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DEVELOPMENT OF THE CHEMICAL COMPOSITION OF WATER DURING SEEPAGE IN NATURAL SURROUNDINGS : MAIN RESULTS OF AN EXPERIMENTAL STUDY

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ABSTRACT

The results presented are drawn from a study whose purpose was to observe and understand the various phenomena that come into play as water acquires its chemical composition in the course of its seepage towards an aquifer. This study is based on observations made at an experimental site in northern France, on the chalk aquifer.

The aquifer "recharge" zone is made up of three successive horizons : silt (3 m), silt and chalk with a high proportion of clay (1 m), and chalk (4 m). The water of these three horizons was observed from both the hydrodynamic (water transfers) and the chemical aspects.

The results obtained bring out the following points :

- From the initial 25 centimetres onwards, the water acquires 50-60 % of the aquifer mineralization level, attaining 75-80 % on arrival in the aquifer.
- The waters in each of these layers are relatively independent with respect to one another in their chemical composition. This independance may be explained by the existence, even in an environment presumed to be continuous, of favoured flow-paths which act as breaks, cutting off the different layers from one another. It would seem that there is a distinction to be drawn between the chemical composition of gravitational-flow water and that of water in the matrix.
- The clayey level, located between 3 and 4 m seems to be the seat of substantial bacterial activity and acts as a major barrier to certain elements, notably nitrates.
- The study of the dissolved calcium and calcite equilibria shows that it is necessary, even in this system of slow transfers, to take the kinetic aspects of dissolving into account for the simulation of this environment.

INTRODUCTION

For some years now, the emergence of pollution problems has led to reflection on the possibilities of action to protect underground water resources or decontaminate them after accidents. At present, however, it would seem that it is necessary, both to explain the origin of the chemical facies observed and to organize the effective prevention of pollution risks, to give special attention to a better understanding of the mechanisms by which water gradually acquires its chemical composition in natural conditions.

In the past few years, there have been a number of publications showing the interest being taken in this subject. A great many laboratory research studies have been conducted, notably to determine the importance and characteristics of the adsorption of various elements or compounds, particularly cations, on clays. At the same time, there have also been a number of studies on anions (BOWDEN et al., 1974 ; S.S.S.RAJAN, 1978 ; W.W. WOOD, 1978 ; ref. 2-7-10-11). In contrast, there have been few so-called "in situ" studies which consist in following the development of the chemistry of the seepage water in natural conditions, through the first metres in the ground. R.DURAND (1978, ref. 5) observed, in lysimetric boxes, the development of the chemical composition of water that had seeped through three meters of chalk. The essential results brought out are that the water acquires its main chemical features very rapidly. The potassium is subjected to rapid variations which would depend on the water regime of the ground. At the aquifer level, there may be a light drop in calcium content which would be caused by calcium carbonate precipitations. The study which comes closest to our work, on both conception and results, is the one prepared by W.W. WOOD and D.C. SIGNOR (1975) -ref. 9- who, using porous cells, observed the modifications in the chemical composition of water in the unsaturated zone during an artificial recharge in an experimental site. The main phenomena observed and analysed by these authors are cationic and anionic exchanges and the adsorption and desorption of ions.

DESCRIPTION OF EXPERIMENTAL SITE AND EQUIPMENT

Geographical location

The site chosen for our experiments is in the northern region of France, about 10 km south-west of Lille (Fig. 1) :

- experimental plot (about 100 m^2) situated in a sector corresponding to a piezometric dome. The chemical composition of the aquifer water is due solely to the various equilibria that are set up between the rainwater and the rocks passed through during seepage ;
- the aquifer concerned is that of the chalk (Upper Turonian made up of glauconitic and phosphatic chalk) ;
- the thickness of the unsaturated zone varies from 8 to 13 m, depending on the fluctuations of the aquifer. This unsaturated zone is made up of a 2.8 m layer of

silt which is separated from the chalk by an intermediate, more clayey layer made up of silt, chalk and flint (2.8 m to 3.6 m). From the 3.6 m level onwards, this zone is made up of marly chalk.

