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Physico-chemical exchanges and transfer of pollution in aquifers

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1 INTRODUCTION

This paper is divided into two parts. The first one is a mathematical analysis of different laws for physic and chemical exchanges occuring during a natural flow in an aquifer. The second part shows, with field experiments at Bonnaud (Jura), how it is possible to determine the parameters of an exchange law in order to forecast the long term evolution of the concentration of a solute which has reached the aquifer.

2 INTRODUCTION TO THE FIRST PART

This part will deal with the study of the concentrations in the water of an aquifer after an injection of tracer. The hypothesis relative to the aquifer are :

- homogeneous and isotropic aquifer,
- uniform and permanent flow.

The evolution of the concentration will result of three phenomenous :

- advection : it is displacement of the tracer with the flow,
- dispersion,
- physic and chemical exchanges between phase.

It is assumed that there are no exchanges with the lower and upper boundaries of the aquifer. The general equation is :

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} - \frac{1-n}{n}\cdot\frac{\partial S}{\partial t}$$

with the relation

$$\frac{\partial S}{\partial t} = f(C,S)$$

C = concentration in the liquid phase (water)
S = concentration in the solid phase (aquifer)
D = dispersion coefficient
n = kinematic porosity
u = effective velocity
t = time
x = distance

Many exchanges laws may be studied : an exchange law may be reversible or not, its equilibrium equation (or "isotherm") may be linear or not (e.g. Langmuir scheme), see J. Rochon 1978.

We choose to study some of these laws which seem to be the most useful.

2.1. Linear exchanges with linear exchange kinetic

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} - \frac{1-n}{n}k_c(k_e C - S)$$

$$\frac{\partial S}{\partial t} = k_c(k_e C - S)$$

which may be writen with dimensionless variables :

$$\frac{\partial C_R}{\partial t_R} = D\frac{\partial^2 C_R}{\partial x_R^2} - \frac{\partial C_R}{\partial x_R} - C_a \cdot N_e (C_R - S_R)$$

$$\frac{\partial S_R}{\partial t_R} = N_e (C_R - S_R)$$

with

$$x_R = x/L \qquad t_R = t/\frac{L}{u}$$

$$C_R = C.L.n/m \qquad S_R = S.k_e.L.n/m$$

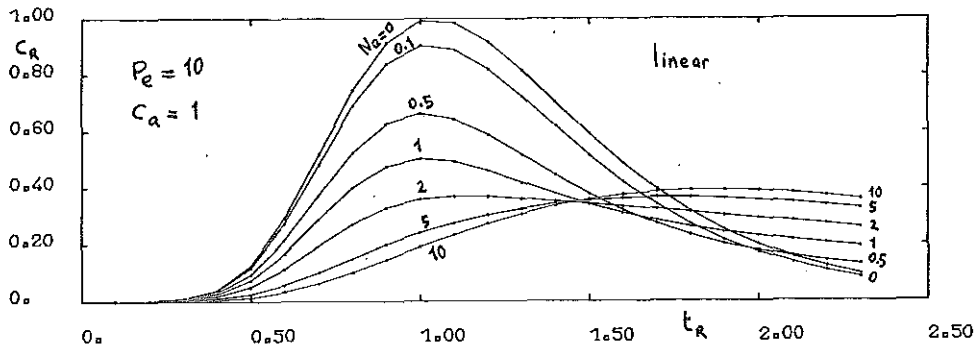
Three dimensionless numbers appears :

$P_e = \frac{uL}{D}$ it is the Peclet number

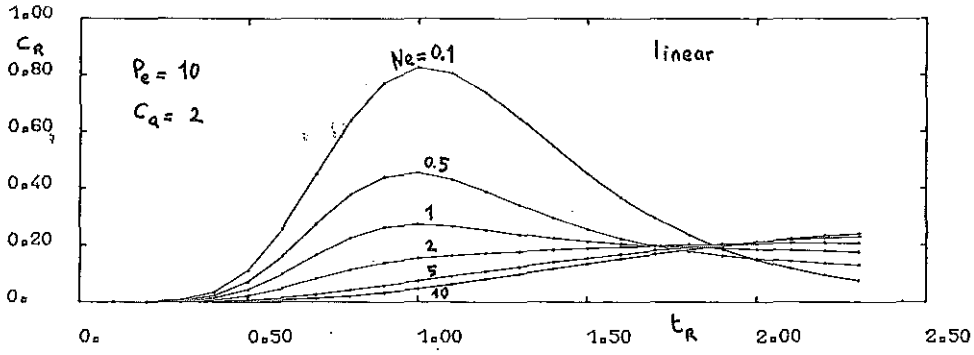
$N_e = \frac{L.k_c}{u}$ it is the number of Echanges during the advection along the distance L

