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NATURAL FLOW AND VERTICAL HETEROGENEITIES IN A SEDIMENTARY GEOTHERMAL  
RESERVOIR (PARIS BASIN, FRANCE) : GEOCHEMICAL INVESTIGATIONS

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ABSTRACT

Three geothermal wells tapping the Dogger aquifer were studied in detail for their variations in chemical composition with time or conditions of exploitation. Analytical improvements for the determination of Cl, SO<sub>4</sub>, Ca, Mg, Na and K make it possible to detect variations respectively of 0.15, 0.8, 0.6, 1.8, 1.8 and 1.4 %. Despite the fact that the natural flow may be important in some parts of the basin aquifer, we conclude that this factor is not responsible for the small variations noticed in mineralization within the one year survey period. The results concerning reactive and nonreactive species are best explained if a vertical heterogeneity of the chemistry of the fluid is assumed. A number of calcareous sub-layers, already demonstrated by geological studies, contribute to varying degrees to the production of the hot water. The changes in pumping rates, which are fixed according to external requirements, play a major role in the hydrodynamic and chemical disequilibrium of the wells. The consequences for the geothermal exploitations are emphasized.

INTRODUCTION

Intensive exploitation of the Dogger limestone aquifer for geothermal purposes has drawn attention to the need for detailed knowledge of the characteristics of the reservoir in order to manage and protect the resource (Rojas et al., 1987). Fluid velocity and chemical heterogeneity of the productive layers may have a marked influence on the lifetime of the installations if the location and orientation of the doublets do not take these parameters into account or if the change in composition of the fluid with time increases corrosion and scaling in the well casing, heat exchangers and surface network. In the Val de Marne Department (south of Paris), the increasing number of wells has brought to light hydraulic contacts between adjacent exploitations. So far, a few tracer experiments (131-I) on single wells for two doublets located south of Paris, at Fontainebleau and Cachan, suggest relatively important natural flow towards the north-

west in the south of the basin (De Marsily et al. 1986). This may be linked to an actual recharge of the aquifer which consist in this area of a dilute but warm water, evidenced by isotopic and chemical indications (Criaud et al., 1986 ; Fouillac et al., 1986 ; Marty et al., 1988). On the other hand, unpublished work by the Institut Mixte de Recherches Géothermiques shows that the chemistry of a fluid collected at the wellhead for a given site may change with the working conditions (pumping rate) and/or the period of sampling. However the range of variation in chemistry was of the same order of magnitude as the relative precision of standard analytical procedures.

We present here the results of a detailed survey for three case studies, in the south and east of the basin, where minimum and maximum salinities respectively of the geothermal fluid are encountered (figure 1). The needs were to improve the analytical methods and quantify the precise variations in chemical composition with time and conditions of exploitation (these consist mainly of variable pumping rates causing differing pressure conditions at wellheads). The aim was to develop a geochemical tool useful for hydrodynamic studies. Because downhole sampling at different depths could not be carried out (due to the presence of immersed pumps), all samples were collected at the wellheads. Sampling at three sites has been carried out over a year or more and at various pumping rates. Total dissolved solids and downhole temperatures for the wells are respectively 6.5 g/l and 74°C (Fontainebleau), 23.5 g/l and 79°C (Créteil) and 35 g/l and 85°C (Coulommiers). Only a limited number of chemical parameters was selected for this survey. We have included highly soluble ions such as Cl or SO<sub>4</sub>, concentrations of which are not controlled by fluid-mineral equilibria in this aquifer (Bastide, 1985), and reactive cations such as Na, Ca, Mg and K which can be affected by water-rock interactions. The former are expected to result from mixing phenomena, while the latter would reflect

different extents of water-rock interaction. We assume that no reequilibration of the fluid happens during ascent in the well, i.e. the concentrations of these species do not vary between the aquifer and the surface. This is supported by the fact that only the deposition of iron sulfide has been reported in the casing (Honegger et al., 1986).

