Hydrogeological investigations in southern Tuscany (Italy) for coastal aquifer management

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Abstract: Ongoing hydrogeological investigations in the Grosseto Province (southern Tuscany, Italy) aim to develop a correct model for the management of coastal aquifers, which are affected by seawater intrusion due to overexploitation for various purposes. This study updates and integrates hydrogeological knowledge of the area; in addition, it proposes a monitoring network and remedial actions. Completed analyses reveal the presence of coexisting flow systems of different rank which allow the mixing of freshwater and saltwater, both superficial (recent) and deep (old), in various proportions.

Hydraulic head measurements reveal the important impact of pumping on the flow of groundwater, with the formation of a negative hydraulic head in areas of intense withdrawal (water supply systems, fish farms). Geochemical data indicate that the chemical composition of groundwater is mainly determined by the mixing of seawater with waters circulating in the cavernous limestone and in neo-autochthonous sediments. The definition of conceptual models for the aquifers allowed the development of numerical models for hydrodynamic and hydrochemical simulations, which provide useful in-

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formation on the general evolution of systems under different stress conditions. The study assessed schemes to counteract seawater intrusion, taking into account the characteristics of the multi-aquifer system of the Albegna plain (replacement of the amount pumped for irrigation with treated wastewater and/or surface water stored in reservoirs; artificial recharge of the aquifer through injection wells or infiltration basins containing treated wastewater and/or infiltration channels which divert the flood water of streams) and of the adjacent carbonate aquifer (requalification of pumping systems in fish farms; redesign of the network of public-supply wells). Lastly, a network of existing wells and additional observation wells was identified for quality and quantity monitoring of aquifers.

Riassunto: Indagini idrogeologiche sono in corso nella Provincia di Grosseto (Toscana meridionale, Italia) con il principale obbiettivo di sviluppare un corretto modello di gestione degli acquiferi costieri, il cui sovrasfruttamento per vari usi ha causato fenomeni di intrusione salina; questo lavoro presenta i risultati ottenuti nell'aggiornamento ed integrazione delle conoscenze idrogeologiche e nell'impostazione della rete di monitoraggio e degli interventi di contrasto. Le indagini eseguite evidenziano la coesistenza di sistemi di flusso di rango diverso che consente il miscelamento in varie proporzioni di acque dolci e salate sia superficiali (recenti) che profonde (vecchie). Il rilevamento piezometrico mostra il pesante condizionamento operato dagli emungimenti sul flusso di falda con la formazione di aree a carico idraulico negativo coincidenti con le maggiori zone di captazione (acquedotto, impianti ittici); l'interpretazione geochimica indica che la composizione chimica delle acque sotterranee è controllata essenzialmente dal miscelamento tra l'acqua di mare e le acque circolanti nel Calcare cavernoso e nei sedimenti neoautoctoni. La definizione dei modelli concettuali degli acquiferi ha consentito lo sviluppo di modelli numerici di simulazione idrodinamica e idrochimica atti a fornire utili informazioni sull'evoluzione generale dei sistemi sotto differenti condizioni di sollecitazione. Sono stati valutati interventi per il contrasto dell'intrusione salina, coerenti con le caratteristiche del sistema multi-acquifero della pianura dell'Albegna (sostituzione del quantitativo estratto a scopo irriguo con acqua reflua depurata e/o acqua superficiale trattenuta con invasi artificiali; realizzazione di impianti di ricarica artificiale della falda mediante pozzi di iniezione o bacini di infiltrazione delle acque reflue depurate e/o canali di infiltrazione di portate invernali dei corsi d'acqua) e dell'adiacente acquifero carbonatico (riqualificazione dei sistemi di pompaggio degli impianti di piscicoltura; riprogettazione della rete dei pozzi dell'acquedotto). Infine, è stata individuata una rete di monitoraggio quali-quantitativo degli acquiferi basata su pozzi preesistenti e pozzi-spia aggiuntivi.

