M. BRONDI (*) - M. D. FIDELIBUS (**)
R. GRAGNANI (*) - L. TULIPANO (**)

HYDROGEOCHEMICAL STUDY AND DISTRIBUTION OF SOME TRACE ELEMENTS IN THE MOST IMPORTANT COASTAL SPRINGS AND GROUNDWATERS OF THE APULIAN REGION (SOUTHERN ITALY)

SUMMARY

Hydrogeochemical surveys were carried out on coastal springs and wells drawing waters from the deep aquifer throughout Apulian region from the Gargano to the Salentine Peninsula.

Analyses of the main constituents as well as a numerous series of minor constituents were conducted on each water sample.

From a geochemical point of view some groundwaters show a calcium-magnesium-bicarbonate chemism being peculiar to the leaching of sedimentary formations. Springs show a sodium-chloride, calcium-sulphate chemism according to the mixing processes with sea water.

Meaningful correlations between Li, B and Cl were found, thus allowing a classification of all examined waters in three distinct groups. Their different characteristics, on the other hand, are in agreement with the different hydrogeological situations within an aquifer mostly homogeneous from the lithological standpoint.

The main differentiation reason of Li and B behaviour versus Cl content seems to be dependent upon a different age of intruding sea water.

Furthermore Ra and Rn contents of examined waters are considered related to Cl content.

(*) Laboratorio di Geochimica Ambientale E.N.E.A. - Pas Scamb. Geoch. C.S.N. Casaccia - Italia.
(**) Istituto di Geologia Applicata e Geotecnica - Facoltà di Ingegneria - Università di Bari.

1. FOREWORD

Apulia is a typical karst region almost lacking in surface water resources: underground waters represent the only supply source available in loco.

Owing to particular hydrogeological conditions of most territory, up till now the aspects related to the modes by which ground water feeding, flowing and discharge phenomena take place, have not been fully clarified.

Really not much is know about real underground waters circuits and actual residence times in the aquifers.

Like methodologies based on isotopic contents analysis of groundwaters, or on the study of those water properties likely to act as environmental tracers, the geochemical methodologies can contribute, as well in a more exhaustive manner, to a better understanding of the subjects under study.

Within the present study an investigations and samplings campaign was carried out all over Apulian territory.

Such operations were made on ground waters in drilled wells and in a series of coastal springs.

The purpose of such a campaign was to provide further information about phenomena governing the evolution of ground water chemical features relating to feeding processes, residence times in the aquifer and encroaching sea-water influence on fresh groundwater. This being a contribution which carries on the hydrogeochemical researches previously undertaken [9, 8, 12, 18, 22].

2. AN OUTLINE ON THE REGION HYDROGEOLOGY

The Apulian region presents geological, morphological-structural and, consequently, hydrogeological features being quite different from zone to zone.

The whole territory can be divided into four distinct hydrogeological units made up by the Gargano, the Tavoliere, the Murgia and the Salento.

Actually the Murgia and the Salento form a sole system, but owing to the different permeability characteristics referring to aquifers substantially similar by a lythological point of view, the distinctions in two units is thought right.

There are plenty of works on Apulian hydrogeology [5 and its bibliography] then here it is better to provide only some information helpful for the understanding of chemical phenomenologies we are treating.

All over Apulia territory underground waters feeding is given by a rate of rainwaters penetrating the subsoil, generally during October-April period.

The local permeability conditions and geometrical characteristics of aquifers, into the four hydrogeological units, determine the flowing conditions of underground waters finding, anyway, their base level at sea level.

Gargano, Murgia and Salento show hydrogeological conditions peculiar to coastal aquifers [6, 10, 11, 17, 20]: fresh water floats on salt water of sea origin, and, along the coasts of the above units, the ground water discharge into the sea through subaereal and subaqueous springs occurs.

Obviously ground waters are affected by salt water, essentially as change of the primary chemical characteristics.

Such an influence is more or less remarkable owing to a series of factors generally connected with hydrodynamic characteristics of such aquifers with particular reference to space distribution of permeability features, typical of carbonate, fissured and karst aquifers markedly anisotropic.

Furthermore other factors may contribute to stress this influence; the most important one is the massive ground water taking happening in broad areas of Apulian region [19].

As for the Tavoliere, it is enough to remember there exists a double hydrological system: a deep aquifer made up by mesozoic carbonate masses sunk and covered by transgressive Pliocene - clays, while soils permeable by porosity, ending the plio - pleistocene series, form the shallow aquifer [4].

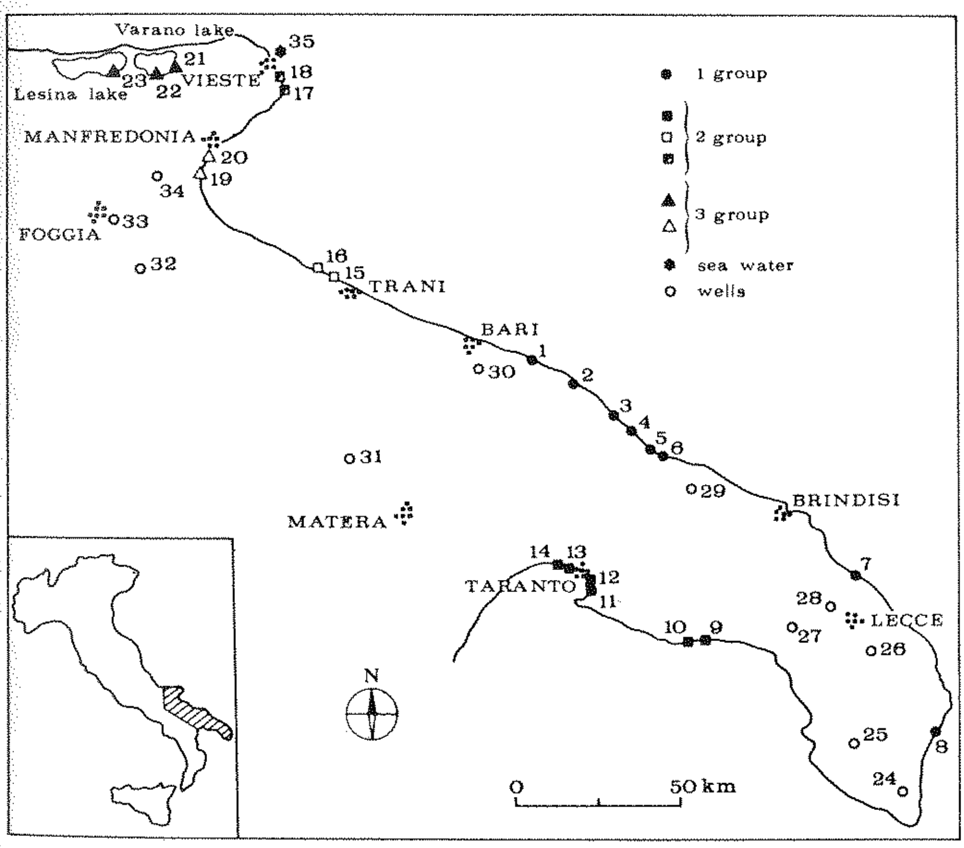

Fig. 1 - Sampling map. Symbols marking the sampling spots refer to the different chemical compositions of waters.

