

Regional flow of intruding sea water in the carbonate aquifers of Apulia (Southern Italy)

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Apulian coastal carbonate aquifers suffer from salinization that only in the coastal areas is connected with modern sea water intrusion. Salt groundwaters sampled inland show chemical characteristics variably modified with respect to those of modern sea water. To the west of the emerged platform, carbonate formation, sunk as a graben, is covered by thick argillaceous deposits of Plio-Pleistocene age: salt waters deeply diagenised have been recognised there. Beside observation wells, only a few drillings reach salt groundwaters: information about their occurrence and mobility was thus indirectly obtained through the hydrochemical study of brackish coastal spring waters. Using major, minor and trace ions as natural tracers of the different salt water end-members, salt water components of the brackish coastal spring waters were hypothesised, thus allowing a scheme of the occurrence and the mobility of salt groundwaters within the Apulian territory to be outlined.

Geological and hydrogeological setting

The Apulian carbonate platform of Mesozoic age elongates from Gargano Promontory to Salentine Peninsula (Fig. 1). The present structural setting of Mesozoic carbonate series was originated by an ample synclinal which was later transformed, due to faulting, into a huge Horst, corresponding to the present outcropping formations, Gargano Promontory and the Murgia-Salento system. Faulting began during Cretaceous and the Horst reached an almost definitive order at the end of the tectonic phase which occurred between Pliocene and lower Pleistocene. To the W the Mesozoic rocks sank as a graben: the consequent Plio-Quaternary transgression filled the graben of mainly argillaceous sediments, having a maximum thickness of about 6000 m, in connection with the more depressed part of Mesozoic basement. While Murgia and Salento can be considered stable areas, the Gargano is still affected by active tectonics: the main fault which separates Gargano from Tavoliere (Candelaro fault) is seismo-genetic. The structural setting of the whole platform allows the identification of four hydrogeological units: Gargano, Tavoliere, Murgia and Salento (Fig. 1).

Gargano aquifer does not correspond to the whole extension of the Promontory, owing to the existence of carbonate facies almost impermeable, as limestone and marly limestone with interbedded flintstones, beside facies very permeable due to fissuring and karstification, constituted by limestone and dolomitic limestone (Cotecchia & Magri, 1966). Salt water of marine origin is found in coastal areas under fresh groundwater. In the central area of the Promontory fresh groundwater show piezometric heads between 30 and 50 m: salt waters should be at depths of about 1000 m under m.s.l. and more, however no drillings are available to control their occurrence, owing to high elevations (reaching 1000 m above m.s.l.). Two main aquifers are recognised in the Tavoliere. The Quaternary shallow porous aquifer, having a thickness of a few tens of meters, is limited at the bottom by the top of the Plio-Pleistocene formation: it consists of strips of regressive deposits (sands and conglomerate) and of alluvial material. Mesozoic carbonate rocks at the bottom of transgressive deposits constitute the deep aquifer, where groundwaters are in hydraulic continuity with those of Gargano and Murgia. Normally fresh or slightly brackish groundwaters flow in the shallower part of the basement, at depths lesser than a few hundred meters under m.s.l.: going inland, approaching the central part of foreland, groundwater becomes progressively more saline. Fresh groundwater is recognised only when the hydraulic head is able to maintain salt water at a depth lower than that of the basement top. The hydrogeological units of Murgia and Salento can be considered as a single aquifer, since great part of Murgia groundwater discharges into the Salento aquifer (Tulipano et al., 1990).

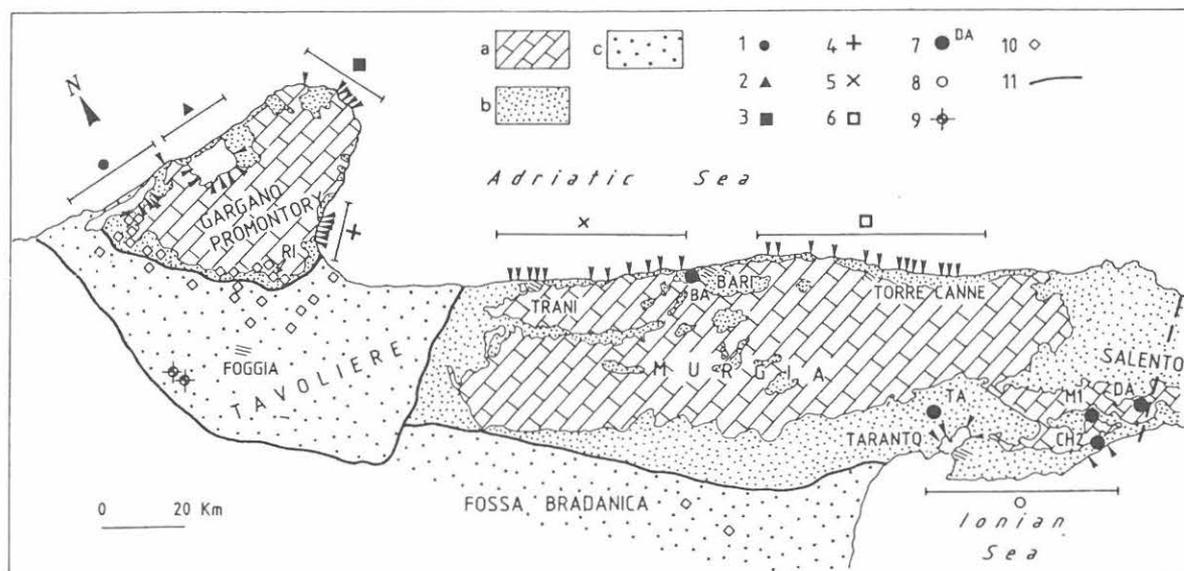


Fig. 1. Map of the Apulia region: a) outcropping Mesozoic carbonate formation; b) thin Quaternary deposits; c) Plio-Pleistocene formation of the Tavoliere and Fossa Bradanica; 1) Lesina springs; 2) Varano springs; 3) Vieste springs; 4) Manfredonia springs; 5) NW Bari springs; 6) SE Bari springs; 7) observation-wells; 8) Taranto springs; 9) oil-exploration wells; 10) drilled wells reaching the carbonate basement; 11) boundary of hydrogeological units.

