Mem. Descr. Carta Geol. d'It.
XC (2010), pp. 51-66,
figg. 12, tabb. 2

Hydrogeologic-hydrogeochemical multidisciplinary study of the confined gravelly aquifer in the coastal Pisan Plain between the Arno River and Scolmatore Canal (Tuscany)

Studio multidisciplinare idrogeologico-geochimico dell'acquifero confinato in ghiaie nella fascia costiera pisana tra il Fiume Arno ed il Canale Scolmatore (Toscana)

BUTTERI M. (*), DOVERI M. (**),
GIANNECCHINI R. (***), GATTAI P. (*)

Abstract - The gravelly horizon of the Pisa plain multilayered system, located at a depth between 50 and 100 m below the sea-level and about 10-20 m thick, is a confined aquifer tapped by a large number of wells. It contains a very important water resource for drinking, industrial and irrigable uses, although in some cases the groundwater is of poor quality.

In order to evaluate if in the coastal area between the Arno River and Scolmatore Canal this aquifer is interested by seawater intrusion and to understand the mixing mechanisms with fresh water, a multidisciplinary study was carried out by means of hydrostratigraphic correlations, water level collection and chemical and isotopic analysis. In particular, three on-site surveys were carried out in June and August 2008 and April 2009. In most of the measured points, piezometric values below the sea-level were collected; particularly depressed levels were registered in August 2008 near the coastline in the southern part of the study area (Calambrone zone) and in the internal part to North (S. Piero a Grado zone). Water-wells sampled along the coast, less than 1.5-2 km far from the coastline, show chemical composition and $\delta^{18}O$‰ values indicative of seawater-fresh water mixing. This phenomenon, in agreement with piezometric conditions, is more evident in the southern zone, toward the Scolmatore Canal, where the fraction of salt water, calculated using the mass balance model of Cl, Br and $\delta^{18}O$‰, is about 7-8%.

Most of the other samples, collected up to 5 km from the coastline, were not interested by seawater; in these cases, groundwater shows the same characteristics found toward the internal part of the Pisa plain, with relatively low TDS and $\delta^{18}O$‰ indicative of recharge average altitudes higher than local altitudes. Only two samples, collected in the North-East portion near the Arno River, showed chemical and isotopic characteristics indicative of a seawater presence of about 8-9%. In these cases, $\delta^{18}O$‰ values clearly show that the seawater intrusion does not directly occur in the gravelly aquifer, but trough the shallow sandy aquifer, which in this zone is in contact with the gravel.

Key words: Hydrochemistry, Hydrogeology, Northern Tuscany, Piezometric condition, Seawater intrusion, Water isotopes.

Riassunto - Il livello in ghiaie dell'acquifero multistrato della Pianura di Pisa, che si trova in generale ad una profondità compresa tra 50 e 100 m sotto il livello del mare ed è spesso circa 10-20 m, costituisce un acquifero confinato interessato da numerosi pozzi di emungimento. Esso contiene certamente una delle principali risorse idriche per approvvigionamento idropotabile, industriale e agricolo, sebbene, in diversi casi, l'acqua non sia di ottima qualità.

Al fine di valutare se nell'area costiera pisana meridionale, compresa tra il Fiume Arno e il Canale Scolmatore, tale importante acquifero sia interessato da fenomeni di intrusione marina, nonché per conoscere i meccanismi di miscelazione tra acque dolci e acqua di mare, è stato effettuato uno studio multidisciplinare mediante correlazioni idrostratigrafiche, rilevamento dei livelli piezometrici e analisi chimiche ed isotopiche delle acque. In particolare, sono state effettuate tre campagne di misura (Giugno e Agosto 2008 ed Aprile 2009).

In ciascun punto di misura è stato rilevato il livello piezometrico riferendolo al livello del mare; aree con superficie piezometrica particolarmente depressa sono state rinvenute

(*) Geologist, external collaborator
(**) Consiglio Nazionale delle Ricerche - Istituto di Geoscienze e Georisorse, Pisa
(***) Dipartimento di Scienze della Terra - Università di Pisa

in Agosto 2008 nella parte più meridionale dell'area di studio (zona Calambrone) ed in quella più interna settentrionale (zona S. Piero a Grado). I campioni di acqua raccolti lungo costa, entro 1,5-2 km dalla linea di riva, mostrano composizione chimica e δ^{18}O‰ indicativi di mescolamento tra acque di falda e acqua di mare. Questo fenomeno, in accordo con le osservazioni piezometriche, risulta più marcato nel settore meridionale dell'area, verso il Canale Scolmatore, dove la frazione di acqua salata, valutata usando bilanci di massa di Cl, Br e δ^{18}O‰, è intorno al 7-8%. La maggior parte degli altri campioni analizzati, raccolti fino a 5 km dalla linea di riva, non è interessata da fenomeni di intrusione marina; in questi casi, le acque sotterranee mostrano le stesse caratteristiche rinvenute nella parte interna della piana di Pisa, con un TDS relativamente basso e valori di δ^{18}O‰ indicativi di quote medie di ricarica maggiori delle quote locali. Soltanto due campioni, raccolti in prossimità dell'Arno nella parte più interna a Nord, mostrano caratteristiche chimiche ed isotopiche attribuibili alla presenza di acqua di mare in percentuali di circa 8-9%. In tali casi, i valori di δ^{18}O‰ mostrano chiaramente che l'intrusione di acqua di mare non avviene direttamente nell'orizzonte ghiaioso, ma attraverso gli acquiferi sabbiosi superficiali, che, in questa zona, sono in contatto diretto con le ghiaie più profonde.

PAROLE CHIAVE: Idrochimica, Idrogeologia, Intrusione marina, Isotopi dell'acqua, Piezometria, Toscana settentrionale.

1. - INTRODUCTION

The coastal plains usually represent preferential areas regarding the anthropic, industrial and agricultural settlements. This is due in particular to their easiness of access and transport, the water availability and the fertility of fields. In the world, more than 150 millions of people live below the altitude of 1 m a.s.l. and 250 millions live below the altitude of 5 m a.s.l. (UNESCO, 2007). Moreover, the tourist attitude which usually characterizes the coastal areas causes a significant seasonal increase of the population.

As a consequence, these regions are characterized by strong human pressure, which often lead to the deterioration of the environmental system, and in particular of the water resource. The pollution phenomena as well as the overexploitation of the groundwater cause a progressive qualitative and quantitative worsening of the water store. One of the most recurring effects is the variation of the natural equilibrium between fresh and sea waters, with consequent advancing of the seawater intrusion in the coastal aquifers (CUSTODIO, 2002). Recent studies (ERICSON *et alii*, 2006) moreover show that in many coastal regions in the world this process is accentuated by sea-level rise (up to 12.5 mm per year), mainly caused by a reduction of the supply of solid materials from the rivers (WALLING & FANG, 2003). However, other causes are represented by the subsidence phenomena, natural eustatic and climatic variations.

Many Italian coastal areas are involved in the seawater intrusion phenomenon (BARROCU, 2003; CAPACCIONI *et alii*, 2005; GIAMBASTIANI *et alii,* 2007; ANTONELLINI *et alii*, 2008); in Tuscany several critical situations linked to the salinization of the coastal aquifer have been highlighted by many authors (ROSSI & SPANDRE, 1994; BARAZZUOLI *et alii*, 1999; GRASSI & NETTI, 2000; GIMÉNEZ FORCATA *et alii*, 2001; GIANI *et alii*, 2001; PRANZINI, 2002; GRASSI *et alii*, 2007; DOVERI *et alii*, 2009).

In order to face the above mentioned problems regarding the interference between seawater and freshwater and to plan the water resource management, specific studies aimed at defining a detailed outline of the aquifer systems are needed. This study is included in a wide project that concerns the whole Versiliese-Pisana coastal plain which forms the Migliarino-San Rossore-Massaciuccoli Regional Park. This area has a high environmental value, due to its great variety of natural settings, ranging from dunes to sandy shores and from hygrophilous forests to marshlands.

In particular, in this study the occurrence of the seawater intrusion in the gravel confined aquifer (BALDACCI *et alii*, 1994) is analyzed in the area between the Arno River and the Scolmatore Canal (fig. 1a), with an extent of about 7-8 km from the coastline.

The problem was already approached by others authors (ROSSI & SPANDRE 1994; GRASSI & ROSSI 1996; SPANDRE *et alii*, 1999; FRONDINI *et alii*, 2001; GRASSI & CORTECCI, 2005). This aquifer is an important and strategic resource for the area, because it is the only able in providing a substantial volume of water in order to satisfy the request of the agricultural and zootechnical firms, tourist structures (in particular bathing establishments), and, not the last, the drinking use. Such human pressure could move forward the salt wedge in this aquifer.

In this work, the coastal aquifer salinization was analyzed by means of a multidisciplinary approach: integration of the hydrostratigraphic knowledge, verification of the piezometric conditions, analysis of chemical features and isotopic contents of the water sampled in three periods (June and August 2008, April 2009). In particular, this work is aimed at analyzing the present situation about the contamination of the first gravel aquifer of the Pisan coastal plain and at comprehending the mechanism of the fresh-salt water mixing. Referring to the last issue, the isotopic analysis represents a significant approach, also considering the availability of past isotopic surveys carried out in zones close to the studied area (GRASSI & CORTECCI, 2005) and in its surroundings (MUSSI *et alii*, 1998; DOVERI, 2004; DOVERI *et alii*, 2009).

