

## **$^{222}\text{Rn}$ ACTIVITY IN A KARST COASTAL AQUIFER UNDER ACTIVE SEAWATER INTRUSION.**

**Maria Dolores FIDELIBUS** (a), **Michele SPIZZICO** (a) and **Luigi TULIPANO** (b)

(a) Bari Politechnics, Department of Civil and Environmental Engineering,  
Via Orabona 4, I-70125 Bari, ITALY

(b) University of Rome "La Sapienza", Dep. Hydraulics Transportation and Roads -  
Via Eudossiana 18, I-00184 Rome, ITALY

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### **ABSTRACT**

$^{226}\text{Ra}$  and  $^{222}\text{Rn}$  are considered by oceanographers as potential tracers of coastal and submarine groundwater discharge (SGWD). The use as tracers is based on the occurrence that  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  concentrations in coastal discharge are a few orders of magnitude greater than in coastal seawater. The paper is aimed at studying these isotopes inland in the aquifers, in order to fill the gap of knowledge about their behaviour before they reach the coastal discharge.

A part of the Salento karstic coastal aquifer (Southern Italy) has been selected as representative for the presence of many coastal and submarine springs and the occurrence of seawater intrusion, which represents the main process indicated as relevant in the production of high isotope activities. The significance of the presence and behaviour in coastal zone of  $^{222}\text{Rn}$  is examined. Base knowledge has been established by means of laboratory experiments. The terra rossa, final product of limestone dissolution, resulted the main source of  $^{226}\text{Ra}$  in the aquifer. In the common conditions found in freshwater environments, where Ra is blocked in "terra rossa",  $^{222}\text{Rn}$  comes from this source. In dynamic conditions (physical laboratory model)  $^{222}\text{Rn}$  activity demonstrates to be more influenced by  $^{226}\text{Ra}$  activity of terra rossa and its specific surface than flow velocity. Moreover the interpretation of the role of  $^{222}\text{Rn}$  has been carried out on the light of the mechanisms that regulate the presence in groundwaters of  $^{226}\text{Ra}$  in relation to seawater intrusion (desorption in high ionic strength). Lab experiments allow to state the extent of  $^{226}\text{Ra}$  desorption from terra rossa at different water salt content. The interpretation of the Rn contents related to numerous coastal springs and groundwaters belonging to the karst coastal aquifers of Puglia region and to the selected area lead to put forward some hypotheses about the factors, which should regulate the activity of  $^{222}\text{Rn}$  in the concerned aquifers.

### **INTRODUCTION**

Most data dealing with the presence of radium isotopes ( $^{223}\text{Ra}$ ,  $^{224}\text{Rn}$ ,  $^{228}\text{Rn}$  and  $^{226}\text{Rn}$ ) and  $^{222}\text{Rn}$  (coming from the decay of  $^{226}\text{Ra}$ ) in coastal areas belong to oceanographic studies. Recently these isotopes came to the attention of oceanographers involved in the evaluation of terrestrial element fluxes to the oceans.  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  are considered potential tracers of coastal and submarine groundwater discharge (SGWD).  $^{222}\text{Rn}$  concentrations in groundwater are, in fact, 3-4 order of magnitude greater than in coastal seawater: Cable et al., 1996, used this occurrence for tracing the submarine groundwater discharge in the Gulf of Mexico. They established that the distribution of high  $^{222}\text{Rn}$  activities in Florida shelf waters was closely related to the presence and localization of submarine springs. Moreover, the  $^{222}\text{Rn}$  was used to evaluate the magnitude of the submarine groundwater discharge (SGWD) into the same Gulf. Hussain et al., 1999, used  $^{222}\text{Rn}$  to evaluate the amount of fresh groundwater discharge in the Chesapeake Bay.

These examples show the peculiar viewpoint of the oceanography, but the presence of  $^{222}\text{Rn}$  in the coastal discharge should be regarded according to the hydrogeological viewpoint as well in order to understand the origin of the fluxes. As suggested by Moore (1999), the two viewpoints can be reconciled introducing the new term of subterranean estuary, i.e. "a coastal aquifer where groundwater derived from land drainage measurably dilutes seawater that has invaded the aquifer through a free connection to the sea".

Present study deals with  $^{222}\text{Rn}$  activity distribution in groundwaters and in discharge waters of a coastal karst aquifer: following the Moore's suggestion, the work is aimed at connecting  $^{222}\text{Rn}$  behaviour inland to its activity in coastal discharge. The interpretation of the groundwater  $^{222}\text{Rn}$  distribution and the justification of the concentrations found in coastal discharge need of background information on the factors which potentially regulate the presence of the said isotope (and its parent  $^{226}\text{Ra}$ ) in the hydrogeological environment.