$C_a = \frac{1-n}{n}k_e$ it is the Exchange Capacity of the aquifer

This system of two dimensionless differential equations has been solved by finite differences with B.R.G.M. numerical code M.O.D.E.L. (J. Ausseur, B. Kanehiro, J.P. Sauty, 1979) and made it possible to design dimensionless type curves describing the



Graph 1. Linear exhanges : influence of the Number of exchange Ca = 1



Graph 2. Linear exchanges : influence of the Number of exchange Ca = 2

evolution of concentrations following a slug injection of tracer. The calculations have been performed for a Peclet number equal to 10, a number of exchange ranging from 0.1 to 10 and a Retention Capacity from 0.1 to 5. Graphs 1 and 2 shows the type curves for Ca = 1 and Ca = 2.

2.2. Exchanges according to Langmuir isotherm

The equilibrium equation is :

$$S_e = \frac{k_e C}{1 + C/C_d}$$

with

C_d = half saturation concentration in the liquid phase (water)

S_e = equilibrium concentration in the solid phase (aquifer)

The exchange kinetic is of second order :

$$\frac{\partial S}{\partial t} = k_c \left(k_e C \cdot \frac{S_e - S}{S_e} \right)$$

The transformation of the variable is the same as in the previous chapter. The dimensionless equation may be written :

$$\frac{\partial C_R}{\partial t_R} = \frac{1}{P_e} \cdot \frac{\partial^2 C_R}{\partial x_R^2} - \frac{\partial C_R}{\partial x_R} - C_a \cdot N_e (C_R - S_R - C_R S_R / S_a)$$

$$\frac{\partial S_R}{\partial t_R} = N_e (C_R - S_R - C_R S_R / S_a)$$

with a fourth dimensionless number

$S_a = \frac{C_d \cdot L \cdot n}{m}$ it is the Saturation Constant.

if Sa is equal to infinity which means no saturation effect, the system of equations is similar to the system describing the linear exchanges.

As the solution depends on four dimensionless numbers, it is not possible to draw a set of type curves.

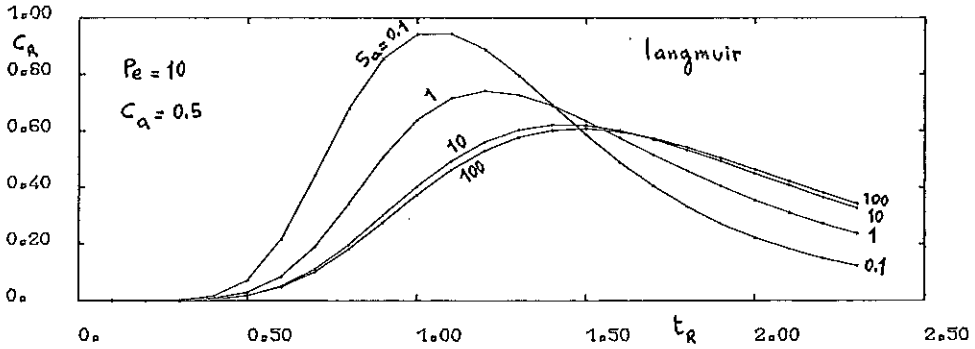
We choose to draw type curves for instantaneous exchanges corresponding to N_e equal to infinity.

If the Peclet number is determined, only two dimensionless number are left : Ca and Sa. Type curves have been drawn to study the influence of each of these numbers. See graphs 3 and 4.