In the Murgia fresh groundwater floats on salt water, certainly in the coastal zone, where it is recognised through observation- or deep wells. Inland, salt water should occur at depths of thousands of meters below sea level, due to the values of fresh water hydraulic heads, higher than 200 m. a.s.l.: however, permeability characteristics of rocks at these depths are unknown. In Salento fresh groundwater floats everywhere on intruding sea water, due to very low piezometric heads, not higher than 4 m above m.s.l..

Peculiar aspects of sea water intrusion in the territory

Previous researches (Tulipano & Fidelibus, 1984, Fidelibus & Tulipano, 1986 and 1990) dealt with the chemical characteristics of salt groundwaters sampled in Murgia and Salento carbonate aquifers. These salt waters represent diagenetically modified sea water: they are typically dominated by Na^+ and Cl^- , but exhibit Ca^{2+} enrichment and a variable degree of Mg^{2+} depletion with respect to modern sea water. The low Mg/Ca ratios (if no otherwise specified, concentrations in the ratios are expressed in meq/l), ranging from 4 to 1.5, allowed to differentiate the salt groundwaters from sea water, having average ratio of 5: the other major constituents showed less sensible changes, while minor and trace constituents as strontium and lithium were distinctly enriched (Fig. 2). ^{14}C contents (Fig. 3) measured in a few salt groundwaters of Apulia region indicated that the decrease of Mg/Ca ratio could be connected to increasing residence times (Fidelibus, 1992). Corrected ages were not calculated: however, if the 50% of ^{14}C is considered of biogenic origin, the apparent ages are of thousands of years (for example about 18.000 years for the CH1 well).

However these findings were not enough to define the mobility of salt waters within the considered carbonate aquifers. Thus an attempt was made in order to recognise if some of them took part in the coastal discharge, mixed with fresh groundwaters. Recognition of the characteristics of salt water component of coastal brackish springs of Murgia and Salento was attained using calcium, strontium and particularly lithium, as capable to trace the connection with the different salt end-members. These natural tracers showed the maximum range of variation in salt groundwaters compared to other constituents (Fig. 2). Ca^{2+} and Sr^{2+} gave only general indication, being involved in water-rock interaction due to mixing (Fidelibus & Tulipano, 1990). Lithium was considered, instead, to be a specific tracer able to differentiate the salt water end-members.

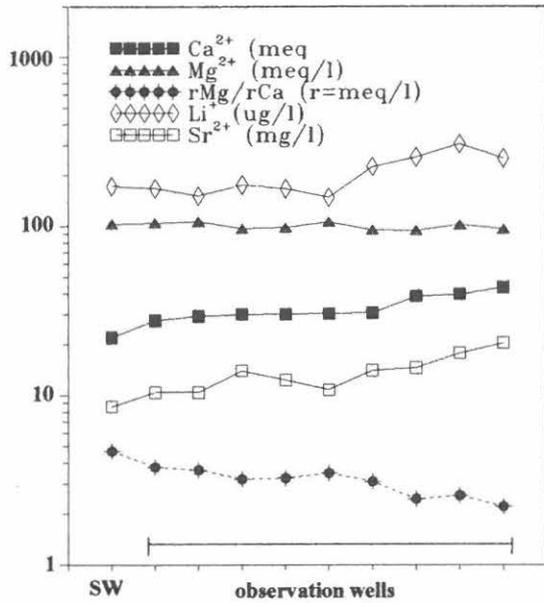


Fig. 2. Variation of major and minor ions concentrations (normalised to 19,000 ppm of chloride) and Mg/Ca ratio in salt groundwaters sampled in Murgia and Salento aquifers with respect to sea water.

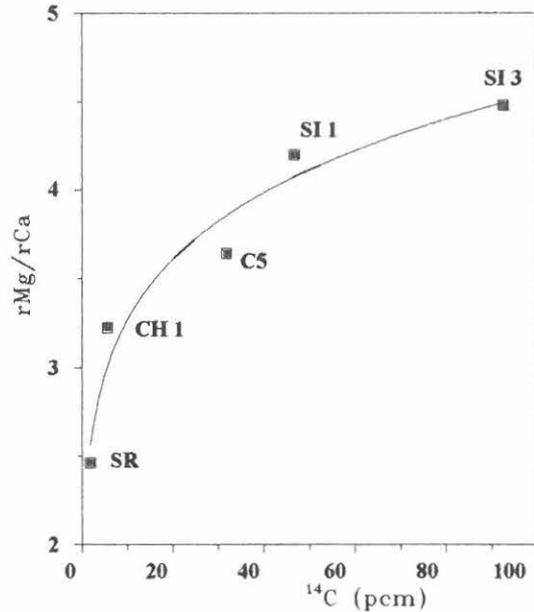


Fig. 4. Cross plot of rMg/rCa (r stands for meq/l) versus ^{14}C contents for some salt groundwaters sampled in the observation wells of Salento aquifer.