## FACTORS REGULATING THE PRESENCE OF $^{226}\text{Ra}$ AND $^{222}\text{Rn}$ IN A COASTAL AQUIFER

After separation from its uranium-bearing rock, radium resides in the dissolved phase: its mobility is limited in fresh water environments by adsorption on to solids on a timescale of the order of minutes. Salinity of groundwaters and presence of other dissolved ions that may affect the radium adsorption distribution coefficient control radium mobility.  $^{226}\text{Ra}$  is, in fact, preferentially adsorbed on clay sediments when clay are immersed in waters of low ionic strength and preferentially desorbed (than afterwards dissolved in groundwater) when clays come in contact with waters of high ionic strength. In practice, the  $^{226}\text{Ra}$  mobility is mainly controlled by ionic exchange direction, which depends in turn on the variations of salinity in a coastal aquifer. Variations of salinity are strictly linked to the dynamics of coastal aquifers, so  $^{226}\text{Ra}$  should be blocked in sediments during prevailing recharge (refreshing) and mobilised during active seawater intrusion.

It has been already stated that, in presence of exchangers, the ion-exchange processes are the governing geochemical processes activated by the dynamics of the seawater intrusion: this way ionic exchange regulates the transport of metals and pollutants to the oceans. The ionic exchange between water and sediments become significant when the ionic concentrations vary along a groundwater path, as due to pollution or to the movement of the salt water/fresh water interface. In such cases, the ionic exchange intervenes to vary water chemical composition in order to bring back the water-clay system to the equilibrium: the phenomenon can completely alter the cationic concentrations through a process known as ion-chromatography. Therefore, hydrochemical variations of the quality of ground waters occur along groundwater flow path in coastal aquifers when exchangers are present. These variations are useful in the reconstruction of the cyclic succession of seawater intrusion and refreshing/recovery steps, allowing, moreover, reconstructing the original quality of the water in the sampling points (Gimenez et al., 1995).

Such situations have been studied through laboratory simulations based on the principle of the ionic chromatography. They used column filled up by aquifer material in equilibrium with seawater or fresh water: after equilibration they injected respectively freshwater or seawater into the column and analysed the effluent at fixed time steps. The process is named *elution chromatography* when the dominant cat ion (for ex.  $\text{Na}^+$ ) present in the injected solution has a low affinity for the exchange sites: the results obtained from this type of chromatographic process allow simulating situations like the active intrusion of seawater in aquifers, formerly in equilibrium with fresh water. Limiting the discussion to the main cat ions Na and Ca, during active intrusion, when sea/saltwater reach zones of the aquifer previously occupied by fresh waters, the clay-water system reacts provoking the release of  $\text{Ca}^{2+}$  (occupying great proportion of exchange sites) and the parallel adsorption of  $\text{Na}^+$ : this way a reaction of *inverse exchange Na/Ca* develops.

The process is named *displacement chromatography* when the fluid injected in the chromatographic column contains ions having towards exchange sites greater affinity in comparison with that peculiar of ions held by the clay. This type of chromatography applies to real situations when fresh waters (where  $\text{Ca}^{2+}$  ions predominate) displace salt waters from sediments in equilibrium with marine waters (in which  $\text{Na}^+$  ions prevail). A *direct exchange Ca/Na* occurs during this recovery step (better known as refreshing) (Appelo & Postma, 1993).

The development of the variations, for both intrusion and refreshing steps, depends, for every cat ion, on the relationship between the amount of the ion adsorbed in the solid fraction and its concentration in solution. This rule makes the intrusion faster than refreshing due to the different amounts of displacing ions transported with a same water volume, respectively of seawater or freshwater. Moreover, the development of inverse or direct exchange reactions in the two different processes results in the appearance of different hydrochemical facies in the two different steps.

The important fact is that radium belongs to the Group II of alkaline earth elements: this means that his behaviour is similar to that of calcium. As calcium concentration can be greatly enhanced in ground waters as seawater enters the aquifer due to the presence of many other ions, the same can occur to radium and radium isotopes. They can be displaced from exchange sites with consequent built up of their concentration in transition zone.

So, in a dynamic environment as the coastal zone, the process of seawater intrusion can scavenge  $^{226}\text{Ra}$  adsorbed in clay sediments, enriching groundwaters of the mixing zone which discharge into the sea through coastal and submarine springs. The inversion of the process, i.e., the arrival in the same zone of fresh water, promotes new conditions for  $^{226}\text{Ra}$  adsorption. This means that in a coastal aquifer, the migration of radium may be retarded or conversely enhanced, according to ionic strength variation and ion exchange. This, as outlined by Krest et al, 1999, results in non-conservative addition of dissolved radium in the mixing zone.

The direct relation of  $^{226}\text{Ra}$  concentration with water salt content has been observed by many authors, as well as the action of ionic exchange on its desorption from clays. Already in 1964, Tanner proposed that the abundant cat ions present in saline waters should compete with radium for exchange sites. Conversely, waters with low ionic strength were considered favourable for radium adsorption into the aquifer matrix. Moore (1997), studying the fluxes of barium and radium at the mouth of Ganges-Brahmaputra River, hypothesises that, when the river discharge is low, the fluxes of radium and barium are controlled by SGWD, being barium and radium desorbed from particles of the aquifer due to seawater intrusion. Moreover, in 1999, Moore underlines that seawater intrusion (high ionic strength) causes the desorption of ions adsorbed on sediments with a consequent flux of desorbed metals and nutrients to the sea. He takes into account the dynamics of intrusion, noticing that this flux to the sea changes in quality when fresh waters (low ionic strength) flush sediments.