#### SAMPLING AND ANALYTICAL PROCEDURES

##### Sampling

For the three wells concerned, samples were collected at different times of year, under different conditions of exploitation of the geothermal installation. The pumping rates consequently vary approximately between 80 m<sup>3</sup>/h (summer) and 250 m<sup>3</sup>/h (winter). A special survey was undertaken in Coulommiers in May 1987, with five steps at different pumping rates. Six hours were allowed for stabilization before new pumping rate conditions were fixed. The first sampling was carried out after 3 hours and a second one after 6 hours. In all cases, water samples were collected at the wellheads. The sampling period spread over more than one year but all the determinations were carried out at the same time in the laboratory, in order to avoid time drifts due to the devices.

pH, temperature, alkalinity and sulfide concentration were measured on site following the procedure already described in Criaud et al. (1986). In the case of Fontainebleau, where the sulfide content reaches 30 mg/l, a special sample was collected for sulfate determination in order to avoid the oxidation of sulfide and subsequent artificial increase of sulfate concentration before analysis. This method was also used for the Coulommiers samples, where sulfide content may reach 0.5 % of the sulfate content but this was unnecessary in Crêteil because the sulfide content is negligible compared to sulfate. Two procedures were tested : in the first, a known amount of cadmium acetate was added to the sample immediately after sampling. In the second mercuric nitrate was used. All reagents and samples were weighed to improve the precision.

##### Analytical methods

**Chloride:** The method involves potentiometric titration with silver nitrate, an Ag/AgCl electrode and a reference electrode. Because the aim of the study was to quantify precise and tiny relative variations rather than very exact determinations, no attempt was made to correct for the bromide and other halogenides which are titrated along with chloride.

The reproducibility of the method is 0.12 % for 10 determinations of the chloride content of Coulommiers water, which is the most saline fluid. This result was found to be satisfactory for the main objectives of the study. Duplicate analysis were performed routinely.

**Calcium:** Complexation of alkaline earths by EDTA offers a very suitable method for the determination of calcium. The use of a titration device under control of a specific optical fiber which transmits a light beam ( $\lambda = 660$  nm) considerably improves the reproducibility of end point determination, giving a reproducibility of 0.6 % for 10 determinations. It is affected mainly by the quantity of indicator, the time for stabilization and the large variation of the photometric signal after each drop of the EDTA reagent. Ba and Sr are titrated together with Ca but again it was assumed that the concentrations of Sr (30 to 70 mg/l) and Ba (approx. 0.1 mg/l) and their relative variations are of little importance compared respectively to the concentrations of calcium and their variations in these fluids.

**Magnesium:** The Mg concentration was calculated from the difference between the results of the titration of calcium on the one hand and the sum of Ca + Mg on the other hand. Ca + Mg was also determined by complexometric titration using black eriochrome as indicator and the 660 nm phototrode. The concentrations of Sr and Ba and their variations were neglected as compared to the magnesium content for the reasons mentioned above. Reproducibility was 0.15 % for 10 determinations of Ca + Mg. Depending on the Ca/Mg ratio, the reproducibility for Mg alone is thus 1.4 % for Fontainebleau, 2.3 % for Crêteil and 2.4 for Coulommiers.

**Sulfate:** The method is based on the determination of barium in excess after removal of the cations of the sample with ion exchange cationic resin, and addition of barium chloride with precipitation of barium sulfate. The complexometric titration with EDTA and the use of the 550 nm phototrode for the determination of the end point provide an accurate method if the excess of barium is kept small. The reproducibilities for the indirect determination of sulfate in the samples were respectively 0.8 % for Fontainebleau and 1.1 % for Coulommiers. For the fluids containing dissolved hydrogen sulfide and treated on site, the addition of cadmium acetate did not give satisfactory results for the more saline fluids because of the low pH and the consequent inefficient removal of cations by the resin, but mercuric nitrate was found suitable for both Fontainebleau and Coulommiers.

**Sodium and potassium:** Na and K were determined by flame emission spectrophotometry. All samples were diluted and the emission measured at 589 and 766.5 nm respectively. The standard solutions were prepared with chemical composition and Na/K ratios close to those of the samples. The reproducibility is 1.3 % for K and 1.8 % for sodium.

## RESULTS

The variation of the chemical components displays variable relative trends in different wells. Table 1 summarizes the maximum deviations compared to the reproducibility of the analytical methods.

	Maximum deviations %			Analytical reproducibility %
	1	2	3	
Cl	1,7	0,6	0,6	0,1
Ca	1,1	1,2	0,6	0,6
SO <sub>4</sub>	7,1	0,5	1,6	0,8
Na	3	1,5	1,3	1,8
Mg	12,9	2,6	0,5	1,8
K	5,7	2,8	2,1	1,4
Ca + Mg	4,5	0,9	0,6	0,15

1: Fontainebleau ; 2: Crêteil ; 3: Coulommiers

Table 1: Maximum deviations of the chemical parameters during the one year survey and analytical reproducibility