Introduction

Coastal aquifers are highly sensitive to anthropogenic disturbance; inappropriate management of coastal aquifers can lead to irreversible damage and their destruction as freshwater sources. About 70 % of the world population dwells in coastal zones; in the last decades, the percentage of groundwater used for domestic purposes has increased by more than 40 % on a worldwide basis (Cheng and Ouazar, 2004). The effective management of coastal aquifers requires the balancing of many competing demands, and typically requires the use of numerical models, field investigations, and the development of a consensus on management options proposed by local governments and other concerned groups (Maimone et al., 2004). Modelling lies at the heart of the planning process; in particular, numerical models are used to test the conceptual model and to evaluate present and alternative exploitation scenarios, taking into account not only technical aspects but also economic, legal, social and political ones (Wang and Anderson, 1982; Canuti and Giuliano, 1986; Bear and Verruijt, 1987; Emch and Yeh, 1998; van Dam, 1999; Maimone et al., 2004; Bear, 2004).

The quality and quantity of groundwater resources along Italian coasts has been declining for some time; the impact of the growing population is alarming, especially in the southern regions, where 45 % of the total resident population lives in coastal areas (Barrocu, 2003). The southern coast of Tuscany is largely affected by seawater intrusion (Bencini and Pranzini, 1992, 1996; Barazzuoli et al., 1999, 2005, 2006, 2008; Angelini et al., 2000; Bencini et al., 2001; Bianchi et al., 2006a,b; Nocchi and Salleolini, 2007, 2009) and by the consequent deterioration of the quality of groundwater and the local anomalous accumulation of heavy metals (Grassi and Netti, 2000; Protano et al., 2000; Agati et al., 2001); this is due to intense pumping for different purposes, especially during summer, when the water demand for agriculture and tourism is highest and the natural availability of water is lowest. The problem has been aggravated in the last few decades by the progressive decrease in the potential renewable water resources of southern Tuscany (Barazzuoli et al., 2003) due to a reduction in total annual precipitation, and will be aggravated by the expected rise in sea level associated with global warming (Bates et al., 2008). The southern end of the Grosseto district is currently experiencing seawater intrusion owing to an irrational exploitation of the aquifer through hundreds of wells of different type and depth and with different pumping rates. The deterioration of groundwater quality is currently a limiting factor for local economic growth; agriculture has either been completely abandoned or has been directed towards crops which can tolerate saltwater but are of inferior quality.

In this context, the authors have planned a pluriannual program of hydrogeological research, with the principal aim of developing a robust numerical model essential for monitoring saltwater intrusion and managing water resources. This work updates and integrates existing hydrogeological knowledge of the coastal area of Grosseto between the Osa River and Chiarone Stream; it also proposes a network of monitoring wells and remedial actions. This area provides a good example of the situation in the geological framework of the Mediterranean coasts.

Study area

The area studied extends for about 280 km² at the southern extremity of Tuscany (Fig. 1). The morphology is primarily hilly; the highest peak, no more than 354 meters above sea level (m asl), is the Poggio del Leccio hill. The north-central area is part of the drainage basin of the Albegna River, which crosses the plain from ENE to WSW with an average annual discharge at the mouth of about 5 m³/s; the remainder of the area is covered by small basins which discharge into the sea. Mean precipitations are slightly less than 700 mm/year, with a minimum in July and maximum in October-November; the mean annual temperature is about 16 °C, with a minimum of 9 °C in January and maximum of 25 °C in August. According to the climate classification proposed by Thornthwaite (1948), the investigated area can be considered subarid C₁ (Barazzuoli et al., 1993).

