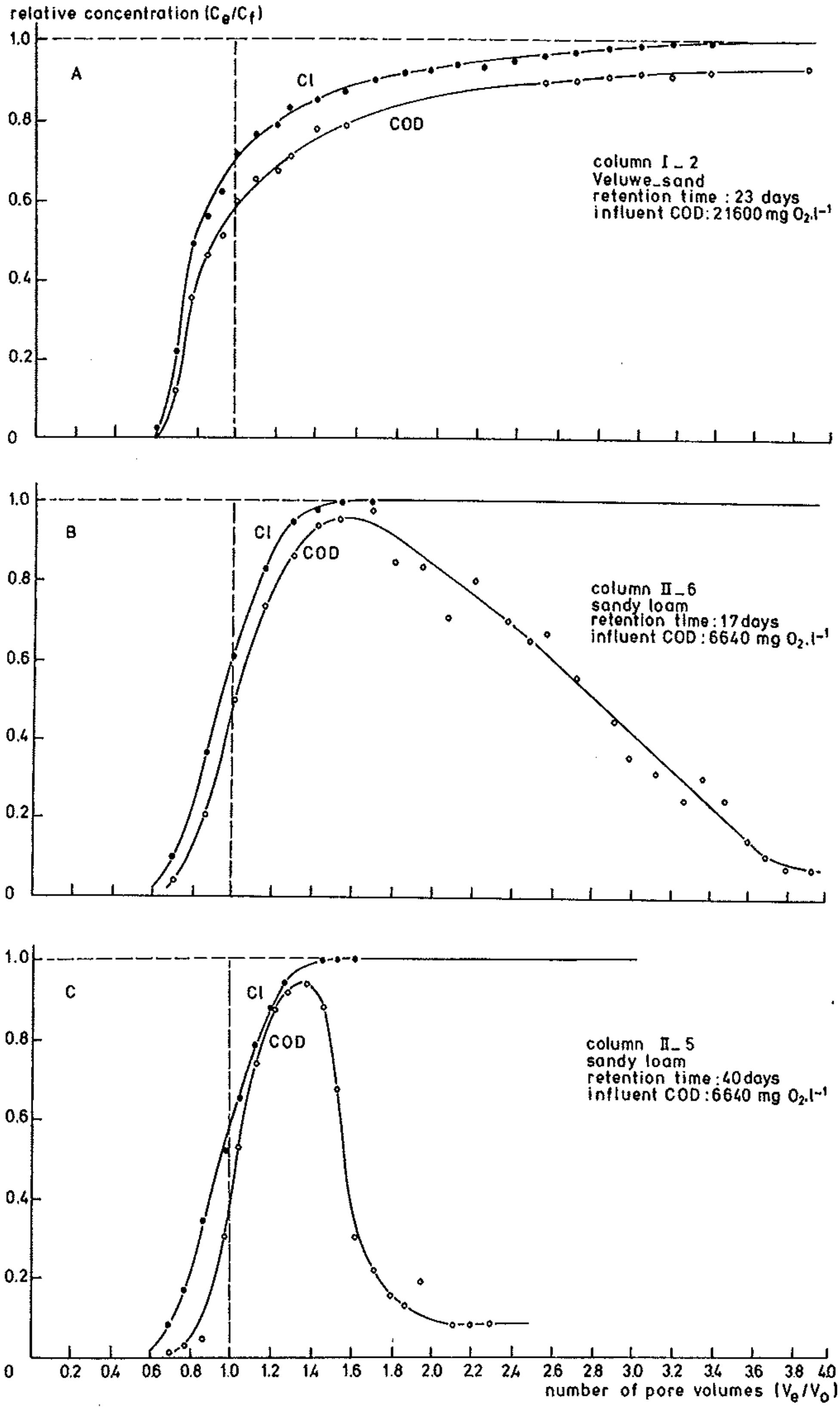


Fig. 3. Breakthrough curves for organic solutes, measured as COD, compared with the reference curve (Cl). The COD-reduction is caused here by methane fermentation (water saturation of the columns respectively 42% (A) and 100% (B and C), temperature 20°C)

mention 3000 mg.l^{-1} (as acetic acid) as a maximum allowable concentration. This aspect is studied by percolating sandy loam soil columns with leachate at different degrees of dilution (BORST, 1978). The results are demonstrated in Fig. 4. The feed solutions were added here to air-dried soil columns, which means that 'breakthrough' is achieved as soon as the first effluent appears and therefore the COD of the effluent is high from the beginning. Apparently the lag period before the start of the methane fermentation is the longer the higher the concentration of organic acids. Without dilution the acid concentration is probably too high, for even after a percolation period of 10 months no significant COD-reduction was observed (column II - 7). In the other two columns the lag period was about 37 days (II - 9) and 55 days (II - 8) after breakthrough.