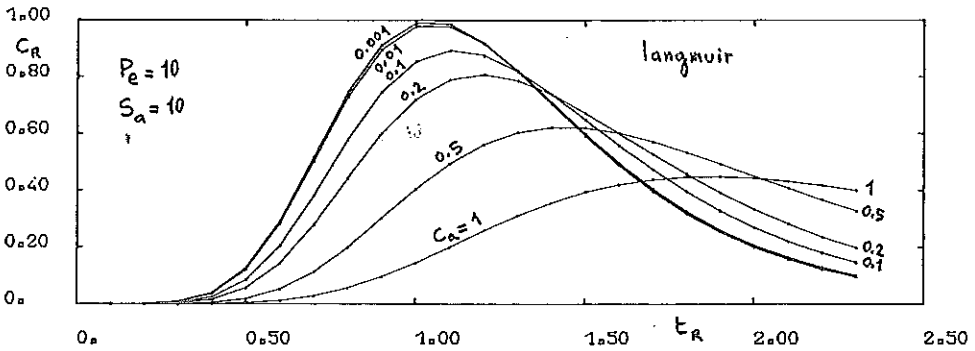
2.3. Ionian exchanges

The hypothesis are the following :

- the sum of the cations in the liquid phase is T,
- the sum of the cations in the solid phase is Qo,
- the anions are not adsorbed by the solid phase,
- the total quantity of injected cations is m.



Graph 3. Influence of the Saturation Constant



Graph 4. Influence of the Retention Capacity

The relation between phases is the following :

$$S_e = \frac{k\, Q_0 C}{T + (k-1)C}$$

when the equilibrium is reached or at any time, if the exchange kinetic is instantaneous. k is the constant of the mass action law.

The sum of all the cations in solution was equal to To. At the time of injection, it is increased at the injection point and then is described by the law of dispersion without exchanges :

$$\frac{\partial T}{\partial t} = D\frac{\partial^2 T}{\partial x^2} - u\frac{\partial T}{\partial x}$$

The reason is that the anions are not adsorbed which is an hypothesis, so the sum of the anions in solution is not involved in exchanges. The electrical neutrality tells that the sum T of the cation too will not be involved in exchanges (see J. Rochon, 1979).

Assuming that the exchange kinetic is instantaneous, it is possible to derive the following equilibrium relation which holds at any time

$$S = \frac{k_a C}{T_R + C/C_d}$$

with the following transformations :

$$T_R = T/T_0$$

$$k_e = k\, Q_0 / T_0$$

$$C_d = T_0/(k-1)$$

The equilibrium relation has the same expression than Langmuir one, when T_R is equal to unity, i.e. for low concentrations of injection.

The dimensionless system of differential equations is :

$$\frac{\partial C_R}{\partial t_R} = \frac{1}{P_e}\frac{\partial^2 C_R}{\partial x_R^2} - \frac{\partial C_R}{\partial x_R} - \frac{C_a}{(T_R + C_R/S_a)^2}\left(T_R\frac{\partial C_R}{\partial t_R} - C_R\frac{\partial T_R}{\partial t_R}\right)$$

$$\frac{\partial T_R}{\partial t_R} = \frac{1}{P_e}\cdot\frac{\partial^2 T_R}{\partial x_R^2} - \frac{\partial T_R}{\partial x_R}$$

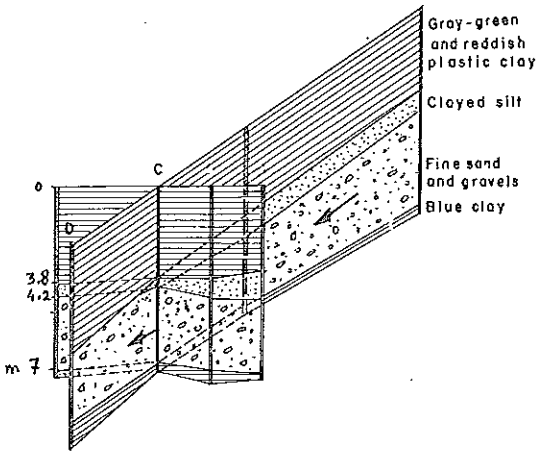
when Co $\ll$ To, $T_R \simeq 1$ and is constant, and these equations are similar to Langmuir scheme. However the second equation which has no exchanges term shows that the variation of T is much faster than the variation of C. After a time equal to about twice the advection time the evolution of concentrations is identical to Langmuir scheme.