From a geological point of view, the zone is characterized by the presence of several tectonic units of Liguride, Austroalpine and Tuscan facies, on which continental and marine Neogene Tuscan deposits rest unconformably (Decandia and Lazzarotto, 1980; Bonazzi et al., 1992); this area is also characterized by extensive outcroppings of "*Calcare cavernoso*" (cavernous limestone), which is a predominantly autoclastic breccia with numerous karst landforms (Iandelli and Piccini, 2006). The outcropping rocks can be divided into two main groups of different permeability through a qualitative classification according to formation:

- Quaternary and Neogene complexes. These deposits have weak or non-existent cementation and show predominant primary permeability due to interstitial porosity. The degree of permeability varies: it is moderate-high in the Neogene conglomerates, sandstone and sand, travertine, terraced alluvial deposits, shores, and in the horizons of coarse aeolian sediments, but zero to low in the Pliocene clays, transition deposits, present and recent alluvial deposits, and in the horizons of fine aeolian sediments.
- The pre-Neogene complex is characterized by diagenetic formations showing predominant secondary permeability due to fissuring or fissuring and karst. The degree of permeability varies: it is medium-high in the Triassic dolomitic limestones and Cretaceous-Eocene calcarenites, but zero to low in the Palaeozoic-Triassic metamorphic rocks and Cretaceous-Eocene argillaceous, calcareous and arenaceous flysch.

Results of hydrogeological research

Geometry and structure of the aquifers

The main geometric-structural and hydrogeological characteristics of the aquifers were reconstructed on the basis of the general geological reconstruction, vertical resistivity sounding and wells/ boreholes reaching a depth of up to 400-500 m.

The Albegna River plain is characterized by the presence of a Plio-Pleistocene multi-aquifer system (Angelini et al., 2000; Nocchi, 2002, 2004; Barazzuoli et al., 2005, 2008) consisting of several gravely and sandy layers which are combined into three main aquifer layers (Fig. 2); these aquifers are generally separated by aquitards composed of clayey deposits with silt or sand in various proportions, but they sometimes combine to form a single-layer aquifer. Another aquitard consisting of sandy-clayey silt is present at the top.

This hydrogeological system overlies an impervious clayey basement, except at the borders of the plain, where hydraulic connections with the outside are possible through permeable rocks. In the south-eastern sector, exchanges of water between the cavernous limestone and the aquifer layers occur through faults; although the natural outflow is from the limestone towards the alluvial deposits, in recent years the flow has sometimes reversed due to intense withdrawals from the carbonate aquifer for the public water system. A similar situation, but with a reduced flow of water, also occurs in the northern sector, where the fault along the Osa River causes the flysch formations and cavernous limestone to crop out. The aquifer system



Fig. 1: Geological-hydrogeological sketch map of the study area in southern Tuscany (Italy) and location of the hydraulic head observation points (*A*, *C*) and groundwater sampling points (*B*, *C*): the red points represent the wells used for fish farming, whereas light blue points indicate public-supply wells

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Fig. 2: Schematic cross-section and conceptual model for the multi-aquifer system in aeolian and alluvial sediments of the Albegna River plain (Barazzuoli et al., 2008, modified). The vertical exaggeration is about 20x

is mostly recharged by the direct infiltration of precipitation falling on the plain; it is also recharged by infiltration into the aquifer layers outside the plain (lateral flows, in the northern and eastern sector) and by the flow of water through the contact alluvial deposits and the cavernous limestone (lateral and vertical flows in the south-eastern sector). The natural outflow is into the sea and the Albegna River; intensive withdrawal from the aquifer through wells is the artificial outflow. Water exchange within the aquifer occurs due to both natural (leakage, close of aquitards) and artificial causes (multiscreened wells). The Albegna River plays an important role in this system by draining the aquifer along most of its course; it feeds the aquifer in different periods of the year, depending on the sector.