While the deep aquifer can't be reached easily, at least in the most central areas of the Tavoliere, the shallow aquifer, whose bottom surface is made up by the roof of the clayey formation, in the run of the last decades underwent so massive water takings through wells as to bring about a remarkable lowering of piezometric surface [4].

3. SAMPLING AND ANALYTICAL PROCEDURES

Samples were taken from a series of springs draining groundwater of the Murgia, Gargano and Salento, and from a series of wells drilled within the above three hydrogeological units. Some of the springs have been matter of hydrological investigations [16].

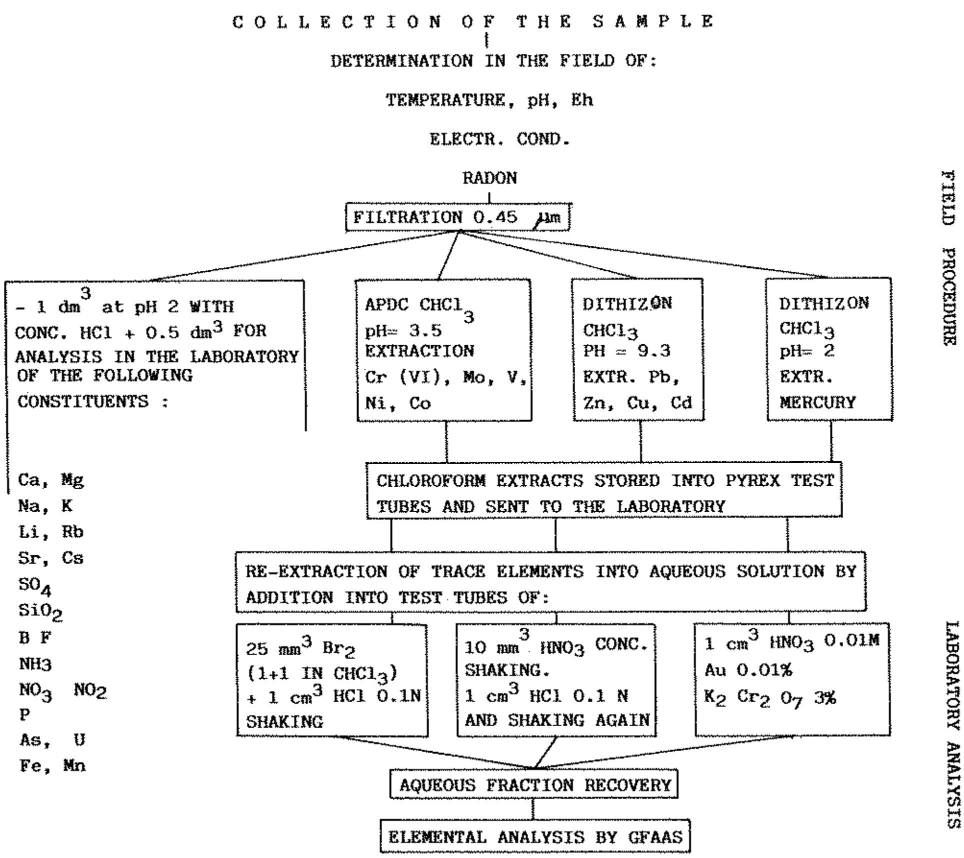

Fig. 2 – Analytical procedure scheme

Three samples were taken from wells drilled in the Tavoliere, one of which, n. 34, finds brackish waters permeating the Mesozoic carbonate formation, confined by the transgressive Plio-Pleistocene series.

The sampling spots are shown in Fig. 1 with a different symbolism. The samples have been analyzed for major, minor and trace constituents. The general scheme of the applied procedures in shown in Fig. 2.

The elements were analyzed by using different techniques as follows:

1) Ca, Mg, Na, K, Li, Sr and Cs	by A.A.S. of emission (Perkin Elmer 5000)
2) Fe, Mn, As	by G.F.A.A.S. (HGA 5000 Perkin Elmer)
3) SO_4	by turbidimetry
4) SiO_2, F, B, NH_3, NO_2, P	by autoanalyzer (Tecnico)
5) U	by fluorimetry
6) I, Br	by specific electrode
7) Rn	by degassing water. The extracted Radon was collected in a ZnS cell and measured by an alpha counting Radon Detector (Edard 100)
8) Ra	according to MASTINO G. [14]

Some procedures are reported by BRONDI et al. [1].

4. RESULTS AND DISCUSSION

The analytical results are reported in Table 1.

Water varies in salinity, in fact the wells waters have generally salt contents less than 1 g/l while the springs have contents of several g/l.

The reaction values in percent of major cations and anions are reported in the Chebotarev diagram of Fig. 3. We can see that all the springs are in the part corresponding to a sodium chloride-calcium sulphate chemism; on the other hand some wells show a calcium-magnesium-bicarbonate chemism, some others are in the central part of the diagram.

It is clear that the principal process that governs the chemism of these waters is the mixing of karst waters with sea-water. It must be noticed that Salento wells are in the part of diagram that stresses very clearly an evident, direct or indirect sea contamination.

By examining the relationship between some major constituents and minor or trace ones some differences between springs become evident.

TABLE 1 – Analytical results.