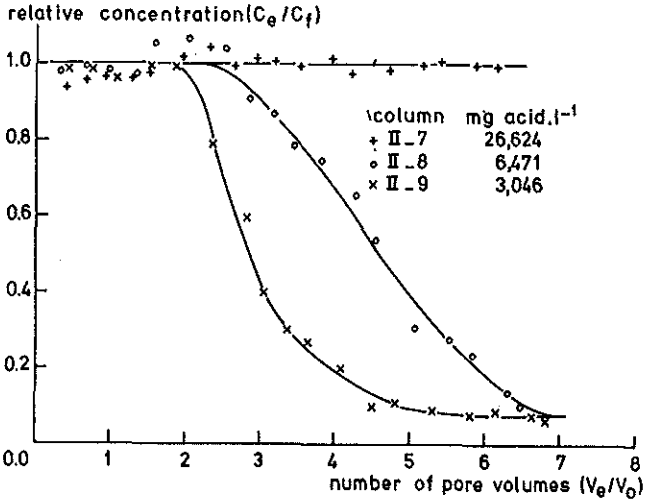


Fig. 4. COD-reduction as a result of methane fermentation in sandy loam soil columns in relation with the acid concentration (presented as acetic acid) in the feed solution (retention time in the columns about 20 days, temperature 20°C)

For column II - 8 the decomposition rate was calculated as 33.8 x 10^{-7} mg O_2.cm^{-3}.s^{-1} and for column II - 9 as 15.1 x 10^{-7} mg O_2.cm^{-3}.s^{-1}. In both cases the COD of the influent was reduced to a constant level of about 7% of the influent COD, probably representing rather persistent organics. So also here the conclusion holds, that the decomposition rate will be even higher at a higher rate of supply with organic acids.

In the effluent there were no organic acids left. Before and during the start of the methane fermentation higher organic acids with longer C-chains are broken down to acetic acid. This process is known at the β-oxidation process, i.e. fragments with 2 C-atoms are separated from the acids with longer C-chains until finally only acetic acid is left. When the organic acid has an odd number of C-atoms the last fragment left is propionic acid, which is also converted to acetic acid (α-decarboxylation). These conversions are reflected in the concentration of the different acids in the effluent (Fig. 5).