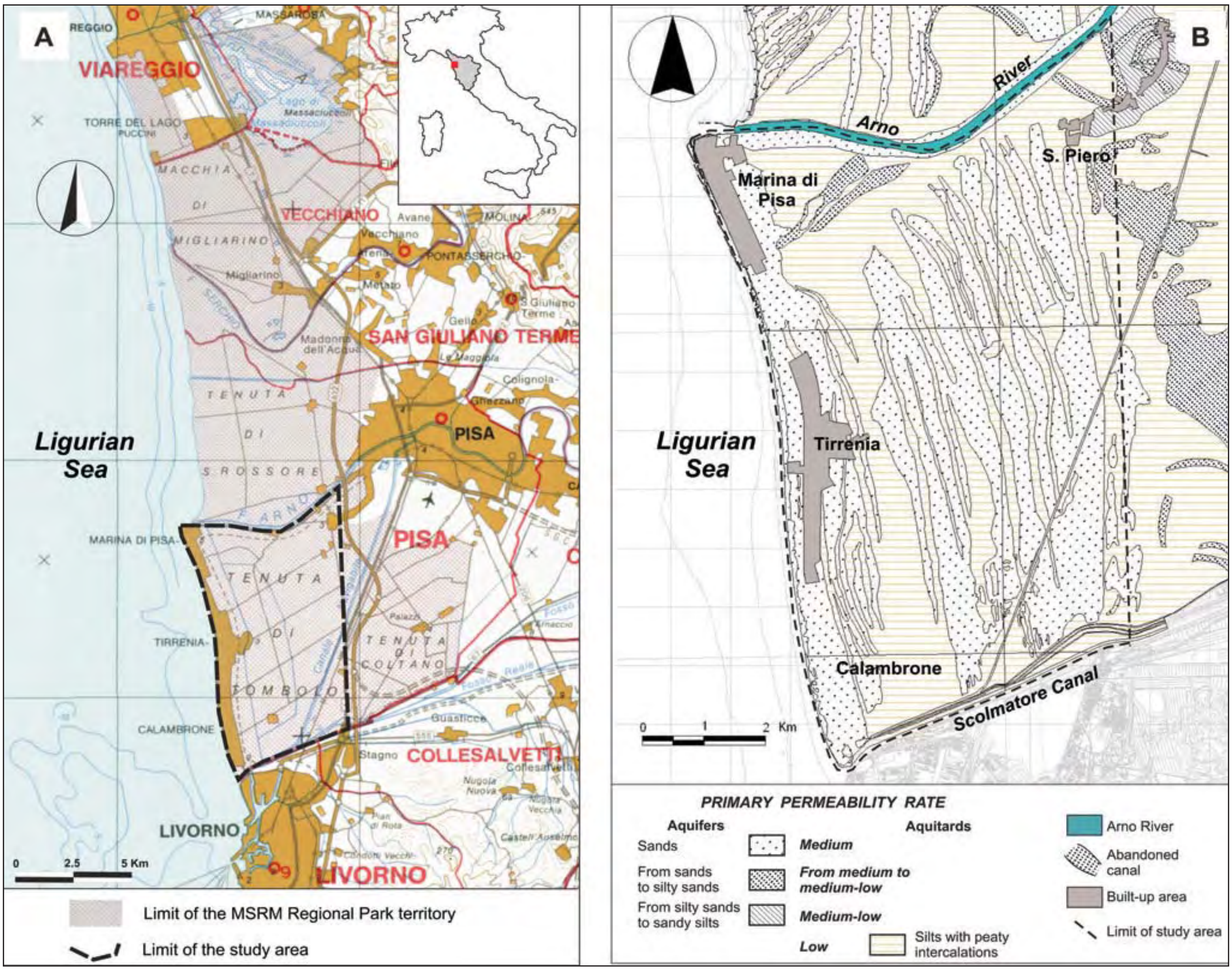

Fig. 1 - a) Location map of the study area (cartographic base by REGIONE TOSCANA, 1988). b) Permeability map, derived from the *Provincia di Pisa* (2005) geological map. - *a) Inquadramento geografico dell'area di studio (base cartografica da* REGIONE TOSCANA, *1988). b) Carta della permeabilità, elaborata sulla base della carta geologica della Provincia di Pisa (2005).*

2. - GEOLOGICAL AND GEOMORPHOLOGICAL SETTING

The Pisan coastal aquifers are included in a more complex depositional system, which constitutes the post-orogenic filling of the graben named Versiliese-Pisan Basin. This basin extends from the mouth of the Magra River to the North, to the surroundings of Pisa and Livorno to the South (MAZZANTI & PASQUINUCCI, 1983; FEDERICI, 1993). This structure is formed by a sub-triangular tectonic depression (direction NW-SE) and is delimited by the Apuan Alps, Oltre Serchio Mountains and Pisan Mountains to the East, the submerged Viareggio ridge to the West, and the Livornesi and Casciana Mountains to the South.

From Upper Miocene, the bedrock of the depression (characterized by formations of the Tuscan and Ligurian Units) was interested by deposition of marine, marine-transitional and continental incoherent sediments (GIANNINI & NARDI, 1965; RAU & TONGIORGI, 1974). The last mainly derive from the Magra, Serchio and Arno rivers basins.

Variations of the sea-level attributable to ice-age episodes are documented in the studied area during the Middle Pleistocene. The Würm II ne-gative one is particularly significant for the Pisan plain area. This phase is proved by clastic deposits of the ancient *Paleo*-Arno River, chiefly rich in pebbles coming from Pisan Mountains and Garfagnana area, which were transported by the ancient *Paleo*-Serchio River. In fact the latter, which drains the Garfagnana area, flowed in the past into the *Paleo*-Arno River through the Bientina depression (East of Pisan Mountains) (MAZZANTI & PASQUINUCCI, 1983). Afterwards, fluvial-lacustrine silt settled on these deposits, due to a reduced fluvial activity, probably linked to both the cessation of sea-level fall, and to a climatic drying up (DELLA ROCCA *et alii*, 1987). Above the fluvial-palustrine silt aeolian sands lie.

The combined effect of formation of dunes and progressive sea-level rise prevented an easy coastal outlet of the main rivers, originating marshes and lagoons and the deposition of finer materials also containing peat and lignite (Fancelli, 1984). This type of environment remained typical of the Pisan plain till historic present (Della Rocca *et alii*, 1987).

3. - HYDROGEOLOGICAL FEATURES

In order to define the shallow hydrogeological conditions of the area included between the Arno River and the Scolmatore Canal, a permeability map was elaborated (fig. 1b). In particular, the available geological map of the area (Provincia di Pisa, 2005) was converted into a permeability map on the basis of both literature information and of the grain size properties of the materials, in agreement with a previous classification of Baldacci *et alii* (1994).

The hydrogeological units have been classified as aquifer and aquitards after parametrization with estimates of permeability ranges. The aeolian and shore deposits, constituted by medium-fine sand, have a medium permeability (about 10^{-4}-10^{-5} m/s, according to Baldacci *et alii*, 1994). Sometimes, in the dune sands silt and peat levels occur, resulting in local lowering of permeability of the sands. The sandy deposits, belonging to ancient abandoned rivers, the "Sabbie e limi di Vicarello" formation (sand and silt) and the overlying alluvial deposits (silty sands) range in permeability from medium to low. The fluvial-palustrine materials have a low permeability, due to the presence of silt.

In the Pisan plain subsurface, below the discontinuous superficial phreatic aquifers, of poor practical interest, there is a complex multi-level confined aquifer that contains two major confined aquifers defined, from the top to the bottom, "1st sandy confined aquifer" and "1st gravelly confined aquifer" (Baldacci *et alii,* 1994); the hydrostatigraphic, hydrodynamic, piezometric and hydrochemical features of such aquifers were defined and described by several authors (Rossi & Spandre, 1994, 1995; Baldacci, 1999; Frondini *et alii*, 2001; Grassi & Cortecci, 2005).

The roof depth of the 1st sandy confined aquifer changes from 20-30 m to the South of the Arno River, to 50-60 m in the Pisa area; then, it goes up again northward (Baldacci *et alii*, 1994). It is prevalently constituted by sandy deposits (Dini, 1976). The recharge of this aquifer is mainly located in the coastal dune area between the Arno and Serchio rivers, in the piedmont of the Pisan plain (where the sandy deposits are directly in contact with the fan gravelly materials), and through the alluvial deposits of the Serchio River at the Ripafratta Strait (Spandre *et alii*, 1999). This aquifer becomes phreatic close to the coastal area, because it is in hydraulic connection with the dune system (fig. 2).

The 1st gravelly confined aquifer is included in *Arno e Serchio da Bientina* conglomerates, represented by clastic fluvial deposits (pebbles of quartz, anagenite, limestone) with high permeability, which originated during the migration of the Serchio and Arno riverbeds (Della Rocca *et alii*, 1987). According to Baldacci *et alii*, 1994 (data obtained by pumping tests) the hydraulic conductivity of the gravelly aquifer is about 10^{-3} m/s, and locally reaches 10^{-2} m/s. The alluvial origin of such deposits implies some discontinuities in a bidimensional representation (see section 1 in fig. 2), which does not exclude possible hydraulic connections in the third dimension. However, these conglomeratic levels are connected to the sea at least in the mouth of the ancient *Paleo*-Arno river, individuated by Serge (1955) and Mazzanti & Pasquinucci (1983). In agreement with Baldacci *et alii* (1994) the recharge of this aquifer is principally due to the direct infiltration on the Vicarello hills, through the pebbly bodies which lie in the piedmont areas and in the intermountain valley of the Pisan Mountains, and through the alluvial deposits of the Bientina area.

The analysis of many stratigraphic logs of the coastal area, provided by the Province of Pisa Administration, allowed us to integrate previous stu-dies (Baldacci *et alii*, 1994, 1998; Baldacci, 1999), describing the hydrostratigraphic structure of the study area by means of two longitudinal and three cross-sections (fig. 2). The gravelly level seems more continuous in the SW area, among Tirrenia, Tombolo and Calambrone villages (fig. 2, sections 2, 3, 4, 5). As cited above (fig. 2, sections 1, 4), the gravel horizon is characterized by several lenticular alluvial bodies, partly overlapped. In the S. Piero a Grado zone (fig. 2, section 1), the discontinuous gravelly levels are interposed between the main sandy aquifer (fed also by the dune system) and the deeper gravelly aquifer. Hydraulic connections are also possible between the two main aquifers by vertical exchange phenomena through the semi-permeable thin horizons which separate such aquifers (Baldacci, 1999). In general, the principal gravelly levels are less than 10 m thick and are located at 50 m below the land surface in the southern part of the study area and at about 100 m northward (fig. 2, section 4).