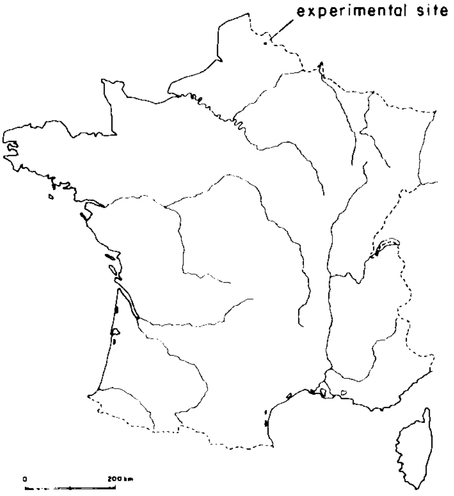

Fig. 1.

Equipment

We paid particular attention to observing the unsaturated zone while causing the least possible disturbance to the chemical phenomena and the water transfer processes. This is why, rather than making observations through lysimetric boxes, we preferred to employ a methodology that has made progress during the past few years and has been the subject of numerous publications : namely, the use of porous cells to collect samples of water, tensiometers and moisture profiles through neutron probes to follow up transfers.

Because of the depths at which certain porous cups and tensiometers had to be placed, these were set up horizontally from the walls of a 1.80 m diameter well, 2 m from these walls (Fig. 2).

The distance of 2 m was chosen in order to prevent any disturbance that could be caused by the edge of the well. Measurements of moisture along horizontal sections at various levels from the well showed that the influence of the edges was felt only up to about 50 cm.

The aquifer fluctuates between 8 and 13 m. In order to follow these variations, a piezometer was set up in the vicinity of the site. Figure 3 shows the various instruments placed on this site.

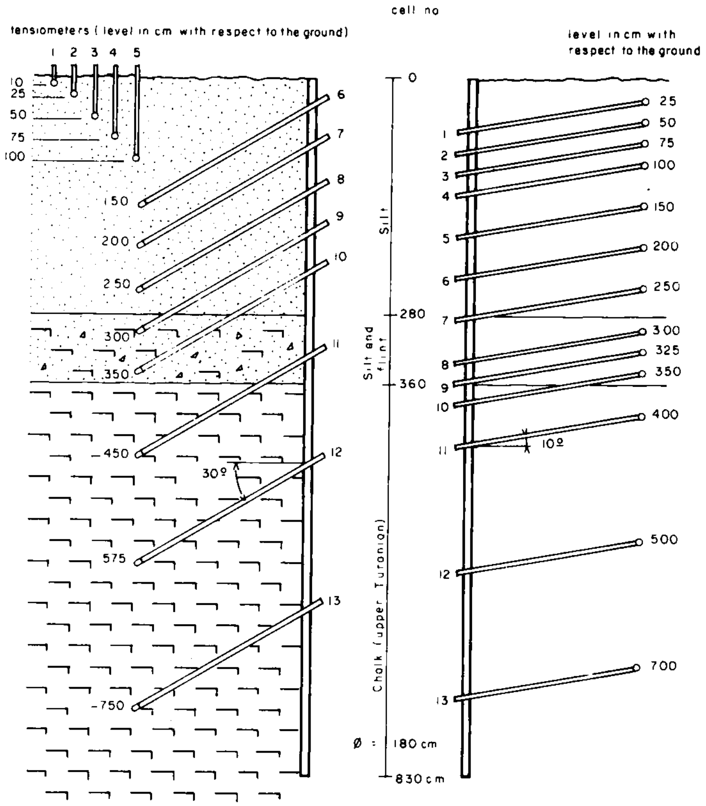

Fig. 2. Location of porous cells and tensiometers in the well.

