SALINIZATION PROCESSES IN THE CASTELLON PLAIN AQUIFER (SPAIN)

Fidelibus, M.D.*; Gimenez, E.**; Morell, I.**; Tulipano, L.***

* *Istituto di Geologia Applicata e Geotecnica*
  Facoltà di Ingegneria
  Politecnico di Bari
  70125 BARI
  ITALY

** *G.I. Medio Ambiente y Recursos Naturales*
   Departamento de Ciencias Experimentales
   Universidad Jaume I
   12080 CASTELLON
   SPAIN

*** *Dipartimento Idraulica Trasporti e Strade*
    Facoltà di Ingegneria
    Università degli Studi di Roma "La Sapienza"
    00184 ROMA
    ITALY

SUMMARY

A process of salinization due to marine intrusion has been detected in the detrital coastal aquifer of the Castellón Plain, especially in its northern and southern areas. This intrusion has been caused by overexploitation of the areas in relation to the low rate of recharge. Hydrogeochemical study reveals that the chemical characteristics of the analyzed waters originate from the mixing of three different water components: intruding sea water, fresh water from rainfall infiltration and saline water with a characteristic sulphate-calcium-magnesium facies, coming from border aquifers. This last important flow is locally regulated by the tectonic relations existing between the triassic formations, outcropping at the Plain border and constituting its substratum, and the plio-quaternary deposits forming the Plain. Given that this substratum often presents structural heights, the thickness of the superficial aquifer ranges from more than 200 meters in the central area to nearly 80 meters in the northern and southern part of the Plain. Where the thickness of the plio-quaternary materials is less there exists a good hydraulic connection between both aquifers. Basically the salinization detected in the aquifer is due both to a marine intrusion process and one of mobilization and withdrawal of deep flowing waters reaching the shallow aquifer because of overexploitation. The aim of this research is to establish a reliable hydrogeological model of this salinization process, involving also a modifying process such as cation exchange.

1. INTRODUCTION

The coastal Plain of Castellón (Fig.1) is an important agricultural zone with 85% of its area occupied by citric crops. Also, there is a great number of ceramic factories. The population of the area is about 300,000. In the North, superficial water from the Mijares river is used for agricultural practices, whereas in the rest of the area supply water is pumped from the plio-quaternary aquifer.

1: Gravels, conglomerates, sands and clays. 2: Limestones
3: Dolomies (including clays and gypsum) 4: Sandstones
5: Sandstones

1   PLIOQUATERNARY
2   CRETACEOUS+JURASSIC
3   UPPER + MIDDLE TRIASSIC
4   LOWER TRIASSIC
5   PALEOZOIC

(☆) Springs of Mesozoic aquifers
(●) samples Benicasim Sector
(■) samples Central Sector
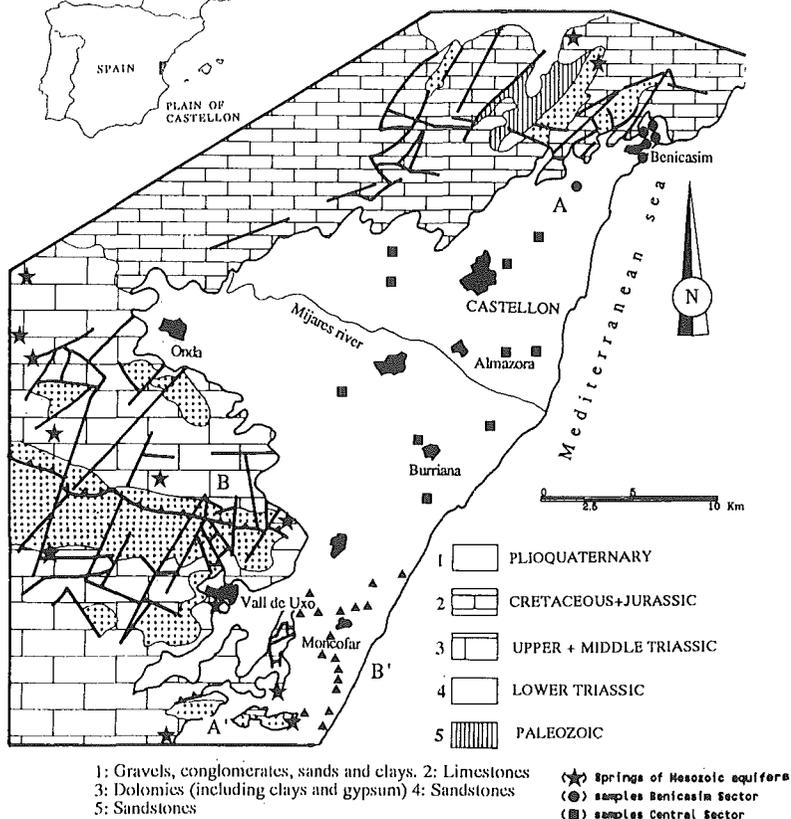(▲) samples Moncofar Sector

Fig.1. Geological map of the study area and location of sampling point

In the southernmost area (Moncófar) salinized water was found over 20 years ago. Several studies carried out in this area concluded that sea water intrusion due to overexploitation was at the origin of salinization [9]: actually the close study of the chemical characteristics of these waters emphasises that the processes which caused the salinization of this portion of the shallow aquifer are far more complex.