Sampling point	Codex Number	Temp °C	pH	EH	Cond Mho	Ca eq/l	Mg eq/l	Na eq/l	K eq/l	HCO_3 eq/l	SO_4 eq/l	Cl eq/l	F mg/l	B mg/l	Sr mg/l	Li µg/l	SiO_2 mg/l	P_2O_5 mg/l	NO_3 mg/l	NO_2 mg/l	NH_3 mg/l	Rb µg/l	U µg/l	Ra pCi/l	Rn pCi/l	Fe µg/l	Mn µg/l	Al µg/l	Zn µg/l	Cu µg/l	Pb µg/l	Cd µg/l	Cr µg/l	As µg/l	V µg/l	Mo µg/l	Ni µg/l	Co µg/l	Hg µg/l
1	14367	17.0	7.2	+310	11-2	93-4	18-3	68-3	16-4	59-4	91-4	86-3	32-2		16-1	32-0	16-0					23-0			27+1														
2	14368	18.0	7.1	+385	21-3	12-3	36-3	16-2	39-4	72-4	18-3	19-2	51-2	93-1	29-1	69-0	12-0					43-0			22+2														
3	14369	18.5	7.2	+265	26-3	14-3	42-3	19-2	50-4	58-4	23-3	23-2	65-2	11-0	33-1	82-0	90-1					52-0			39+2														
4	14370	18.0	7.3	+290	19-3	11-3	29-3	15-2	32-4	61-4	15-3	16-2	55-2	86-1	30-1	59-0	96-1					35-0			30+2														
5	15365	18.0	7.2	+405	16-3	12-3	27-3	11-2	32-4	66-4	16-3	13-2	28-2	70-1	26-1	46-0	96-1	1-3	23-1	40-3	50-3	28-0	16-1	35-1	13+2	34-1	75-2	16-1	17-1	15-2	37-3	23-3	70-3	72-2	20-1	25-1	90-2	80-4	43-4
6	15366	19.0	7.0	+405	23-3	16-3	42-3	17-2	50-4	61-4	24-3	19-2	47-2	13-0	35-1	70-0	99-1	1-3	98-2	72-2	40-3	54-0	19-1	54-1	33+2	36-1	35-2	10-0	12-1	17-2	45-3	58-3	10-2	88-2	18-1	56-1	93-2	80-4	40-4
7	15373	18.0	7.4	+275	10-3	79-4	18-3	74-3	23-4	43-4	95-4	96-3	44-2	62-1	18-1	36-0	90-1	20-3	80-1	30-3	47-3	22-0	25-1	45-1	30+2	11-0	30-2	50-1	60-2	14-2	20-3	30-3	30-2	93-2	17-1	70-2	57-2	11-3	24-4
8	15372	28.0	6.6	-015	49-3	45-3	79-3	41-2	12-3	34-4	53-3	51-2	19-1	59-0	15-0	55+1	11-0	25-3	71-2	39-2	24-1	17+1	74-2	18-0	18+1	80-1	42-1	30-1	57-2	24-2	12-4	37-3	80-3	16-1	34-2	15-2	37-2	58-3	
9	15362	18.0	7.0	+355	58-4	73-4	10-3	39-3	13-4	60-4	62-4	47-3	23-2	42-1	21-1	32-0	11-0	1-3	38-1	30-3	1-4	16-0	35-1	12-1	50+1	70-1	95-2	32-1	15-1	14-2	20-3	27-3	73-2	48-2	45-1	33-1	65-2	90-4	58-4
10	15361	17.6	7.4	+545	43-4	64-4	72-4	25-3	80-5	58-4	41-4	32-3	27-2	[illegible]	21-1	25-0	32-0	1-3	63-1	5-3	1-4	15-0	33-1	56-2	14+1	98-1	95-2	95-1	79-2	11-2	50-4	20-3	80-2	42-2	33-1	23-1	28-2	40-4	70-4
11	15408		7.0			61-4	61-4	23-3	63-5	57-4	33-4	26-3	28-2		16-1	27-0																							
12	15409		6.9			69-4	89-4	35-3	81-5	61-4	50-4	41-3	24-2		19-1	39-0																							
13	15360	18.4	7.3	+655	36-4	60-4	67-4	20-3	60-5	55-4	35-4	27-3	23-2	26-1	17-1	22-0	11-0	1-3	47-1	5-3	10-3	12-0	21-1	61-2	34+1	44-1	70-2	84-1	11+1	13-2	17-2	32-3	20-1	37-2	34-1	14-1	75-2	11-3	80-5
14	15410		6.7			69-4	64-4	15-3	47-5	62-4	33-4	19-3	36-2		24-1	39-0																							
15	15356	19.0	6.4	+385	51-4	13-3	12-3	40-3	12-4	85-4	60-4	51-3	50-2	48-1	24-1	60-0	16-0	15-3	32-1	5-3	1-4	28-0	20-1	54-2	24+1	10-0	12-1	66-1	15-1	32-2	62-3	52-3	20-2	48-2	19-1	27-1	13-1	14-3	50-4
15b	15407		6.5			96-4	11-3	42-3	10-4	87-4	57-3	51-3	42-2		18-1	78-0																							
16	15357	19.0	7.4	+345	56-4	94-4	11-3	39-3	12-4	83-4	56-4	47-3	44-2	43-1	25-1	50-0	16-0	1-3	36-1	5-3	1-4	20-0	20-1	17-2	34+1	10-0	80-1	86-1	96-2	22-2	33-3	53-3	17-2	64-2	26-1	27-1	50-2	11-3	24-4
17	15405	21.0	7.2	+360	92-4	11-3	12-3	64-3	16-4	48-4	74-4	77-3		49-1	25-1	67-0	11-0					28-0			71+1														
18	15404	19.0	7.1	+320	12-3	13-3	17-3	82-3	21-4	48-4	10-3	10-2		61-1	24-1	82-0	11-0					34-0			10+3														
19	15369	22.0	7.2	+465	76-4	10-3	98-4	49-3	15-4	60-4	62-4	65-3	24-2	82-1	30-1	14+1	13-0	1-3	58-1	25-2	60-4	27-0	17-1	13-1	12+2	50-1	12-1	14-1	53-2	67-2	80-3	18-3	10-2	66-2	80-2	46-2	40-2	60-4	74-4
20	14406	19.0	7.1	+320	76-4	99-4	11-3	51-3	14-4	58-4	53-4	62-3		62-1	30-1	13+1	11-0					37-0			11+2														
21	15402	14.0	7.2	+360	49-4	64-4	67-4	31-3	74-5	43-4	35-4	36-3		17-1	11-1	25-0	84-1					12-0			50+1														
22	15403	14.0	7.3	+350	32-4	51-4	44-4	19-3	48-5	40-4	24-4	22-3		86-2	74-2	15-0	60-1					11-0			43+1														
23	15401	15.0	7.2	+330	41-4	63-4	64-4	27-3	71-5	52-4	30-4	32-3		25-1	15-1	52-0	84-1					17-0			20+1														
24	15371	18.0	7.4	+455	14-4	39-4	38-4	60-4	21-5	55-4	84-5	79-4	21-2	62-2	40-2	32-1	84-1	1-3	54-1	60-3	60-4	25-1	19-1	13-1	19+1	50-1	45-2	64-1	62-0	60-2	15-3	41-3	31-2	53-2	46-1	45-2	75-2	90-4	24-4
25	15370	17.0	7.3	+405	12-4	33-4	38-4	55-4	18-5	50-4	80-5	70-4	23-2	61-2	40-2	63-1	72-1	1-3	53-1	5-3	10-3	30-1	16-1	59-2	18+1	56-1	50-2	12-1	64-0	82-2	10-3	70-3	27-2	24-2	27-1	55-2	11-1	16-3	80-5
26	15374	18.0	7.3	+375	83-5	37-4	17-4	23-4	16-5	39-4	42-5	37-4	14-2	52-2	30-2	17-1	90-1	1-3	12-0	70-3	60-4	30-1	16-1	78-2	77+1	26-1	30-2	12-1	25-0	70-2	17-3	15-3	49-2	56-2	23-1	43-2	15-2	50-4	70-4
27	15375	14.0	7.3	+285	19-4	50-4	39-4	87-4	47-5	58-4	15-4	11-3	21-2	16-1	75-2	10-0	12-0	1-3	14-0	29-2	60-4	90-1	28-1	39-2	30+1	80-1	80-1	28-1	11-0	46-2	17-3	12-3	37-2	16-2	31-1	50-2	65-2	17-2	75-4
28	15363	15.0	7.1	+505	15-4	47-4	29-4	47-4	30-5	57-4	85-5	56-4	17-2	86-2	50-2	49-1	13-0	1-3	11-0	60-3	10-3	40-1	46-1	13-1	45+1	60-1	53-2	38-1	30+1	38-2	37-3	74-3	42-2	40-2	33-1	35-2	27-2	80-4	62-4
29	15384	17.0	7.4	+455	85-5	42-4	27-4	21-4	70-6	60-4	31-5	25-4	80-3	25-2	25-2	58-1	11-0	1-3	33-1	30-3	40-3	18-1	10-1	13-2	27+1	38-1	70-2	34-1	20+1	21-1	37-3	22-3	19-2	16-2	39-1	25-2	70-2	80-4	30-4
30	15358	14.0	7.2	+455	92-5	47-4	43-4	73-5	10-5	85-4	13-5	99-5	15-2	61-2	25-2	33-1	18-0	1-3	81-1	10-2	51-3	30-1	19-1	18-2	24+1	36-1	80-2	24-1	45+1	60-1	75-3	13-3	27-2	14-1	26-1	11-2	75-2	11-3	30-4
31	15359	18.0	7.3	+455	65-5	32-4	22-4	75-5	10-5	49-4	42-5	79-5	27-2	61-2	14-1	34-1	13-0	1-3	56-1	25-3	20-3	32-1	19-1	18-2	26+1	54-1	65-2	69-1	65-0	18-3	10-2	26-3	27-2	48-2	28-1	74-1	25-2	50-4	47-4
32	15367	16.2	7.4	+385	86-5	44-4	90-5	26-4	30-5	50-4	85-5	20-4	77-2	74-2	40-2	13-0	27-0	1-3	19-0	70-3	17-3	12-1	46-1	30-3	40+1	32-1	11-1	20-1	14-0	39-2	55-3	15-3	10-2	16-2	35-2	55-2	32-2	80-4	43-4
33	15368	18.0	7.3	+395	10-4	59-4	13-4	27-4	50-5	54-4	17-4	20-4	63-2	11-1	80-2	12-0	27-0	1-3	28-0	14-2	54-3	75-1	58-1	30-3	48+1	64-1	30-2	20-1	67-1	80-2	10-2	17-3	55-2	42-2	22-1	50-2	17-2	12-3	30-4
34	14274	21.4	6.3	+220	41-3	47-3	74-3	36-2	88-4	12-3	38-3	45-2	12-1	33-0	17-0	76+1	18-0					17-0	13-0		13+1														
35	14213				54-3	20-3	12-2	46-2	10-3	27-4	64-3	61-2	12-1	23-0	74-1	21+1	30-2	20-3			78-3	12+1							89-1	13-1	13-2	60-3	13-2		48-2	11-0	12-1	19-2	33-4