These findings indicate that brackish groundwaters, when in the aquifer there are exchangers, should have  $^{226}\text{Ra}$  concentrations higher than freshwaters.

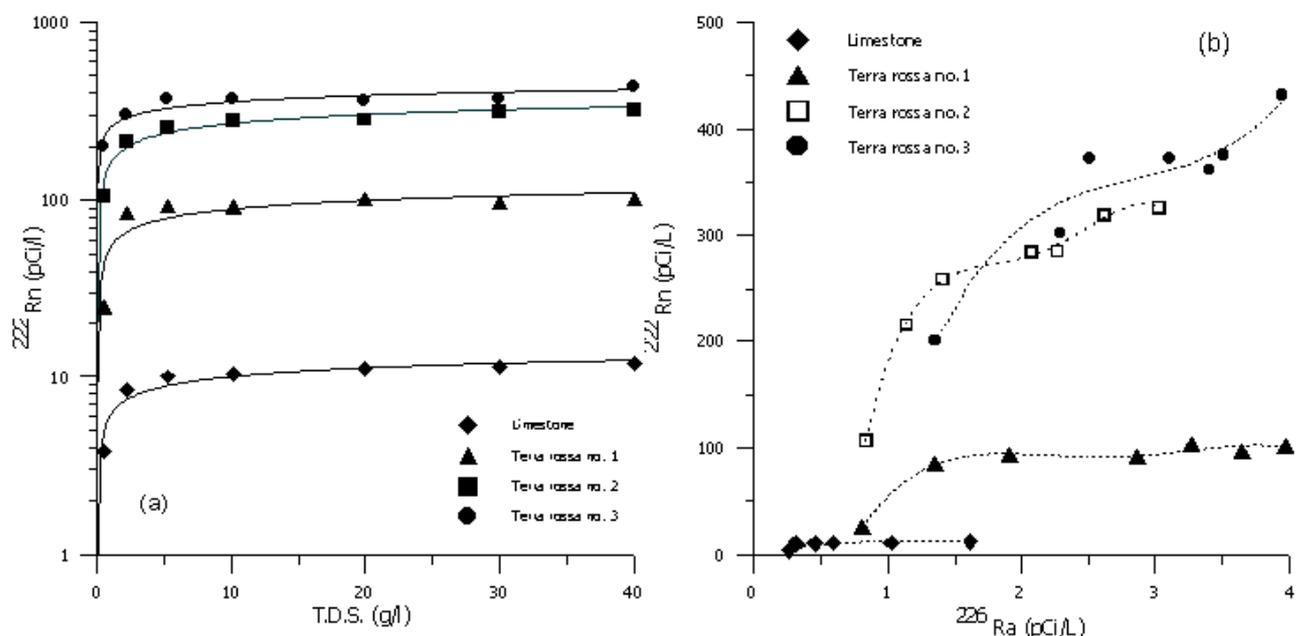
The new aspect of the problem in coastal aquifers subject to seawater intrusion is that, in determining the factors affecting the final  $^{222}\text{Rn}$  concentrations in groundwater, we should consider also the ionic exchange that cause the desorption of  $^{226}\text{Ra}$  parent: this means that new  $^{222}\text{Rn}$  can be produced directly in the liquid phase along groundwater paths. This way, radioactive decay of high concentrations of desorbed  $^{226}\text{Ra}$  could explain why, added to the other effects, which lead to its build up in the fresh waters,  $^{222}\text{Rn}$  reaches high concentrations in brackish waters.

## **$^{226}\text{Ra}$ AND $^{222}\text{Rn}$ IN CARBONATE AQUIFERS: ROLE OF "TERRA ROSSA". LAB EXPERIMENTS.**

In karst aquifers hosting fresh groundwaters, most part of  $^{226}\text{Ra}$  escaped from uranium-bearing carbonate rocks is blocked in "terra rossa", which is the final product of limestone dissolution. A recent experimental study (Tadolini et al., 1997, Spizzico & Sciannamblo, 2000) supports this statement. A number of rainwater samples (noticeably without radon) have been left in contact 38 days (time to reach radioactive equilibrium between  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$ ) with different *terra rossa* samples (having known  $^{226}\text{Ra}$  activity) taken in the Salento Peninsula (South Italy).  $^{222}\text{Rn}$  activities measured in the supernate resulted proportional to the variable  $^{226}\text{Ra}$  content of the *terra rossa*. In absence of flow,  $^{222}\text{Rn}$  concentration was found higher near the surface of sediments (due to diffusion) and linked to the specific surface available for contact between liquid and solid phases. The experimental results in dynamic conditions (physical laboratory model) outline that the overall amount and distribution of *terra rossa* in the volume of the model controls the  $^{222}\text{Rn}$  activity more than flow velocity: when in contact with carbonate rock with a very low amount of *terra rossa*,  $^{222}\text{Rn}$  content results comparatively lower.