2. GEOLOGICAL AND HYDROGEOLOGICAL FEATURES

The plio-quaternary formation of the Castellón Plain, prevalently continental, is litho-logically constituted by gravel, wedge-shaped conglomerate and clayey layers irregularly distributed; this formation, whose thickness reaches up to 200 m, covers the mesozoic substratum of limestone, dolomitic limestone and sandstone. This mesozoic substratum outcrops at the border of the detrital aquifer, and consists of Triassic (Buntsandstein, Muschelkalk and Keuper facies), Jurassic and Cretaceous sediments. The Buntsandstein facies is formed of sandstone.

The sedimentation of the Muschelkalk facies occurred in a shallow seawater environ-ment; the frequent eustatic variations with sporadic intertidal phases produced, apart from the precipitation of limestone, the precipitation of gypsum and anhydrite. The rock under-went an epigenetic dolomitization to the extent that in fact, about 80% of this facies is markedly dolomitic, even though it shows signs of posterior calcitization [5]. Moreover a middle level of marnes with gypsum (of approximately 10 m) appears between the dolomitic limestones.
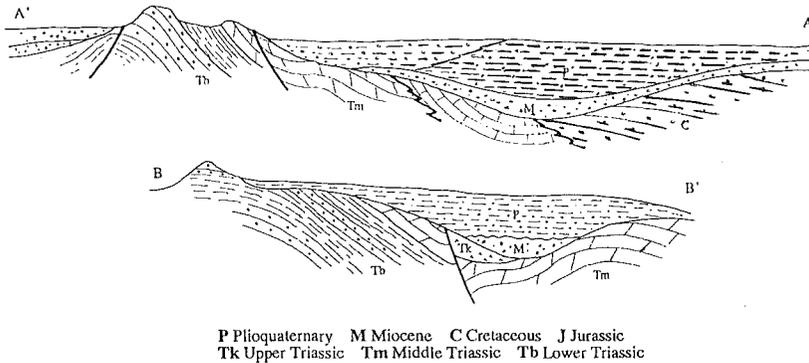

P Plioquaternary   M Miocene   C Cretaceous   J Jurassic
Tk Upper Triassic   Tm Middle Triassic   Tb Lower Triassic

Fig.2 Geological sections along lines A-A' and B-B'

The Keuper, sedimented subsequently to the Muschelkalk, in an evaporitic environ-ment, is constituted of clays, marnes and abundant gypsum. The limestone, marnes and dolomitic limestone of the Jurassic and Cretaceous ages, make up the remaining mesozoic materials.

Mesozoic formations have a clear Iberic Range alignment (WNW-ESE) with complex tectonic features. A set of faults more or less perpendicular to the structures breaks them, creating uneven blocks sunk in steps beneath the plio-quaternary materials. The thickness of the detrital material is not regular: both in the southern and northern areas it is only a few meters thick, with an irregular presence of substratum (cross-section A-A' and B-B' in Fig. 2)

The plio-quaternary aquifer can be considered as a multi-level aquifer because of the clay layers interbedded between conglomerates. Nevertheless, because of the hydraulic connection between levels and both lateral and vertical changes of facies, the aquifer can be considered as a single unit. Transmissivity values range normally from 3,000 to 6,000 m²/day and the storage coefficient varies between 5% and 10% [9].

The groundwater recharge arises from infiltration of rainfall (rainfall is about 470 mm/ year), lateral flow from the bordering aquifers and natural infiltration of superficial water, mainly coming from the Mijares river; in total it can be assumed that the recharge to the plio-quaternary aquifer is about $290 \cdot 10^6$ m³/year. The natural outflow occurs through concentrated coastal springs and diffuse flow into the sea (Fig. 3).
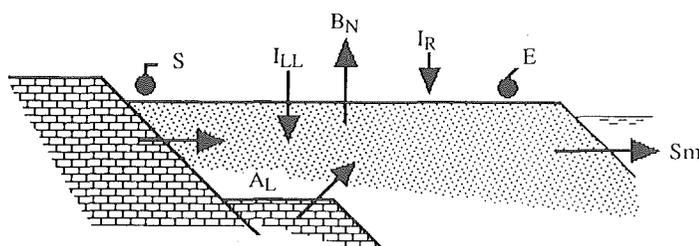

Fig. 3 - Hydrogeological scheme of Castellón Plain. Sm:subterranean flow to the sea; AL: lateral flow from mesozoic aquifers; BN: net abstraction; IR: infiltration from irrigation with superficial waters; ILL: infiltration of rainwater; S:springs ; E: drainage in wetlands

The groundwater of the Castellón Plain circulates in a prevalently orthogonal direction towards the sea, starting from hydraulic heads which, in the more internal zones, even exceed 100 m. a.s.l. and has a very high slope of piezometric surface of the order of 10%. The trend of the piezometric surface of Fig. 4(a), which refers to the year 1985, shows how in the southern zone of the aquifer, in particular between Villareal, Vall de Uxó and Moncófar there is still a notable piezometric drawing down which reaches values higher than 2 m. b.s.l. Some years ago, the concomitance of a succession of years of drought and an increase in extractions, had drawn down the piezometric surface in the same zone even more than 8 m. b.s.l.