A salt water component older than modern sea water could be ascribed to most of Murgia springs, while almost all the coastal springs of Salento Peninsula exhibit a salt water component quite similar to sea water. The study of a few coastal springs discharging near to the submerged part of Murgia carbonate formation, implied that a salt water more ancient than those already known, should be involved in the mixing. Joined interpretation of both the geographic distribution of salt groundwaters of different age and the recognition of different salt water components in the brackish springs, allowed to put forward initial hypotheses upon the underground pathways followed by sea water from intrusion fronts to the coastal discharge in Murgia and Salento aquifers (Fidelibus & Tulipano, 1986 and 1990).

Further information about salt waters was provided by the analysis of a sample coming from the shallower part of carbonate basement of Tavoliere close to Gargano unit. This salt water appeared to be the most drastically altered salt water found in Apulia: it showed extremely high Ca^{2+} enrichment and exhibit remarkable changes in some major and minor constituents. The very low value of Mg/Ca ratio occurred with appreciable depletion of sodium, magnesium, potassium and sulphate and the greatest observed enrichment in strontium and lithium. The hydrochemical study of the coastal brackish springs of Gargano (Fidelibus, 1992) established that most of them had a salt water component very similar to that sampled in the Tavoliere carbonate basement: the same salt water could satisfy the required characteristics of the salt water component hypothesised for the coastal springs of Murgia close to the boundary with Tavoliere and Fossa Bradanica. These last findings suggested more ancient waters than those found in coastal zones, and likely existing in the basement, could reach the coastal discharge, following pathways that presupposed very large distances to be covered.

Wells reaching the shallower part of the basement provide mostly fresh and brackish waters: unfortunately not enough facts are known concerning either the occurrence of salt waters in the deepest part of the carbonate basement or their principal chemical constituents. Only a few oil-exploration wells have seldom reached the basement, the interest of investigation being ordinarily limited to Plio-Pleistocene formation due to the presence of oil or gas reservoirs: consequently, just a few data on salinity are available. Waters found between 1000 and 2000 m in the basement showed salinity in the range 20-30 g/l. Even if waters have been found in oil drilling operation, normally sampling conditions are unknown: given that innumerable possibilities exist for errors in sampling of this sort, the only two chemical analyses available must be considered with caution.

The hypothesis which will be discussed, is that salt waters existent into the carbonate basement of Tavoliere and Fossa Bradanica could actively mix with fresh waters of outcropping aquifers, at least in the zones close to the outcropping formation. The study aims at recognising the role played by these fluids in the salinisation of coastal springs, in order to contribute at clarifying, on a regional scale, the complex behaviour of all the salt water end-members.

Data presentation

The study is based on the chemical analyses of salt and brackish waters sampled in the whole Apulia region. Salt water samples ($Cl > 300$ meq/l) are represented by: (1) sea water of the Adriatic and Ionian side sampled far from the coast; 2) salt groundwaters from the observation-wells pertaining to the Murgia aquifer (namely TA, SR, CH2, M1, DA, BA) and 3) salt groundwaters from drilled wells reaching the carbonate basement of Tavoliere close to Gargano unit (RI, PG). One salt water sample (L1) comes from the carbonate formation reached by an oil-well at 1600 m of depth in the Tavoliere; another salt water sample (MZ1) comes from the sandy Pliocene levels intercepted in the 1172-1213 m of depth range in a close oil-well. For these last samples no information about minor and trace elements is available. Brackish groundwaters were sample in some wells reaching the shallower part of carbonate basement.

Furthermore, waters from numerous brackish coastal springs have been sampled. Springs outflowing along the Gargano coastline belong to four main groups, namely Lesina, Varano, Vieste and Manfredonia (Fig. 1), having a total discharge rate of $5 \text{ m}^3/\text{sec}$. Salinity ranges from 0.5 to 14 g/l. Temperature ranges from a minimum of $14 \text{ }^\circ\text{C}$ for the Varano springs to maximum values of $27 \text{ }^\circ\text{C}$ of some springs of Lesina group. Coastal springs outflowing along Adriatic and Ionian coastlines of Murgia region are divided in three main groups, Bari NW, Bari SE and Taranto (Fig. 1), which include, respectively, the big concentrated springs of Trani, Torre Canne and Taranto. Average total discharge rate of concentrated springs is higher than $5.5 \text{ m}^3/\text{sec}$: this figure do not takes into account submarine and minor spring discharge. Salinity ranges from 2 to 21 g/l and temperature from 17 to $19 \text{ }^\circ\text{C}$. Southernmost coastal springs of Salento aquifer, due to a little involvement in coastal discharge of salt waters different from modern sea water, will not be included in the study.

Chemical characteristics of salt waters in relation to their diagenetic history.

Fig. 4 shows the cross-plots of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Li^+ , Sr^{2+} , SO_4^{2-} , HCO_3^- versus Cl^- for coastal springs waters, brackish and salt groundwaters and modern sea water. Because of its generally conservative behaviour, chloride has been used to infer the origin of the waters. The salt waters exhibit distinct behaviour: dispersion in the diagrams defines the domain of the possible end-members of the mixing.