The experiments confirmed that in fresh groundwaters of karst aquifer the high  $^{222}\text{Rn}$  concentrations could originate only from *terra rossa*, present in the fissures and fractures (Tadolini & Spizzico, 1998). High radon activities should characterise zones of high diffuse permeability due to both karstic features and fractures, owing to the possibility in this condition of increasing the contact area between water and sediments.

In order to prove that the enrichment of radium (and radon) in brackish waters is due to desorption of  $^{226}\text{Ra}$  from *terra rossa*, four different samples, one of pure carbonate rock and three of *terra rossa*, belonging to different zones of Puglia region (Southern Italy) have been mixed in fixed proportion respectively with no. 6 seawater and diluted seawater samples, having T.D.S. ranging from 40 to 0.5 g/L. The 24 combinations of water and soil have been left standing for 38 days till the attainment of  $^{226}\text{Ra}$ - $^{222}\text{Rn}$  radioactive equilibrium. Afterwards the supernate has been separated from sediments:  $^{226}\text{Ra}$  has been measured by gamma spectrometry and  $^{222}\text{Rn}$  by  $\alpha$  activity in scintillation counters. Figure 1a shows the four curves (for the four soil/rock samples) representing the variation of the measured  $^{222}\text{Rn}$  activities with TDS: the trends are of logarithmic type. For each TDS radon activity is higher for contact with *terra rossa* than with carbonate rock.  $^{226}\text{Ra}$  activity/TDS relationship follows an almost similar trend. Figure 1b shows the relationship between Rn and Ra (of polynomial type).



**Figure 1** (a):  $^{222}\text{Rn}$  activities vs. T.D.S. related to the waters in radioactive equilibrium with four rock/soil samples; (b):  $^{222}\text{Rn}$  vs.  $^{226}\text{Ra}$  for the same waters

The respective gradients  $\Delta[\text{Rn}] / \Delta\text{TDS}$  and the  $\Delta[\text{Ra}] / \Delta\text{TDS}$  are higher in the range 0.5–5 g/L than in the range 5–40 g/L: this should indicate that most radium desorption occurs in the first range.

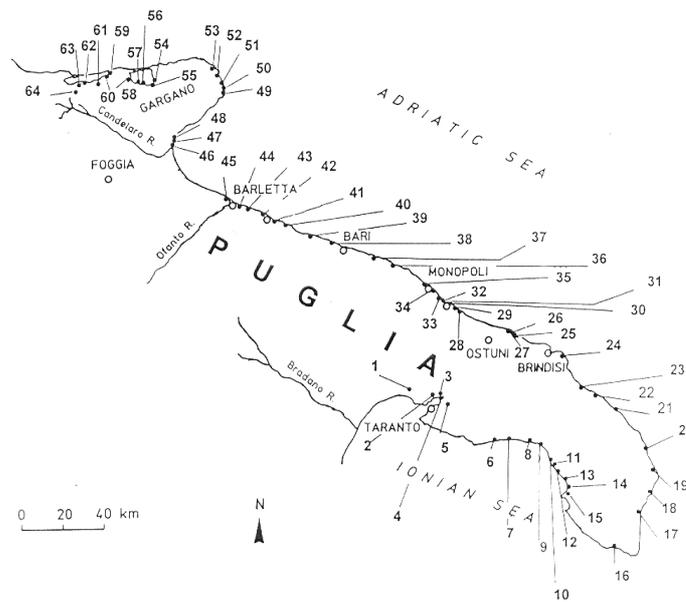
The liquid samples not used for Rn and Ra measurements have been moreover degassed for eliminating radon: then they have been left standing for other 38 days without any further contact with rock/soil. New  $^{222}\text{Rn}$  was found in the water samples originated from the desorbed  $^{226}\text{Ra}$  present in the liquid phase.

Lab experiment results are in accordance with starting statements:

1. *terra rossa* is the main reservoir of  $^{226}\text{Ra}$  in the carbonate aquifer;
2.  $^{226}\text{Ra}$  is desorbed from *terra rossa* according to the ionic strength increase of the water in contact, but most desorption occurs up to 5 g/L;
3.  $^{222}\text{Rn}$  activity is mainly due to the decay of  $^{226}\text{Ra}$  blocked in rock/soils in fresh groundwater, while it is due to the above source plus the desorbed radium when in brackish water.