3 INTRODUCTION TO THE SECOND PART

All the tracer experiments in uniform flow which are analysed in this part took place in 1974 at Bonnaud, near Lons-le-Saunier (Jura - France). The experiments were desi-gned together by two teams : the Bureau de Recherches Géologiques et Minières (BRGM) and the Section d'Application des Radio-éléments du Commissariat à l'Energie Atomi-que (SAR-CEA). The aim of the research was to study extensively with field experiments the underground migration of various matters soluble in water. All the results are described in B. Gaillard, J. Guizerix, J. Margat, J. Molinari, P. Peaudecerf, 1976.

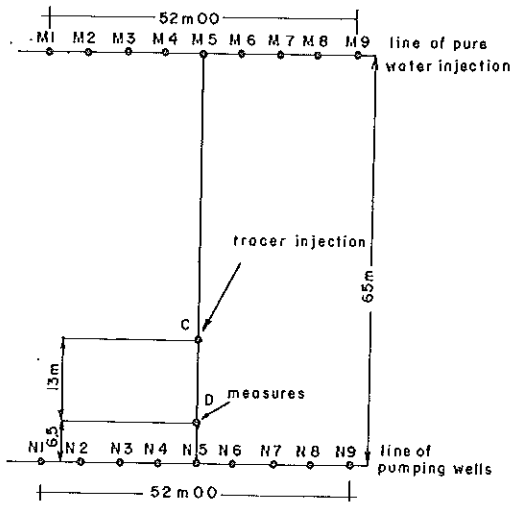
3.1 Description of the experiment field

The aquifer has the following characteris-tics :
- the water table is of limited thickness (3 to 4 m) which helps for the measurements,
- the aquifer is confined which implies no influences of the fluctuation of the water table and no exchanges with the non satura-ted zone,
- the aquifer is not thick and is well de-fined,
- the naturel variations of level are small,
- the hydraulic conductivity is high which helps the advection of the injected tracers (transmissivity : 10^{-3} m^2/s)



Graph 5. Longitudinal and transversal geological cross-sections of aquifer

In order to get a uniform gradient and in-crease the velocities to keep the experiment duration reasonable, a uniform flow has been imposed and controlled by a set of in-jection wells (M) and pumping wells (N) with constant rates (see graph 6).



Graph 6. Situation of wells

3.2 The field experiment to be analysed

Among all the experiments three of them have been selected and are analysed in the follo-wing lines. Each injection took place in well C and measurements were in well D, 13 meters further. The main characteristics of these experiments are gathered in table 1.

Table 1. Main characteristics of the field experiments at Bonnaud

Injected matter	I-Na	Rhodamine WT	Uranine
Mass injected (g)	20	4	40
Date of injection	23/10/74	18/10/74	25/10/74
Uniform flow 10^{-3} m^3/s	3.39	2.42	2.36
Incidents		36 hours stop	
Maximum concentration measured µg/l	295	17	105
Estimation of residual concentration (from previous experiments µg/l)	40	4	6

3.3 Method of interpretation

The three experiments have been analysed se-parately by ajustment of the parameter with a mathematical model. The number of parameter is 4 : D, u, k_c, k_e and also the cross-section area of the part of the aquifer in which the migration takes place.

Other experiments with "perfect" tracers like tritium for which there are no exchanges have been performed on the same experiment field. The analysis of these experiments (P. Peaudecerf, J.P. Sauty, 1978) made it possible to determine the parameters describing advection and diffusion :
- effective velocity u = 3.8 10^{-5} m/s (3,3 m/day),
- (kinematic porosity n = 33 %),
- diffusion coefficient D = 2,5 10^{-5} m^2/s (2.2 m^2/day).

These parameters lead to a dispersivity $\alpha = D/u = 0.66$ m and a Peclet number : $Pe = uL/D = 19.8$ (L = distance = 13 m).

This high value of Peclet number shows that the advection term is much larger than the diffusion one.

The experiments with the other matters (I-Na, Rhodamine WT, Uranine) have been analysed with these same values for D, u and n. The analysis have been done only by ajusting the parameters of exchanges between phases.

