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PARDET

A computer programme for calculating parameters
and exchange isotherms from breakthrough curves

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1. INTRODUCTION

In this report a systems approach for determining dispersion length, retardation factors, porosity and exchange isotherms from column experiments is presented. This approach has been described before by ROEST and RIJTEMA (1983). Here, the theory has been extended to the calculation of retardation factors and exchange isotherms. The Fortran 77 programme, Pardet, that calculates the parameters from experimental results is presented.

Finally some column experiments reported by HOEKS et al (1984) will be used to illustrate the operation of the programme.

2. PROCESSES

The basis for the transport of solutes through the soil is the convection-dispersion equation.

For soil columns used in column experiments the one dimensional equation is valid because these columns have a large length to width ratio. The equation is written as follows:

$$(q' + \theta) \frac{\partial c}{\partial t} = - F_d \frac{\partial c}{\partial x} + F_d \alpha_L \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where: c = the concentration at point x and time t

F_d = the drainage flux

θ = the effective pore space involved in transport and mixing of solutes

α_L = the dispersion length

q' = the capacity of the exchanger

Assuming linear adsorption means that the tangent of the adsorption isotherm, q' , is constant:

$$q' = \frac{\Delta q}{\Delta c}$$

Take V^* as the mean actual velocity of the solute then

$$V^* = F_d / (q' + \theta) \quad (2)$$

and D^* as the dispersion coefficient,

$$D^* = F_d \alpha_L / (q' + \theta) \quad (3)$$

then equation (1) becomes:

$$\frac{\partial c}{\partial t} = -V^* \frac{\partial c}{\partial x} + D^* \frac{\partial^2 c}{\partial x^2} \quad (4)$$

The distribution ratio, R_d , is defined as the quantity adsorbed relative to the quantity in the solution:

$$R_d = \frac{\Delta q}{\theta \Delta c} = \frac{q'}{\theta} \quad (5)$$

2.1. Two solved problems

In soil column experiments normally two type of experiments are carried out. The first case is a continuous injection with a tracer of concentration c_f in the soil column with initial concentration c_i . And the second possibility is the injection of a tracer applied at an infinitely short time.

Case 1. A constant continuous injection with a tracer at $x = 0$ with $c = c_f$ and initial concentration in the soil solution of c_i . BEAR (1972) solved this problem by applying the Laplace transform to eq. (14). The solution is:

$$c = \frac{c(x,t) - c_i}{c_f - c_i} = \frac{1}{2} \operatorname{erfc} \left\{ \frac{-(x - V^*t)}{2\sqrt{D^*t}} \right\} \quad (6)$$

Eq. (6) is illustrated in Fig. 1.

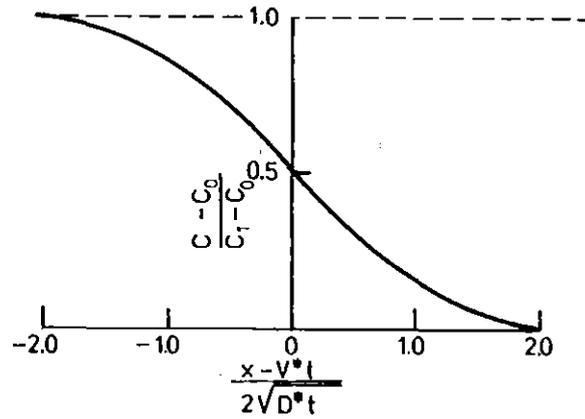


Fig. 1. Progress of a front

Case 2. A tracer injection applied during an infinite short time period (Dirac delta function) at $x = 0$ with $c = c_f$ and $c_i = 0$. According to BEAR (1972), applying the method of characteristics the solution is:

$$c = \frac{c(x, t)}{c_f} = \frac{1}{\sqrt{4\pi D^* t}} \exp\left\{-\frac{(x - v^* t)^2}{4D^* t}\right\} \quad (7)$$

Eq. (7) is illustrated in Fig. 2.