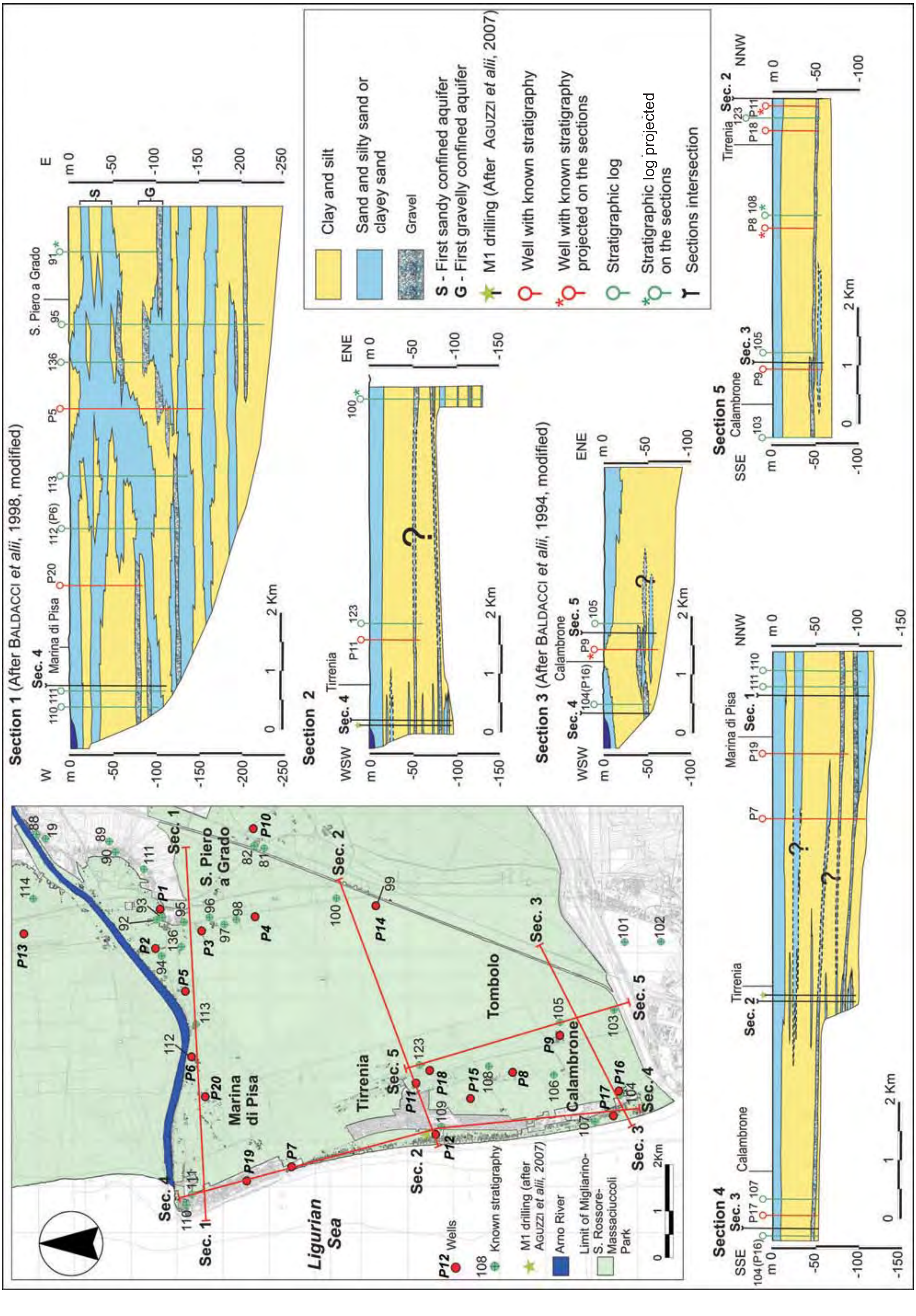

Fig. 2 - Hydrostratigraphic cross-sections of the southern coastal Pisan plain. - *Sezioni idrostratigrafiche della porzione meridionale della pianura costiera pisana.*

This hydrostructural outline generally confirms the model of the local groundwater circulation proposed by Baldacci *et alii* (1994) and Rossi & Spandre (1994, 1995), with two main aquifers (sandy and gravelly) sometimes composed by more levels in hydraulic connection among them and with the sea floor.

4. - ON-SITE SURVEYS AND ANALYTICAL METHODS

The research was carried out by several steps. Firstly, in order to obtain piezometric data, the water wells which intercept the gravelly aquifer were chosen (fig. 3) by means of existing hydrogeological documents and on-site surveys. For each well, the absolute elevation (in m a.s.l.) of the topographic surface was obtained using a specific planimetric-altimetrical survey with a double-frequency instrument Leica GPS 1200 Series (planimetric precision in mm ± 10 +1 ppm; altimetrical precision in mm ± 20 +1 ppm) in RTK (Real Time Kinematics) modality, with correction from single station (nearest site).

Three field surveys were carried out in June and August 2008 and April 2009, respectively. With regard to the first one, the piezometric level, temperature and electric conductivity were measured and the chloride concentrations were determined on a selection of water-wells.

In the subsequent surveys, the alkalinity (through titration with HCl 0,1M) and pH were measured in addition to the others data. Some water samples (raw and filtered-acidified) were collected for chemical and isotopic analysis. Sampling was done in 20 wells tapping the gravelly aquifer, and in one point of the Arno River (only in April 2009) at two different depths (1 and 4 m under water level). The determination of the anions Cl^-, SO_4^{2-}, Br^-, NO_3^- was obtained by ion chromatography, while the cations Na^+, K^+, Ca^{2+}, Mg^{2+} were analyzed by means of optical ICP. The $\delta^{18}O$‰ and δ^2H‰ (Fritz & Fontes, 1980) were determined by means of mass spectrometry in gas phase, after sample preparation using vacuum lines and isotopic equilibration at 25°C with CO_2 ($\delta^{18}O$‰) and at 460 °C with Mg (δ^2H‰). The used reference isotopic standard is V-SMOW (Hoefs, 2004) and the standard error is ±0.1 ‰ and ±1 ‰ for $\delta^{18}O$‰ and δ^2H‰ respectively.

The use of environmental isotopes in this type of study yields more useful information than classic chemical elements do. In fact, the isotopic contents are not influenced by interaction processes between water and solid matrix in normal temperature conditions. This implies that the isotopes preserve information about the origin of the infiltration water and, referring to the coastal aquifer, permit to discriminate if the water salinity is really attributable to the seawater-fresh water mixing or if it is attributable to dissolution phenomena in sea deposits, which are present in the study area.

The piezometric and physical-chemical data obtained on site are shown in table 1, while the results of the chemical and isotopic analysis are shown in table 2.

5. - PIEZOMETRIC LEVELS AND ELECTRIC CONDUCTIVITY (EC)

Because of the random distribution of water-wells and of the absence of data for some wells, the piezometric maps shown in figure 4 are only representative of the broad piezometric configuration and are not aimed to describe the flow patterns in detail. These maps substantially evidence the presence of water levels generally below the sea-level on most of the territory and of two local piezometric depressions, in the S. Piero a Grado (wells P1-P2-P3) and Calambrone (wells P8-P9) zones respectively.

Further considerations are possible taking into account the seasonal variations of the water level and the existing relationship between water level (figs. 3, 4 and 5) and the groundwater electric conductivity (EC) (figs. 3 and 5). Referring to the June and August 2008 surveys, all the piezometric data show values below the sea-level, with a relative drawdown in August more than 1 m in comparison with the June data. Such a drawdown (maximum in the wells P2 and P3, S. Piero a Grado area), of about -1.40/-1.50 m, is mainly related to the intense pumping which is typical of the summer period for the study area. An exception is represented by the well P1, probably due to the pumping before June 2008, which could have significantly influenced the measured piezometric level. As regards the April 2009 survey, despite the measured piezometric levels are still below the sea-level, we can note a general raising of more than 1 m with respect to the two previous surveys. The major rise of the water level was individuated in the wells P2 and P10, with 1.96 m and 2.25 m respectively in comparison with the August 2008 situation. This might result from the combination of abundant rainfall from autumn 2008 to winter and spring 2009 and significant pumping reduction during the same period.

With regard to the wells P15, P16, P17, P18 and P20, only April 2009 data are available, thus the comparison with the previous surveys is not possible. What's more, only in these water-wells, ex-

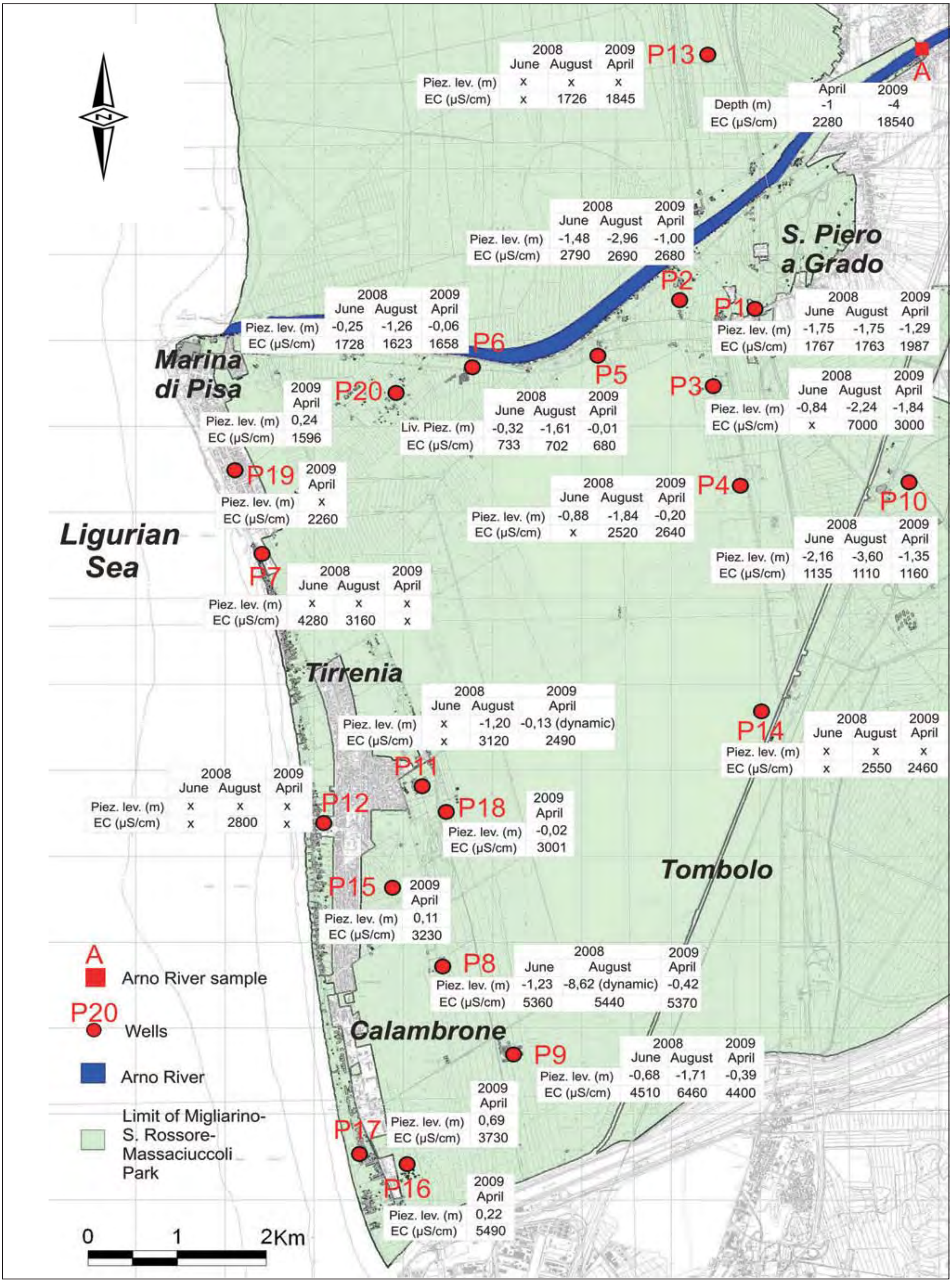

Fig. 3 - Location of the water sampling points and piezometric and electric conductivity (EC) data.
- Ubicazione dei punti d'acqua campionati e dati piezometrici e di conducibilità elettrica.