3.3.1. Choice of the model of exchange

Various injections have been realised on the same location with the same tracers but with different injected mass (ratio of 10). None of these test show any mass effect ; in other words, for a given tracer, and after a given duration the concentration is proportionnal to the injected mass of tracer. Moreover, as the capacity of cationic exchange Q_o of the aquifer and the chemical nature of the water To are not known, it has not been possible to try any interpretation with ionian exchange scheme or Langmuir scheme. The model which has been chosen is then the reversible and linear exchanges. It must be noted that, as the duration of the measurements is sometimes short and as some incidents occur during the experiments, it should have been illusory to use a more complicated model with more parameters.

3.3.2. Determination of the parameter

For each experiment two parameters have been determined :
- the kinetic constant k_c (corresponding to the half exchange time : $t_d = Ln2/k_c$),
- the equilibrium constant k_e.

The corresponding dimensionless parameters are :
- number of exchanges : $Ne = L.kc/u$
- retention capacity : $Ca = k_e (1-n)/n$

The interpretation scheme is one dimensional so the transverse difusion is neglected The flow is assumed to take place in a prism of aquifer of section A (thickness h and width l) in which the concentration is uniform. The thickness of the aquifer ranges between 2.9 m at injection point to 2.5 m at measurement point. The width l is not known. It is possible to compute it by the ratio of the injected mass to the initial injected concentration which is a parameter of the model.

The parameters obtained after calibration are gathered in table 2.

Table 2. Parameters of exchange

	I-Na	Rhodanine WT	Uranine
kinetic constant kc (10^{-6} s^{-1})	3.0	8.0	7.5
half exchange time td (days)	2.7	1.0	1.1
equilibrium constant ke	0.22	1.12	1.49
number of exchanges Ne	1.03	2.74	2.57
Retention capacity Ca	0.45	2.27	3.03
equivalent width of prism l (m)	6.7	8.4	6.7

The comparison of the measured and computed concentration appear on graph 7 to 9. These graphs show that the calibration is reasonable, keeping in mind the incidents which occur during the experiments and also the fact that the concentration measurements seems sometimes affected by erratic variations.

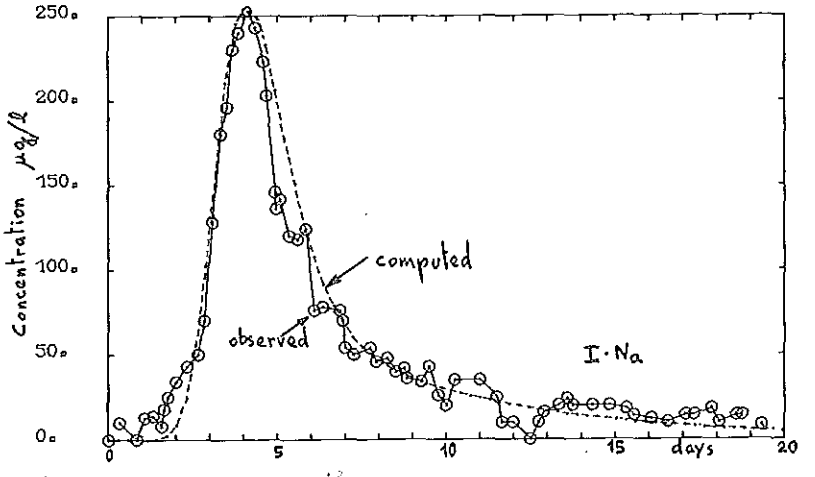
3.4. Interpretation of the exchange parameters

The experiment with Sodium Iodide (I-Na) shows little exchange because the Retention Capacity is small (Ca = 0,45) and the kinetic of exchange is slow (Ne = 1.0).