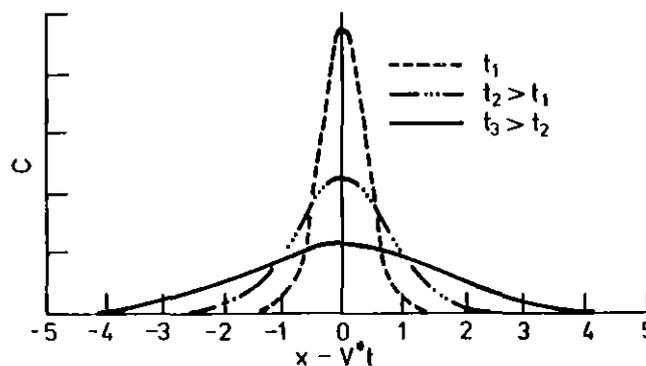


Fig. 2. Progress of a slug

Eq. (6) and (7) describe the shape of breakthrough curves. The influence of adsorption, porosity, velocity and dispersion on the breakthrough curve can be read from these equations. These formulas have a great resemblance with the equation of the normal distribution (eq. 8). PRICKETT et al (1981) applied the statistical form of the breakthrough curve in his random-walk method in describing dispersion. In this report

the statistical mean and variance of the measured breakthrough curves will be used to calculate the dispersion length, porosity and retardation. This is in fact an inverse approach.

3. STATISTICS

The normal distribution is a distribution for which the density function can be written as follows:

$$n(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left\{-\frac{(x - \mu)^2}{2\sigma^2}\right\} dx \quad (8)$$

where: μ = the mean

σ^2 = the variance

The cumulative distribution of $n(x)$ is given by:

$$N(x) \equiv \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^x \exp\left\{-\frac{(z - \mu)^2}{2\sigma^2}\right\} dz \quad (9)$$

take $y = \frac{z - \mu}{\sigma}$ and according to MODD and GRAYBILL (1963) this becomes:

$$N(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\frac{x-\mu}{\sigma}} e^{-\frac{1}{2}y^2} dy \quad (10)$$

take $y = \frac{y}{\sqrt{2}}$ and eq (10) becomes

$$\frac{-1}{\sqrt{\pi}} \int_{\frac{x-\mu}{\sigma\sqrt{2}}}^{\infty} e^{-y^2} dy \equiv \frac{1}{2} \operatorname{erfc}\left(\frac{-(x - \mu)}{\sigma\sqrt{2}}\right) \quad (11)$$

Take the mean traveltime of the solute as \bar{t} at point x , then eq. (7) becomes an equation in the x plane and can be compared with eq. (8) (or compare eq (11) with eq (6)). $c(x)$ and $n(x)$ describe the concentration front in the column at a certain time \bar{t} . The comparison gives for μ and σ^2 the following results:

$$\mu = \bar{x} = v^* \bar{t} = \frac{F_d \bar{t}}{\theta} \cdot \frac{1}{(1 + R_d)} \quad (12a)$$

and

$$\sigma^2 = 2D \bar{t} = \frac{2F_d \alpha_L \bar{t}}{\theta} \cdot \frac{1}{(1 + R_d)} = 2\alpha_L \mu \quad (12b)$$

Deriving an equation for the t space at a chosen x needs rewriting of eq (7). This is the case for a breakthrough curve with $x = L_t$, where L_t is the column length.

Rewriting eq (7) using the substitution $x = t$, $t = \frac{x}{v^*}$ and $dt = \frac{1}{v^*} dx$ and dividing by v^{*2} yields:

$$\frac{c(L_t, t)}{c_f} = \frac{1}{4\pi D * L_t / v^{*3}} \exp \frac{-\left(t - \frac{L_t}{v^*}\right)^2}{\frac{4D * L_t}{(v^*)^3}} \quad (13a)$$

This gives for μ and σ^2 the following result:

$$\mu = \bar{t} = \frac{L_t}{v^*} = \frac{\theta L_t}{F_d} (1 + R_d) \quad (13b)$$

and

$$\sigma^2 = \frac{2D * L_t}{(v^*)^3} = \frac{2\alpha_L L_t}{(v^*)^2} = \frac{2\alpha_L \theta^2 L_t}{(F_d)^2} (1 + R_d)^2 \quad (13c)$$