Fig. 4 and 5 show the diagrams of chloride versus lithium content and chloride versus boron content. Mainly in the chloride-lithium correlation we can see that generally the samples can be distinguished in two groups.

A group is represented by the springs of Gargano, Trani and Taranto whose Li/Cl and B/Cl ratios are higher than those of sea-water.

Another group includes springs of Adriatic coast southeast of Trani. Their Li/Cl and B/Cl ratios are close to those of sea-water.

The remarks made for Li/Cl ratios are confirmed to a minor extent also for Rb/Cl and Sr/Cl ratios.

R-Mode Factor Analysis has been effected; its synthetic results are shown in Tab. 2.

The analyses were carried out by selecting the eleven most important variations (Ca, Mg, Na, K, Cl, B, Sr, Li, Rb and Rn).

Two factors were determined, the former is tightly connected with Mg, Na, K, SO_4, Cl, the latter with Sr, Li, while Ca, B, Rb affect in the same manner the two factors.

In such data processing the chemical analysis of S. Cesarea spring (No. 8) [3], well 34, sea-water (No. 35) as well as of other samples lacking in some parameters of those examined, were not taken into account.

The two so determined factors are shown in the diagram of Fig. 6 and state that Gargano, Trani and Taranto springs are clearly separated from the remaining Adriatic coast springs.

Naturally this differentiation results from the direct Li-B relationship (Fig. 7).

From this last diagram it's noteworth noticing that Li/B ratio is quite peculiar to the two above mentioned situations, by deriving, for the 1st group a value of the characteristic ratio Li/B higher than the one relative to the 2nd group.