Salt waters from observation-wells show a general Ca^{2+} enrichment (Fig. 4a) and Mg^{2+} and K^+ depletion (Fig. 4b and 4d), while sulphates are only occasionally depleted (Fig. 4e). Salt waters from carbonate basement and from Pliocene sands show marked chemical variation with respect to sea water: they show Mg^{2+} , K^+ and SO_4^{2-} depletion and Ca^{2+} and HCO_3^- enrichment. Na^+ depletion is observed in RI and L1 samples from carbonate formation, while MZ1 in Pliocene sands shows higher Na/Cl ratio with respect to sea water. The enrichment and depletion of major, minor and trace constituents follow the tendency of more striking changes usually recognised for the same constituents in subsurface waters of marine origin enclosed in different sedimentary rocks of ancient basins (Chave, 1960). Major reactions recognisable as responsible of salt waters diagenesis are: (a) Ca^{2+} - Mg^{2+} exchange due to water-carbonate rocks interaction, (b) Na^+ - Ca^{2+} or Na^+ - Mg^{2+} base exchange and (c) SO_4^{2-} reduction.

In carbonate environments, simultaneous enrichment of Ca^{2+} and depletion of Mg^{2+} have been explained as mainly due to water-rock interaction processes as dolomitisation, dissolution and

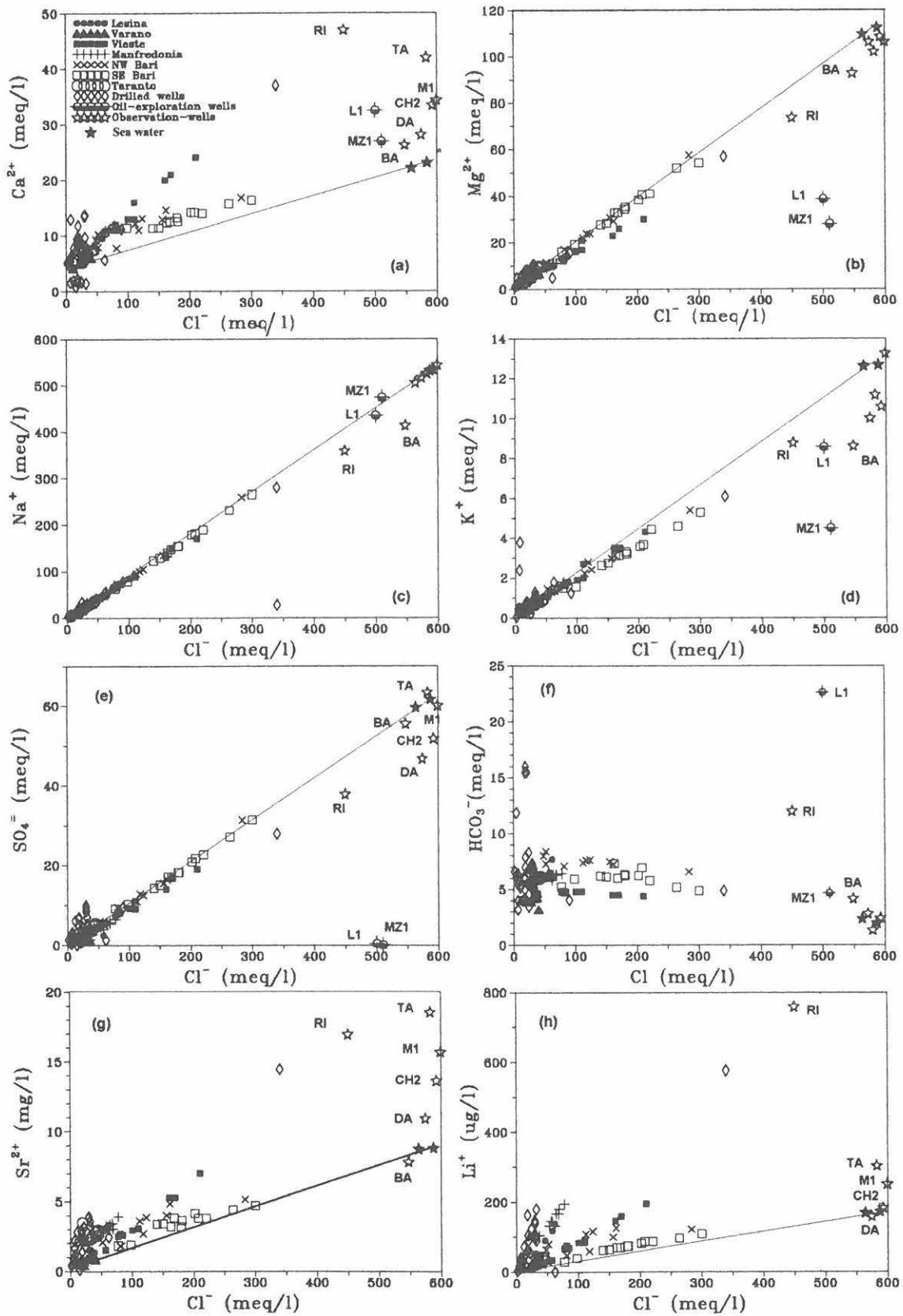


Fig. 4 - Cross - plots of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , HCO_3^- concentrations versus Cl^- contents for the coastal spring waters, brackish and salt groundwaters, and sea water. Lines stand for fresh water-sea water conservative mixing.

precipitation (Tulipano & Fidelibus, 1984, Fidelibus & Tulipano, 1986). Ca^{2+} - Mg^{2+} exchange reaction (dolomitisation) has been reported as cause of Mg/Ca ratio decrease in salt waters of ancient carbonate basins (Land, 1987): progressive decrease of Mg/Ca ratio was observed according to increasing age of aquifer rocks. The same reactions can also take place in brackish conditions (Folk & Land, 1975, Hanshaw et al., 1971, Matthews, 1971, Magaritz et al., 1980). Land (1987) stated that the decrease of Mg/Ca ratio is controlled by equilibrium between calcite and dolomite and is strongly dependent on temperature.