### Fontainebleau

The most important variations with time were observed in the fluid from Fontainebleau which is the most dilute in the basin. Unfortunately the pumping rates could not be monitored for this well. If the results are interpreted as a function of time, then the concentrations of chloride, potassium and sodium tend to increase within the one year survey period, while those of calcium and magnesium decrease. This would favor the assumption of a natural "horizontal" flow of the fluid within the aquifer. This circulation should be quite important to be consistent with the extent of chemical changes evident on the very small time-scale of one year. The main objection to this assumption is that the natural flow (Rojas et al., 1987) and the isosalinity curves (Criaud et al., 1986) in this part of the basin imply rather that the salinity of the fluid decreases with distance (figure 1). On the other hand the exploitation of the aquifer with various pumping regimes is unlikely to provoke such movements of the fluid near the well.

Another approach is to compare the variations of the chemical components relative to each other. From table 1, it appears that Cl, Na, Ca and K vary significantly and can be used as indicators of geochemical phenomena. Although Cl would be preferable, we have also taken Na into account to illustrate the main variations of the other elements. It can be seen in figure 2 that the mineralization of the geothermal fluid shows no regular variations according to chronological order of the samples, thus confirming that the "horizontal" circulation of the water is not responsible for

the observed variations. The behavior of Cl, Na, K and HCO<sub>3</sub> are best explained if we assume that the water collected at the wellhead results from the mixing of slightly different fluids. Flow rate measurements after the end of drilling had shown the existence of at least three productive geological facies, each of them subdivided into several productive layers which could be interconnected (Rojas et al., 1987). Since some samples deviate significantly from the trend observed for Na versus Cl (both of which are considered here as non-reactive) on figure 2a, it may be concluded that more than two different fluids cause the changes in chemical composition. The results for K lead to the same conclusion.

In contrast, the Mg content clearly decreases with the Cl (figure 2d). Since dissolved Mg is controlled by the solubility of dolomite in the Dogger fluids (Bastide, 1985), the different Mg/Cl ratios in the various sub-aquifers can be related to different temperatures. Another consequence of this would be the positive correlation of salinity with temperature for these sub-layers.

### Crêteil

The operating conditions of the geothermal wells vary according to the hot water requirements and the main factor that could be responsible for the variations observed is the variable pumping rate. This is not accurately known for the Fontainebleau samples, but Crêteil is very suitable for examining the effects of both time and pumping rates on the chemistry of the fluid. The available data are for discharge rates between 96 and 220 m<sup>3</sup>/h and were measured over ten months. Figures 3a, b, c and d show that the samples taken at lower and upper regimes are respectively the least and the most mineralized, the two other points being very close to each other with respect to both analytical determinations and pumping rate measurements. It must be emphasized that the relative variations (table 1) are close to the standard deviation of analytical methods for Na, Ca and SO<sub>4</sub>, but despite this, the variations are remarkably consistent on figure 3. A mixing model involving two or more fluids could account for these correlations. So far the importance of the circulation of the fluid within the aquifer is not known in this area, but vertical variations in the chemistry are likely to occur at Crêteil, which would satisfactorily explain the geochemical results.

The calcium is in this case much more reactive than at Fontainebleau, its concentration decreases as sodium (or chloride) increases. This may be linked to a slight rise of temperature, and to the solubility of calcite.

There is no evidence in Crêteil for time variations on the chemistry of the fluid.

### Coulommiers

This fluid is the most mineralized of any in the basin, and very little modification of the chemical composition was observed within the one year survey period (table 1). The greatest variations were obtained for sulfate and potassium. On figures 4a and 4b the concentrations in K versus  $\text{SO}_4$  and Cl are plotted. The points display a rough positive correlation which is not linked to the order of collection. No systematic relation is found between the discharge rate or composition but this again may be due to imprecise knowledge of the exploitation parameters during the first part of the survey. Mixing of fluids from separate layers of the main aquifer with constant Cl/K and  $\text{SO}_4$ /K ratios would explain these patterns.