Tab. 1 - *Piezometric and physical-chemical data collected on site (^: sampling depth from water level; *: dynamic level; n.m.: not measured; location of sampling points in figure 3).*
- Dati piezometrici e chimico-fisici ottenuti in sito (^: profondità di campionamento rispetto alla quota del pelo libero dell'acqua; *: livello dinamico; n.m.: non misurato; ubicazione dei punti di campionamento in figura 3).

Water point	Well depth (m)	JUNE 2008			AUGUST 2008				APRIL 2009			
		Piezometric level (m a.s.l.)	Conductivity (µS/cm at 25°C)	T (°C)	Piezometric level (m a.s.l.)	Conductivity (µS/cm at 25°C)	pH	T (°C)	Piezometric level (m a.s.l.)	Conductivity (µS/cm at 25°C)	pH	T (°C)
P1	100	-1.75	1767	18,6	-1,75	1945	6,83	19,1	-1,29	1987	6,82	18,2
P2	105	-1.48	2790	17,7	-2,96	2640	7,25	17.7	-1,00	2680	7.25	17.6
P3	97	-0.84	n.m.	n.m.	-2,24	8750	7,52	17,1	-1,84	3000	6,98	15,2
P4	101	-0.88	n.m.	n.m.	-1,84	2530	6,57	18,5	-0,43	2640	6,74	18,7
P5	154	-0.32	733	15,4	-1,61	723	10,30	16.1	-0,01	680	9.97	14.8
P6	131	-0,25	1728	20,6	-1,26	1762	7,19	20,0	-0,06	1658	6.86	18.1
P7	110	n.m.	4280	20,9	n.m.	3400	7,16	20,0	n.m.	n.m.	n.m.	n.m.
P8	50	-1.23	5360	19,5	-8.62*	5560	7,33	20,5	-0,70	5370	7,09	19,8
P9	54	-0.68	4510	20,7	-1,71	6460	7,20	19,5	-0,39	4400	6,78	17,0
P10	72	n.m.	1135	17,6	-3,60	1190	7.27	17.8	-1,35	1160	6.94	17.9
P11	55	n.m.	n.m.	n.m.	-1,20	3120	7,16	20,0	-0.13*	2490	6,99	20,6
P12	80	n.m.	n.m.	n.m.	n.m.	2800	6,78	20,6	n.m.	n.m.	n.m.	n.m.
P13	100	n.m.	n.m.	n.m.	n.m.	2040	6,55	20,0	n.m.	1845	6,68	19,0
P14	60	n.m.	n.m.	n.m.	n.m.	2550	6,90	16,80	n.m.	2460	6.96	16.9
P15	55	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	0,11	3200	6.91	17.6
P16	43	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	0,22	5490	6,86	15,3
P17	55	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	0,69	3730	7,24	17,6
P18	70	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	-0,02	3100	6,92	18,6
P19	92	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	2260	6,92	17,5
P20	85	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	0,24	2596	7,08	17,0
Arno River (depth 1 m)	1^	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	2280	6,93	16,6
Arno River (depth 4 m)	4^	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	18540	7,06	16,1

cept one (P18), we recorded water levels above the sea-level (maximum +0.69 m a.s.l. in P17).

After all, considering all the data collected, in two areas (S. Piero a Grado and the area between Tombolo and Calambrone, figs. 3, 4 and 5) the piezometric level is particularly depressed below the sea-level. On the other hand, in these areas the main farms are present. Such a piezometric situation was already highlighted by ROSSI & SPANDRE (1994) and BALDACCI *et alii* (1999).

In the water-wells belonging to these areas we also recorded higher EC values (7,000 and 6,460 µs/cm, in P3 and P9 respectively in August 2008). However, we can observe in general high values of EC (frequently more than 3,000 µs/cm) in all the wells close to the coastline between Marina di Pisa and Calambrone villages, with a tendency to raise southward. With the exception of P2, P3 and P4 (S. Piero a Grado area), almost all the water sampled in the well of inland zones are characterized by electric conductivity relatively low, often minor than 2,000 µs/cm.

From June 2008 to April 2009 we can observe significant variations of EC only at P3 and P9, with higher values in August 2008, corresponding to the lower piezometric level. The maximum EC (18,500 µs/cm) was recorded for the Arno River close to the bottom of the bed (-4 m from the surface of the water). This is clearly attributable to the seawater which goes upstream for several kilometres, as documented for this area by various authors (LA RUFFA & PANICHI, 2000; CORTECCI *et alii,* 2002).

6. - CHEMICAL AND ISOTOPIC CHARACTERISTICS OF THE WATER

Figure 6 shows that most samples of groundwater are usually characterized by an intermediate chemical composition Ca-Na/HCO_3-SO_4, Ca-Na/HCO_3-SO_4-Cl or Ca-Na/HCO_3-Cl. Among the remaining samples, P10 is Ca/HCO_3, P13 Ca/SO_4, while P2-P8-P16-P17 and P3-P9 sampled in August 2008 have a composition Na/Cl (see fig. 3 for the location of the water sampling points).

In general, we can observe that up to middle values of TDS (fig. 7) the salinity is mainly regulated by HCO_3 and sometimes by SO_4. On the contrary, high values of TDS depend on Cl contents.

Regardless of the TDS values, some water samples show particularly low values in SO_4, due to the phenomenon of reduction by bacteria, as highlighted by GRASSI & CORTECCI (2005) during studies on the internal portion of the Pisan Plain.

After all, the chemical composition points out that in the study area the gravelly aquifer is characterized by a water circulation with prevalently Ca/HCO_3-SO_4 composition, which evolves towards Na/Cl composition caused by seawater mixing. This process is confirmed by the fact that the samples with high Cl contents have Na/Cl and Br/Cl ratios comparable to those of the seawater (figs. 8 and 9).

The significant influence of sulphate in the groundwater chemical features, not involved in seawater mixing, is attributable to a feeding component from the Mesozoic calcareous aquifer, in hydraulic connection with the gravel aquifer (GRASSI & CORTECCI, 2005). In fact, this calcareous aquifer outcrops on the hills close to the Pisan Plain and constitutes its bedrock as well. The water circulating in this aquifer is mainly characterized by Ca-SO_4, as demonstrated by chemical analyses of some springs located in the Pisan Mountains edge (GRASSI *et alii*, 1994).

In agreement with the electric conductivity and piezometric level, the chemical features show that the seawater-freshwater mixing is particularly evi-

Tab. 2 - *Chemical and isotopic data (n.d.: not determined; location of sampling points in figure 3).*
- Dati chimici e isotopici (n.d.: non determinato; ubicazione dei punti di campionamento in figura 3).

Sampling period	Water point	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	Cl^{-} (mg/l)	NO_3^{-} (mg/l)	SO_4^{2-} (mg/l)	HCO_3^{-} (mg/l)	Br^{-} (mg/l)	$\delta^{18}O$‰	$\delta^{2}H$‰
JUNE 2008	P2	n.d.	n.d.	n.d.	n.d.	507,1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	P6	n.d.	n.d.	n.d.	n.d.	220,4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	P8	n.d.	n.d.	n.d.	n.d.	1256,3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	P9	n.d.	n.d.	n.d.	n.d.	780,4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
AUGUST 2008	P1	176,5	49,7	145,3	7,8	159,0	0,4	408,8	482,0	0,5	-6,60	-41,5
	P2	89,3	35,6	401,7	9,6	479,3	6,6	208,5	518,6	1,7	-6,02	-36,4
	P3	140,1	136,2	1019,1	38,9	1926,9	25,8	142,8	671,1	5,9	-5,37	-34,9
	P4	291,4	73,7	179,9	12,4	186,7	<0.2	546,9	707,7	0,6	-6,82	-38,7
	P6	156,6	45,6	145,6	6,5	177,8	<0.2	263,0	457,6	0,6	-6,55	-39,4
	P7	248,7	76,1	314,2	16,6	452,4	6,7	370,8	762,7	1,9	-6,59	-38,6
	P8	119,6	71,5	892,9	24,0	1395,2	<0.2	23,6	875,5	6,1	-6,18	-36,6
	P9	137,0	160,1	969,9	41,4	1542,6	0,8	62,9	1421,6	6,1	-6,25	-39,4
	P10	93,5	25,3	110,4	5,7	114,5	0,3	82,3	408,8	0,4	-6,60	-41,1
	P11	259,5	85,0	292,8	17,5	352,5	27,6	487,4	799,3	1,5	-6,87	-39,8
	P12	246,0	77,5	256,6	14,0	331,9	1,7	445,2	780,0	1,4	-6,65	-40,0
	P13	236,2	49,9	119,1	14,7	110,7	14,0	553,5	451,5	0,3	-6,86	-42,9
	P14	263,5	95,1	185,1	10,9	199,2	<0.2	509,8	841,0	0,6	-6,79	-41,1
APRIL 2009	P1	193,2	51,8	182,5	9,5	190,1	n.d.	454,4	488,1	0,6	-6,62	-38,1
	P2	77,5	34,1	440,2	9,7	424,6	n.d.	235,8	494,2	1,6	-6,01	-32,8
	P3	88,9	42,9	210,4	7,7	295,6	n.d.	79,3	482,0	1,2	-5,96	-32,8
	P4	203,4	70,9	287,1	17,7	282,1	n.d.	378,3	677,2	1,0	-6,40	-37,1
	P6	149,8	44,1	151,4	5,8	172,0	n.d.	260,6	457,6	0,7	-6,52	-37,0
	P8	114,7	67,2	923,5	21,9	1332,5	n.d.	22,3	915,2	5,8	-6,25	-37,0
	P9	149,0	129,5	622,5	25,4	821,0	n.d.	83,4	1446,0	3,4	-6,72	-38,6
	P10	93,3	24,7	116,6	5,0	114,5	n.d.	81,9	457,6	0,4	-6,59	-38,9
	P11	127,8	75,3	301,1	16,0	318,2	n.d.	361,3	567,4	1,3	-6,68	-40,3
	P13	234,2	48,2	128,7	14,8	115,3	n.d.	554,9	457,6	0,3	-6,79	-39,9
	P14	248,5	85,5	188,5	9,0	182,4	n.d.	512,2	793,2	0,5	-7,03	-38,9
	P15	170,7	82,8	385,5	19,9	521,0	n.d.	209,7	890,8	1,7	-6,75	-37,6
	P16	282,3	96,5	712,3	18,1	1406,0	n.d.	237,9	640,6	6,3	-5,88	-36,2
	P17	195,1	61,0	490,0	14,0	847,0	n.d.	147,7	488,1	3,5	-6,09	-35,0
	P18	253,6	82,3	308,1	18,1	395,0	n.d.	461,1	848,1	1,5	-6,71	-40,3
	P19	212,9	51,1	200,7	7,9	282,3	n.d.	238,0	665,0	0,8	-6,53	-36,7
	P20	130,5	32,8	148,5	7,9	195,6	n.d.	60,8	500,3	0,6	-6,29	-40,0
	Arno River (depth 4 m)	n.d.	n.d.	3450,2	127,9	6223,0	n.d.	879,8	298,0	19,6	-4,13	-23,1
	Arno River (depth 1 m)	n.d.	n.d.	311,9	12,9	289,0	n.d.	138,2	256,3	0,9	-6,40	-38,2