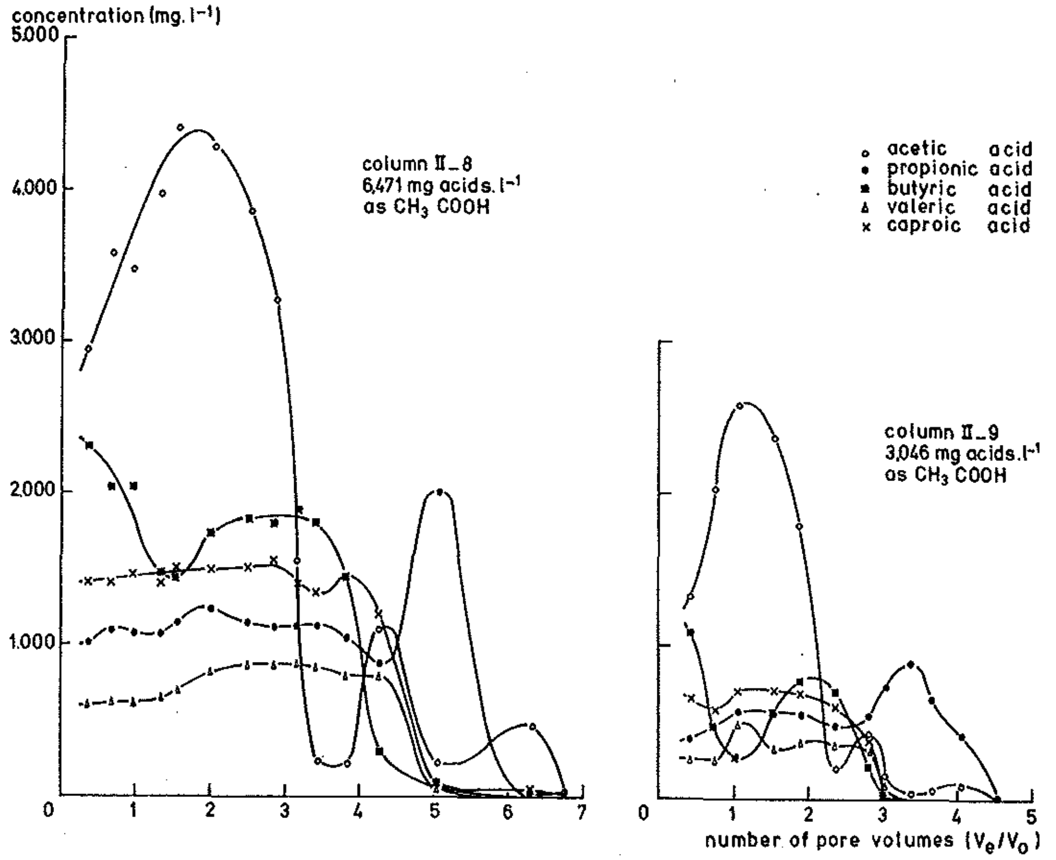


Fig. 5. Degradation of organic acids preceding and during the methane fermentation process, as it was reflected in the acid concentrations in the effluent of sandy loam soil columns (temperature 20°C)

Especially the initial conversion of butyric acid to acetic acid is clear from these data. Finally acetic acid and propionic acid are the only acids left and when the methane fermentation in the column has reached its maximum rate these acids are also broken down. From that moment on there are no organic acids left in the effluent.

From these experiments it became clear that the maximum allowable acid concentration for methane fermentation can be much higher than the limit mentioned in literature. In column II - 8 the acid concentration in the influent amounted 8,550 mg acids per liter, equivalent with 6,471 mg acetic acid per liter. In column II - 7 the acid concentration amounted 35,060 mg acids per liter, which is equivalent with 26,624 mg acetic acid. This concentration was apparently too high.

At the end of the experiment (318 days after the start) the influent COD of column II - 8 was gradually raised by decreasing the degree of dilution until finally the COD of the pure leachate was reached (Fig. 6). Initially the methane fermentation was not disturbed although the effluent COD increased up to a level of about 12,500 to 15,000 mg $O_2.l^{-1}$. In this stage the decomposition rate increased to about 64 x 10^{-7} mg $O_2.cm^{-3}.s^{-1}$. Finally the fermentation process was nevertheless disturbed. Probably the buffering capacity of the soil was to low to maintain the pH of the soil solution in the range of 6.5 to 7.0. The pH-lowering is supposed to be the main reason for the limitation of the fermentation process more than a direct toxic effect of the organic acids (see also LETTINGA, 1977).

4.3. Adsorption and desorption

The adsorption complex in soils is formed by clay particles (< 2μ) and humic compounds, which are dominently negatively charged. This means that mainly the positively charged cations will be adsorbed. Only Fe- and Al-(hydr)oxides may be positively charged, at least at low pH-values (below pH 6 to 7), and so they may adsorb negatively charged anions. In the here discussed column experiments no significant adsorption of anions was observed.

The adsorption of cations onto negatively charged adsorption

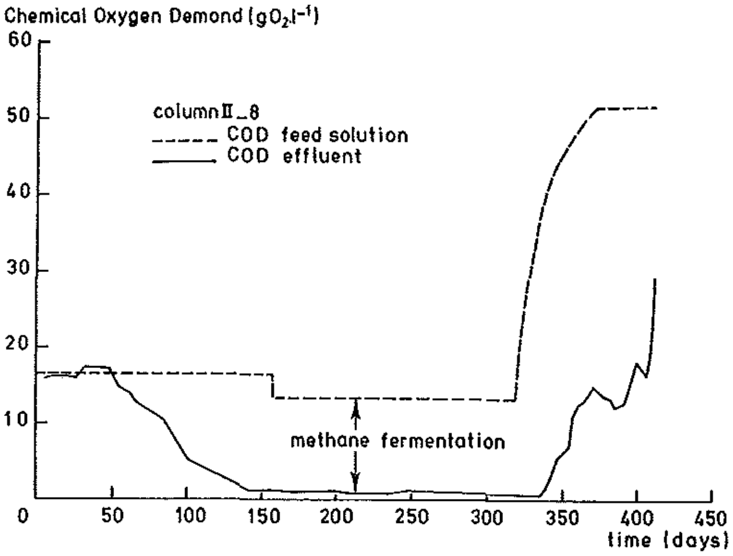


Fig. 6. The effect of a gradual rise of the COD of the feed solution on the methane fermentation process in a sandy loam soil column, as it was reflected in the COD-value of the effluent