The carbonate aquifer system east of the Orbetello Lagoon is characterized by an extensive and complex circulation of waters (Fig. 3); the aquifer is highly permeable due to fracturing and karstification and is heavily exploited for irrigation, domestic and fish farming purposes (Bianchi et al., 2006a,b; Nocchi and Salleolini, 2007, 2009). Conduits, fractures and matrix pore systems coexist in the aquifer; field observations and data suggest that the permeability associated with the secondary elements (conduits and fractures) is of the same magnitude as that associated with the matrix. This aquifer sits above an impervious basement consisting of Triassic metamorphic rocks and extending to maximum depths of 350-400 m in the coastal area of Ansedonia; the flow along the freshwater/saltwater interface may therefore even derive from considerable depths, with the upwelling of waters of different age, salinity and temperature. The aquifer is mostly recharged by the direct infiltration of precipitation falling on the outcropping cavernous limestone; it is also recharged by a probable regional flow (lateral flow, in the north-eastern sector).

The natural outflow is into the sea, the lagoon and the Albegna plain; artificial outflow from the aquifer occurs through intensive pumping of wells.



Fig. 3: Schematic cross-section and conceptual model for the aquifer system in the cavernous limestone located east of the Orbetello Lagoon (Bianchi et al., 2006b, modified). The vertical exaggeration is about 2x.

In part due to the lack of numerical calibration and validation, the conceptual model based on hydrogeological data gathered south of the Melone River is much less reliable than the ones described above. This area is characterized by the absence of an active hydrographic network and by the abundance of fine sediments which favour surface runoff and preclude the presence of important aquifers, as confirmed by the low productivity of most wells.

In contrast to the situation in the Albegna plain, the formation of Quaternary and Neogene sediments is here linked almost exclusively to the dynamics of the sea; continental sedimentation has produced layers of greater grain size but of limited thickness and extension. In particular (Fig. 4): the Quaternary deposits in the coastal area contain horizons of varying productivity consisting of sandy-gravely lenses in a predominant limy-clayey lithology with low permeability; in the hilly sector, instead, there are formations with medium-high permeability (travertine deposits, Pliocene conglomerates, cavernous limestone) in which wells with good yield have been sunk. In most cases recharge of the aquifer occurs through direct infiltration of rainfall on various permeable outcrops; within the cavernous limestone, there is a possible contribution of a regional flow of groundwater with characteristics similar to those described earlier. Natural discharge occurs through diffuse flow into Lake Burano and the sea; artificial discharge is by pumping from wells. Water exchange within the Quaternary sediments is likely due to both natural (leakage, close of aquitards) and artificial causes (multiscreened wells).



Fig. 4: Schematic cross-section and conceptual model for aquifers in the Quaternary and Neogene sediments and cavernous limestone south of the Melone Stream: HD = Holocene deposit; PM = Pleistocene marine clay and sand; MC = Miocene conglomerate; CL = cavernous limestone. The vertical exaggeration is about 3x.

Piezometric surface and hydraulic properties

The most recent hydraulic head measurements were carried out in February and July 2009 in 97 wells; these were integrated with piezometric heads measured previously in fish farms (Bianchi et al., 2006a,b) and considered still valid for 2009, given that pumping for fish farming purposes is necessarily constant and piezometric levels are virtually stable. Note that, due to continuous groundwater extraction from the various wells in the area, it was only possible to measure the dynamic water level; hydraulic head data thus do not reflect the natural equilibrium conditions, especially in the summer months, when the demand for water increases due to irrigation and tourism. In order to verify the actual altitude of the measurement points, GPS measurements were carried out in April 2005 and May 2008 to determine the topographic elevation of 45 points in all. Since both fresh and salt water occur in the area, the method proposed by Post et al. (2007) was used to convert water level measurements to fresh water heads; a maximum correction of 1.29 m was obtained in the higher salinity well of fish farms. In general, water level measurements were locally well correlated, suggesting that there is adequate hydraulic continuity among the different aquifers in the coastal zone; as previously stated, geological, hydrodynamic and hydrochemical data indicate that the south-eastern sector of the Albegna plain is characterized by exchanges of water between the cavernous limestone and the Plio-Pleistocene sediments. Hydraulic head measurements from each monitored well can thus be considered the local value of the a single piezometric surface generated through the re-equilibration of pressure among the various aquifers; piezometric surfaces were reconstructed using hydraulic head measurements from all observation wells.