As one observes from the diagram of Fig. 4(b) which regards the piezometric oscillations measured in a well of the Moncófar area, the maximum of the drawing down was registered in 1979. Starting from 1982, one can notice a slow but almost constant recovery in the piezometric level, which, at least for the well under discussion has by now reached "normal" levels, or rather, higher than the average sea level.
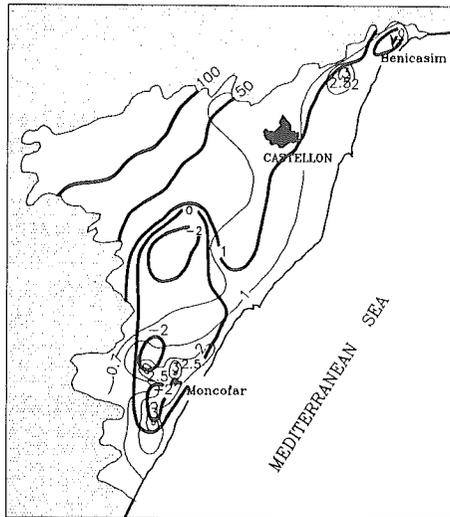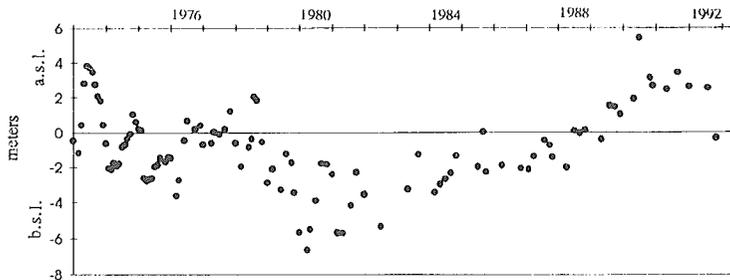
Fig. 4 - (a) Piezometric contour lines (m) (thick line) and salt content distribution (T.D.S., g/l, narrow line); (b) Trend of hydraulics heads in a well of the Moncófar area

As far as the hydrogeology of the outcrops of the mesozoic base surrounding the Plain is concerned, the formation of the Bundsandstein, made up of orthoquarzitic sandstone, can be considered as an aquifer with reduced permeability due only to fissures, while the Muschelkalk, at least in its lower part, can be considered as an aquifer with good permeability characteristics due to fissuring and karsting phenomena. The complex tectonic, especially at the southern border of the plain, has a decisive influence on the behaviour of the triassic aquifers; in fact they normally result isolated from the impermeable soils belonging to the higher and lower levels of the Bundsandstein and to the intermediate portion of the Muschelkalk besides the clayey materials of the Keuper. Without doubt, however, hydraulic connections may exist between the aquifers because of tectonic accidents. The Jurassic and Cretaceous rocks, outcropping in the Central-Northern area may constitute good aquifer levels when they are lithologically formed of limestone and/or dolomitic limestone; also these aquifers contribute to the lateral feeding of the Castellón Plain.

3. HYDROGEOCHEMISTRY

3.1. Hydrochemical characteristics

Considerations regarding the hydrochemical characteristics of the waters of the Castellòn Plain refer to samples taken from a network of 33 wells; their distribution over the territory is shown in Fig.1.

The contents in major constituents, represented on a Piper diagram, allow the differentiation of these waters into three main groups (Fig. 5):
Type 1) Sodium - chloride waters, corresponding to samples taken in the northern sector (Benicasim);
Type 2) Sulphate - bicarbonate - calcium - magnesium waters, corresponding to samples taken from the Central sector of the aquifer;
Type 3) Chloride - sulphate - calcium - magnesium waters, corresponding to the southern sector of the aquifer (Moncófar).
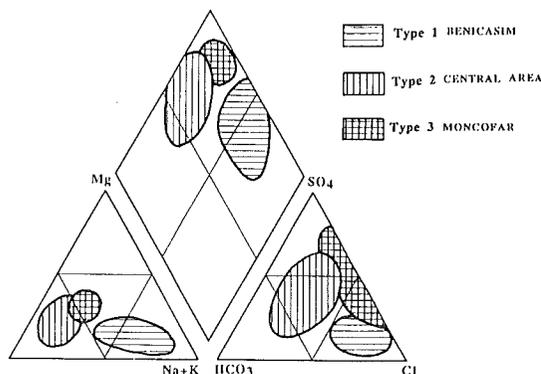

Fig.5 - Piper Classification.