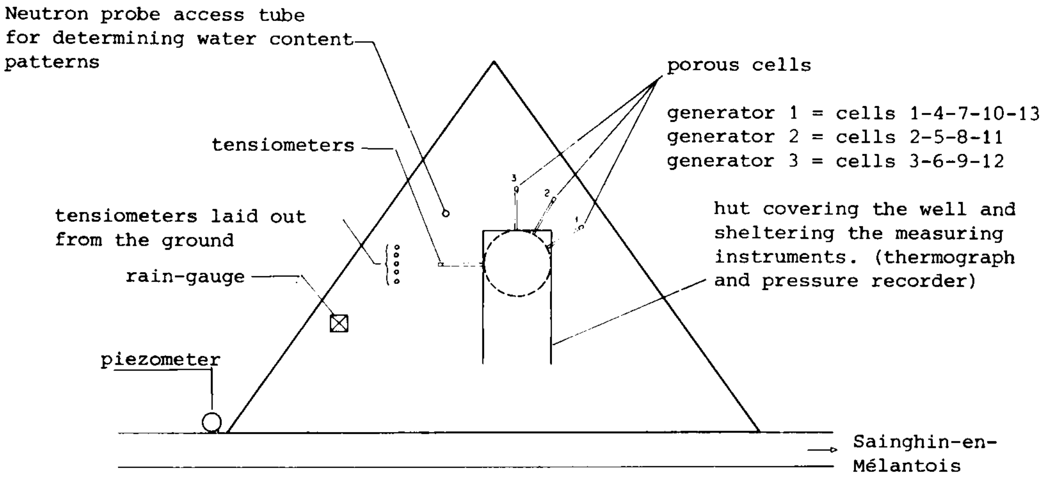

Fig. 3. Layout diagram : equipment of the experimental site.

PROGRAMME OF MEASUREMENTS

At the same time as the chemical processes in the waters was being studied, transfers of water in the ground were followed up by the recording of water content and hydraulic heads and by interpretation through models, according to the techniques described and used by certain authors like J.P. BELL and S.S.S. MacCULLOCH (1966), J.F. DAIAN and G. VACHAUD (1971), D. HILLEL et al. (1972), F.A. DAUDET and G. VACHAUD (1977) (ref. 1-3-6-4). This part of the research programme made it possible to specify the hydrodynamical behaviour of the system, as far as this can be done given the present state of knowledge in the field, and notably to specify the periods in which a recharge takes place and the volumes of water brought into play.

In the chemical part of the programme, we sought to show and explain the phenomena that cause the chemical composition of the water to develop and change from that of rainwater to that of groundwater. Table 1 gives these two compositions at either extreme of the profile studied.

TABLE 1

Chemical analysis of rain-water and ground-water

			Rain-Water (sampling September+October (1977)	Ground-water (sampling February 1978)
pH			5.5	6.75
resistivity (ohms x cm) at 20°C			16 950	1 190
Ca^{2+}	mg/l		5	193
Mg^{2+}	"		-	6.2
Na^{+}	"		1.4	16.8
K^{+}	"		0.5	0.9
HCO_3^-	"		5	330.6
Cl^-	"		2.9	54
SO_4^{2-}	"		13.9	180
NO_3^-	"	NO_3	4.9	43
NH_4+	"	NH_4	5.6	0.3
NO_2^-	"	NO_2	4.9	-
Total mineral nitrogen	mg/l $N\text{-}NO_3$		31	
F^-			0.09	0.1
Zn^{2+}			0.11	0.020
Fe^{3+}				0.012
Sr^{2+}				0.037
Silice	"	SiO_2		10

Between these points, the chemical quality was followed up from samples of water taken by porous cells set up along the section. Five chemical profiles were drawn up over a period of one year.