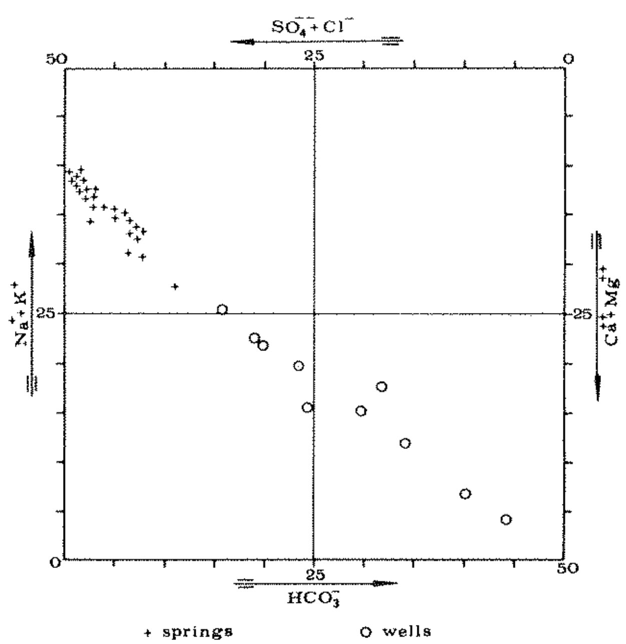

Fig. 3 - Chebotarev diagram

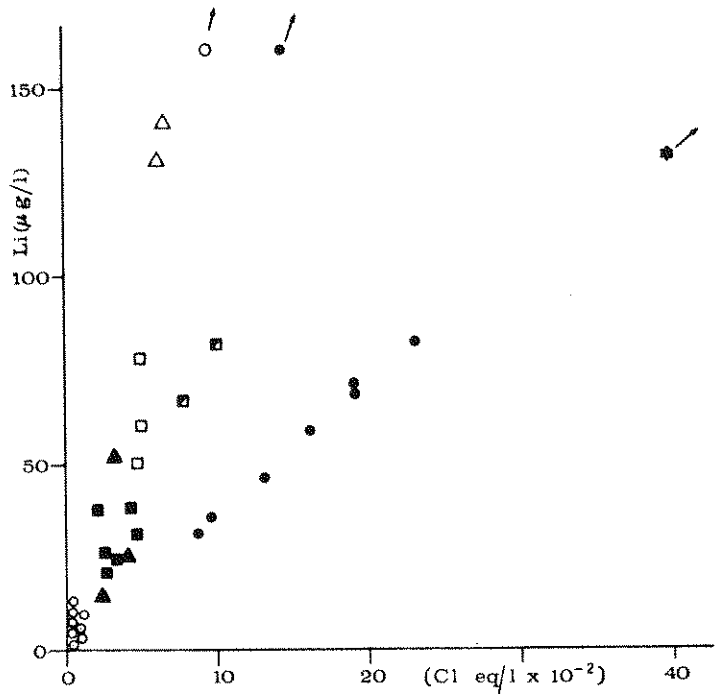

Fig. 4 - Cl-Li correlation (for the symbols see Fig. 1).

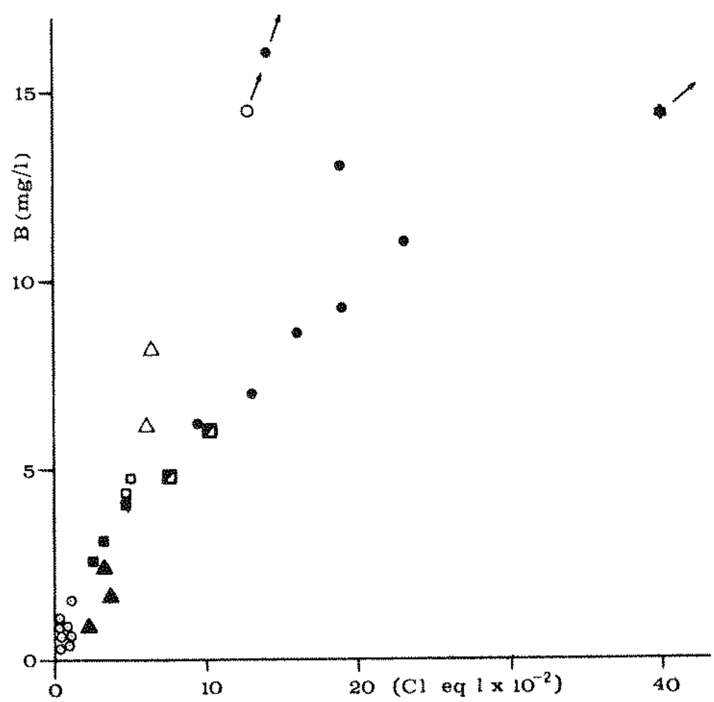

Fig. 5 - Cl-B correlation (for the symbols see Fig. 1).

Actually a further division can be operated if we consider the relationships between the first mentioned Li/B ratio and Cl, shown in Fig. 8, where beside the distinct differentiation compared to the others of the springs group located between Bari and Lecce, one could further distinguish those of Taranto, Trani and Vieste areas from Manfredonia and Varano ones.

With such a division the 1[st] group includes the present seawaters as well, while the 2[nd] group includes very ancient intruding seawater intercepted in the well No. 34.

Moreover, group No. 3 can be further divided since Manfredonia springs, under the same value of Li/B characteristic ratio, show absolute contents of the two ions definitely higher than Varano springs ones (Fig. 7).

It is evident as above reported, that the intruding sea water undergoes a geochemical metamorphism because of its interaction with the rocks. During this interaction sea-water becomes richer in Li, B, Sr, Rb, and sometimes in other trace elements.

Evidently, this enrichment is to be related to seawater residence times in the aquifer, and consequently the same elements, or better the mutual charac-

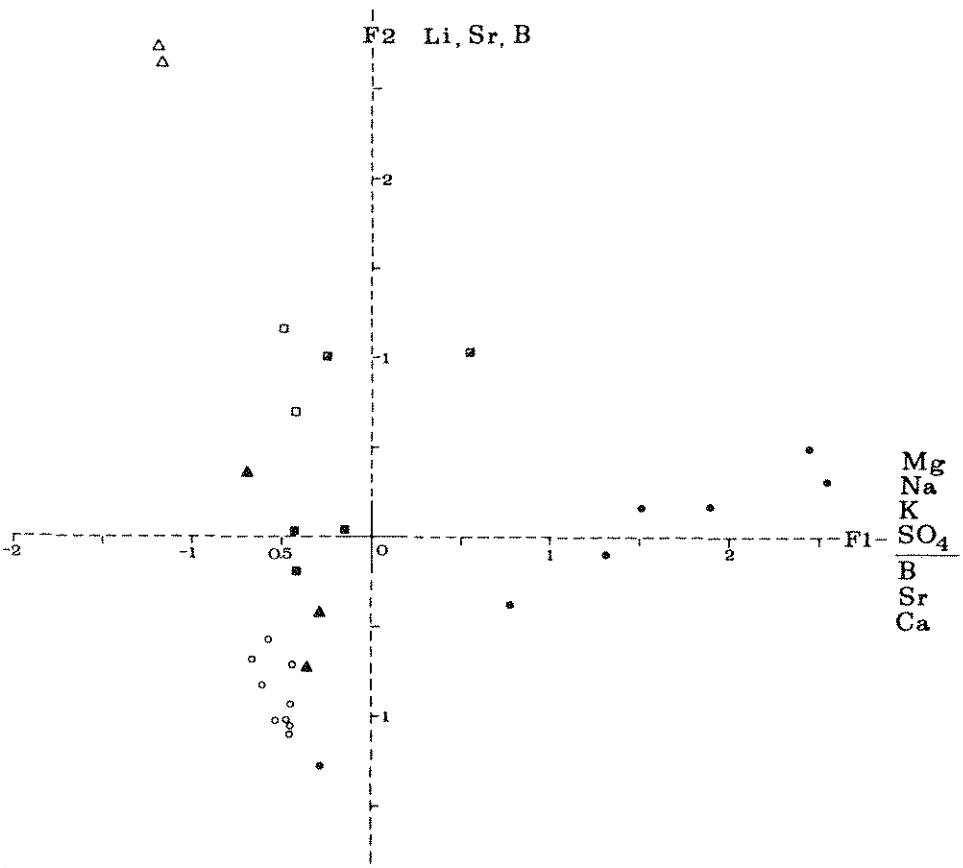

Fig. 6 - R-mode Factor Analysis (for the symbols see Fig. 1)