The chemical characteristics of all of these waters definitely reveal the influence of a salinization process caused by intruding sea water. At first sight the characteristics of the waters may be described as resulting from the diverse influence of three different end-members: one component of sea water of a sodium-chloride type, one of feeding freshwater of a bicarbonate - calcium - magnesium type and the third, of a sulphate-calcium-magnesium facies. In Fig. 6(a) which shows the contents in SO_4^- with respect to those in Cl^-, one notes that all the waters fall within the field delimited by these three components. Considering SO_4^- as the conservative tracer of the influence of sulphate waters (low in chlorides and therefore with a high SO_4/Cl ratio) and Cl^- as the conservative tracer of mixing with seawater (characterized by a lower SO_4/Cl ratio), the fresh water-sea water alignment, along which the representative points of the waters of the Benicasim sector are found, clearly represents the only influence of intruding sea water on fresh waters; diversely all the waters of the Central sector of the plain, which follow the fresh water-sulphate water alignment and which result
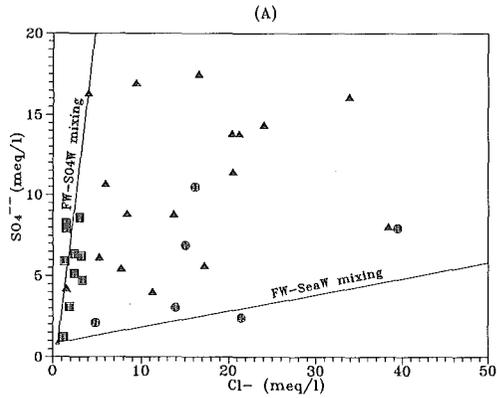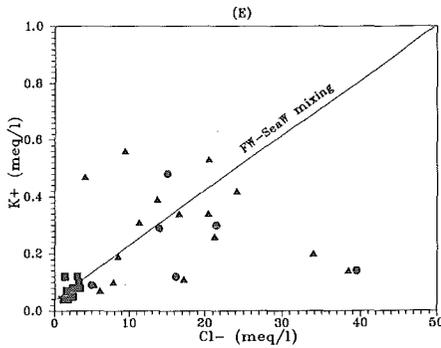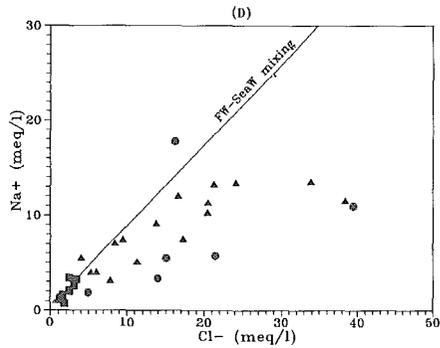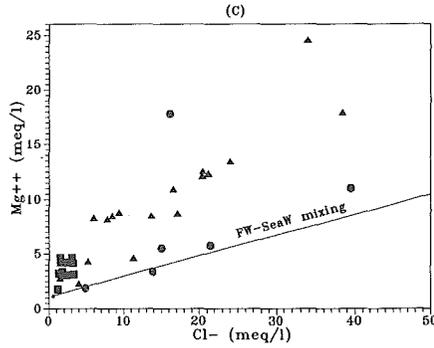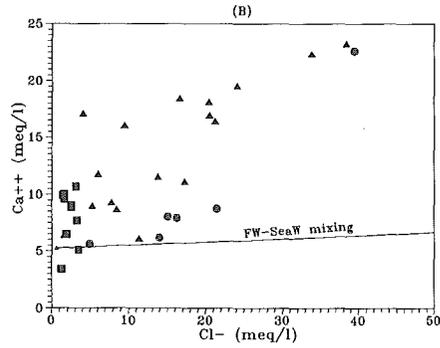
(A)

Fig. 6(a) — Chloride and sulphate concentrations in relation to the fresh water — sea water mixing line and sulphate water — fresh water mixing one

Fig. 6(b),(c),(d),(e) — Chloride contents versus major constituents concentrations in relation to the fresh water — sea water mixing line

slightly or not at all affected by salinization caused by sea water intrusion, show characteristics of mixing with waters which are rich in sulphates.

A third group of waters results from the concurrent effect of mixing with intruding sea water and sulphate waters. This last group of waters, whose representative points occupy intermediate positions, is almost entirely constituted of waters from the Moncófar zone. Therefore, at least in the more complex case of the Moncófar zone, a mixing of three different components is definitely present.

To recognise the relative influence of each end-member on the final composition of all examined samples, the real concentrations of each major constituent have been compared with those resulting from theoretical mixing between a representative sample of the fresh water component, (La Salud spring), and one of the salt component (seawater sampled off the Castellón Plain coast). With this aim the chloride ion, which is present in very limited quantities both in fresh and sulphate end-members, was chosen as a conservative parameter in the calculation of the theoretical mixing (closed system). The differences between the observed and expected concentrations are expressed as ΔIon (in meq/l): these result positive compared to the conservative mixing for Ca^{++}, Mg^{++} and SO_4^{--} (excess), while for Na^+ and K^+ they are either zero or negative (deficits) (Fig. 6(b),(c),(d),(e)).
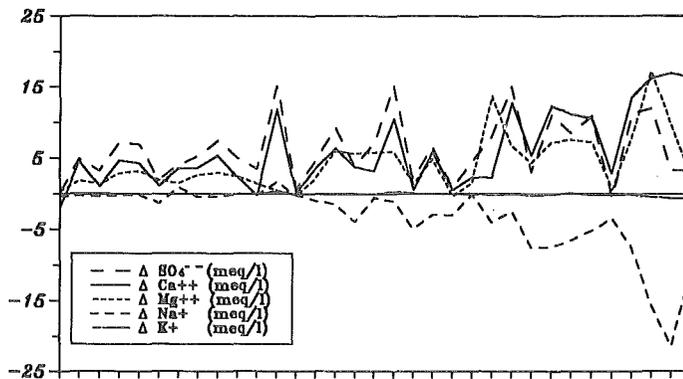