The pumping conditions were carefully controlled for the second part of the study at Coulommiers. The changes were made in 5 stages of 6 hours of fixed pumping rates. The deviations for most of the elements determined are hardly noticeable with regard to analytical error.  $\text{SO}_4$ , Cl and K only show significant variations (figure 4). Other considerations based on iron contents (Ouzounian et al., 1987 and unpublished results by IMRG) tend to indicate that hydrodynamic equilibration of the well is still not attained after 6 hours of pumping at a constant rate. When the second set of samples (collected after 6 hours) is considered, a fair correlation between K and  $\text{SO}_4$  is observed (figure 4d). Na and  $\text{SO}_4$  concentrations also display a positive correlation when all the points are plotted. This is consistent with the hypothesis of mixing of two or more fluids. The influence of several producing layers is assumed, in view of geological considerations. So far, no information concerning the circulation rate of the fluid within the aquifer in the east of the basin is available. With regard to the results of the two parts of the chemical survey, we believe that the main influence demonstrated is in modifications of the pumping conditions. The relative percentages of water produced by the Dogger sub-aquifers seem to vary in a complex manner, according to the equilibration time required and the relations between mineralization and pumping rates, which are not simple (as far as the analytical precision is sufficient).

### DISCUSSION

Previous geochemical investigations came to the conclusion that the origin of the fluid collected at the wellheads of about a hundred wells is complex. Local trends make it possible to distinguish at least three different mixing phenomena, according to specific ratios such as Cl/ $\text{SO}_4$  or Cl/B, but Cl/Br or Cl/Na, which are rather homogeneous at the basin scale, arguing for a common origin and a global mixing model. The very

precise determinations made for this study can be used to compare the ratios between Cl,  $\text{SO}_4$  and Na obtained for the three wells of Fontainebleau, Créteil and Coulommiers, each belonging to a different group (Criaud et al., 1986), with those obtained at local or regional scale. The Dogger aquifer pattern for Cl versus Na defines a correlation according to the equation: ( $n = 55$  wells)  $(\text{Cl}) = 1.917 (\text{Na}) - 774.9$  with  $r = 0.9898$ , while for Fontainebleau and Créteil significantly lower slopes were found for the mixing lines calculated from figures 2 and 3. The variations of the chemistry at Coulommiers are too small to allow such confident interpretation. Differences in Na/ $\text{SO}_4$  ratios confirm the local trends previously pointed out (Criaud et al., 1986). We thus emphasize the fact that three degrees of mixing could account for the complex evolution of the Dogger fluids:

- At the regional scale (200 km), the natural flow is responsible for a variety of mineralizations and temperature distributions. Certain chemical indications favor the hypothesis of a common parent for these waters (Cl/Br and Cl/Na ratios).
- At the local scale (10 km or less), certain groups of fluids are clearly characterized by their Cl/B and Cl/ $\text{SO}_4$  ratios as well as isotopic properties (Seine St Denis, Val de Marne, Fontainebleau, eastern and western wells) (Fouillac et al., 1986).
- Any particular producing well taps a number of sub-strata which constitute the Dogger aquifer and are obviously not homogeneous in chemistry. Because most of the wells are exploited at different pumping rates, with a consequent hydrodynamic disequilibrium, the relative contribution of each layer to the chemical composition at the wellhead varies depending on the sampling period.

The variations of chemical composition demonstrated by this work result mainly, or entirely, from the varying contributions of the vertical sub-systems constituting the Dogger aquifer. The relative proportions involved depend on site, pumping rate and equilibration time. The other influences (regional or local "horizontal" flow) could possibly be displayed by geochemical methods if longer experiments could be undertaken, especially for the wells of moderate salinity, because analytical problems could be solved more easily.

### CONCLUSIONS

The variations of the chemical composition of three geothermal wells were monitored carefully over a year or more and if we except Fontainebleau, the variations are very small (< 3%). This study has been possible because analytical methods for the determination of Cl,  $\text{SO}_4$ , Mg, Ca, Na and K

have been improved. The techniques involved are independent, i.e. chemical interferences can hardly explain the observed correlations between the concentrations of some elements, and consequently we believe that they are significant. Despite the fact that greater precision is needed for Na and K, it is remarkable that their variations often correlate well with those of other species ( $\text{SO}_4$ , Cl, Mg or Ca).

Several mechanisms can account for the modification of the chemistry of the fluids at Fontainebleau, Créteil and Coulommiers. A complex and permanent disequilibrium of the hydrodynamics of the wells is probably due to changing conditions of exploitation, which are adapted to the external requirements for heating. Examination of the chemical data permits to conclude that the variations of the pumping rate play a major role. Slight differences in the chemistry of the fluids produced by the association of several strata are assumed. In contrast the gradual evolution of chemistry with time (on a one year scale) is unnoticeable. Though evidence exists for a "rapid" horizontal circulation of the fluid in some parts of the basin, the chemical changes induced on the human scale are negligible compared to analytical uncertainties. Other experiments, such as the use of tracers, are required to monitor this kind of circulation. Nevertheless, the vertical zonation of the wells that is observed for chemistry as well as for lithology, is expected to have a marked influence on the concentrations of highly reactive species (iron and sulfide, e.g.).