The sample-taking cells were all put under depression (0.7 bar), 15 days before the collection of water. The volume of water collected in each cell varied according to the cell (from 0.1 to about 1 litre). The samples were filtered on the spot so as to facilitate the interpretation of the results concerning "in situ" chemical equilibria, namely those relating to temperature, pH, conductivity, dissolved oxygen and HCO_3 ion content. The analyses relating to the other major ions and some trace elements (Fe^{3+}, Mn^{2+}, Sr^{2+}, F^-) were done in the laboratory.

To assist in the interpretation of these results, the distribution of the various kinds of ions in solution as well as the state of equilibrium between the water and the various minerals were calculated using the WATEQ programme (A.H. TRUESDELL and B.F. JONES, 1974 - ref.8).

MAIN RESULTS OBTAINED

Trend of the chemical profiles

The chemical pattern profiles prepared at various periods of the recharge of the aquifer, that is to say with or without movement of water in the ground, all show a trend rather similar to that of total mineralization (Fig. 4).

As in most of the studies on this subject, it is observed that the water rapidly acquires its chemical features in the first centimetres. After 25 cm of seepage, it has acquired 50-60 % of its final (aquifer) level of mineralization. All the same, this acquisition of chemical properties does not develop in a regular manner until the aquifer is reached. Numerous points of discontinuity are observed, all situated at the same levels regardless of the sample-taking period. These points of discontinuity are located notably at the level of the interfaces between the three layers of ground. The substantial mineralization of the waters contained in the intermediate weathering layer should be noted, this mineralization being 25-35 % higher than that of the water taken from the bottom of the section.

These discontinuities could be explained by phenomena of dilution between the water of porosity (in the matrix) and the moving water that circulates through macropores or indeed through favoured flow-paths (diagram in Fig. 5). This is what seems to be shown by the interpretation of the results recorded for the study of water transfers.

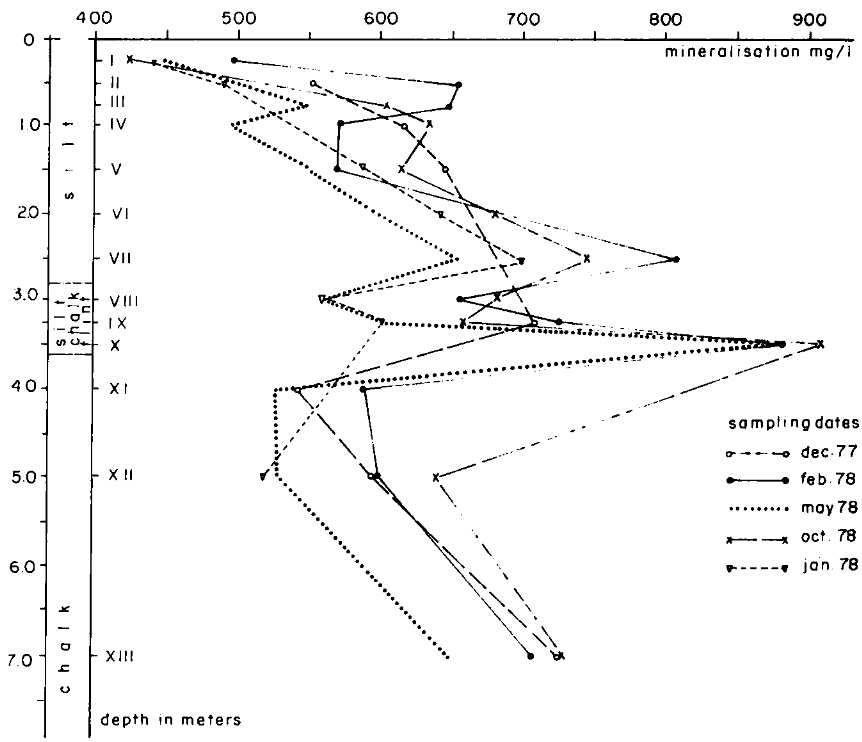

Fig. 4. Profile of T.D.S.