sites in the soil is a reversible process, i.e. adsorbed ions may be exchanged with ions in the soil solution. Therefore the adsorption capacity of a soil is referred to as the cation exchange capacity (C.E.C.). This exchange process is clearly demonstrated by the data in Table 3. By percolating a sandy loam soil with leachate from a waste tip the initially adsorbed Ca- and Mg-ions have been exchanged with Na-, K-, NH_4-, Fe-, Zn- and Ni-ions from the leachate. Consequently the adsorption of cations is not only dependent on the C.E.C. and the concentration in the feed solution but also on the amount of cations, initially present on the adsorption sites in the soil.

The effect of adsorption on breakthrough curves is illustrated in Fig. 7 for the cations Na, K and NH_4. The distribution ratios can be calculated from these curves in the way described in Section 2 (Fig. 1). A few data about distribution ratios are summarized in Table 4.

In all soil types Na is only slightly adsorbed. Compared with that the adsorption of K and NH_4 is considerably higher, indicating

Table 3. Adsorbed amounts of cations (in % of C.E.C.) in a sandy loam soil before and after percolation with leachate of waste tip (C.E.C. = 7.8 meq per 100 gram of soil)

Cation	Adsorbed amount in % of C.E.C.	
	before percolation with leachate	After percolation with leachate
Na	0.0	33.6
K	4.6	10.6
NH_4	0.2	8.6
Ca	91.1	28.8
Mg	3.9	0.3
Fe	0.2	17.6
Zn	0.0	0.2
Ni	0.0	0.2

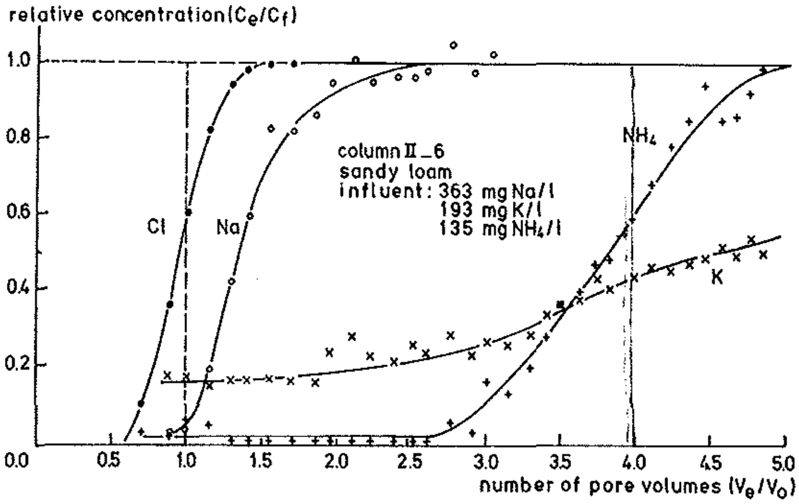


Fig. 7. Breakthrough curves for Cl, Na, NH_4 and K in the effluent of a sandy loam soil column

a high affinity between these ions and the adsorption sites. This is especially true in the Winsum clay and the sandy loam. Possibly fixation of K and NH_4 in the crystal grid of the clay minerals may

Table 4. Distribution ratios (R_D) of cations in the leachate in different soil types and at different concentration levels (des. = desorption;* = estimated)

Cation	Column	Soil type	Concentration in feed solution mg/l	Distribution ratio R_D
Na	I - 2	Veluwe sand	998	0.058
	II - 6	Sandy loam	363	0.46
	II - 10	Sandy loam	5,650	0.12
	II - 11	Winsum clay	5,650	0.38
	II - 12	Humic sand	5,650	0.25
K	I - 2	Veluwe sand	601	0.48
	II - 6	Sandy loam	193	4 *
	II - 10	Sandy loam	2,070	0.69
	II - 11	Winsum clay	2,070	2.3
	II - 12	Humic sand	2,070	0.53
NH_4	I - 2	Veluwe sand	604	0.32
	II - 6	Sandy loam	174	2.9
Fe	II - 10	Sandy loam	1,075	1.1
	II - 11	Winsum clay	1,075	2.9
	III - 1	Humic sand	2,080	1.6
	III - 2	Veluwe sand	2,080	0.73
Zn	II - 10	Sandy loam	56	2.6
	II - 11	Winsum clay	56	3.8
	III - 1	Humic sand	53	4.5
	III - 2	Veluwe sand	53	des.
Cd	III - 1	Humic sand	5	1.9
	III - 2	Veluwe sand	5	0.21
Ni	III - 1	Humic sand	7	2.5
	III - 2	Veluwe sand	7	0.38