This kind of geochemical method, based on wellhead sampling can be useful for the knowledge of the geothermal reservoir and to detect vertical heterogeneities, even when downhole sampling cannot be carried out.

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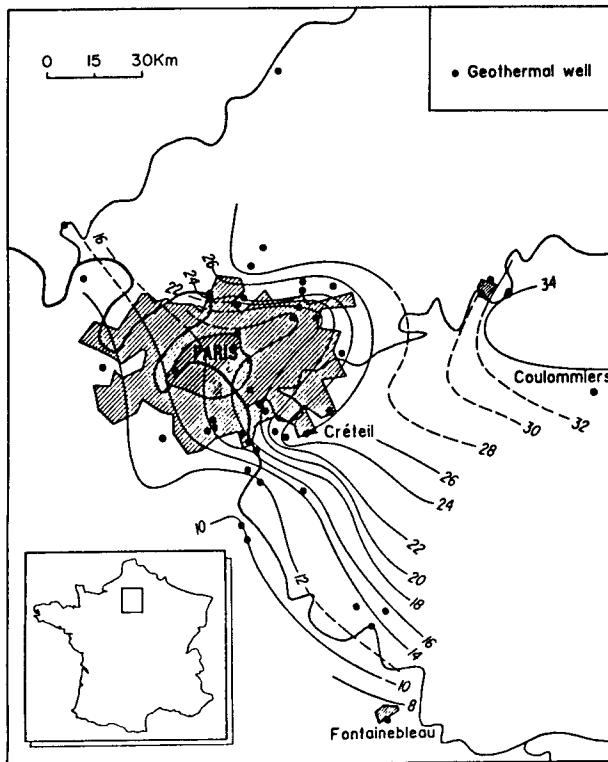


Figure 1 : Location map of the geothermal wells in the Paris basin.  
-12- : isosalinity Curves obtained after geothermal and oil wells data.

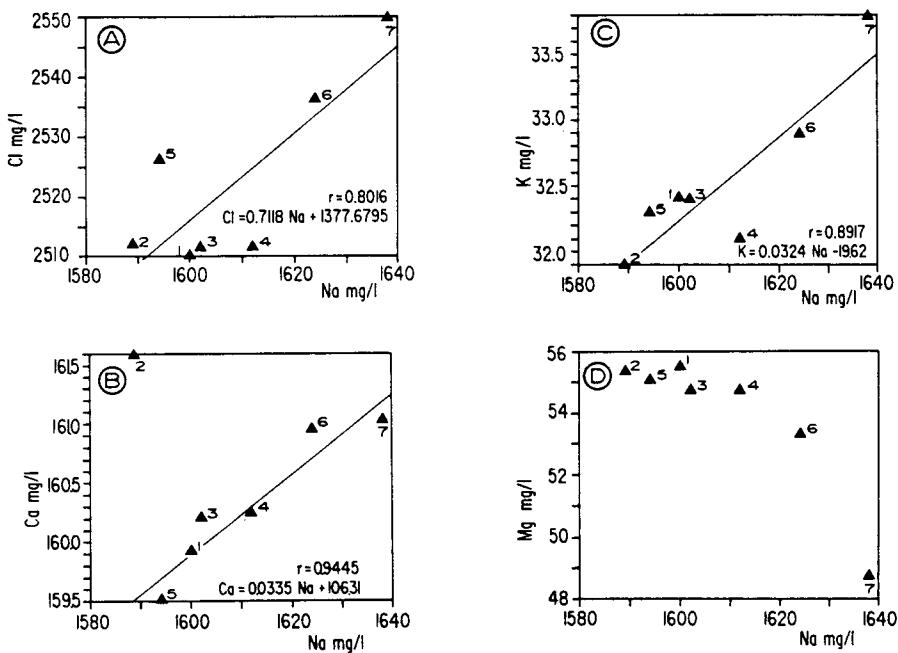


Figure 2 : Fontainebleau. Variation diagrams for Cl, K, Ca and Mg relative to Na during one year - Results are consistent with a mixing model - Numbers represent sampling dates : 1=June 1986 2=Aug 1986 3=Oct 1986 4=Nov 1986 5=Nov 1986 6=Feb 1987 7=Apr 1987 8=May 1987.