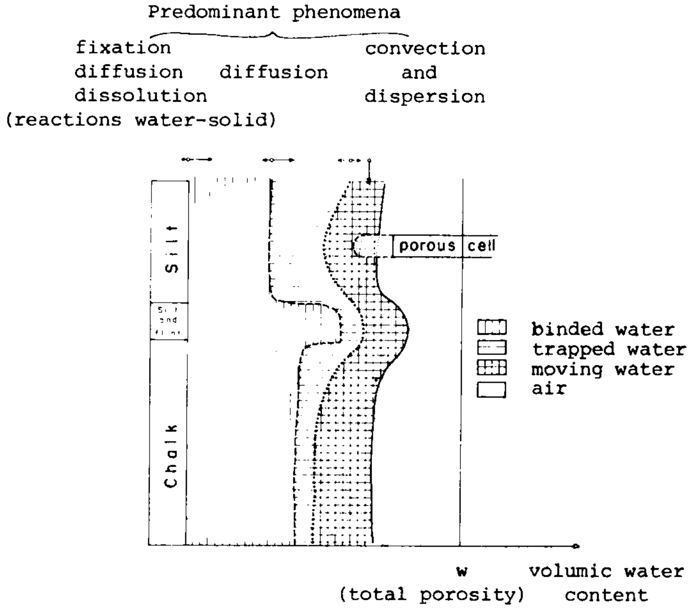

Fig. 5. Theoretical model of the main physico-chemical phenomena of exchange and transfer in a natural profile during infiltration.

Nitrate content of water in the intermediate layer

In the samples taken in May, June and September 1978, nitrate content levels of about 160 mg/l were observed. This figure even approached 280 mg/l in October, while the nitrate content of the water at the silt and chalk layers is about 20 and 50 mg/l respectively (Fig. 6).

The clays (montmorillonite and a smaller proportion of illite) that characterise this layer would seem to play the role of a very major barrier to this anion. This barrier effect has been observed in numerous research studies, but mainly for cations. It is possible that this nitrates-fixing effect is, in fact, due to the ammonium ions which are linked to clays in an exchangeable or fixed form or in the form of organic complexes, these compounds being transformed into nitrates under the action of nitrifying bacteria. For this level would seem to be a seat of microbial activity not found elsewhere, apart from the aerobic surface layer. The following may be put foward as proof of this microbial activity :

- the waters extracted from this clayey layer have pH values tending to show light acidification as compared to water taken from silt or chalk (CO_2 produced by bacterial activity ?).
- the level of organic carbon content (necessary for bacterial development) is similar to that of the surface layer (the first metre), which is the favoured place for bacterial phenomena (cf. Table 2).

TABLE 2

Content of total organic carbon in soil

depth (meters)	content (in %)
0.5	0.13
1	0.11
2	0.10
2.5	0.07
3	0.13
3.5	0.11
4	0.07
4.5	0.05
5	0.06
7	0.04