## **<sup>226</sup>Ra AND <sup>222</sup>Rn IN THE COASTAL SPRING WATERS OF THE PUGLIA REGION**

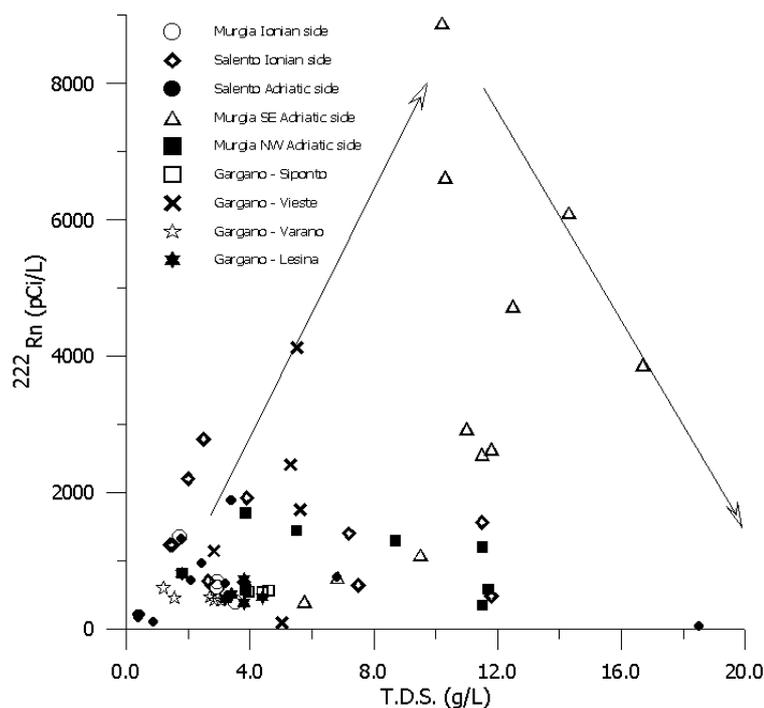
The first survey aimed at recognising the activity of <sup>226</sup>Ra and <sup>222</sup>Rn in the karst coastal aquifers of Puglia region (Southern Italy) dates back to 1982. <sup>226</sup>Ra concentrations in a limited number of brackish spring waters (max salt content 14 g/L) resulted higher (0.2–8 pCi/L) than in fresh groundwaters (0.03–1.3 pCi/L) (Brondi et al., 1983). Brackish springs showed anomalous (200–10000 pCi/L) <sup>222</sup>Rn concentrations as well, generally 1 order of magnitude higher than in freshwaters. <sup>226</sup>Ra and <sup>222</sup>Rn activities increase more or less linearly with water T.D.S., leading to a linear relationship between <sup>226</sup>Ra and <sup>222</sup>Rn. The origin of these anomalous values did not find any conclusive explanation at that time. On the light of previous considerations and experimental data, these old data come now more realistic: the effect of the ionic exchange also in karst aquifers can evidently produce appreciable <sup>226</sup>Ra desorption from the scarce clay sediments owing to salinization of fresh waters.



**Figure 2** Location of the 64 coastal springs sampled in Puglia region.

Another recent survey aimed at evaluating <sup>222</sup>Rn activity in a larger number of coastal and submarine springs (no. 60, Figure 2) belonging to the coastal karst aquifers of the Puglia region. The survey covered the range of salt content between 0.5–20 g/L. Figure 3 outlines the variation of <sup>222</sup>Rn activity with respect to T.D.S.. Data related to natural water samples are 1-2 orders of magnitude higher than lab data obtained for waters of same salt content: lab experiments evidently do not take into account all the factors controlling Rn activity and their natural variability. As matter of fact, the variability of Ra activity in terra rossa can be greater than that of the samples considered in the lab experiments.

Most part of <sup>222</sup>Rn increase occurs, according to the experiments, in the range 0–10 g/L (radon reaches max concentrations of about 8000 pCi/L). Exceeding 10 g/L, radon activity decreases. All samples are within the triangle limited by the two main steps: this normally indicates a three end-member conservative mixing (with or without overlapping geochemical processes) or a two member conservative mixing with overlapped geochemical processes brought about by mixing.



**Figure 3**  $^{222}\text{Rn}$  vs. T.D.S. for the coastal springs belonging to Puglia karst coastal aquifers

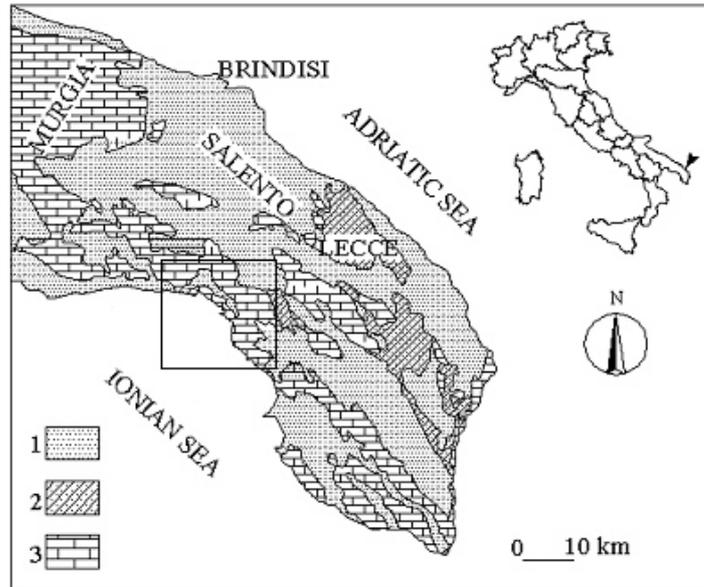
In the second case, the two-steps behaviour of radon should be explained as consequent to that of radium. In the first step nearly all radium desorption takes place enhancing radon activity (non-conservative behaviour of two end-member mixing); afterwards, the dilution effect of seawater, which has almost zero content of radon, prevails (conservative mixing).