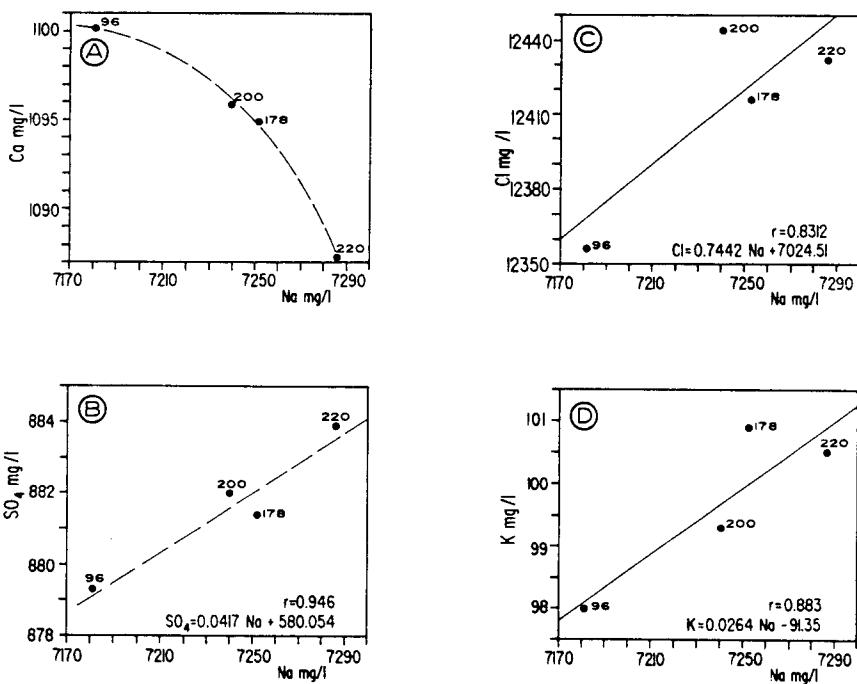


Figure 3 : Créteil. Effects of variable pumping rates (m<sup>3</sup>/h) on Ca, Cl, SO<sub>4</sub> and K versus Na content.

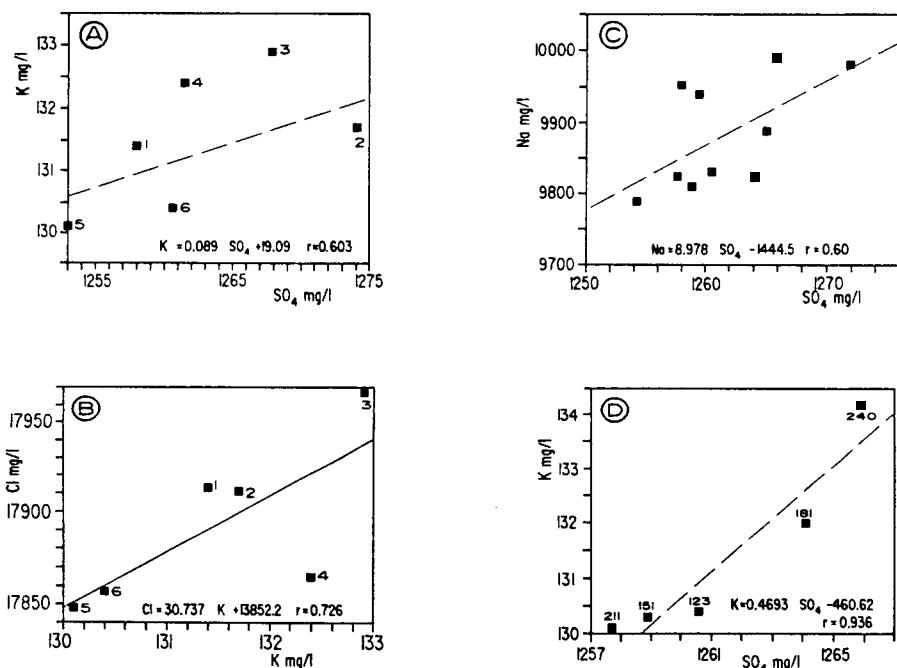


Figure 4 : Coulommiers.

(A) and (B) Effects of time on the variations of K and Cl relative to SO<sub>4</sub> and K

1=Aug 1985 2=Aug 1986 3=Dec 1986 4=Dec 1986

5=Apr 1987 6=May 1987

(C) Correlation between Na and SO<sub>4</sub> - All results are from May 1987 with various pumping rates.

(D) Effects of pumping rates on K versus SO<sub>4</sub> contents (May 1987) - Numbers represent pumping rates.