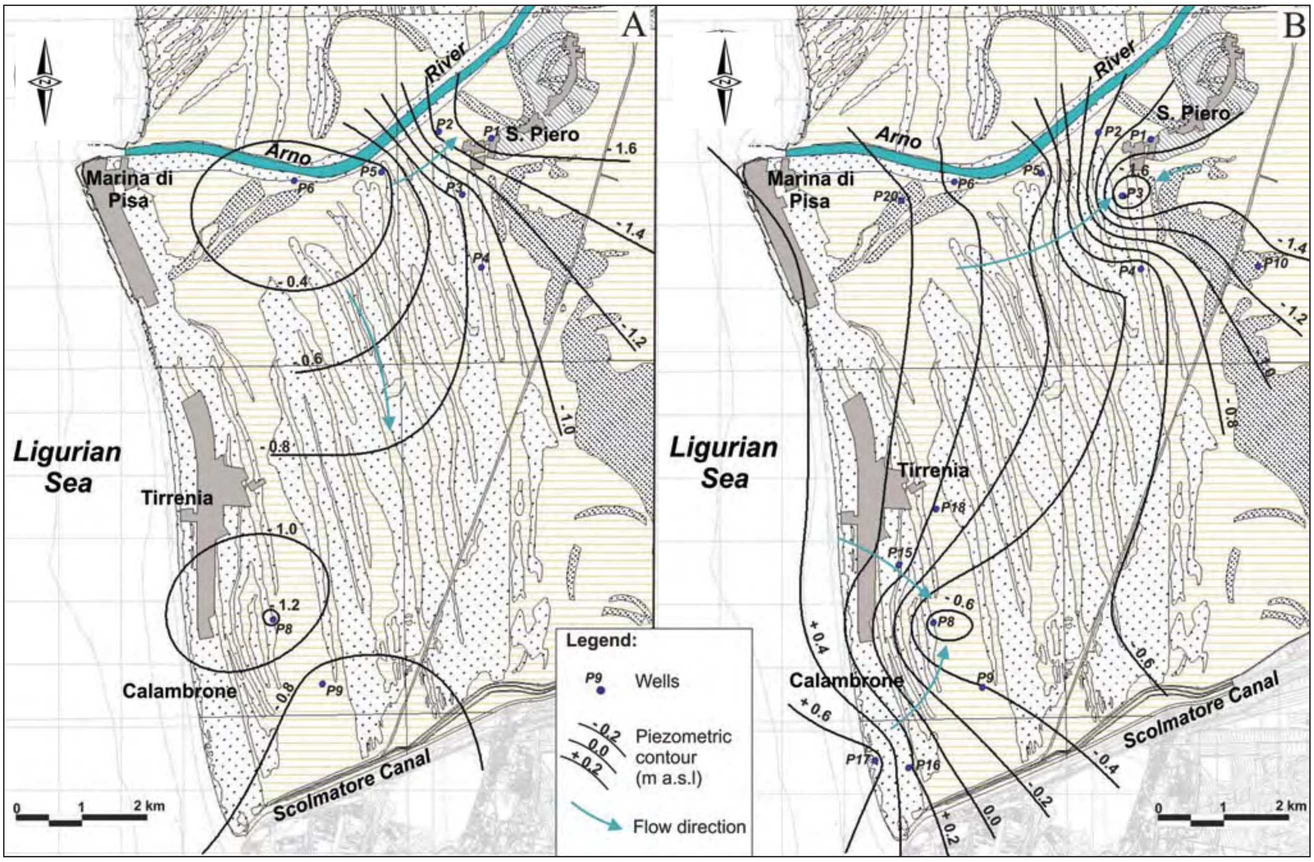

Fig. 4 - Piezometric sketch map of the confined gravelly aquifer: A) June 2008, B) April 2009 (see fig. 1b for the legend of the base map).
- Carte piezometriche schematiche relative all'acquifero ghiaioso confinato: A) Giugno 2008; B) Aprile 2009 (vedi fig. 1b per la legenda della cartografia di base).

dent in the S. Piero a Grado area (P2, P3) and in the southern portion of the study area, between Tombolo and Calambrone (P8, P9, P16, P17). As shown in figure 6, such mixing in many cases is not conservative and this is principally caused by the mentioned phenomenon of sulphate reduction which includes the removal of SO_4 and a relative enrichment of HCO_3 in solution.

The analysis of the Cl contents permits to individuate some groundwater samples (P1, P6, P10, P13, P14, P20) with concentration ranging 110-200 mg/l, in agreement with the observations of GRASSI & CORTECCI (2005) about the gravelly aquifer in the internal portion of the plain. Such values could reasonably represent the "Cl background value" in the groundwater of the gravelly aquifer reaching in the coastal plain. In the other sampling points, higher Cl values were registered from more than 300 mg/l up to more than 1900 mg/l (P3 in August), depending the seawater-freshwater mixing degree.

Considering the wells sampled in two of three surveys at least (fig. 10), we can observe that the groundwater with lower Cl concentration show a general stability with time of this element. On the contrary, a pronounced variability is recognizable in the wells that show higher values (in particular P3 and P9). From a quantitative point of view, this indicates that seawater mixing depends on the different seasonal conditions in terms of both recharge and pumping. In fact, higher values of Cl concentration is present in August, namely in the period characterized by low recharge amount and high withdrawal, which determine the lower piezometric levels.

On the basis of Br and Cl contents, the max percentage of seawater in samples is about 8-9% in S. Piero a Grado area (P3 in August) and 7-8% in the area between Tombolo and Calambrone (P9 in August, P8 in August and April).

As regards the isotopic contents, the diagram in figure 11 shows that most groundwater samples are grouped into values of $\delta^{18}O$‰ and $\delta^{2}H$‰ of about -6.5/-6.8 and -37/-40, respectively. Such values are typical of the water circulating in the confined gravelly aquifer of the internal portion of the Pisan Plain (GRASSI & CORTECCI, 2005) and are representative of recharge altitude higher than the plain. Actually, the rainfall at Pisa has $\delta^{18}O$‰ medium yearly contents in the order of -5.3 and -