← hier zit Ew en Cd van deze grond al in een getal. mag dus niet extrapoleren naar andere gronden met andere Cd en Ew

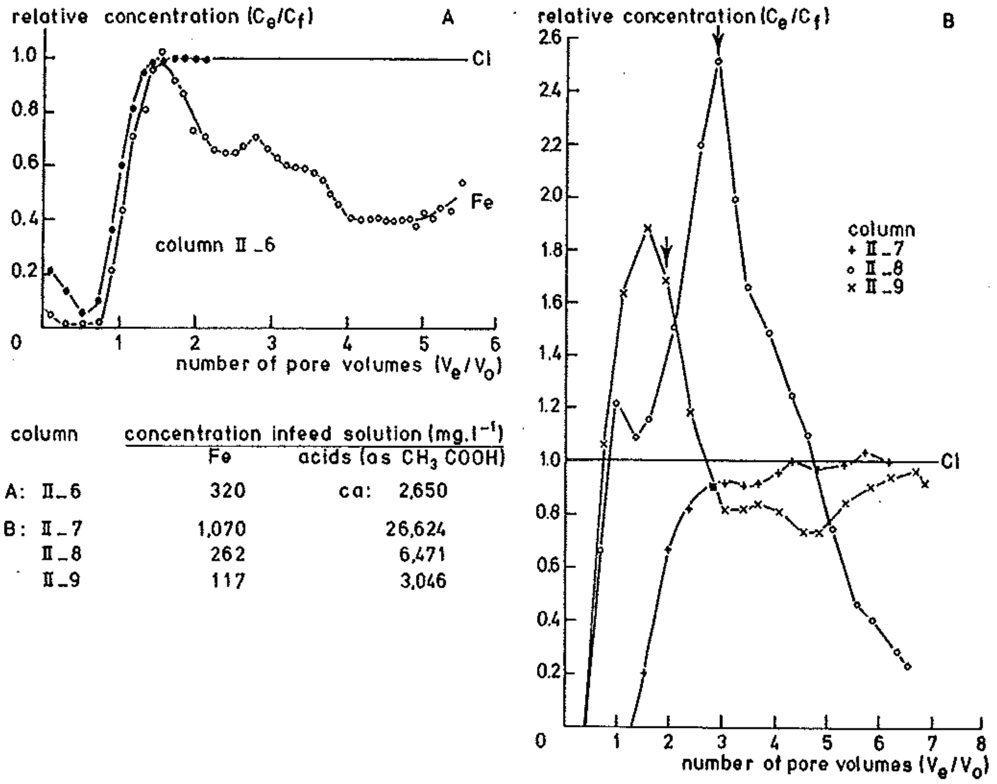
also have influenced the adsorption. The distribution ratios are not only dependent on the relative proportions of the cations in the solution, but also on the absolute concentrations. The distribution ratio is higher as the leachate is more diluted.

The metal ions Fe, Zn, Cd and Ni are not only involved in adsorption processes but also in chemical equilibrium reactions. The adsorption of these metals is therefore strongly dependent on the nature and rate of other processes, which vary with the environmental circumstances in the soil (see also Section 4.4). Metal ions may form complexes with inorganic or organic anions, and then they may behave completely different in adsorption processes.

4.4. Chemical reactions

The experimental breakthrough curves of various leachate components have indicated that chemical reactions may have a dominant influence on the behaviour of certain solutes in soil. The breaktrough curves for Fe in sandy loam soil columns, as demonstrated in Fig. 8, indicate that in the presence of organic acids the Fe-ion is nearly as mobile as the Cl-ion. The Fe-concentration in the effluent rises rather quickly until the concentration level of the feed solution is reached or even much higher if Fe is desorbed and dissolved from the soil. The afterwards observed fall in concentration has only taken place in columns with methane fermentation and this fall coincides with the COD-fall. So the behaviour of Fe is apparently related with the biodegradiation of organic acids. In the presence of organic acids Fe-ions probably from complexes with the acids. Apparently these complexes are not involved in adsorption or precipitation reactions.