TABLE 2 – R-mode Factor Analysis

VARIMAX FACTOR LOADINGS MATRIX

Var	Comm		
Ca	0.9148	0.683	0.670
Mg	0.9861	0.935	0.335
Na	0.9835	0.915	0.382
K	0.9886	0.916	0.387
SO_4	0.9887	0.923	0.370
Cl	0.9843	0.907	0.401
B	0.9704	0.766	0.620
Sr	0.9257	0.558	0.784
Li	0.9610	0.230	0.953
Rb	0.9772	0.731	0.665
Rn	0.3902	0.549	0.298

VARIMAX FACTOR SCORES

Samp. P.	Codex No.		
2	14368	1.8928	0.1642
3	14369	2.5511	0.3125
4	14370	1.5031	0.1695
5	15365	1.3019	-0.0960
6	15366	2.4419	0.4945
7	15373	0.7772	-0.3693
8	15371	-0.4226	-1.0844
9	15362	-0.1463	0.0360
10	15361	-0.4260	0.0276
13	15360	-0.4362	-0.1891
15	15356	-0.4927	1.1496
16	15357	-0.4292	0.7045
17	15405	-0.2346	1.0007
18	15404	0.5498	1.0358
19	15369	-1.2157	2.7361
20	14406	-1.1615	2.6051
21	15402	-0.2905	-0.4213
22	15403	-0.3711	-0.7025
23	15401	-0.6965	0.3578
25	15370	-0.4631	-1.0484
26	15374	-0.4626	-1.0975
27	15373	-0.4436	-0.7121
28	15363	-0.4622	-0.9329
29	15364	-0.5330	-1.0269
30	15358	-0.4846	-1.0351
31	15359	-0.6683	-0.6810
32	15367	-0.6014	-0.8248
33	15368	-0.5761	-0.5725

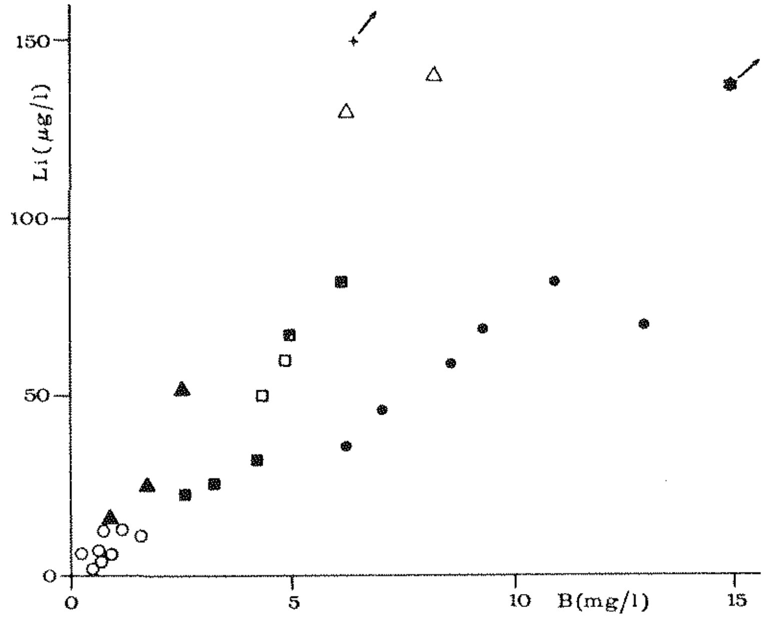

Fig. 7 - B-Li correlation (for the symbols see Fig. 1).

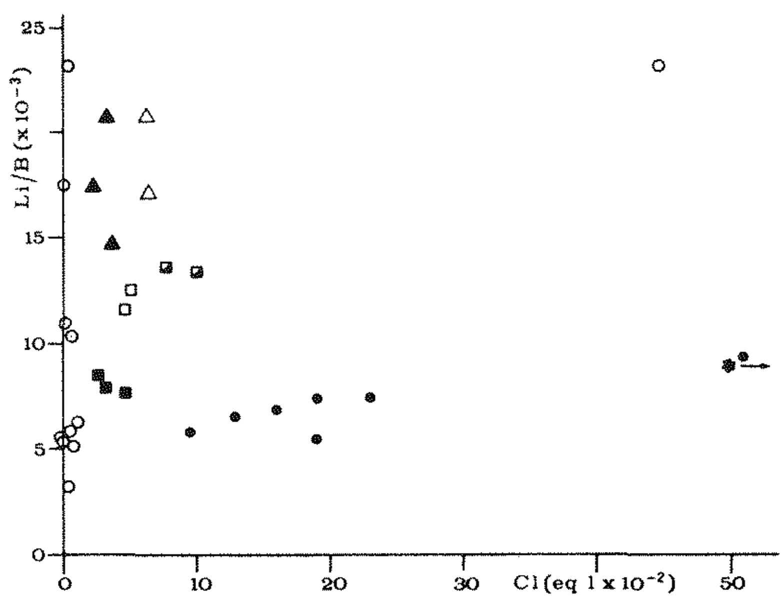

Fig. 8 - Cl-Li/B correlation (for the symbols see Fig. 1).