Sulphate reduction clearly affects salt waters of CH2, DA and RI wells. The average SO_4^{2-} /Cl ratio (Fig. 4e) of modern sea water is 0.1, while in subsurface waters of ancient basins it rarely exceeds 0.07 (Chave, 1960): according to this values, old salt waters of L1 and MZ1 oil-exploration wells have very low sulphate concentration, respectively of 20 and 4 mg/l. SO_4^{2-} can be reduced by anaerobic bacteria at temperatures lower than 80°C, while thermo-chemical reduction prevails at higher temperatures. In these processes CO_2 and H_2S are produced: salt waters from Tavoliere basement near Candelaro fault (RI) show very high bicarbonate concentrations (Fig. 4f) and, in the same zone, recurring presence of H_2S is observed in connection to the highest temperatures. The reduction process can produce either high or lower pH, depending on conditions and materials involved. A reductive environment and a pH decrease should favour dissolution of carbonate minerals: this way sulphate reduction could be ascribed of further changes of Mg/Ca ratio.

The feasibility of Na^+ - Ca^{2+} or Na^+ - Mg^{2+} base exchange was demonstrated in the coastal carbonate aquifer of Garraf by Pascual & Custodio (1990). Nadler et. al (1980), following laboratory experiments, stated that small amounts (a few percent) of clay in the carbonate rocks could be sufficient to produce appreciable changes in Na^+ , Ca^{2+} and Mg^{2+} concentrations in salt waters by base exchange. The wells BA and RI show in fact appreciable depletion of Na^+ . Moreover, K^+ depletion is generally observed. MZ1 sample, from Pliocenic sands, shows the maximum depletion; in the same sample, as well as in the L1 sample from the upper part of the deep carbonate basement, very high depletion of Mg^{2+} is detected (Fig. 4b). K^+ and Mg^{2+} depletion can be probably put in connection with diagenetic conversion, due to compaction of buried sediments, respectively of montmorillonite to illite and kaolinite to chlorite: it would mean that the effect of processes taking place in the transgressive deposits surrounding carbonate reservoirs might be felt in adjacent formations. Pelitic or siltitic-argillaceous levels, sometime of appreciable thickness, have been found within the carbonate Apulian formation. Furthermore, *terra rossa*, originated by alterations of limestone and constituted mainly by kaolinite and enriched with iron and aluminium hydroxides, is disseminated in cavities and fractures of the whole carbonate platform. A few stratigraphies of wells drilled in the basement in the SE part of Fossa Bradanica show argillaceous materials in the fractures. This way clays can be considered as responsible of part of observed chemical variations.

Sr^{2+} and Li^+ are abundant in all analysed salt waters. Sr^{2+} content (normalised to 19.000 ppm of chloride) in sea water is of 7 to 8 ppm, while salt waters show higher normalised values (maximum 19 ppm). Sr/Cl ratio in subsurface waters of ancient basins is always higher than that of modern sea water: however, the increase in strontium is sometimes higher than could be justified by dissolution of carbonate, unless, as observed in fresh karst groundwater (Tulipano et al., 1990), strontium concentration rises in liquid phase at each dissolution-precipitation cycle, owing to incongruent dissolution of strontium-rich skeletal aragonite.

Lithium is commonly enriched in sampled salt waters: RI sample shows lithium enriched up to 700% with respect to sea water. A very low Li/Cl weight ratio ($\cong 10^{-6}$) characterises modern sea waters, while in many oil-field waters the ratio increases up to the value of 10^{-3} . Lithium cannot enter the lattice structure of the minerals of other alkali-metals, thus its presence in carbonate can only be linked to clay fraction. Clay minerals selectively remove lithium from natural waters, becoming lithium-enriched: however lithium is unstable in the lattice structure due to its charge. A small rise in temperature is enough to cause lithium to leave the mineral: a very small difference in temperature at which the rock-water interaction takes place brings about an increase of lithium content in water of a factor of 100 to

10.000 times, allowing to consider lithium an useful pathfinder in hydrogeochemical exploration of hydrothermal systems (Bronzi et al., 1973). Contents in thermal waters are in fact extremely high: 1000 ppb are normal for thermal springs, reaching 10 ppm as well. Besides temperature, other processes are likely to produce an increase of lithium content in groundwaters of sedimentary basins: for instance, laboratory experiments (Kharaka et al., 1973) indicated that, under compaction, the filtering through clays, acting as semi-permeable membranes, could produce squeezed fluids selectively richer in lithium than hyper-filtrate solutions, being lithium the species which passes preferentially with respect to the other monovalent and divalent cations.

The significance of chemical diagenesis seems roughly in relation with the increasing sampling depth and/or the temperature: salt waters in the carbonate basement or in the transgressive deposits surrounding carbonate formations show the more remarkable modifications.