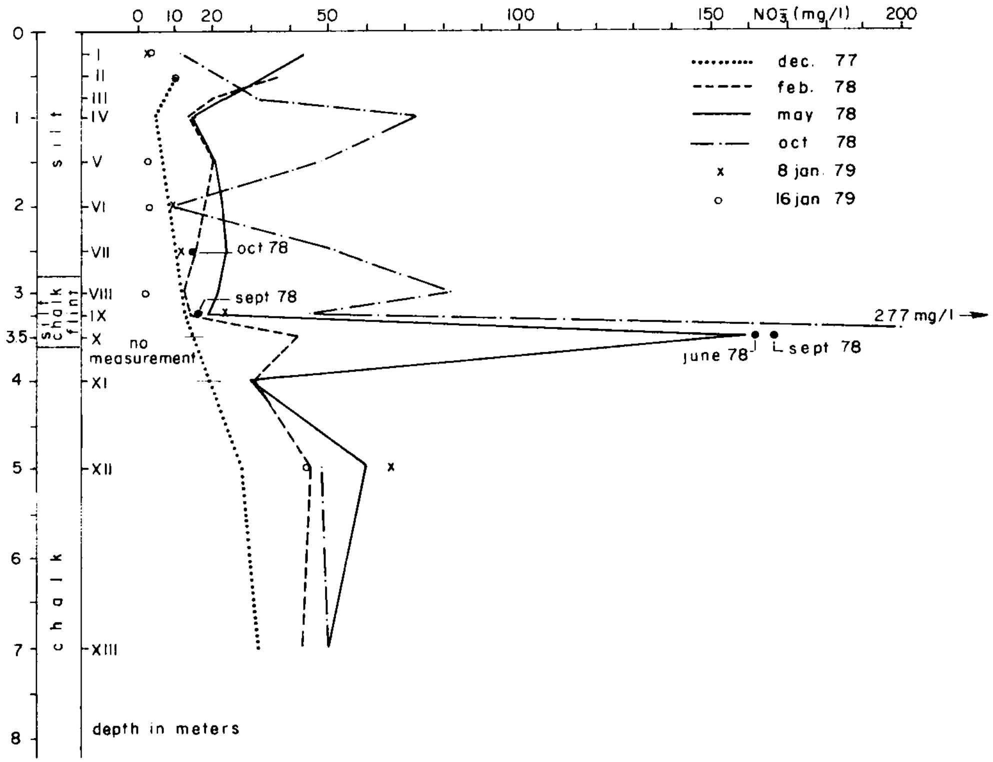

Fig. 6. Profile of NO_3

Equilibrium of dissolved calcium and calcite

The study of the dissolved calcium/calcite equilibria show that, in our case, the water mineral equilibria are reached only when the time of water-rock contact is extremely long. This is to say that these equilibria are reached only outside of the aquifer recharge periods when there is no longer any transfer of water in the macropores, and that the water samples taken correspond somewhat to matrix water.

Equilibrium with dissolved calcium and calcite :

DECEMBER 1977 *All samplings are under saturation except porous cups 11 and 13*	:	Begining of the recharge of the aquifer (at the end of November).
FEBRUARY 1978 *All samplings are under saturation*	:	Recharge of the aquifer.
MAY 1978 *5 samplings are upper saturation (porous cups 3, 5, 7, 8, 10)*	:	End of the recharge of the aquifer.

OCTOBER 1978 *All samplings are upper saturation*	:	Discharge of the aquifer. No transfers of water in soil.
JANUARY 1979 *7 samplings are upper saturation (porous cups 4,6,7,8,9,11,12)*	:	Begining of the recharge of the aquifer (late for this hydrogeological year).

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Observation : Although there is perfect correlation with the movements of water in the ground, there should, all the same, be some restrictions imposed on the validity of the measurements of the pH values and the Ca^{2+} and HCO_3^- ions. These relate to the mode of sample-taking which entails a depression of about 0.7 bar in the porous cells and a period of about 8 days during which the samples of water stay in these cells. These factors could give rise to modifications in the chemical equilibria due, notably, to the variation of the partial pressure of CO_2.

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CONCLUSIONS

The setting up of substantial equipment enabled us to follow the development of the chemical composition of a portion of water in the course of its seeping through the grounds up to the aquifer. The trend of the profiles observed shows that the development is not gradual but that, on the contrary, the chemical composition undergoes numerous changes which could be due to the effects of dilution between the so-called moving waters, which circulate easily beneath low hydraulic gradients in the macropores or ground fissures, and the matrix waters which are more static and which can enter into chemical equilibrium with the solid phase. This shows how worthwhile it would be to have "chemical" studies linked to the hydrodynamical aspect which could reinforce the interpretation of the phenomena observed.

Among the various phenomena observed, the role of the intermediate layer arising out of the weathering of the chalk is of special interest and is worth examining in greater depth, particularly with respect to the role that the clays may play in relation to the nitrates. This is all the more important as this layer is found in most "silt-on-limestones" systems.

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