Fig.7 - Δ ions related to the ground waters of the Castellon Plain.
The data are ordered according to increasing levels of chloride concentrations.

As clearly appears from Fig. 7, to explain these differences, in most cases, one has to take into account the intervention of modifying phenomena and/or a mixing with a third type of water; the phenomena probably involved, which will be examined in more detail later on, are above all the processes of cation exchange.

3.2. Modifying phenomena: processes of cation exchange.

The values of ΔNa^+ and ΔK^+, progressively more negative in relation to the increase in the chloride content, and the considerably more positive values of ΔCa^{++} and ΔMg^{++} in more salinized waters, may be justified by a water-soil interaction process, that is by a cation exchange between waters salinized by sea water intrusion and clayey materials, present in abundance in the continental plio-quaternary deposits.

Similar cation exchange processes are described by various authors: Nadler et al.[10]; Howard et al.[7];Tellam et al.[14]; Custodio [3]; Ikeda [8]; Pascual et al.[11]. All of these authors refer to sea water intrusion processes accompanied by cation exchange prevalently involving the exchange $Ca^{++} \rightarrow Na^+$ with consequent enrichment in Ca^{++} in the ground waters.

To identify the type of exchangeable complex of involved clayey materials, some samples of clay, taken from various zones of the aquifer, were leached with a solution of ammonium acetate: the analyses of the resulting solutions show that Ca^{++} occupies an extremely high proportion (>80%) of the exchange sites, while the percentages of the presence of Mg^{++}, Na^+ and K^+ are respectively less important.

The same clays were put in contact both with brackish waters and sea waters with the aim of simulating the process of exchange: in both cases the waters resulted rich in Ca^{++}, with an equivalent loss of Na^+, K^+ and Mg^{++}. The Mg^{++}, however, represented only a tiny proportion in the process of exchange, so one can affirm, that the cation exchange produced in the clays of the Plain in contact with waters affected with salt water contamination, only significantly involves Ca^{++}, Na^+ and K^+.

However, when one proceeds to the comparison of ΔCa^{++} and the sum of the deficits $\Delta Na^+ + \Delta K^+$, to confirm whether this process is really responsible for the variations observed with regard to calculated theoretical values, one observes that the values of ΔCa are greater than the value of the exchange indicated by the sum $\Delta Na^+ + \Delta K^+$ (Fig. 8). Therefore an excess of Ca^{++} and Mg^{++} exists which cannot be justified only by the cation exchange phenomenon.
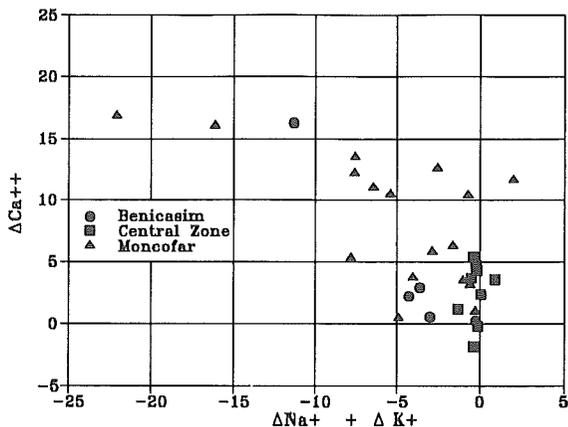
Fig. 8 - ΔCa^{++} versus $\Delta Na^+ + \Delta K^+$ values, indicating the feasibility of the ion-exchange process

3.3. Influence of the sulphate water component

The accordance of the variations (Fig.7) of ΔSO_4^{--}, ΔCa^{++} and ΔMg^{++}, confirmed by the correlation existing between ΔSO_4^{--}, ΔCa^{++} and ΔMg^{++} (Fig. 9(a),9(b)), especially observed in the waters sampled in the Moncófar sector of the aquifer,suggests a common origin for these three ions: the existence of a contribution of waters of a sulphate-calcium-magnesium type.
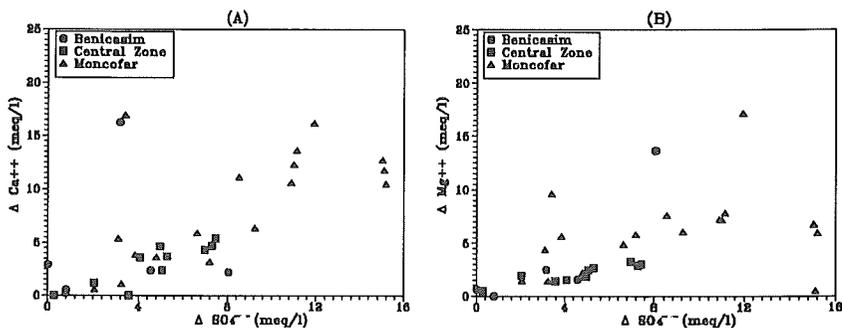