Collected data show that aquifers are generally unconfined (or semi-confined) towards the innermost sectors, but semi-confined (or confined) towards the sea due to the presence of semipervious (or impervious) covers and/or intercalations; the carbonate aquifer is unconfined in the outcropping cavernous limestone and semi-confined (or confined) in the rest of the area studied. The reconstructed piezometric surfaces (Fig. 5) show that withdrawals strongly affect groundwaters, creating areas of negative hydraulic head at the site of the most intensely exploited wells (aqueduct, fish farms); in summer, the greatest depressions occur near the Osa River (up to -4 m asl), in the Ansedonia area (up to -5 m asl of the fish farms) and especially in the Le Forane area, where pumping for domestic use results in piezometric heads of -30 m asl.

The general flow of groundwater is towards the lagoon and the sea. In the Albegna plain, the main flows of water are from the north and north-east; these move towards the Albegna River (the main groundwater drainage axis), through which the waters finally reach to sea. In the hills east of the lagoon, along with the meteoric wa-



Fig. 5: Groundwater level contour map.

ter that infiltrates into the carbonate outcrop directly, there is likely a contribution from regional groundwater circulation. The NNE flow of groundwater in the area between the Melone and Chiarone streams originates in the Capalbio hills.

Variations in piezometric head values between February and July 2009 were on average about -1.8 m, with peaks of almost -10 m; values obviously derive from a combination of the amount of water outflow from and inflow into the aquifers. As for the latter, comparison between the thirty-year average annual precipitation (632 mm) and the present one (1,134 mm, corresponding to a 79 % increase) suggests that the lowering of the piezometric head cannot be attributed to the general decrease in meteoric recharge characterizing almost all of southern Tuscany (Barazzuoli et al., 2003); in particular, the four months prior to February and July 2009 were very humid with respect to the average (with a more than 120 % increase in precipitation), thereby excluding at least the role of very short term recharge. In other words, the drop in piezometric head between February and July seems to simply be the result of spring-summer withdrawals of groundwater for various purposes, especially for agriculture and tourism. The impact of meteoric recharge on the local hydraulic head is better revealed through comparison with the results of measurements made in the same months of the previous year. Although withdrawals were practically the same, in summer 2008 a depression of the piezometric surface formed along the coast between the Osa River and Ansedonia; this was much wider than that observed in 2009. Although the four-month period prior to February 2008 was particularly dry (168 mm of rain, with a 44 % decrease with respect to the average for that period), that prior to July 2008 was very rainy (205 mm, corresponding to a 31 % increase). In other words, there was a significant shift in meteoric recharge in 2008 from fall-winter to spring. This affected the carbonate aquifer especially, which is easily and quickly recharged due to the wide outcrops of cavernous limestone: the average value of the piezometric head in February 2008 (1.37 m asl) was much lower than that measured in February 2009 (5.17 m asl).

The temporal evolution of the piezometric surface for different pumping conditions was analyzed by comparing the current distribution of hydraulic head with that found in previous investigations (Angelini et al., 2000; Nocchi, 2002, 2004; Bianchi et al., 2006a,b); results highlight a gradual shift inland of the zero piezometric line subsequent to increased groundwater withdrawals for various purposes, especially from the carbonate aquifer for the public water system. In summer 1995 vast areas of negative piezometric head, with an average hydraulic head of 2.76 m asl, were measured only in the Albegna plain. These were generated by the demand for water for agricultural use, along with the abundant withdrawals by fish farms in the Ansedonia area, which already at that time affected the carbonate aquifer (although their impact on the groundwater level has not been documented). The continuous increase in withdrawals for domestic use has led to the stable negative positioning of the piezometric level first in the Orbetello Scalo-Ansedonia area and then also in the Le Forane area; as further confirmation, in the Albegna River plain, where there are no public-supply wells, the zero piezometric line probably receded (between 1995 and 2009 the hydraulic head value in July increased on average by more than 2 m) due to a decrease in agricultural activity and its improved efficiency of water consumption, largely compensating the above-mentioned negative trend in the natural renewable resources of water.