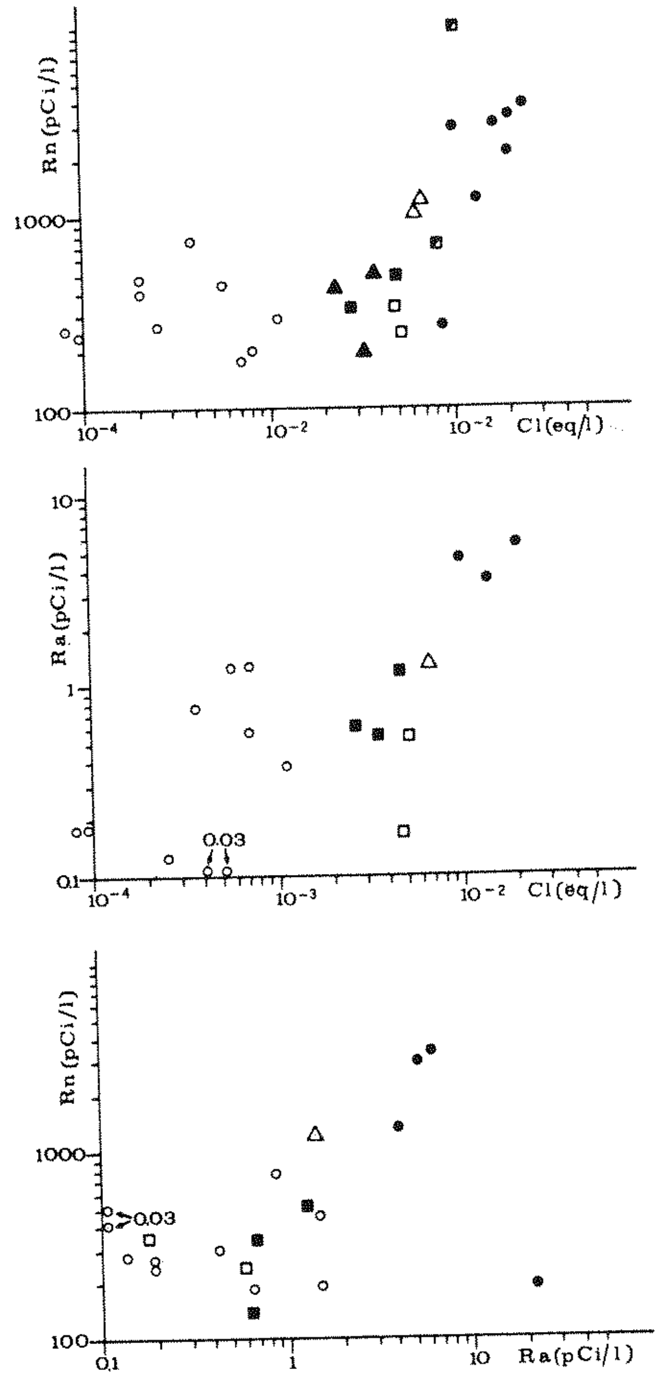

Fig. 9 – Cl-Rn, Cl-Ra and Ra-Rn correlations
(For the symbols see Fig. 1).

teristic ratios can be considered as environmental tracers. Also an increase in temperature may cause an enrichment [2]: an example is shown by S. Ceserea spring (No. 8) [3] that is enriched in the above mentioned elements but right the relationship Li/B versus Cl gives the chance to classify it again, despite the high Li and B contents, in the springs group 1 in type.

Sometimes the Rn has been used like a natural tracer in hydrogeological studies. This element is an inert gas, therefore it has a high mobility but, on the other hand, it is a radioactive element (T/2 = 3,8 d) with short life. For this particular characteristic the study of its behaviour finds important applications in geological field [15, 21].

Magri G. and Tazioli G. S. [13], observed, studying springs and wells in Apulia Region, that, where the Ra content of rocks was uniform an increasing content in Rn was due to an increase in fluids dynamics and viceversa.

The diagrams of Cl versus Rn content, Cl versus Ra content and Ra versus Rn content are reported in Fig. 9. It shows that Rn content is correlated to Cl content in the springs. Only the springs of S. Cesarea (Cl = 510 meq/l) and No. 18 (Rd = 10000 pCi/l) are very scattered in the diagram. In the first case the water was perhaps partially degassed in the sampling point, in the second, (18), high content of radon may be explained by a favourable hydrogeologic situation [13].

The diagrams Ra versus Cl content, and Rn versus Ra content show that the two elements are correlated in the springs. In the last diagram S. Cesarea spring displays an anomalous behaviour as to above mentioned. The average Ra content of ocean is 0,1 pCi/l so that the examined samples are enriched up to 180 times with respect to sea-water. It can be attributed to the water-rocks interaction processes.

5. FINAL CONSIDERATIONS

A first examination of the available data, results in a differentiation of all considered springs in 3 groups.

Each of them is characterized by a different behaviour of the minor elements, though referring to a substancially similar hydrogeological situations as for as the aquifer lithological nature and the chemical influence on fresh water due to intruding sea water are concerned.

The most important consideration likely to be put forward is that probably in various parts of the Apulian aquifer, salt-waters below fresh groundwater show different chemical characteristics right in the minor elements contents and in their mutual relationships.

Such differences affect spring water chemism being a mixing product between fresh waters and salt waters.

This can prove that Trani and Taranto springs drain groundwaters mixed with a sea-water other than the present one characterizing the mixing of springs between Bari and Lecce.

Besides, it is worth considering that Taranto springs represent outflows of concentrated type of the Murgian underground waters circulation [7]. The genesis of this kind of springs is linked to a discontinuity of the clayey formation which prevent, elsewhere, groundwaters discharge into the sea and in the meantime acts as a barrier against present intruding sea waters; these geological conditions are not present in the Adriatic versant, particularly in Bari-Lecce tract.

In other words intruding sea waters, mixed with fresh water which are drained by Taranto springs should be recycled only by sea waters from Adriatic versant, obviously with very long residence times.

Along the coast, in the zone between Bari and Lecce characterized by very favourable permeability conditions, sea water which mix with ground waters before being drained by springs should be present and recycled through the effect of the «cyclical flow». Added to this it is worth saying that water taking conditions in the zones favour the ingression of increasingly more recent sea waters.

The above mentioned distinction may be reasonably referred to sea water residence times very different in the two cases; as a proof of what said, it is

TABLE 3 - Mineral equilibria

	S.P. No. 15	S.P. No. 13	S.P. No. 5	S.P. No. 19
ANHYDRITE	- 1.459	- 1.957	- 1.289	- 1.599
APATCHLR	13.239	11.745	11.864	12.853
APATFLUR	16.506	15.002	14.289	15.348
ARAGONITE	- 0.652	- 0.030	0.030	0.112
CALCITE	- 0.601	0.021	0.080	0.165
CHALCEDONY	0.065	- 0.147	- 0.210	- 0.105
DOLOMITE	- 0.981	0.460	0.995	0.706
HEMATITE	7.626	20.687	13.243	17.254
MAGNETITE	3.436	15.610	10.352	14.902
FLUORITE	- 4.005	- 5.128	- 5.002	- 5.070
GYPSUM	- 1.111	- 1.591	- 0.923	- 1.278
ILLITE	1.910	5.076	3.064	2.760
KAOLINITE	3.186	5.270	3.127	2.979
MAGNESITE	- 1.101	- 0.382	0.092	- 0.279
MONT CA	3.289	5.765	3.164	3.202
MONT K	2.927	5.341	3.010	2.872
MONT MG	3.377	5.863	3.332	3.296
MONT NA	3.231	5.640	3.315	3.188
MUSCOVITE	11.758	15.707	13.249	12.690
QUARTZ	0.666	0.458	0.393	0.489

worth to notice that the well 34 intercept waters with a saline content very close to the typical one of sea water; but this waters can be considered very ancient since they are trapped in the cretaceous limestones which are covered in the Tavoliere by the transgressive clayey deposits.