For the first most complex case (three end-member mixing) it has to be taken into account that other salt end-members than present seawater can be involved in the mixing in the Puglia carbonate aquifers (Fidelibus & Tulipano, 1996, Barbieri et al., 1998). Salt waters of different age and different chemical composition (due to diagenesis) have been in fact recognised in the discharge waters of most part of the above coastal springs and have been sampled through deep wells reaching salt water inland. Unfortunately no data about  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  have been collected. However, Kraemer & Reid, 1984, point out that saline formation waters of the Gulf Coast region can have radium as high as 28 pCi/L. Moreover, Tamar et al., 2000, assert that saline waters in the Rift Valley reach  $^{226}\text{Ra}$  values of 340 pCi/L and Rn values of more than 27000 pCi/L. This means that old salt waters present inland in the Puglia karst aquifers could have appreciable  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  contents. The presence of an old end-member should affect mainly the first step; the second step should not be affected by the eventual presence of another end-member in the studied aquifers, because all the springs with salt content higher than 12 g/L show generally a present seawater component (Fidelibus & Tulipano, 1996).

$^{222}\text{Rn}$  activities in the first salinity range are, moreover, higher than those obtained by desorption experiments: one of the reason of this behaviour should be the natural variability of Ra activity of terra rossa. Samples used in the experiments cannot evidently include all the variability range.

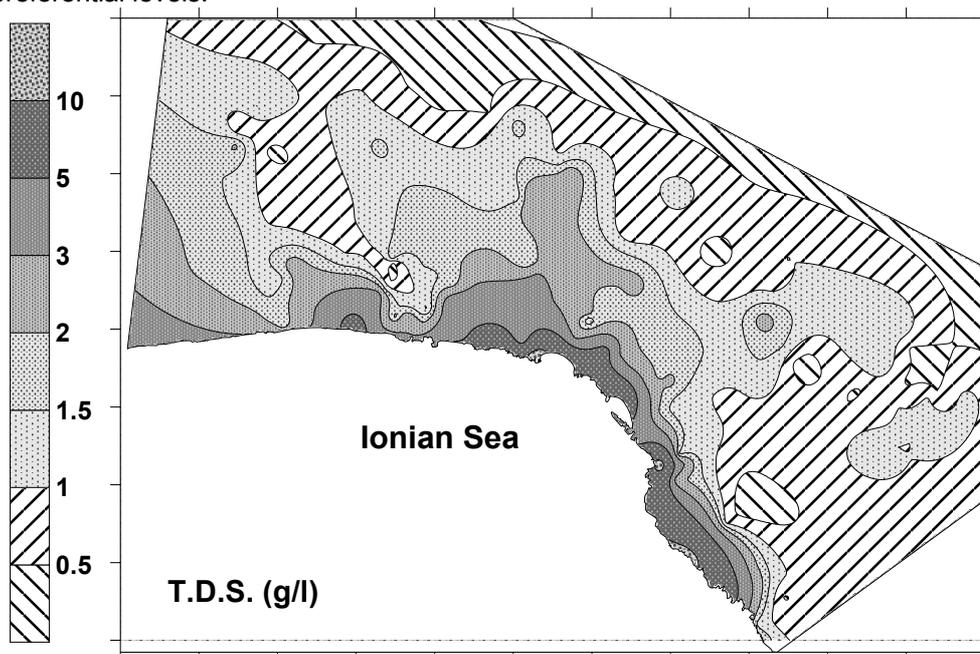
## BEHAVIOUR OF $^{222}\text{Rn}$ IN THE COASTAL KARST AQUIFER OF PORTO CESAREO

A part of the Salento coastal karst aquifer (location in Figure 4) facing the Ionian Sea (Porto Cesareo area) has been selected with the aim of studying the behaviour of  $^{222}\text{Rn}$  from inland to the coastal discharge. The strongly anisotropic aquifer is made up by limestone and dolomitic limestone of Cretaceous: the aquifer has a high permeability degree due to both fissuring and karst development.