The formation of metal-organic acid complexes became clear from batch shaking experiments (BEKER, 1977). Two soils were shaken with synthetic solutions containing metal ions with or without organic acids. The data in Table 5 illustrate that the adsorption of heavy metals is strongly reduced in the presence of organic acids, especially in the Veluwe sand with the lower organic matter content (0.45%). In the humic sand (6.5% organic matter) the reduction in adsorption is less pronounced. It is most likely that the metal ions can form complexes either with the organic acids in the solution or with insoluble humic compounds in the soil. Complexes with humic compounds are supposed to be much more stabile and this may be the reason of the relatively slight reduction in adsorption in the humic soil. This seems especially true for the metals Cu and Pb. Research of SCHNITZER (1969) has shown that Cu and Pb form very stabile complexes



column	concentration infeed solution (mg.l^{-1}) Fe	acids (as CH_3COOH)
A: II_6	320	ca: 2,650
B: II_7	1,070	26,624
II_8	262	6,471
II_9	117	3,046

Fig. 8. Breakthrough curves for Fe in sandy loam soil columns in relation with the fermentation of organic acids. The start of the methane fermentation process in the columns is indicated with arrows near the curves

with fulvic acids. From the here presented results it is not possible to decide whether the 'adsorption' of the metals is a pure electrostatic adsorption process or a chelation reaction with organic matter in the soil.

The breakthrough curves for Cu and Pb in column experiments are not typical adsorption curves (Fig. 9). In the humic sand the effluent concentration remains about constant at a level of 30% of the influent concentration, indicating that chemical processes (e.g. chelation with humic compounds) control the effluent concentration.

The Veluwe sand (column III - 4) contained a high Cu-content in the initial state (21.8 mg per kg of soil). This is probably the reason for the high Cu-leaching during breakthrough of the leachate.

Table 5. The effect of complex formation with fatty acids on the adsorption of heavy metals (with acids = addition of C_2, C_3, i - C_4, C_4, i - C_5, C_5 and C_6, total concentration 23,600 mg.1^{-1} as acetic acid; Fe-concentration about 5 mg.1^{-1})

Metal	Adsorbed amounts in % of added amounts			
	Veluwe sand		Humic sand	
	with acids	without acids	with acids	without acids
Ni	14	79	78	92
Cd	9	90	64	98
Cu	36	100	99	100
Zn	-35	90	63	91
Pb	46	100	92	100

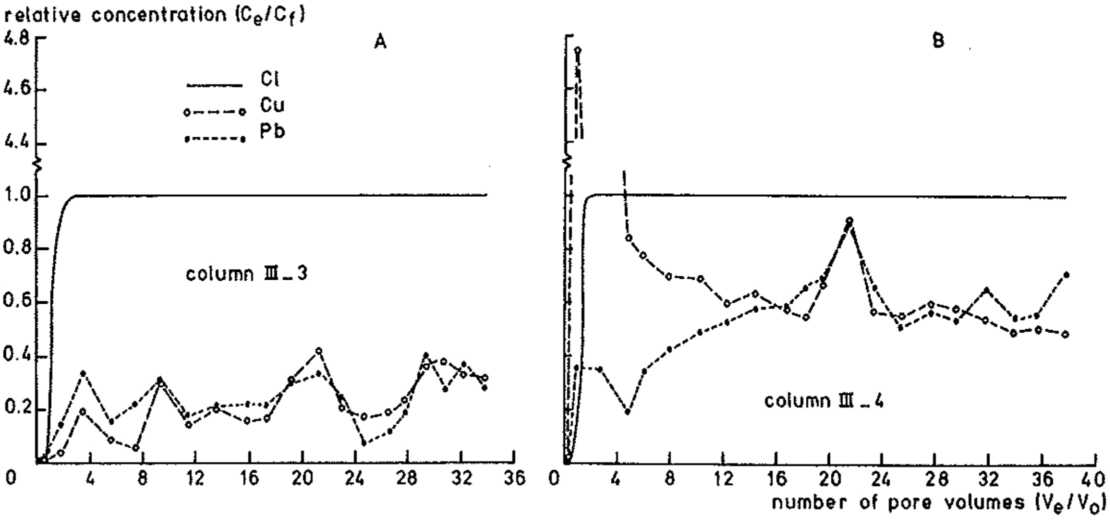


Fig. 9. Breakthrough curves for Cu and Pb in humic sand with 6.5% organic matter (A) and Veluwe sand with only 0.45% organic matter (B). The acid concentration is in both cases 24,590 mg.1^{-1} (as CH_3COOH). Concentration of Cu and Pb in the feed solution was 5 mg.1^{-1}