Eq (13b) and (13c) are also given by ROEST and RIJTEMA (1983). Due to their discretisation in the x plane they find:

$$\sigma_t^2 = \frac{L_N L_T}{(v^*)^2} \quad (\text{eq 13d})$$

and

$$\mu_t = \frac{L_T}{v^*} \quad (13e)$$

Where L_N is the Δx or layer thickness. From eq (13c) can be deduced that:

$$L_N = \frac{2D^*}{V^*} = 2\alpha_L \quad (14)$$

Summarizing; from the analytical solutions given in Chapter 2 it can be deduced that the response of a soil column to an input of c_f is equal to the normal distribution. A continuous injection with concentration c_f gives a response that equals the cumulative normal distribution.

4. SYSTEMS APPROACH

Considering the soil column as a linear system that responds to an input and gives as a result an output, the measured input and output can be handled with the theory of system analysis.

The measured breakthrough curve can be considered as the cumulative curve that is the result of a continuous feed of the column. The first derivate of the breakthrough curve can be considered as the impulse response of the column (as has been shown in Chapter 2) as a result of an injection applied during an infinite short time.

The cumulative curve is given by:

$$H(t) = \int_0^t h(t) dt \quad (15)$$

where $h(t)$ = the impulse response

$H(t)$ = the cumulative curve

The statistical moments of the impulse response characterize the shape of this curve:

$$M_i = \frac{\int_0^{\infty} t^i h(t) dt}{\int_0^{\infty} h(t) dt} \quad (16)$$

where M_i = the i^{th} moment relative to the origin

The first moment gives the mean time:

$$\mu_t = \bar{t} = M_1 \quad (17a)$$

The second moment gives the variance. The standard deviation of $h(t)$ relative to the mean time is:

$$\sigma_t^2 = M_2 - (\bar{t})^2 \quad (17b)$$

According to NASH (1959) the relation between input, output and impulse response is:

$$M_i\{y(t)\} = M_i\{x(t)\} + M_i\{h(t)\} \quad (18)$$

where $y(t)$ = system output

$x(t)$ = system input

The breakthrough curve that has been measured normally is a discrete curve because at a regular time interval concentrations have been measured. The sampled cumulative curve, $H(t)$, consists of N points with variables c_i and t_i , see Fig. 3.

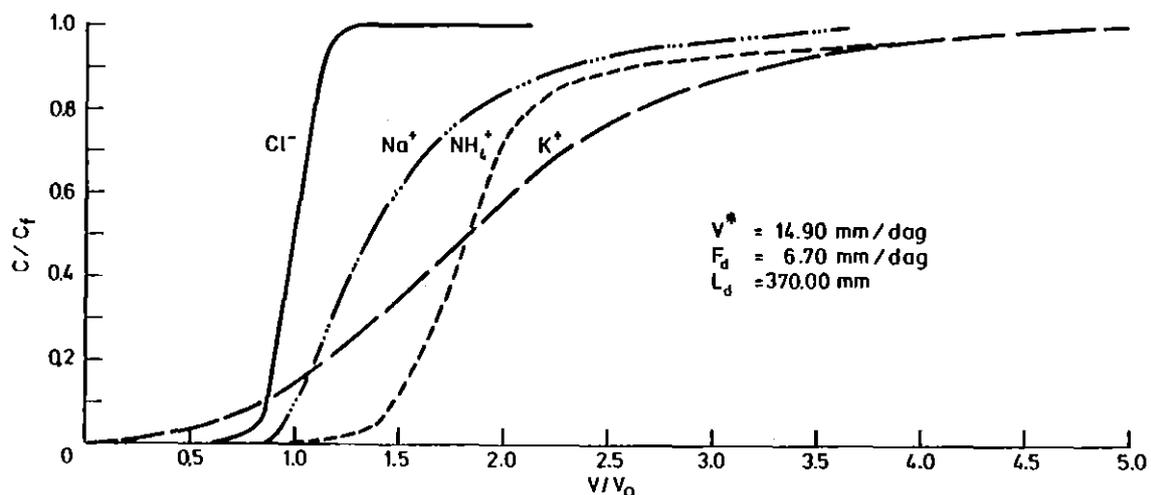


Fig. 3. Handfitted breakthrough curves experiment II
 (experimental data after HOEKS et al., 1984)