Direct knowledge of the hydrodynamic parameters of these aquifers is poor, whereas estimates based on various calculations are more numerous. Angelini et al. (2000) report on the only pumping tests carried out in the Albegna River plain: two tests refer to wells screened in all aquifer layers, which have an average hydraulic transmissivity (T_a) of 6.10⁻³ m²/s, average hydraulic conductivity (K_a) of 6.10⁻⁴ m/s and average storativity (S_a) of 3.10⁻³; one test refers to a well only screened in the Pleistocene layers (T = $9 \cdot 10^{-4} \text{ m}^2/\text{s}$, $K = 4.10^{-5}$ m/s, $S = 3.10^{-4}$). The authors estimate the aquifer transmissivity distribution by multiplying K_a and the saturated thickness matrix; transmissivity values range from zero, where the pre-Neogene basement crops out, to 21.10-3 m²/s in the Albinia area, with an average value of 9.10-3 m²/s. The calibration for steady-state conditions (Barazzuoli et al., 2005, 2008) assigns hydraulic conductivity values of 10⁻⁴ - 10⁻⁵ m/s to the aeolian deposits and Pliocene sediments and of 10⁻³ - 10⁻⁵ m/s to the fluvial terraces; the estimated K_{vert} for the aquitards is 5.10⁻⁸ m/s. As for the carbonate aquifer, calibration for steady-state conditions yielded hydraulic conductivity values ranging from $6 \cdot 10^{-3}$ m/s to $6 \cdot 10^{-5}$ m/s, with an average value of about 6.10⁻⁴ m/s (Nocchi and Salleolini, 2007, 2009), in keeping with the results of a tracer test on the local cavernous limestone (Bianchi and Fanciulletti, 2000). South of the Melone Stream, the only known pumping test carried out in a well screened in the cavernous limestone yielded a transmissivity of $1\cdot10^{-4}$ m²/s. Data for the wells indicate a specific capacity of $2-3\cdot10^{-4}$ m²/s for the cavernous limestone, of $2-9\cdot10^{-4}$ m²/s for the Pliocene conglomerates and of $1-6\cdot10^{-4}$ m²/s for the Pleistocene sediments.

Groundwater quality

The main physical-chemical characteristics of groundwater were defined through electrical conductivity measurements (completed at the time of the piezometric surveys) in 72 wells and analysis of water samples from 35 wells to determine major ion concentrations. Previously collected data on withdrawals in fish farms were also taken into account (Bianchi et al., 2006a,b); these data were considered also valid for the 2009 period, given that the continuous withdrawals maintain the water chemistry practically stable.

The distribution of electrical conductivity highlights the remarkable difference in total salinity between the central-eastern sector and the area near the coast; values range from 300-1,000 μ S/cm (at 20 °C) in some wells drilled in the carbonate aquifer (confirming the flow of freshwater from the cavernous limestone) to maximum values greater than 5,000 μ S/cm in the sector between Orbetello Scalo and Ansedonia, which is in large part characterized by negative piezometric heads. Values were constantly greater than 2,000 μ S/cm in the coastal strip between the Osa River and Albinia up to about 6 km inland, where negative piezometric heads are commonplace only in dry years.