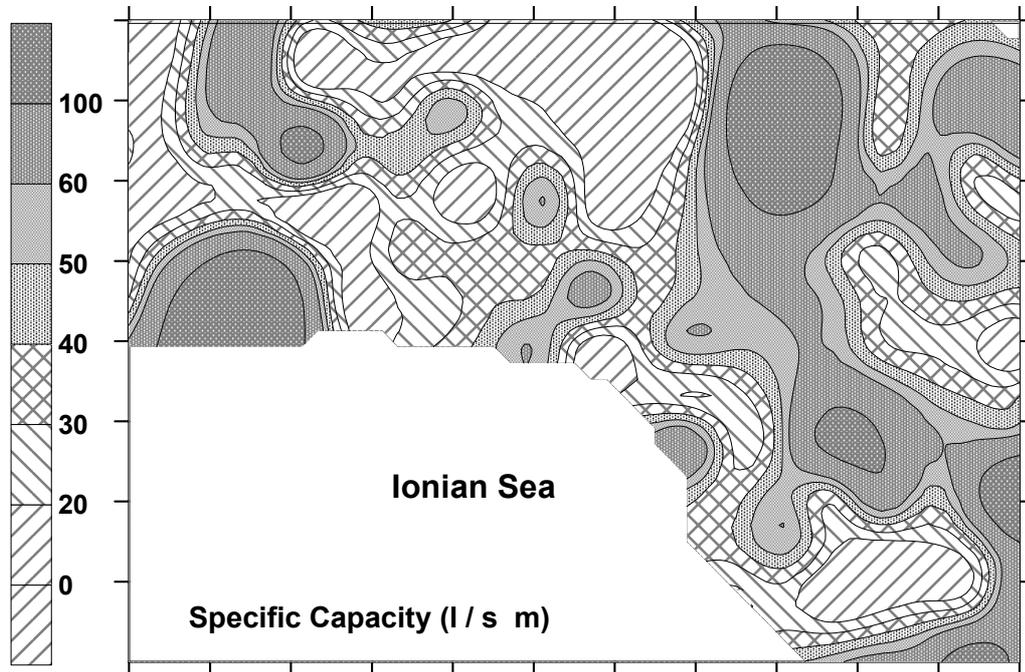
**Figure 4** Geological map of Salento Peninsula and location of the selected study area  
 1) Calcarenes, sands and clays (Plio-Quaternary) 2) Calcarenes, marly calcarenites (Miocene)  
 3) Limestones, dolomitic limestones (Cretaceous)

Transgressive deposits (calcarenes, sands and clays), which age ranges from Miocene to Quaternary, cover partially the basement (Figure 4). However, Cretaceous formation is almost everywhere present at sea level and groundwater flows in phreatic conditions, floating on intruding seawater. Water table shows low hydraulic heads, seldom exceeding 3 m above m.s.l. and gradients are very low as well ( $0.25 \text{ ‰}$ ). The repeated changes in the sea level, due to tectonic and glacio-eustatic events in the Tertiary and Quaternary, determined a renewal of karstification in the transition zone due to the change of the base level of groundwater circulation and even the development of secondary porosity at various depth under sea level, due to the vertical displacements of the transition zone itself. In the north-western part of the selected area, groundwater flows mostly through high permeable preferential water levels which are separated by less permeable levels; in the area situated toward the east the aquifer is highly fractured as well and groundwater flow is more diffuse and not limited to preferential levels.



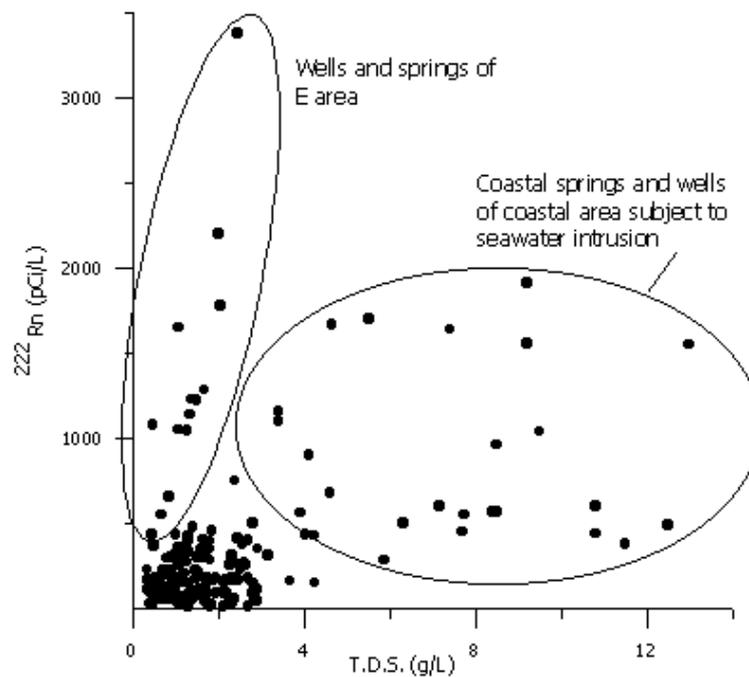
**Figure 5** T.D.S. contour lines for the selected study area

T.D.S. contour line map (Figure 5) shows a salt content variable inland between less than 0.5 and 2 g/L: in the coastal zone and in the central zone in the north direction, salt content is higher than 2 g/L, clearly outlining the trend of seawater intrusion. Along the coast, groundwater discharges through a series of springs, subaerial and submarine.