Fig. 9 - (a) Relationships between ΔSO_4^{--} and ΔCa^{++} values (b) Relationships between ΔSO_4^{--} and ΔMg^{++} values

The hypothesis that a part of the sulphate excess could have originated from fertilizers used in agricultural activities, as other authors have demonstrated [2],[4] has also been considered. For the examined area this hypothesis has to be disregarded as the predominant

cause of sulphate excesses due to the fact that in the zone the use of nitrogenous fertilizers is more prevalent than the sulphatic ones. The different origin of the sulphate excess is moreover demonstrated by the high ratio SO_4/NO_3 generally found in the examined samples, a ratio which may exceed the value of 10, if the concentrations are expressed in meq/l.

The lithological diversity of the formations which border the plain together with the complex structural characteristics, determine a great variety of situations which condition locally the chemical characteristics of ground waters reaching the plio-quaternary aquifer. In fact the three sectors result distinct in terms of both the thickness of the plio-quaternary formation and the lithology of the aquifers on the border. The contribution of the sulphate-calcium-magnesium waters has a greater effect on the waters of the Moncófar sector.

The Muschelkalk is possibly the only important aquifer which contributes an important flow to the plio-quaternary aquifer in this sector. The springs of this aquifer are chemically variable: in general they are of a bicarbonate-calcium-magnesium type, even though they often present high quantities of sulphates (Fig. 10(a)). The waters result undersaturated with respect to calcite and dolomite (Fig. 10(b)).
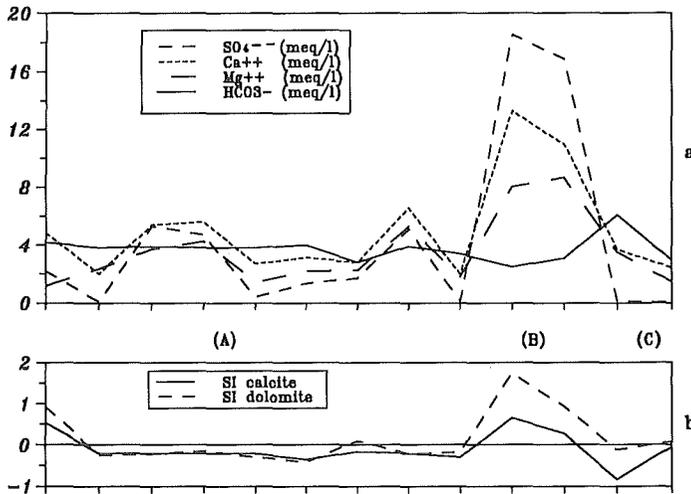

Fig. 10 - (a) Variations of sulphate, calcium, magnesium and bicarbonate concentrations relative to springs of mesozoic aquifers. (b) Variations of the calcite and dolomite saturation indexes relating to the springs of the mesozoic aquifers: (A) Muschelkalk springs (B) Springs influenced by Keuper formation (C) Buntsandstein springs.

Even though the Keuper is practically impermeable, the abundance of gypsum in the facies may have some influence on the chemical composition of the waters of the Muschelkalk and the Jurassic aquifers. In fact, in some contact springs one finds concentrations of $SO_4^=$ higher than 1000 mg/l, accompanied by high levels of Ca^{++} and Mg^{++} (Fig. 10(a)).

The data shown suggest that the dolomitic limestone of the Muschelkalk aquifer may represent an important source of magnesium and calcium. Given that gypsum is present, one can consider the possible interaction of waters rich in sulphate with the dolomitic aquifer: the reaction of dissolution of the dolomite, caused by the solution of gypsum followed by precipitation of calcite, may explain the genesis of the waters drained by the Muschelkalk springs; the presence of calcitization processes which followed the dolomitization of the rock [5] and the condition of undersaturation with respect to the dolomite of the spring waters, support this hypothesis, which is similar to that proposed by Hanshaw et al. [6], Plummer [12] and Wigley et al.[15].

In conclusion, the ground waters of the Muschelkalk aquifer can be representative of the sulphate-calcium-magnesium end-member present in mixing in ground waters of the Moncófar sector of the plio-quaternary aquifer. Depending on the local different contributions of the Muschelkalk aquifer, the ground waters in the Moncófar sector result characterized by different excesses (Δ) in Mg^{++}, Ca^{++}, $SO_4^=$.

4. CONCLUSIONS

It may be concluded that different processes determine the final chemical composition of the water flowing in the plio-quaternary aquifer, some of them being connected with the geochemical characteristics of the different hydrogeological environments involved, others intervening as a consequence of sea water intrusion induced by overexploitation.