Variations in conductivity between July and February 2009 were on average about 450 μ S/cm, with maximum values of 1,100 to 3,100 μ S/cm near the coast; these obviously derived from a combination of the salinity of water inflow into and discharge from the aquifers. Comparison with the results of previous investigations (Angelini et al., 2000; Nocchi, 2002; Bianchi et al., 2006a,b) reveals a temporal evolution characterized by practically stable conductivity values along the entire coastal strip, except in the south-eastern sector of Albinia, where salinity has increased permanently towards the carbonate hills due to intense withdrawals from public-supply wells, in a sector where there are exchanges of water between the cavernous limestone and alluvial sediments.

Analytical data were interpreted through Piper diagram (Piper, 1944) and Cl vs SO₄ correlation. The quality of water was compared with that of the Saturnia and Osa thermomineral springs (Bianchi and Fanciulletti, 2000), the Albegna River (Nocchi, 2004), the sea (Bianchi et al., 2006a,b) and of a typical recent superficial flow of continental water fed by meteoric recharge, with the aim of accurately reconstructing relationships between groundwaters and their hydrogeological history in an area characterized, as others in southern Tuscany, by various salinization phenomena (Bencini and Pranzini, 1992, 1996; Avio et al., 1995; Bianchi et al., 1997; Angelini et al., 2000; Barazzuoli et al., 1999, 2005, 2006, 2008; Bencini et al., 2001; Bianchi et al., 2006a,b). Normal groundwaters in the coastal plains of Grosseto are chemically mature thanks to the progressive concentration of elements along the flow path (aging process); their chemistry is sometimes significantly modified by sulphate- and/or chloride-rich saltwater intrusions (mixing process) and by ionic exchanges with the matrix (cation exchange process).

Figs. 6, 7 and 8 reveal that the main hydrochemical facies coexist in the studied waters and that chemical variability is locally compensated through water/matrix interactions, which are common in coastal aquifers affected by salinization process (Appelo and Postma, 1993; Kim et al., 2003; Capaccioni et al., 2004; Faye et al., 2005).



Fig. 6: Piper diagrams for groundwater samples. Diagrams also show the chemistry of the "Saturnia" and "Osa" thermomineral springs (respectively, TS and TO; Bianchi and Fanciulletti, 2000), of the Albegna River (FA; Nocchi, 2004), of the sea (SW; Bianchi et., 2006a,b) and of a typical recent superficial flow of continental water fed by meteoric recharge (AC).



Fig. 7: Hydrochemical zonation of groundwater based on average analytical data on major ions for February-July 2009; samples n. 79, 115 and 116 refer to a single sampling.

The following briefly describes the five identified facies with reference to average values in February-July 2009.

The HCO₃-Ca facies was detected in 7 out of 35 cases (20 % of the total) and is characterized by the following values: electrical conductivity (EC) = 804 μ S/cm; total dissolved solids (TDS) = 20 meq/L; Cl = 2 meq/L; (Ca+Mg)/(Na+K) = 4.4; SO₄/Cl = 0.7; Na+Cl = 22 %. It is present especially in the inner zones and is linked to a recent and relatively superficial flow of groundwater fed by meteoric recharge. The SO₄-Ca facies was identified in 14 % (5 cases) of all cases and is characterized by: EC = $1,317 \mu$ S/cm; TDS = 38 meq/L; $Cl = 3 \text{ meq/L}; (Ca+Mg)/(Na+K) = 6.7; SO_4/Cl = 4.8; Na+Cl = 15 \%.$ It is found in the wells of the Albegna plain and is therefore ascribed to groundwater flows from the north-east, which are fed by meteoric infiltration and by seepage of stream waters (sample FA); the latter are practically identical to those of the Saturnia thermomineral spring (sample TS) which discharges into the upper Albegna River, largely contributing to its baseflow (0.3-0.6 m³/s: Mancini, 1960; Fanelli et al., 1982). The chemistry of water in wells n. 26 and 50 is linked to the baseflow in the cavernous limestone aquifer, which is

fed by meteoric recharge and by the likely contribution of a regional flow. The *Cl-Na* facies was identified in 13 cases (37 %) and is characterized by: EC = 3,239 μ S/cm; TDS = 79 meq/L; Cl = 29 meq/L; (Ca+Mg)/(Na+K) = 0.9; SO₄/Cl = 0.2; Na+Cl = 62 %.