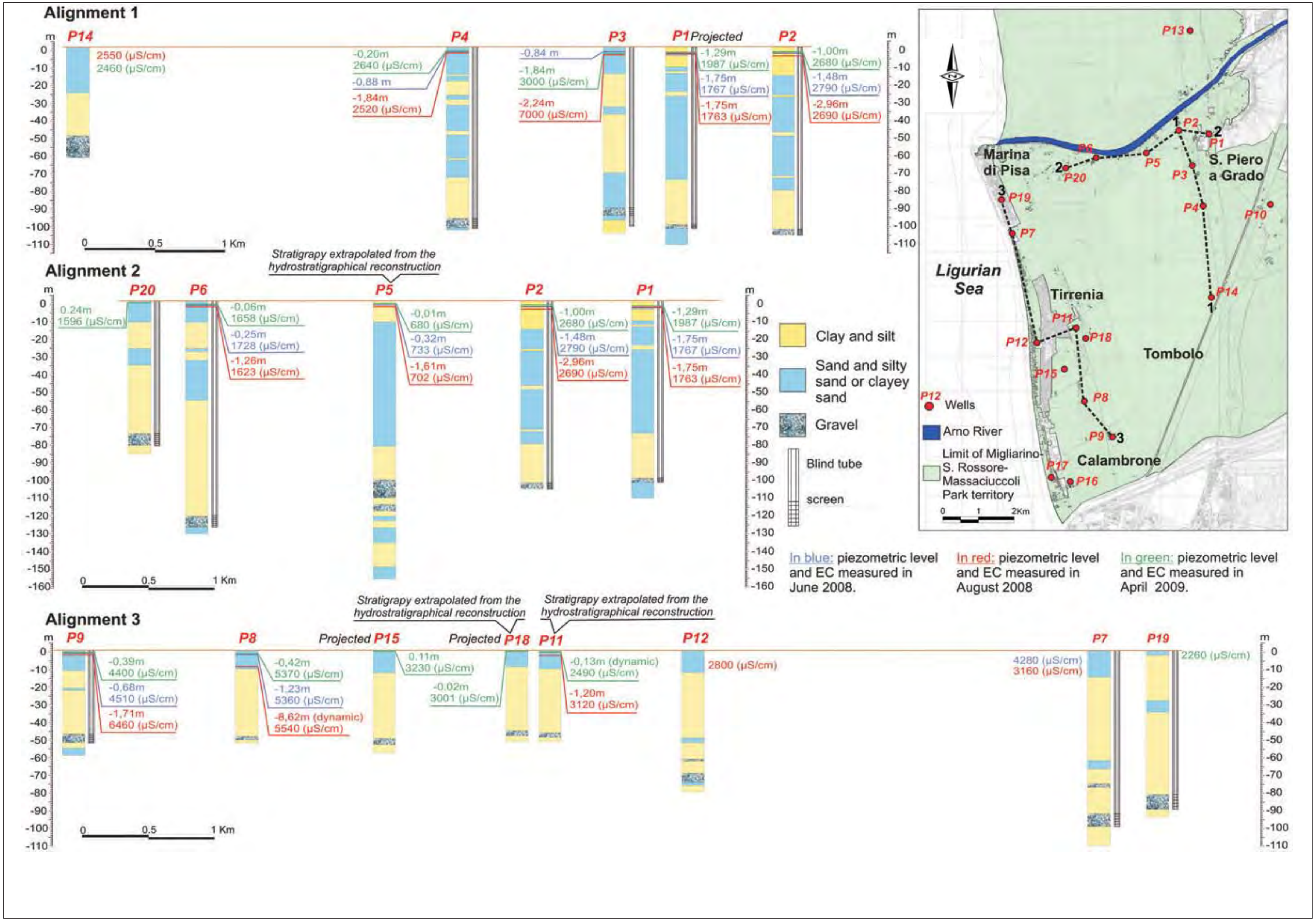

Fig. 5 - Stratigraphic outline of the water wells with piezometric and electric conductivity data (location of wells in figure 3).
- Schema stratigrafico dei pozzi con relativi dati piezometrici e conducimetrici (l'ubicazione dei pozzi è riportata in figura 3).

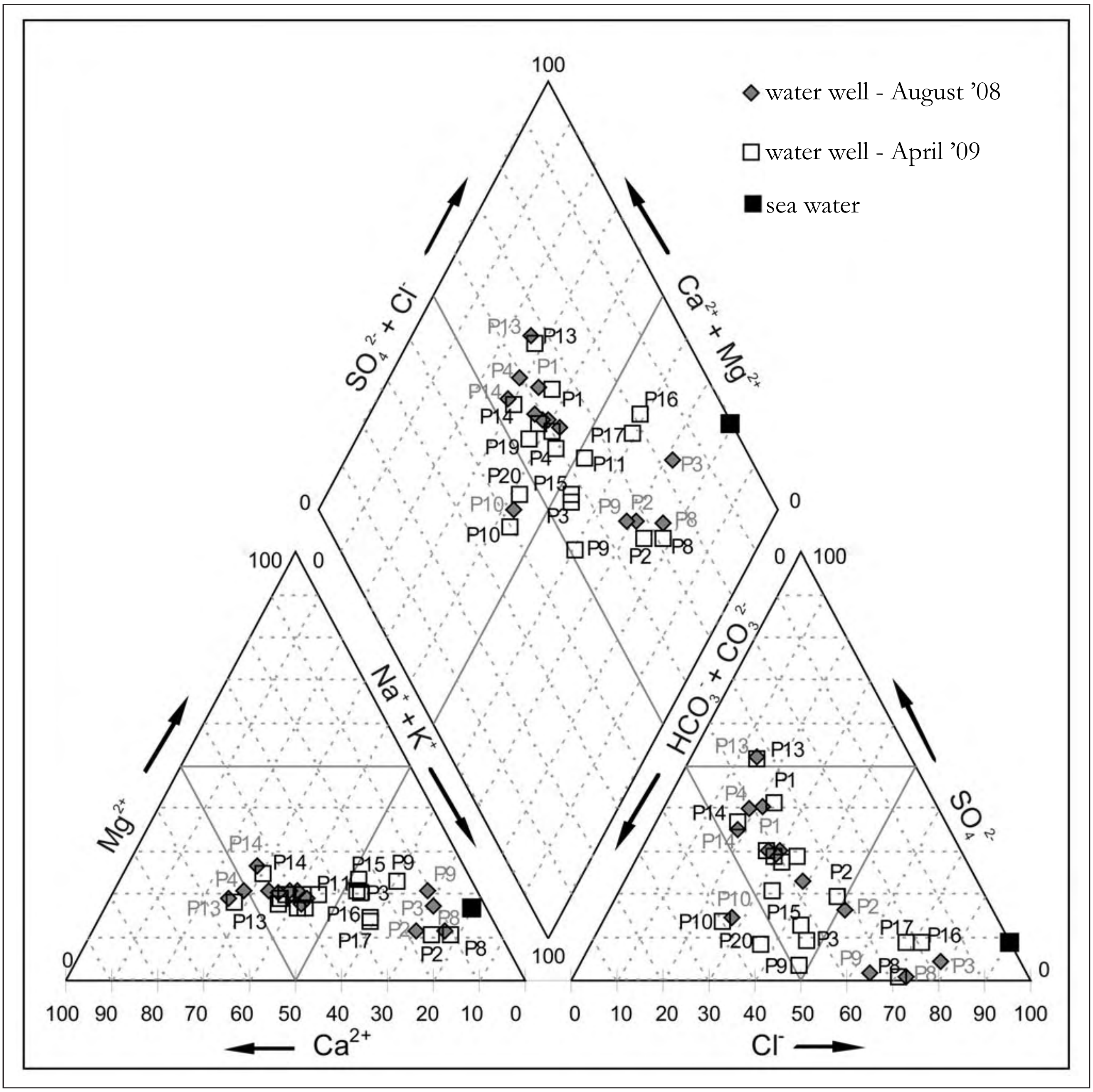

Fig. 6 - Piper diagram (Piper, 1994).
- *Diagramma di Piper (*Piper*, 1944).*

5.8 (IAEA/WMO, 2001; Mussi *et alii*, 1998). Such values are generally found also in the unconfined aquifers of the Versiliese-Pisan coast (Doveri *et alii*, 2009; Doveri, 2004; Baldacci & Doveri, 2008). The lower values that characterize most of the water samples collected in the confined gravelly aquifer highlight a negligible or absent supply linked to the direct infiltration of rainfall in the Pisan Plain. Corroborating the chemical analysis, the isotopic data indicate the contribute from the Mesozoic calcareous aquifer ($\delta^{18}O$‰ at Pisan Mountains springs of about -6.5; Grassi *et alii*, 1994) in addition to the Pisan hills, Lucca Plain and Arno River Plain. The shifting of isotopic ratios for samples P2, P3, P8, P9, P16, P17 and P20 from the main group toward higher values of $\delta^{18}O$‰ and $\delta^{2}H$‰ (fig. 11) is compatible with both local connections between sandy aquifer (with higher isotopic contents) and gravelly aquifer and with a fresh water-seawater mixing. On the other hand, the sample collected in the Arno River is clearly influenced by seawater intrusion, with isotopic con-

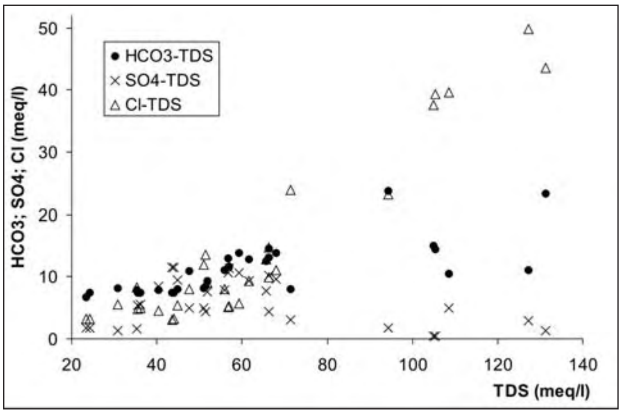

Fig. 7 - Binary diagram HCO3, SO4, Cl vs. TDS.
- Diagramma binario HCO3, SO4, Cl vs. TDS.

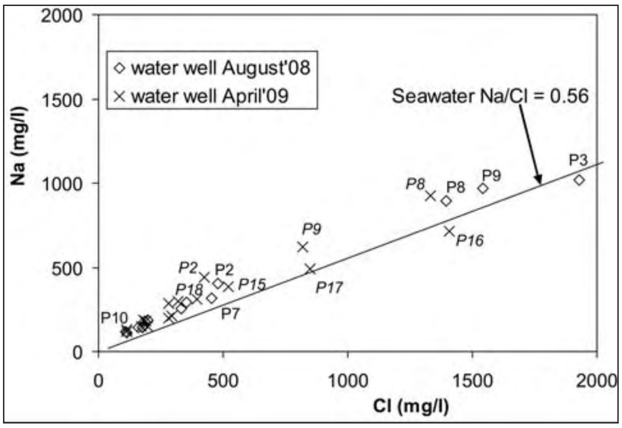

Fig. 8 - Binary diagram Na vs. Cl.
- Diagramma binario Na vs. Cl.

centration even higher than the rainfall at sea altitude.

Comparing the $\delta^{18}O‰$ and Cl contents (fig. 12), we can conclude that the samples interested by seawater intrusion, with different percentage, are included within 2 km from the shoreline (P7, P8, P9, P11, P12, P15, P16, P17, P18, P19) and P2-P3 close to S. Piero a Grado. However, this process occurs in different ways. In fact, the direct capture of the seawater in the gravel aquifer is probable only for the wells nearer to the coast. As regards P2 and P3 (S. Piero a Grado area), fig. 12 shows that in addition to the seawater there is a mixing with the water of the Arno River and/or of the sandy aquifer, which is in connection with the surface in this area. Moreover, considering that between P2 and P3 and the coastline there are other wells that intercept the gravel horizon showing low values of $\delta^{18}O‰$ and Cl, we can state that the seawater fraction individuated in P2 and P3 is not due to the hydraulic connection between sea and gravelly aquifer, but is related to the Arno River or the sandy aquifer. In fact, in this area the two aquifers could be in hydraulic connection, due to the lack or thickness reduction of the silty-clayey aquiclude/aquitard that usually separates them (fig. 2, section 1). However, we can not exclude that the hydraulic connection between the two aquifers is due by technical features of the wells, with water extraction both from the sandy and the gravelly aquifer. This is the most probable cause of the limited shift from the linear mixing *gravel groundwater-seawater* (GG-SW) showed by P16 and P17 samples (fig. 12), collected near the coastline in the southern part of the area.