The Zn-content of the Veluwe sand was also rather high (87 mg per kg of soil) and consequently also Zn-leaching was observed during breakthrough of the leachate. In the batch shaking experiments desorption of Zn was observed in the presence of organic acids. However, desorption of Cu did not occur in these experiments. The Cu-leaching from the column is therefore hard to explain, especially because in a later stage of percolation again Cu-accumulation was observed. Perhaps the high Fe-concentration in the leachate enhanced the Cu-leaching, since Cu may be replaced by Fe in metal-humic acid complexes.

In the presence of high Fe-concentrations especially Zn, Cd and Ni are excluded from adsorption and chelation reactions with humic substances in the soil (see Table 6). The metals Cu and Pb are far less influenced indicating that the organic matter of the soil has a strong preference for Cu and Pb. This is in agreement with the order of stability of divalent metal-fulvic acid complexes at pH 5, mentioned by SCHNITZER (1969): Cu > Pb > Fe > Ni > Mn > Co > Ca > Zn > Mg. So Fe can easily replace Zn, Ni and apparently also Cd, but it can far less easily expel Cu and Pb from the complexes.

Table 6. Effect of high Fe-concentrations on the adsorption of heavy metals, in the presence of 680-880 mg isobutyric acid per liter

Metal	Adsorbed amounts in % of added amounts			
	Veluwe sand		Humic sand	
	5 ppm Fe	3500 ppm Fe	5 ppm Fe	3500 ppm Fe
Ni	51	7	91	18
Cd	64	4	97	30
Cu	96	44	100	97
Zn	47	-72	92	- 3
Pb	100	89	100	98

As soon as the organic acids are broken down, the metal ions may as yet be adsorbed or precipitated. Under reducing circumstances, as these prevail in soils below waste tips, ions like Ca, Mg, Fe and heavy metals may precipitate as poorly soluble carbonates, phosphates or sulfides. The precipitation of FeS was clearly visible in the soil colums as soon as the methane fermentation process had started, Precipitation of $FeCO_3$ is also possible at low redox potential values (-200 mV) in combination with a high CO_2-concentration and a pH-value of about 7 (BREEUWSMA and VAN ENGERS, 1975).

5. DISCUSSION AND CONCLUSIONS

Leachate from waste tips contains a lot of inorganic and organic pollutants. The here discussed soil column experiments have shown that the mobility of these pollutants in soil is largely controlled by chemical or biochemical processes. The presented breakthrough curves are well comparable to the field situation. In the groundwater near a waste disposal site in Delden (Twente, Netherlands) similar breakthrough curves were found (see Fig. 10), illustrating both the retardation effect by adsorption of NH_4 and the biodegradation of organic substances as reflected in the COD-curve (the leachate has a COD of about 40 to 60,000 mg $O_2.l^{-1}$).

Leachate may contain large amounts of organic acids, especially when the fermentation process in the refuse gets stuck in the acid formation stage because the methane fermentation is impeded for some reason. In soil the methane fermentation may also be impeded.
In the column experiments this was especially true at an acid concentration level of about 25,000 mg per liter(as acetic acid) and in sandy soils with a low buffering capacity also at the lower concentration level of about 6,500 mg per liter (as acetic acid). In soil with substantial buffering capacity the methane fermentation process went on favourably even at 6,500 mg acetic acid equivalents per liter, be it that the lag phase preceding the start of the methane fermentation increased with higher acid concentrations. It is supposed that the limitation of the process, as it was observed in sandy soil and at a high acid concentration level, is