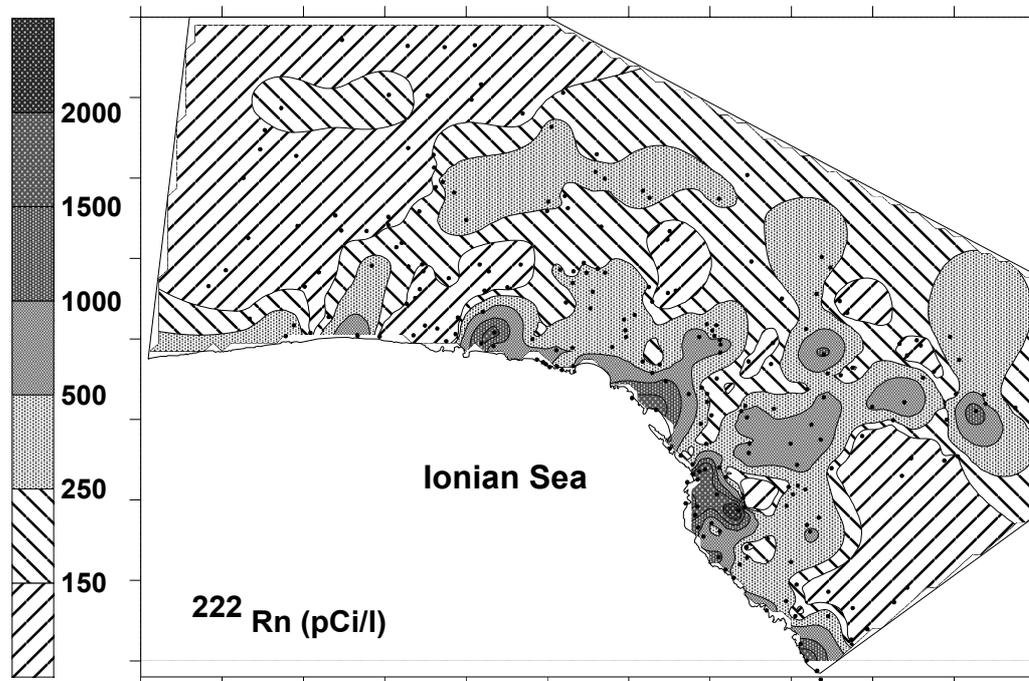
**Figure 6** Specific capacity map for the selected study area.

Specific capacity (Figure 6) calculated from discharge tests with reference to the first meter of drawdown, shows its highest values in the E part of the territory. Being the specific capacity distribution a rough indication of the permeability degree, this should indicate a higher overall permeability in the E area than in the NW area.



**Figure 7**  $^{222}\text{Rn}$  vs. T.D.S. for the groundwaters and spring waters sampled in the selected study area

No. 204 groundwater from irrigation wells and no. 24 coastal spring waters have been sampled in the area and analysed for  $^{222}\text{Rn}$  and TDS (location in Figure 8). Figure 7 shows the relationship between  $^{222}\text{Rn}$  activities and T.D.S.. The highest  $^{222}\text{Rn}$  activities (up to 3400 pCi/L) appear in the TDS range 0.3–2.5 g/L. Groundwaters in the range 3–13 g/L (mainly spring waters) show activities lower (400–2000 pCi/L) than those of the less saline range, probably in connection with the already mentioned dilution effect of the seawater. The most part of waters in the range 0–2.5 g/L have  $^{222}\text{Rn}$  concentrations in the range 10–500 pCi/L. Among them many waters have very low  $^{222}\text{Rn}$  content, between 10 and 100 pCi/L: this is the typical range of fresh karst groundwaters.



**Figure 8**  $^{222}\text{Rn}$  activity distribution for the selected study area and location of sampling spots (wells and springs)

The reconstruction of the  $^{222}\text{Rn}$  activity contour lines (pCi/L) for the selected area is based on the interpolation of the data related to the above-mentioned 204 groundwater samples and 24 coastal spring waters (Figure 8). The  $^{222}\text{Rn}$  distribution allows outlining two main zones of the coastal aquifer: the first located NW, characterised by mean concentrations less than 200 pCi/L, the second, at E, with mean concentrations higher than 200 pCi/L: the peak values above 2000 pCi/L belong to this second area and correspond to a few springs and mainly to wells located inland. According to the specific capacity map, the higher overall permeability (due to contribution of fracturing) of the area located to the E and the more diffuse flow, not limited to high permeable preferential levels, should enhance the extent of contact with terra rossa and explain these high values as due to higher release of  $^{226}\text{Ra}$  by sediments. On the coast, highest concentrations correspond to the fronts of seawater intrusion (Figure 5).

## CONCLUSIONS

Matching all information collected about the selected area, some conclusions on the behaviour of  $^{222}\text{Rn}$  in karst coastal aquifers can be drawn.

- $^{222}\text{Rn}$  activity of brackish waters should reflect:
  - In part the memory of the fresh water component; in the fresh water environment  $^{222}\text{Rn}$  comes from the decay of  $^{226}\text{Ra}$  of variable activity *blocked* in terra rossa;
  - in part the effect of the decay of *desorbed* Ra; its activity in the liquid phase depends on the amount released from sediments under ionic exchange during mixing, which in turn depends on the  $^{226}\text{Ra}$  activity of the terra rossa deposits;
  - the *specific surface* available for contact with mixed waters (which should have relation with the overall permeability) that should enhance  $^{226}\text{Ra}$  release by ionic exchange;

- the effect of the salt-water component that could cause dilution (present seawater with zero Rn concentration) or concentration ( $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  from old salt-water component).

It is not easy to recognise the relative significance of each of above factors in determining the Rn activity in a karst coastal aquifer. The information gained by the study should be of help for oceanographers involved in the recognition and evaluation of submarine and coastal discharge: in karst coastal aquifers, groundwater discharge can transport very different amount of radon not easily related to the salt content of waters.

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