The impulse response can be approximated with the following equation:

$$h_i = \frac{1}{2} \left(\frac{C_{i+1} - C_i}{t_{i+1} - t_i} + \frac{C_i - C_{i-1}}{t_i - t_{i-1}} \right) \quad (19)$$

where $h_N = 0$ the concentration at time t_N equals 0

$h_0 = 0$ the concentration at time t_0 equals 0

According to eq (15), the discrete H(t) curve becomes

$$H(i) = \sum_{k=1}^i h_k \cdot \left(\frac{t_{k+1} - t_{k-1}}{2} \right) \quad (20)$$

Substituting eq (20) into eq (16) gives for the first moment:

$$M_1 = \mu_t = \frac{\sum_{k=1}^{N-1} t_k \left(\sum_{j=1}^k h_j \left(\frac{t_{j+1} - t_{j-1}}{2} \right) \right)}{\sum_{k=1}^{N-1} h_k \left(\frac{t_{k+1} - t_{k-1}}{2} \right)} \quad (21)$$

Substituting eq (20) into eq (16) and (17b) gives for σ^2

$$\sigma_t^2 = \frac{\sum_{k=1}^{N-1} t_k^2 \left(\sum_{j=1}^k h_j \left(\frac{t_{j+1} - t_{j-1}}{2} \right) \right)}{\sum_{k=1}^{N-1} h_k \left(\frac{t_{k+1} - t_{k-1}}{2} \right)} - M_1^2 \quad (22)$$

For each breakthrough curve it is possible to calculate μ_t and σ_t^2 with equation (21) and (22). When equation (13b) and (13c) are used with known μ_t and σ_t^2 some important parameters of the soil column can be calculated. Three applications of the formulas derived above will be discussed in the following chapter.

5. THE PROGRAMME PARDET

Three computer programmes have been developed to apply the formulas derived in the previous chapter.

5.1. Programme PARDET 1

This programme has been written by GROENENDIJK (1985). It calculates the θ and α_L from the breakthrough curve of a non-retarded tracer like Cl^- or NO_3^- .

As input parameters the L_t , F_d , μ_t and σ_t^2 can be measured or calculated with eqs (21) and (22). Using eq (13b) the effective porosity θ is calculated with the following expression:

$$\theta = \frac{\mu_t F_d}{L_t} \quad (23a)$$

Equation (13c) is used to calculate the dispersion length α_L :

$$\alpha_L = \frac{\sigma_t^2 F_d^2}{2\theta^2 L_t} = \frac{1}{2L_t} \left(\frac{\sigma_t F_d}{\theta} \right)^2 \quad (23b)$$

5.2. Programme PARDET 2

This programme calculates the mean distribution ratio, R_d , from the breakthrough curve of a retarded tracer like Na^+ or benzene with q' considered constant

As input parameters the L_t , F_d , μ_t , σ_t^2 , α_L and θ can be calculated or measured. The last two parameters, θ and α_L must be calculated by using the breakthrough curve of a non-retarded tracer (see 4.1). Using eq (13b) the distribution ratio is calculated by the programme:

$$R_d = \frac{\mu_t F_d}{\theta L_t} - 1 \quad (24)$$

The retardation, R , equals:

$$R = \frac{1}{1 + R_d} \quad (25)$$

5.3. Programme PARDET 3

This programme calculates the exchange isotherm of a retarded tracer. The breakthrough curves of a non-retarded tracer like Cl^- or NO_3^- and

of the retarded tracer in question must be known.