Recognition of salt water component in brackish spring waters

Concentrations of major, minor and trace constituents were measured in coastal spring waters and compared with those in modern sea water, brackish and salt groundwaters. As shown in Fig. 4, the cross-plots of Ca^{2+} , Li^+ , Sr^{2+} versus Cl^- yield data arrays which fall above the Ca-Cl, Li-Cl and Sr-Cl trends expected for waters derived from dilution of sea water. Cross-plots of Mg^{2+} , Na^+ , K^+ , SO_4^- versus Cl^- show data arrays which fall under or on the respective dilution trends. The more diluted spring waters can barely be observed at the scale of the graphs: however, a distinct behaviour can be noticed for the springs of high salinity, belonging to two different data arrays, roughly identifying the Gargano and Murgia springs. For sake of clarity the springs pertaining to the two hydrogeological units will be discussed separately.

Gargano springs follow a general trend which inclines to RI water characteristics. Enrichment and depletion calculated for major, minor and trace constituents with respect to concentrations determined by conservative mixing were considered meaningful when higher than respective analytical error. The deficits and the excesses, expressed as $\Delta_{\text{ion}} = C_m - C_{\text{ex}}$ (C_m = measured concentration and C_{ex} = concentration expected by fresh water-sea water conservative mixing) are shown in Fig. 5a and 5c: data are ordered, within each spring group, according to increasing TDS. Almost all springs show changes in major constituents (Fig. 5a) in the same direction of the modifications observed in the salt water sampled in the carbonate basement (RI well) and the changes appear to be, in general, and within each group, in accordance with salt content increase. Δ_{ions} of the more diluted spring waters are not easily decipherable: at very low salinity, oscillation of the concentration of the real fresh end-member with respect to the chosen one, prevails on the effect of mixing; moreover Δ_{ions} include the effects of water-rock interaction processes brought into action by mixing. This way the salt water component of Varano Lake springs, due to very low salinity, cannot be easily outlined: Δ values of most elements are only slightly higher than analytical error. However, the tracing effect of a salt end-member deeply modified predominates at higher salinity. In Fig. 5c lithium and strontium excesses rise according to the salinity increase within each group (with the exception of some springs of Lesina group); however, lithium highest enrichment is observed in some Lesina and Manfredonia spring waters, having a lower salinity with respect to Vieste springs. Temperature variations are in accordance with lithium changes.

Murgia spring waters show less remarkable ion enrichment and depletion with respect to those observed in Gargano (Fig. 5b and 5d): Δ values are shown following the geographical order, going from NW Bari to Taranto. Several Δ_{ion} were not considered, since of the same order of related analytical error. The Bari SE group shows very light depletion in magnesium and sulphates, being calcium enrichment practically constant while salinity markedly varies; the same occurs for lithium and strontium excesses. On the contrary, the Bari NW and Taranto spring groups show calcium excess and sodium depletion in accordance with salinity variations: lithium and strontium follow salinity as well. The Bari NW group evolves from NW to SE showing, in the central springs, the most remarkable effects of an altered salt water; Taranto springs show enhancement of the ion excess and depletion