At present there is no equally acceptable assumption for Gargano springs differentiation.

The mineral equilibria have been studied in some samples by Solmnec program to ascertain some meaningful differences among springs. Some saturation indexes (DELG) are reported in Tab. 3. The solution will be saturated or under saturated according as the index value is >O or <O. In conclusion the examined samples confirm that the analyzed waters have not circulated in very different geological environment.

ACKNOLEDGEMENTS

The authors whish to express their sincere thanks to the officers and to the technicians of the «Ente Autonomo per l'Acquedotto Pugliese» for their collaboration during sampling operation in their installations.

Great appreciation to Dr. Falchi Giannantonio who has offered his precios collaboration to the data processing.

REFERENCES

1 – BRONDI M., DALL'AGLIO M., GHIARA E., GRAGNANI R.: *Heavy Metals in the Environment.* Heidelberg 6-9 September 1983.

2 – BRONDI M., DALL'AGLIO M., VITRANI F.: *Lithium as a pathfinder Element in the Large Scale Hydrogeochemical Exploration for Hydrothermal Systems.* Geothermics, V.2, n. 3-4, pp. 142-153, 1973.

3 – CALÒ G., SPIZZICO M., TINELLI R., ZEZZA F.: *Hydrogeological investigations on the area sourrounding S. Cesarea Terme springs (Southern Apulia).* 8th Salt Water Intrusion Meeting, Bari (Italy), 1983.

4 – COTECCHIA V.: *Gli aspetti idrogeologici del Tavoliere delle Puglie.* L'acqua, A. XXXIV, fasc. 11-12, 1956.

5 – COTECCHIA V.: *Studi e ricerche sulle acque sotterranee e sull'intrusione marina in Puglia (Penisola Salentina).* Ist. Ric. sulle Acque del C.N.R., Quaderni de «La Ricerca Scientifica», n. 20, Roma, 1977.

6 – COTECCHIA V.: *Methodologies adopted and results achieved in the investigations of sea water intrusion into the aquifer of Apulia (Southern Italy).* 6th Salt Water Intrusion Meeting, Hannover (Germany), 1979.

7 – COTECCHIA V., TADOLINI T., TAZIOLI G. S., TULIPANO L.: *Studio idrogeologico della zona della sorgente Chidro (Taranto).* II Conv. Intern. sulle Acque Sott., Palermo, 1973.

8 – COTECCHIA V., TADOLINI T., TITTOZZI P.: *Influenza del chimismo delle piogge sulle acque sotterranee della Puglia.* Geol. Appl. e Idrogeol., vol. VI, Bari, 1971.

9 – COTECCHIA V., TADOLINI T., TITTOZZI P.: *Precipitazioni secche in Puglia e loro influenza sul chimismo delle acque alimentanti la falda sotterranea.* Geol. Appl. e Idrogeol., vol. VIII, Bari, 1973.

10 - COTECCHIA V., TADOLINI T., TULIPANO L.: *The results of researches carried out on diffusion zone between fresh and sea water intruding the land mass of Salentine Peninsula (Southern Italy).* Intern. Symposium of Hydrology of Volcanic Rocks, Lanzarote (Canary Islands), Spain, 1974.

11 - COTECCHIA V., TADOLINI T., TULIPANO L.: *Saline contamination phenomena in the karstic and fissured carbonatic aquifer on the Salentine Peninsula (Southern Italy) and their evolution.* 7th Salt Water Intrusion Meeting, Uppsala (Sweden), 1981.

12 - COTECCHIA V., TAZIOLI G. S., TITTOZZI P.: *Geochimica delle acque della Penisola Salentina in relazione ai rapporti tra le acque di falda, le acque marine sotterranee e il mare.* Geol. Appl. e Idrogeol., vol. X, Bari, 1975.

13 - MAGRI G., TAZIOLI G. S.: *Tecniche di misura del radon in idrogeologia e prime applicazioni alle acque sotterranee della Puglia.* Geol. Appl. e Idrogeol., vol. III, Bari, 1968.

14 - MASTINOG.: *An emanation apparatus with simple operation procedure for measurement of low levels of 226Ra.* Health phis. V. 28, pp. 97-100, 1975.

15 - TADOLINI T., TAZIOLI G. S., TULIPANO L.: *Idrogeologia della zona delle sorgenti Idume (Lecce).* Geol. Appl. e Idrogeol., vol. VI, 1971.

16 - TADOLINI T., TINELLI R., TULIPANO L.: *Discharge conditions and variations of the main hydrological parameters of some coastal Apulian springs relating to sea water influence on groundwater.* 8th Salt Water Intrusion Meeting, Bari (Italy), 1983.

17 - TADOLINI T., TULIPANO L.: *Primi risultati delle ricerche sulla zona di diffusione della falda profonda della Penisola Salentina (Puglia).* I Conv. Intern. sulle Acque Sott., Palermo, 1970.

18 - TADOLINI T., TULIPANO L.: *La misura del contenuto in cloro, bromo e iodio delle acque sotterranee della Penisola Salentina (Italia Meridionale) in rapporto alle acque adi mare di invasione continentale.* III Conv. Intern. sulle Acque Sott., Palermo, 1975.

19 - TADOLINI T., TULIPANO L.: *The conditions of the dynamic equilibrium of ground water as related to encroaching sea water.* Symposium on « Hydrodinamic diffusion and dispersion in porous media ». Pavia, 1977.

20 - TADOLINI T., TULIPANO L.: *The evolution of fresh water-salt water equilibrium in connection with drafts from the coastal carbonate and karst aquifer of the Salentine Peninsula (South Italy).* 6th Salt Water Intrusion Meeting. Hannover (Germany), 1979.

21 - TULIPANO L.: *Ricerche idrogeologiche preliminari sulle acque sotterranee della media valle del Torrente Raganello (Calabria).* Quaderni dell'Istituto di Ricerca sulle Acque del CNR, n. 6, 1972.

22 - TULIPANO L., TADOLINI T., FIDELIBUS M. D.: *Significativi aspetti delle acque sotterranee circolanti nell'acquifero carsico della Penisola Salentina (Italia meridionale).* II Int. Symp. « Utilization of karst areas », Bari, 1982.