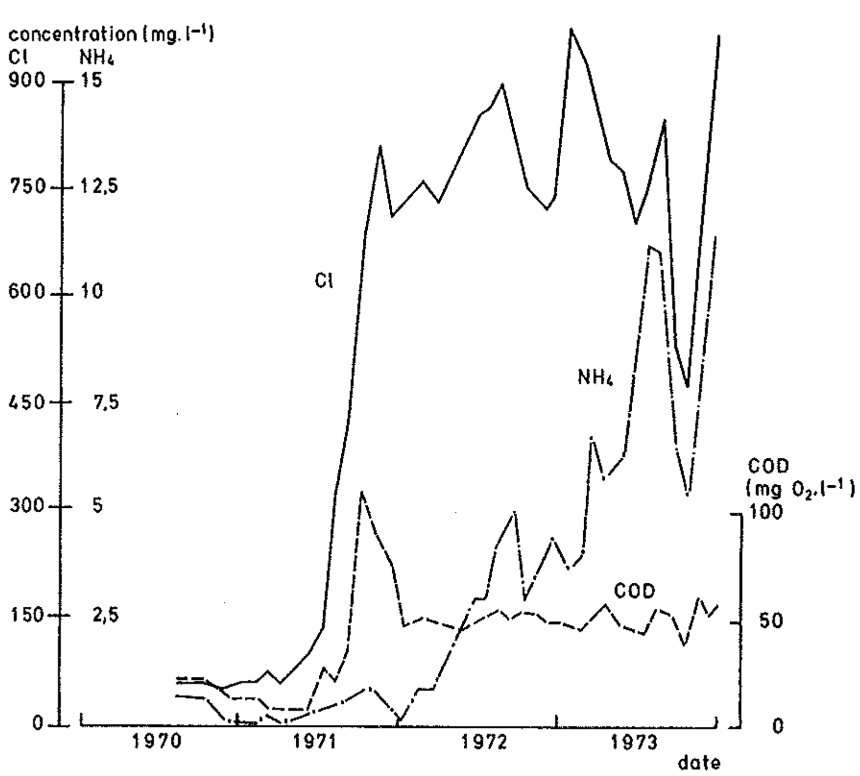


Fig. 10. Breakthrough curves for Cl, NH_4 and COD, as measured in groundwater at 6.0-6.5 meter depth about 10 meter downstream of a waste tip (data from SVA, 1973, 1974)

caused by the lowering of pH (down to pH 5.7) more than by a direct toxic effect of the organic acids. From this point of view it would be most advisable to dump lime containing wastes among the refuse in a waste tip in order to increase the buffering capacity of the waste and thus the methane fermentation rate. It is very likely that with an effective methane fermentation there are no organic acids left in the leachate. The pH of the leachate will rise over pH 7 and the load of heavy metals will be much lower under these circumstances.

Adsorption is mainly important for the positivily charged cations in the leachate. Because of the high concentration level of the macro-elements in the leachate the distribution ratio R_D, which determines the mobility, is rather small. In sandy soils with a low organic matter content adsorption is practically neglectable.
In clay containing soils the adsorption of K and NH_4 is significantly

higher than the adsorption of Na. Possibly these ions are partly fixed in the grid of clay minerals.

In many soils the adsorption sites are largely occupied by Ca- and Mg-ions. Percolation with leachate will therefore result in desorption of these ions. In the column experiments the Ca-concentration in the effluent was much higher than it was in the influent. Probably also dissolution of carbonates has attributed to this increase in concentraties (see also HOEKS, 1977).

Heavy metals are often highly preferentially adsorbed at the low concentration level, as found in the leachate. The behaviour of these metal ions may, however, completely change in the presence of certain inorganic or organic anions. Thus heavy metals may become as mobile as chloride. Batch shaking experiments have shown that the adsorption of heavy metals is strongly reduced in the presence of high amounts of organic acids, especially in soils with a low organic matter content. This is another reason why the methane fermentation in the dumped refuse should be enhanced as much as possible.

Under anaerobic, highly reductive conditions, as these actually prevail in a soil below a waste tip, precipitation of carbonates and sulfides may also be of importance. In the column experiments dissolution of carbonates was observed during the early breakthrough of the leachate. The low pH and the high amount of organic acids in the leachate will have enhanced the dissolution of carbonates. Later on when the methane fermentation has started the pH rises and the redox potential drops. Thus conditions may become favourable again for precipitation of carbonates. In this stage sulfates are reduced and will be precipitated as sulfides. Cations which may be precipitated with carbonates or sulfides are Ca, Mg, Fe, Al and heavy metals like Ni, Cd, Zn, Cu and Pb. Precipitation reactions are usually much more effective in removing cations from the leachate than are the adsorption processes. Nevertheless one should remember that the behaviour of heavy metals may be completely different as long as the organic compounds of the leachate have not yet been broken down.

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