The origin of the excess of $SO_4^=$ and Mg^{++} would therefore be related to the contribution of the Muschelkalk aquifer, while the excess of Ca^{++}, partly linked to the same origin, would result as being further modified by the processes of cation exchange forced by intruding sea water.

Despite all the involved uncertainties, related to other possible interferences on cation-exchange processes which originate from the presence in the ground waters of substances coming from agricultural activities (there is a high level of nitrate pollution owing to the widespread use of ammonium nitrate in the whole area of the Castellón Plain), the good correlation existing between the deficits in sodium and potassium (in relation to the simple mixing) and the quantity of calcium (exceeding the total coming from the mixing and from the dissolution of gypsum and carbonate rocks) (Fig. 11), would confirm the existence of cation-exchange phenomena between Ca^{++} and $Na^+ + K^+$.

The geochemical processes which concur to determine the final chemical composition of groundwaters, and the hydrogeological connections between the Castellón Plain aquifer and the border aquifers which feed it whether laterally (in natural conditions) or from the depth (in overexploitation conditions), are outlined. On this basis some conclusions, concerning the relative prevalence of the above-mentioned phenomena at the origin of the chemical composition of ground waters in the different sectors of the Plain, can be drawn.
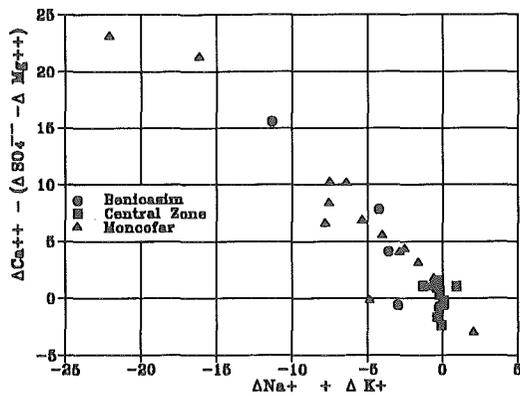
Fig. 11 - $\Delta Na^{++} + \Delta K^+$ and $\Delta Ca^{++} - (\Delta SO_4^{\cdot\cdot} - \Delta Mg^{++})$(in meq/l) relationships. - The ΔCa^{++} - - $(\Delta SO_4^{\cdot\cdot} - \Delta Mg^{++})$ value represents here the total ΔCa^{++} from which has been subtracted the calcium contribution coming from the sulphate water component.
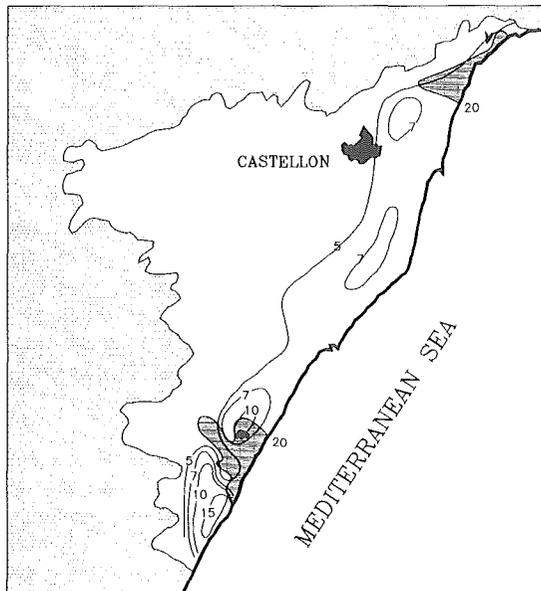

Fig. 12 - $\Delta SO_4^{\cdot\cdot}$ (meq/l) contour lines.-The grey zones represent the areas with chloride content greater than 20 meq/l.

These conclusions may be arrived at with the help of the trends of the contour lines of $\Delta SO_4^{\cdot\cdot}$ (tracer of the contribution of sulphatic waters) and of chloride (tracer of the sea water intrusion) (Fig. 12).

To the same end, the data relevant to the minor constituents such as lithium and

strontium are very useful. In fact these minor constituents reach, in the waters of the Plain, concentrations often much higher than those relating to simple processes of mixing with sea water. The particular tectonic situation of the zone, almost certainly at the origin of the thermal manifestations which may be found in the aquifers that border the Moncófar Plain (there are in fact springs which on emergence have temperatures of up to 60°C) and the diffuse presence of evaporitic materials, render plausible the high concentrations of lithium and strontium which have been observed ([1], [13]).
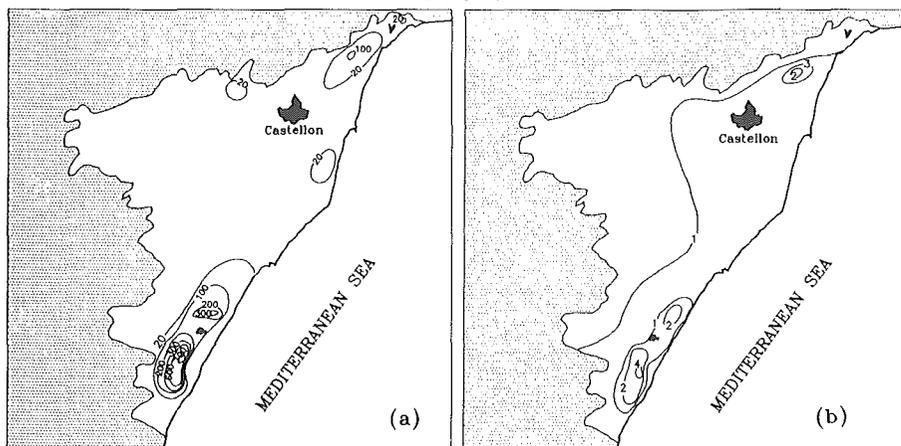

Fig. 13 - ΔLi^+(a)(in ug/l) and ΔSr^{++}(b)(in mg/l) contour lines.