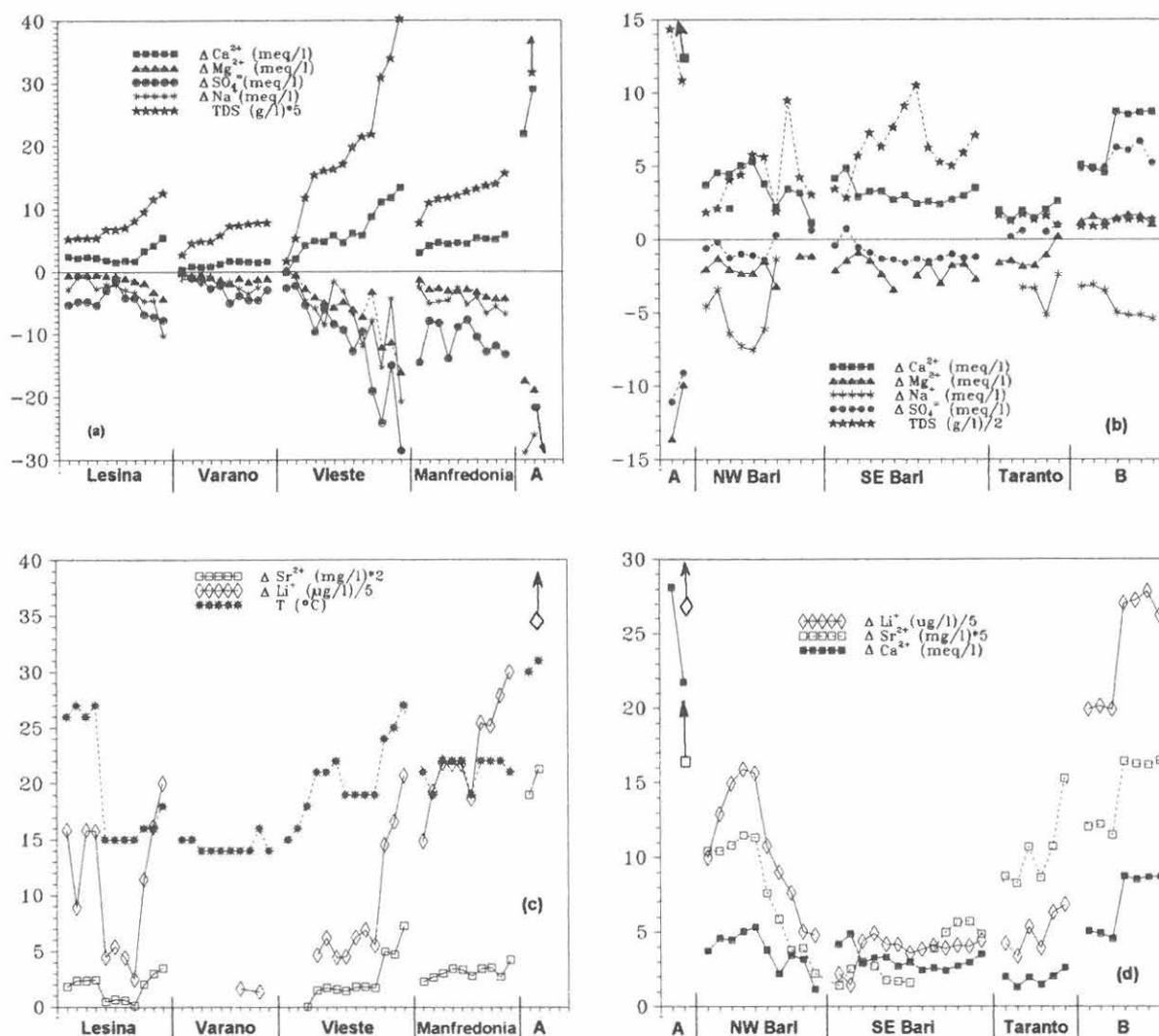


Fig. 5. Enrichment and depletion related to major (a) and minor constituents (c) for coastal spring waters of Gargano Promontory with respect to conservative mixing between fresh and sea water (zero line); data are ordered within each spring group according to TDS increase; A: salt waters of RI well. - (b) and (d) refer respectively to enrichment and depletion of major and minor constituents for coastal spring waters of Murgia aquifer; data are shown in geographical order; B: brackish waters of drilled wells of carbonate basement of Fossa Bradanica.

approaching to the Fossa Bradanica border. In Figs. 5b a 5d the first two samples represent the salt waters sampled in the basement of Tavoliere, while the last seven samples represent brackish waters sampled in the basement of Fossa Bradanica: both groups of waters show an outstanding excess of lithium and diagenetic modifications amplified with respect to those observed in the NW Bari and Taranto spring groups.

Conclusions

Some conclusions can be drawn on the basis of chemical data interpretation. The whole Apulia territory hosts different types of salt waters which can be grouped in three broad families. The first family includes sea water of recent intrusion which is recognised in limited coastal areas of the carbonate aquifers (Fig. 6). The second family gathers the salt waters of ancient intrusion which diagenesis developed essentially in a carbonate environment: mainly calcium, magnesium and strontium concentrations turn out modified with respect to sea water, due to water-rock interaction, roughly being Mg/Ca ratio decrease and strontium enrichment in connection with increasing residence times: this family should occupy a great part of the Murgia aquifer and, even if not directly recognised, in Fig. 6 its presence is outlined also in its central part. The third family differentiates from the second

owing to larger diagenetic changes of chemical composition with respect to sea water: all ions are involved and, besides the interaction with carbonate rocks, interaction with clay sediments is needed to justify part of the observed chemical changes. Very old salt waters, having variable chemical characteristics, belong to this family, and they are supposed to occupy all carbonate basement sunk under Tavoliere and Fossa Bradanica Plio-Pleistocene sediments. These salt (and brackish) waters of the basement show variable, but outstanding, enrichment in lithium.

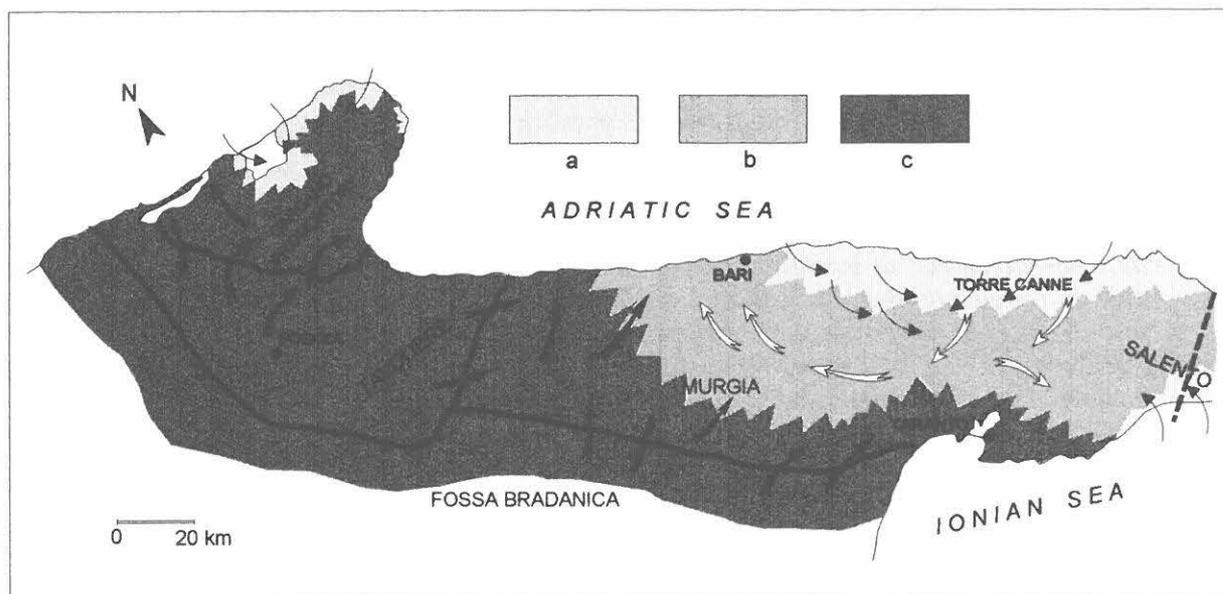


Fig. 6. General outline of the distribution of sea water of modern intrusion (a), sea water of ancient intrusion (b) and very old salt waters of marine origin (c). Arrows indicate the more probable direction of the migration of the different salt waters.