7. - CONCLUSIONS

The confined gravelly aquifer, belonging to the Pisan Plain multi-level system aquifer, presents certain continuity in the coastal area at a depth of

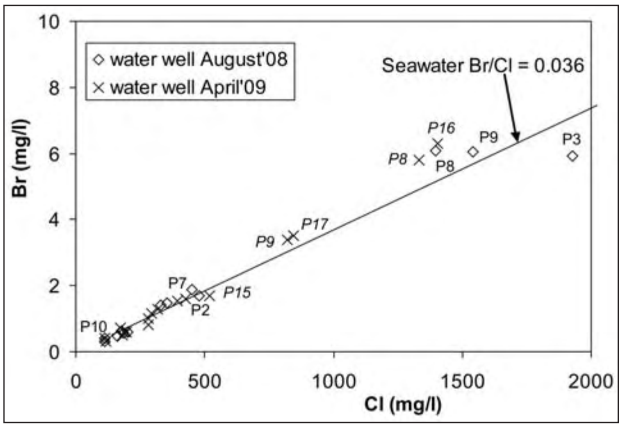

Fig. 9 - Binary diagram Br vs. Cl.
- Diagramma binario Br vs. Cl.

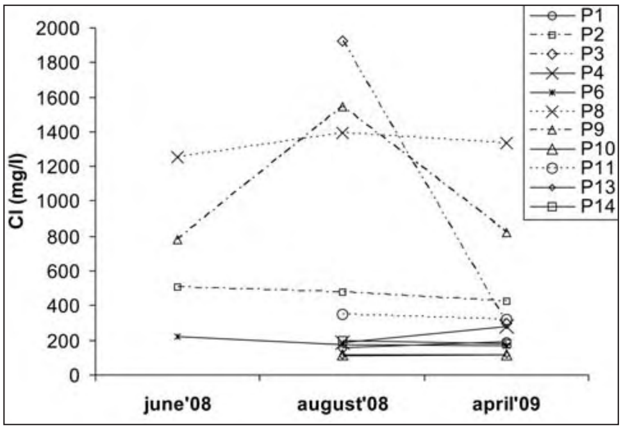

Fig. 10 - Cl concentration in the different sampling periods (location of wells in fig. 3).
- Concentrazione di Cl nei diversi periodi di campionamento (ubicazione dei pozzi in fig. 3).

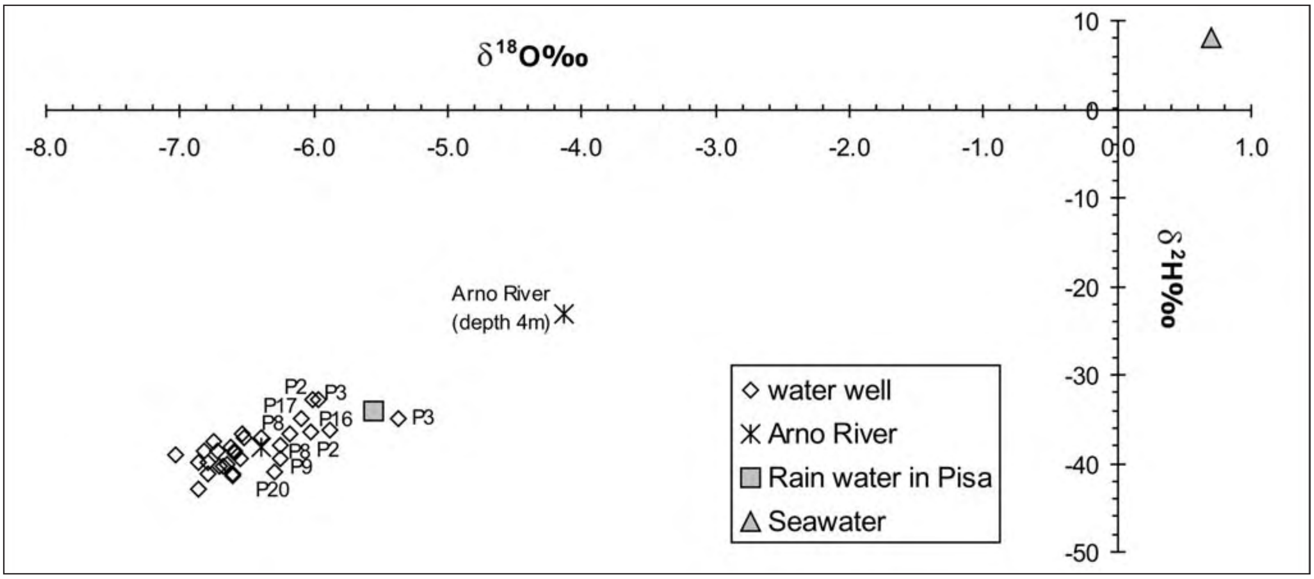

Fig. 11 - Relationship between δ^{18}O‰ and δ^{2}H‰. - *Relazione tra δ^{18}O‰ e δ^{2}H‰.*

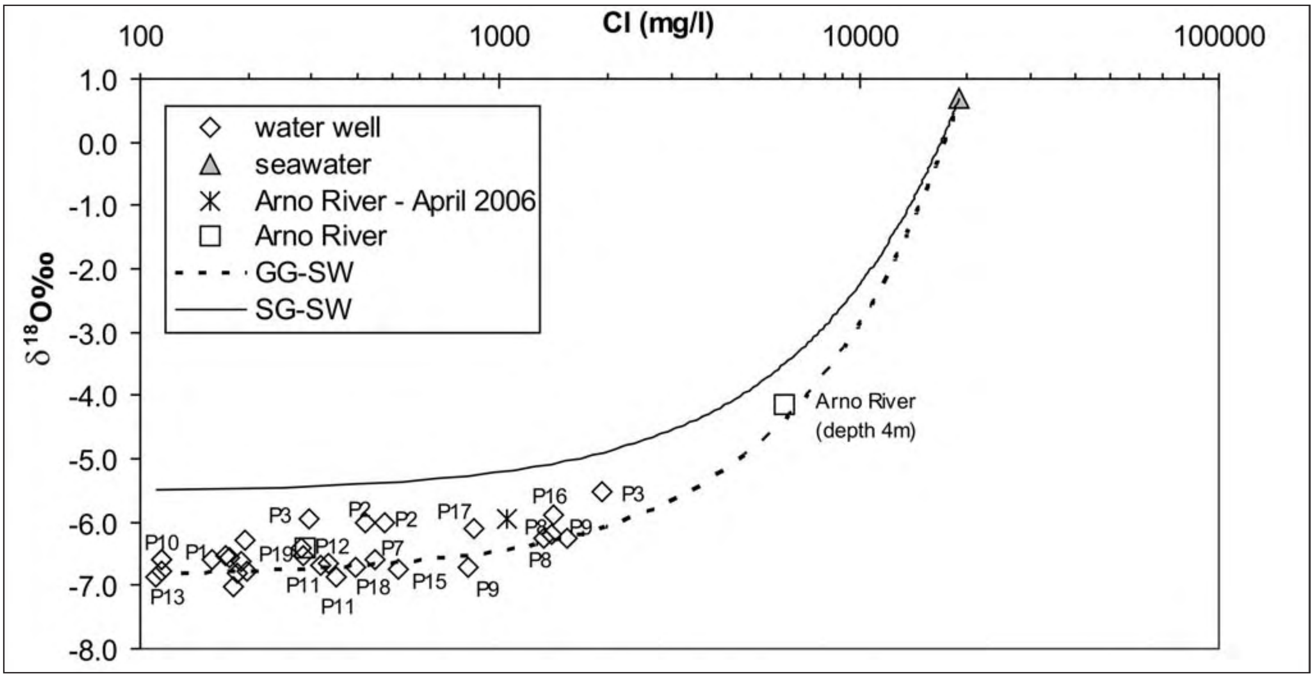

Fig. 12 - Binary diagram δ^{18}O‰ vs. Cl (Arno River-April 2006 after BALDACCI & DOVERI, 2008; GG-SW: gravel groundwater-seawater mixing; SG-SW: sand groundwater-seawater mixing).
- *Diagramma binario δ^{18}O‰ vs. Cl (Arno River-April 2006 da* BALDACCI & DOVERI*, 2008; GG-SW: mixing tra falda delle ghiaie e acqua di mare; SG-SW: mixing tra falda delle sabbie e acqua di mare).*

about 50 m below the land surface. In several zones there are discontinuous gravelly horizons at different depths (higher and lower than 50 m). Across the study area the gravelly level is substantially separated from the overlying sandy aquifer, but locally (e.g. S. Piero a Grado) some in hydraulic connection could exist, due to absence or thickness reduction of the silty-clayey aquiclude/aquitard that usually separates them.

The piezometric level is lower than the sea-level in almost all the survey points (with the exception of some water points of the April 2009 survey). In the southern coastal area (Calambrone) and in the S. Piero a Grado area, the maximum depression of piezometry occurs because of intense pumping related to agricultural and tourist activity. In these zones, the groundwater, usually characterized by relatively low salinity (EC < 2,000 μs/cm at 25°C) and chemical facies Ca/HCO_3-SO_4, shows high EC, δ^{18}O‰, Br and Cl values. This clearly indicates the freshwater-seawater mixing in the order of about 9% as showed by the mass balance based on the Br and Cl contents.

The contemporaneous use of chemical and isotopic data enabled us to highlight two different origins of such a mixing. In particular, up to 1.5-2 km from the southern coastline (Calambrone area) and in a restricted area close to the coastline to the North, the seawater intrusion directly develops in the confined gravelly horizon in contact with the sea floor. In the S. Piero a Grado area the mixing with seawater is controlled by the seawater intrusion that interests the Arno River-phreatic sandy aquifer system and by the hydraulic connection between the last and gravelly aquifer.

Future developments of this research will better identify the relations between aquifers of the plain and among them and the Arno River, in order to evaluate the vulnerability of the main water horizon (gravelly aquifer) and to control the withdrawal.

Aknowledgement

The authors are grateful to the Referees, T. Bonomi and M. Masetti, and to R. Bersezio, whose comments and suggestions effectively improved this paper.