The concentration of both increases with the increase of the excess of $SO_4^=$: Sr^{++} probably does not originate only from the dissolution of gypsum but certainly also comes from the incongruous dissolution of the carbonate matrix of Muschelkalk, while the Li^+ is more strongly linked to the manifestation of elevated geothermic gradients within the aquifers of the border. Then the distribution of the excesses of both the minor constituents in the ground waters of Castellón Plain (Fig. 13), represents a further tool for interpreting the complex hydrogeology of the region.

Ground waters circulating in the Benicasim sector show the intervention of a direct sea water intrusion which is superimposed to a limited contribution, probably only lateral, of sulphatic waters coming from the border aquifers. In fact they result of a chloride-sodium type, with sporadic high contents of sulphate (Fig.14(a)). The contribution of the sulphatic waters is also marked, in the waters characterized by the higher excesses of sulphate, by the presence of slight excesses of lithium and strontium.

Fresh ground waters characterized by a sulphate-bicarbonate-calcium-magnesium facies circulate in the central sector of the aquifer. They represent the final product of a mixing between very fresh waters and mineralized waters marked by higher sulphate contents; no
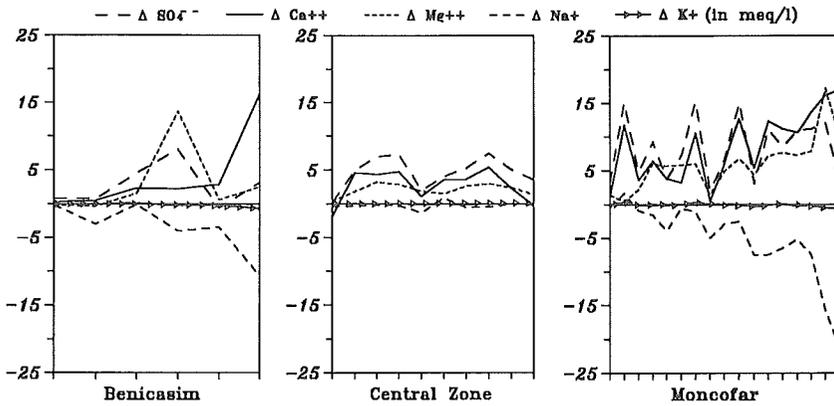
Fig. 14 - Δions related to the groundwaters of the different sectors.- For each sector the data are ordered according to increasing levels of chloride concentrations.

appreciable intervention of intruding sea water and of the relative modifying process of ion-exchange appears in the sector (Fig. 14 (b)). Therefore the main hydrogeological aspect of this sector is an appreciable contribution of sulphate-calcium-magnesium waters, that probably come from the depth, especially in the more coastal zones; the values of the excesses of strontium and lithium confirm these contributions.

The Moncófar sector presents the more complex situation: both the processes of a direct sea water intrusion and a notable contribution of sulphatic waters contribute to the final chemical quality (Fig.14 (c)); these waters are, in fact, of a chloride-sulphate-calcium-magnesium type. In this sector the excesses of sulphate, strontium and lithium reach maximum values; nevertheless it is more important to notice that their distribution over the territory points out that the origin of sulphate waters may be attributed to a heavy withdrawal directly from the depth related to, on the one hand, the presence of structural heights in the mesozoic substratum, and on the other, the strong drawing down in this zone due to overexploitation.

The processes of overexploitation are therefore at the origin of two concomitant facts whose reciprocal prevalence in the territory may reasonably be regulated from the local conditions of permeability characterizing the plio-quaternary aquifer along the coast. Where good conditions of permeability exist along the coast, the overexploitation determines a lateral intrusion of sea water; where instead the permeability, and therefore the level of communicability with the sea, is reduced, the drawing down resulting as a consequence of overexploitation determines the withdrawal of sulphate waters directly from the depth. Deep piezometers reaching the mesozoic aquifer which can concur the evaluation of the relationship between the hydraulic head of the plio-quaternary and the mesozoic aquifers are not available in the zone. Given, however, that the phenomenon of salinization and of the

contemporary mineralisation of sulphate has verified itself in the Moncófar sector in a very evident manner only starting from the years in which drought provoked the strongest drawings, one should consider that in normal conditions the hydraulic head of the plio-quaternary aquifer is prevalent over that of the deep system, while in conditions of overex-ploitation, the hydraulic head of the deep aquifer prevails over the depressurised superficial aquifer.

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