The effects of the involvement of the salt waters deeply modified belonging to the third family are chiefly recognised on brackish waters of coastal springs discharging close to the contacts between the carbonatic formations and the Plio-Pleistocene argillaceous deposits (namely on Lesina, Manfredonia, NW Bari and Taranto spring groups). If only slight, but significant, differences on the characteristics of salt water component are recognised as far as major constituents are concerned, when lithium excesses are evaluated, a more clear distinction of the different situations is obtained.

At the contact between Gargano and Tavoliere, along Candelaro fault, outstanding and localised increases of geothermal gradient (up to 10 °C/100 m) have been recognised by numerous investigations. Part of Lesina and all Manfredonia springs show a remarkable enrichment in lithium, according to the temperatures of the spring waters (of 27 °C maximum): this can be explained by the influence of convective upward flows, rising through the tectonic fault, which convey towards spring discharge deep salt waters enriched in lithium. The influence of these upward flows is not recognised in the Varano lake springs, which are probably slightly salinised due to direct sea water intrusion. Even though the salt water component of Vieste springs, which locate far from the fault, could be considered deeply modified by major chemical data, it is not marked by high lithium excess: this should mean that salt waters present in Vieste brackish springs do not come from the basement, being their diagenetic environment closer to the discharge zones.

NW Bari springs show the clear mark of a salt water similar, as diagenetic modifications on major constituents are concerned, to that involved in the Gargano springs: lithium enrichments are here, in absence of geothermal anomalies, in accordance with total salt increase, indicating an homogeneous old salt end-member to be involved in spring discharge. Approaching Bari town, due to the increasing influence of recent intruded or slightly modified sea water, a progressive decrease of the lithium effect is noticed.

At the contact between Murgia carbonate formation and Fossa Bradanica sediments, high lithium excesses are found in the brackish water of the basement and, in minor extent, in Taranto spring waters. No information about deep salt waters of the zone is available. Extrapolation of the characteristics of analysed brackish waters to a higher salinity, leads to a salt end-member of Ca-Cl-SO₄ type. The possible existence of this type of salt water should be in accordance with the findings of geological exploration drillings which found thick Messinian gypsum strata on the top of carbonate basement in the Fossa Bradanica: these evaporite deposits should be able to originate Ca-Cl-SO₄ brines. As far as the brackish waters of the basement are concerned, they are naturally involved in the groundwater circulation of this part of Murgia aquifer, due to the accordance of their piezometric heads with regional piezometric trend, indicating the natural discharge of the groundwater towards the Taranto Gulf.

A hypothesis about mobility and flow direction of deep salt waters can be put forward on the basis of both the available data and the following considerations. When interpreting the characteristics of the various basement waters, it should be considered that thick argillaceous deposits are in contact with the carbonate basement rocks. In a sedimentary basin it can be assumed that the compaction of argillaceous sediments is the principal cause for flows which, in the course of geological periods, can move large quantities of water. The existence of such flows, caused by compaction in recent sedimentary basins, is evidenced, for instance, by the presence of super hydrostatic pressures in formation waters of sands surrounded by layers of clay. So, in the Plio-Pleistocene deposits of Tavoliere and Fossa Bradanica, compaction could be challenged for arising flow of interstitial solutions, which, due to intercommunicating porosity, could penetrate through the sedimentary rocks and thus participate in all diagenetic processes.

Besides the compaction by simple gravitational loading, a more drastic compression of the sediments can be produced by horizontal compressive stresses of tectonic origin: Hubbert and Rubey (1959) stated that water-filled clays or shales would respond to deformational stresses by an increase of the fluid pressures. Some geological evidences indicate that a tectonic compression, owing to the convergence of thrust sheets of Apennine towards foreland and having direction from W to E, could originate over-pressures in Fossa Bradanica and Tavoliere basins. This would cause the migration of deep fluids which should be forced to rise, emerging as springs, or could be expelled towards permeable sediments of the foreland basin and platform.

As previously discussed, squeezed interstitial solutions would be highly enriched in lithium: this occurrence could explain high lithium excesses in basement waters also in absence of geothermal anomalies; moreover, even if based on a few chemical data, it can be outlined that the salt waters coming from oil-exploration wells drilled in different formations seem to have been subject to very similar diagenesis.

The fact itself that very old salt end-members reach the coastal discharge indicates that these waters are moving, though their migration velocity should be very low. As an example, $6 \cdot 10^6 \text{ m}^3$ of old salt water are outflowing per year through the Trani and Taranto springs. These volumes must be replaced by other salt water, which, owing to the particular characteristics, can only come from contact areas. An hypothesis about regional circulation has been outlined in Fig. 6: this circulation has to be intended in the wider sense, owing to the fact that migration velocity is very slow, probably of the order of a few centimetres per year, as calculated hypothesising the flow through a broad section contact between Murgia and Plio-Pleistocene sediments.

We do not pretend to have fully understood this huge system, most of which is inaccessible, and conclude our remarks with the recommendation that more data are surely needed to reach reliable conclusions.

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