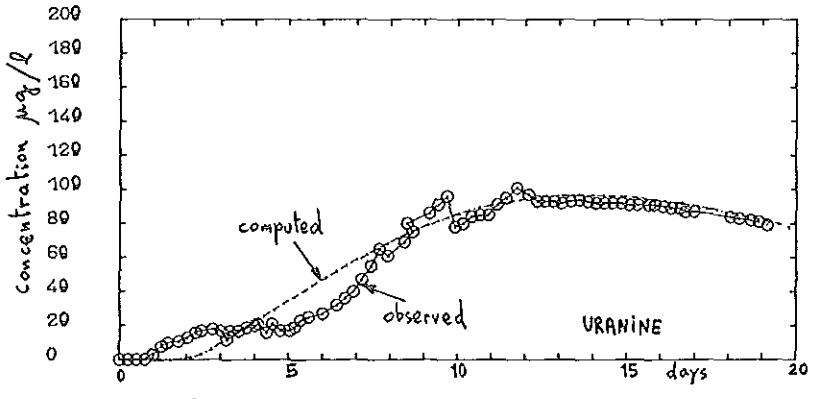
The experiments with Rhodamine and Uramine give results which are quite similar (see graph graph 8 and 9) with much more exchanges : the Retention capacity ranges from 2 to 3, the Number of Exchanges is equal to about 2.5. The computed width of the equivalent prism of aquifer is equal to 7 or 8 meters for the 3 experiments. This width does not describe the lateral extension of the plume of tracer but rather the width of aquifer influenced by the pumping at the measurement point D.

4 CONCLUSION

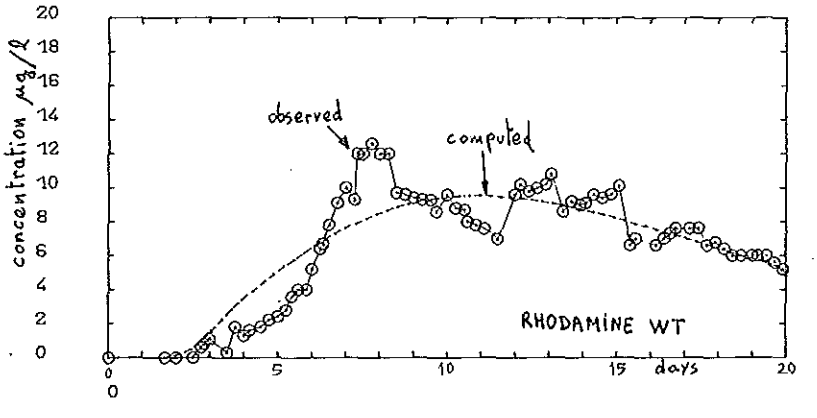
The use of models makes it possible to predict the migration of a pollution in the water of an aquifer, taking into account the physic and chemical interactions of the aquifer. To determine the exchange parameters it is necessary to do the following :
- perform a first experiment on the field



Graph 7. Sodium Iodide



Graph 8. Uranine



Graph 9. Rhodamine WT - Tracer injection at Bonnaud (Jura)

with a "good" tracer (i.e. with no or little exchanges) in order to determine the parameters describing advection and dispersion, perform a second test -preferably a field experiment- with a solute similar to the product to study but which is not a pollutant. When such an experiment may not be performed (for economical reasons or because there is no solute with properties similar to the polluant to study) a dynamic test may be realised in laboratory with a sample of the ground and with the pollutant. From this second experiment, the exchange parameters will be deducted. However a laboratory test will only give a rough estimation of the parameters by not taking into account the heterogeneity of the real field.

NOTATIONS

C = Concentration in the liquid phase

C_a = Retention Capacity

C_e = Equilibrium Concentration

C_R = Dimensionless Concentration in the liquid phase

C_d = Half-saturation Concentration (kg/m^3)

D = Dispersion Coefficient

k = Equilibrium Constant

k_c = Kinetic of exchange constant

k_e = Equilibrium Constant

L = Distance between injection point and measurement point

m = Injected mass of solute or quantity of injected cations

n = Kinematic porosity of the aquifer

N_e = Number of exchanges

P_e = Peclet Number = uL/D

Q_o = Sum of the cations in the solid phase

S = Concentration in the solid phase

S_a = Saturation Constant

S_R = Dimensionless Concentration in the solid phase

T_o = Sum of the cations initially in the liquid phase

T = Sum of the cations in the solid phase

t = Time

t_R = Dimensionless time

u = Effective velocity or poral velocity

x = Distance (m)

x_R = Dimensionless Distance

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