The mean R_d value is calculated in programme PARDET 2. By calculating for each concentration interval a R_d value the exchange isotherm can be estimated. Then instead of the mean travel time the travel time of a selected concentration interval must be substituted. Let t_i be the traveltime of concentration c_i then eq (24) can be rewritten as:

$$t_i = \frac{\theta L t}{F_d} (1 + R_{d,c_i}) \quad (26)$$

Dividing t_i by the traveltime of the non-retarded tracer (e.g. NO_3^-) at the same concentration level yields:

$$\frac{t_i}{t_{\text{NO}_3^-}} = R_{d,c_i} + 1 \quad (27)$$

Applying eq (27) for each concentration of the breakthrough curve results in the tangent curve of the adsorption isotherm. Integrating from $c_o = c_i$ to c_f with $q_o = q_i$ at $c_o = c_i$ gives the adsorption isotherm:

$$q_j = \sum_{k=1}^j \frac{\theta R_{d,k} c_k}{10\rho d}$$

where q_j = the total amount adsorbed at concentration c_j
 ρd = the dry density in kg/dm^3

6. RESULTS

The programmes PARDET have been applied to column experiments reported by HOEKS (1984) to illustrate the programme.

The feed solution consisted of a leachate of a waste tip and the percolation was performed under anaerobic conditions. The data of the column are given in Table 1 and the measured breakthrough curves in Fig. 4.

The handfitted curves from Fig. 3 have been used as input for the programmes PARDET. The results are given in Table 2.

Table 1. Data of column II according to HOEKS (1984)

dry density	1.35	kg/dm ³
CEC	11.5	meq/100 gram
column length, L _t	370	mm
drainage flux, F _d	6.70	mm/day
total porosity	0.478	
Na ⁺ influent concentration	125	meq/dm ³
NH ₄ ⁺ influent concentration	83	meq/dm ³
Cl ⁻ influent concentration	137	meq/dm ³
K ⁺ influent concentration	28	meq/dm ³
total salt concentration	260	meq/dm ³

Table 2. The results calculated by HOEKS
 et al., (1984) versus the results of
 PARDET

	Hoeks et al	PARDET
θ	0.463	0.446 cm ³ /cm ³
α_L	2.3	2.74 mm
\bar{t} (Cl ⁻)	24.9	24.6 days
R _d (NH ₄ ⁺)	0.95	0.906
R _d (K ⁺)	0.84	0.976
R _d (Na ⁺)	0.45	0.645
N (NH ₄ ⁺)	0.261	0.239
N (K ⁺)	0.079	0.076
N (Na ⁺)	0.184	0.195

From Table 2 can be concluded that the calculation results of PARDET do agree with the results given by Hoeks et al. The small differences are the result of the calculation method that has been followed. Assuming that the initial composition of the adsorption complex was 100% calcium, the following normalized exchange isotherms can be calculated with PARDET 3 (Fig. 4).

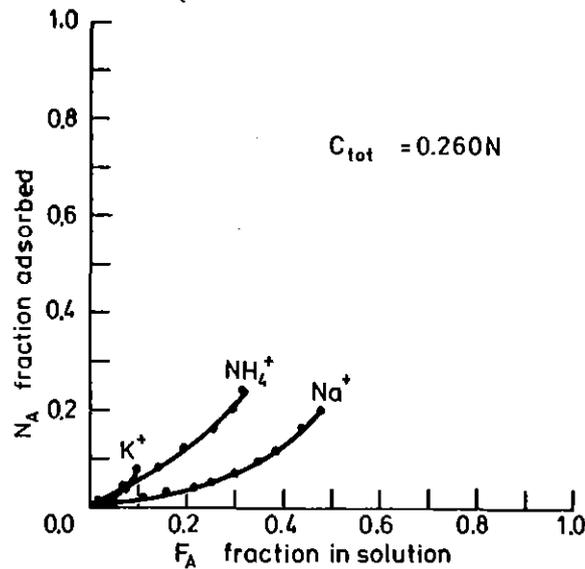


Fig. 4. Three normalized exchange isotherms calculated with PARDET 3 on the basis of the breakthrough curves reported by HOEKS et al., (1984)

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