REFERENCES

Aguzzi M., Amorosi A., Colalongo M.L., Ricci Lucchi M., Rossi V., Sarti G. & Vaiani, S.C. (2007) - *Late Quaternary climatic evolution of the Arno coastal plain (Western Tuscany, Italy) from subsurface data*. Sediment. Geol., **202**: 211-229.

Antonellini M., Mollema P., Giambastiani B., Bishop K., Caruso L., Minchio A., Pellegrini L., Sabia M., Ulazzi E. & Gabbianelli G. (2008) - *Salt water intrusion in the coastal aquifer of the southern Po Plain, Italy*. J. Hydrogeol. , **16**: 1541-1556.

Baldacci F. (1999) - S*truttura e piezometria del "primo acquifero artesiano in ghiaie" della Pianura Pisana*. Atti Soc. Tosc. Sci. Nat. Mem., ser. A, **106**: 90-101, Pisa.

Baldacci F., Bellini L. & Raggi G. (1994) - *Le risorse idriche sotterranee della Pianura Pisana*. Atti Soc. Tosc. Sci. Nat. Mem., ser. A, **101**: 241-322, Pisa.

Baldacci F., Bellini L. & Raggi G. (1998) - *Sistema Acquifero della Pianura di Pisa (Sap) - Carta della permeabilità delle rocce*. Atti Soc. Tosc. Sci. Nat. Mem., ser. A, **105**, 1 tav., Pisa.

Baldacci F. & Doveri M. (2008) - *L'intrusione marina nella fascia costiera versiliese-pisana: Studio Idrogeologico-geochimico degli acquiferi freatici nelle zone Canale Burlamacca-Fosso della Bufalina e Fiume Arno-Fiume Serchio*. Rapporto tecnico-scientifico, CNR-IGG/UNIPI-DST/Parco Regionale MSRM, pp. 111.

Barazzuoli P., Bouzelboudjen M., Cucini S., Kiraly L., Menicori P. & Salleolini M. (1999) - *Olocenic alluvial aquifer of the River Cornia coastal plain (southern Tuscany, Italy): database design for groundwater management*. Environ. Geol., **39**: 123-143.

Barrocu G. (2003) - *Seawater intrusion in the coastal aquifers of Italy*. In: J. Calaferra (Ed.): «*State of seawater intrusion in coastal aquifers of the Mediterranean Coast*». SWIM-SWICA: 207-223, Alicante, Spain.

Capaccioni B., Didero M., Paletta C. & Didero L. (2005) - *Saline intrusion and refreshening in a multilayer coastal aquifer in the Catania Plain (Sicily, southern Italy): dynamics of degradation processes to the hydrochemical characteristics of groundwater*. J. Hydrol., **307**: 1-16.

Cortecci, G., Dinelli, E., Bencini, A., Adorni-Braccesi, A. & La Ruffa, G. (2002) - *Natural and anthropogenic SO_4 sources in the Arno River catchment, northern Tuscany, Italy; a chemical and isotopic reconnaissance*. Appl. Geochem., **17**: 79-92.

Custodio E. (2002) - *Coastal aquifers as important natural hydrogeological structures*. In: E. Bocanegra, D. Martìnes & H. Massone (Eds.) «*Groundwater and Human Development*»: 1905-1918, Bremerhaven, Germany.

Della Rocca R., Mazzanti R. & Pranzini E. (1987) - *Studio geomorfologico della pianura di Pisa*. Geog. Fis. Dinam. Quat., **10**: 56-84.

Dini I. (1976) - *La prima falda artesiana della zona di Pisa*. Provincia - Comune di Pisa.

Doveri M. (2004) - *Studio idrogeologico e idrogeochimico dei sistemi acquiferi del bacino del Torrente Carrione e dell'antistante piana costiera*. PhD Dissertation, Università di Pisa: pp. 178.

Doveri M., Giannecchini R., Giusti G. & Butteri M. (2009) - *Studio idrogeologico-geochimico dell'acquifero freatico nella zona compresa tra il Canale Burlamacca ed il Fosso della Bufalina (Viareggio, Toscana)*. Proc. 3° AIGA Congress. Accepted Giorn. Geol. Appl., 12, 103-119.

Ericson J.P., Vörösmarty C.J., Dingman S.L., Ward L.G. & Meybeck M. (2006) - *Effective sea-level rise and deltas: causes of change and human dimension implications*. Global Planet Change, **50**: 63-82.

Federici P.R. (1993) - *The Versilian transgression of the Versilia area (Tuscany, Italy) in the light of the drillings and radiometric data*. Mem. Soc. Geol. It., **49**: 217-225.

Fancelli R. (1984) - *Tentativo di ricostruzione dell'andamento della falda artesiana tra i -30 ed i -50 m di profondità nel sottosuolo di Pisa e dintorni*. Rapporto CNR - Ist. Int. Ric. Geotermiche, Pisa.

Fritz P. & Fontes J.Ch. (1980) - *Introduction*. In: P. Fritz & J.Ch. Fontes (Eds.), «*Handbook of Environmental Isotope Geochemistry*»: 1-19, Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York.

Frondini F., Zanzari A. & Giaquinto S. (2001) - *Salt water intrusion in Pisa the coastal plain (Central Italy)*. In: R. Cidu (Ed.), «*Proc. Tenth International Symposium on Water-Rock Interaction 2001*», **1**: 513-516, Balkema, Lisse.

Giambastiani B.M.S., Antonellini M., Oude Essink G.P. & Stuurman R.J. (2007) - *Saltwater intrusion in the unconfined coastal aquifer of Ravenna (Italy): a numerical model*. J. Hydrol., **340**: 91-104.

Giani P., Bellucci L., Panichi C. & Podda F. (2001) - *Studio sulla presenza di acqua di mare nel tratto terminale del Fiume Arno con metodologie chimico-isotopiche*. Atti Soc. Tosc. Sci. Nat. Mem., ser. A: 53-60.

Giannini E. & Nardi R. (1965) - G*eologia nella zona nord occidentale del Monte Pisano e dei Monti d'oltre Serchio (Provincia di Pisa e Lucca)*. Boll. Soc. Geol. It, **13**: 210-233.

Giménez Forcata E., Bencini A. & Pranzini G. (2001) - *Salinization in coastal plain of Grosseto: Hydrochemical study*. In: R. Cidu (Ed.), «*Proc. Tenth International Symposium on Water-Rock Interaction 2001*», **1**: 517-520, Balkema, Lisse.

Grassi S. & Cortecci G. (2005) - *Hydrogeology and Geochemistry of multilayered confined aquifer of the Pisa Plain*. Appl. Geochem., **20**: 41-54.

Grassi S., Gianelli G. & Toro B. (1994) - *Studies of Low-Temperature Hydrothermal Systems: San Giuliano Prospect (Pisa, Italy)*. Energ. Source, **16**: 401-423.

GRASSI S., CORTECCI G. & SQUARCI P. (2007) - *Groundwater resource degradation in coastal plains: the example of the Cecina area (Tuscany - Central Italy)*. Appl. Geochem., **22**: 2273-2289.

GRASSI S. & NETTI R. (2000) - *Sea water intrusion and mercury pollution of some coastal aquifers in the province of Grosseto (Southern Tuscany-Italy)*. J. Hydrol., **237**: 198-211.

GRASSI S. & ROSSI S. (1996). *Il cloro delle acque sotterranee della Pianura di Pisa*. Atti Soc. Tosc. Sci. Nat. Mem., ser. A, **103**: 135-142.

HOEFS J. (2004) - *Stable isotope geochemistry*: 5th edition, Springer Verlag, Berlin, pp. 244.

IAEA/WMO (2001) - *Global Network of Isotopes in Precipitation*. Available by: <http://isohis.iaea.org>.

LA RUFFA G. & PANICHI C. (2000) - *Caratterizzazione chimico isotopica delle acque fluviali: il caso del fiume Arno*. In: «*Caratterizzazione chimico isotopica delle acque fluviali: il caso del fiume Arno*»: 1-101, Istituti Editoriali e Poligrafici Internazionali, Pisa-Roma.

MAZZANTI R. & PASQUINUCCI M. (1983) - *L'evoluzione del litorale lunense-pisano fino alla metà del XIX secolo*. Boll. Soc. Geogr. It., **12**: 603-628.

MUSSI M., LEONE G. & NARDI I. (1998) - *Isotopic geochemistry of natural water from the Alpi Apuane-Garfagnana area, Northern Tuscany, Italy*. Miner. Petrogr. Acta, **41**: 163-178.

PIPER A.M. (1944) - *A graphic procedure in the geochemical interpretation of water analyses*. Am. Geophys. Un. Trans., **25**: 914-923.

PRANZINI G. (2002) - *Groundwater salinization in Versilia (Italy)*. Proc. SWIM 17th: 412-421, Delft, Holland.

PROVINCIA DI PISA (2005) - *La Geologia della Provincia di Pisa - Cartografia, Geositi e Banche Dati*. Provincia di Pisa, Area Governo del Territorio-Servizio Difesa del Suolo.

RAU A. & TONGIORGI M. (1974) - *Geologia dei Monti Pisani a sud-est della valle del Guappero*. Mem. Soc. Geol. It., **13** (3): 227-408.

REGIONE TOSCANA (1988) - *Carta Generale del Territorio*. Ed. S.EL.CA., Firenze.

ROSSI S. & SPANDRE R. (1994) - *L'intrusione marina nella falda artesiana in ghiaia nel litorale pisano*. Acque Sotterranee, **43**: 51-58.

ROSSI S. & SPANDRE R. (1995) - *Caratteristiche idrochimiche della prima falda artesiana in sabbia nei dintorni di Pisa*. Acque Sotterranee, **48**: 27-48.

SERGE A. (1955) - *Nota sulla idrografia continentale e marina*. In: «*Note illustrative della Carta Geologica d'Italia, scala 1:100.000, Foglio 111 Livorno*». Serv. Geol. d'It., Roma.

SPANDRE R., CERAGIOLI M. & SPINICCI A. (1999) - *Realizzazione di una carta di vulnerabilità degli acquiferi della Pianura pisana compresa tra la linea di costa, il Canale Scolmatore, il Fosso della Bufalina e la città di Pontedera*. Provincia di Pisa, Settore Pianificazione del Territorio.

UNESCO (2007) - *Global sea-level: past, present and future*. Reprint from IOC Annual Report 2006: pp. 8.

WALLING D.E. & FANG D. (2003) - *Recent trends in the suspended sediment loads of the World's Rivers*. Global Planet Change, **39**: 111-126.