This composition, found all along the coastal area, results from the mixing of continental and marine waters in various proportions determined by the widespread piezometric depressions; the facies occupies the area characterized by piezometric heads less than 2 m asl and chloride concentrations greater 500 mg/L. The marine chemistry is found practically unchanged in several fish farm wells (Ansedonia area), which show the following range of values (Bianchi et al., 2006a,b): EC = 16,440-53,300 μ S/cm; TDS = 347-1,263 meq/L; Cl = 200-716 meq/L; (Ca+Mg)/ (Na+K) = 0.2-0.4; SO₄/Cl = 0.0-0.1; Na+Cl = 79-89 %.

Figure 8 allows the identification of alkaline chloride waters (n. 34, 38, TO), which show an enrichment in sulphates and calcium with respect to those present along mixing line A. This chemical variability can be ascribed to mixing between regional flows of SO_4 -Ca waters and Cl-Na waters of likely marine origin; this also explains



Fig. 8: Cl vs SO_4 correlation plot of groundwater samples: values for February and July 2009. The plot also shows the chemistry of the "Saturnia" and "Osa" thermomineral springs (respectively, TS and TO; Bianchi and Fanciulletti, 2000), of the sea (SW; Bianchi et., 2006a,b) and of a typical recent superficial flow of continental water fed by meteoric recharge (AC).

the formation of waters with a *Cl-Ca* facies, which involves inverse ionic exchange reactions. The latter facies is present especially in wells drilled in the carbonate aquifer of the area behind the alkaline chloride facies (n. 47, 51 and 55) or in the alluvial sediments of the Grosseto plain downstream of the sulphate-calcium facies (n. 98 and 101). It represents 17 % of the total (6 cases) and has the following characteristics: EC = 2,122 μ S/cm; TDS = 55 meq/L; Cl = 15 meq/L; (Ca+Mg)/(Na+K) = 2.1; SO₄/Cl = 0.6; Na+Cl = 41 %.

Figure 8 also shows the mixing line (B) between recent continental water and regional flows of water. The transition occurs for SO₄ values of about 5 meq/L; the two end-members are the water of well n. 48 (located ESE of Albinia) and that sampled in July from well n. 26 (located ENE of Ansedonia). Lastly, the *HCO*₃-*Na* facies was found in 4 cases (11 %) and is characterized by the following values: $EC = 1,434 \,\mu$ S/cm; TDS = 37 meq/L; Cl = 4 meq/L; (Ca+Mg)/(Na+K) = 1.2; SO₄/Cl = 1.3; Na+Cl = 34 %. It is associated with direct ionic exchange reactions in bicarbonate-calcium waters within formations characterized by the relative abundance of the clay fraction.

Note that most samples have the same facies in July and February (88 % of cases), indicating the overall stability of the process of salinization of local groundwaters. The few variations between February and July can mostly be ascribed to advancing seawater intrusion caused by greater withdrawals in spring-summer, as in the case of wells n. 32 (HCO_3 - $Ca \rightarrow Cl$ -Ca), n. 95 (HCO_3 - $Ca \rightarrow Cl$ -Na) and n. 101 (SO_4 - $Ca \rightarrow Cl$ -Ca); the changes observed in well n. 46 (Cl- $Na \rightarrow Cl$ -Ca) are linked to a process of inverse ionic exchange in chloride sea water.

The distribution of chloride (Fig. 9) reveals how the quality of groundwater has deteriorated considerably along the coast up to the Diacciobello locality, where values of about 600 mg/L (well n. 51) are recorded, except in the area by the mouth of the Osa River and in the sector between Burano Lake and the Chiarone Stream. The average total chloride content is nearly 700 mg/L (27 % of the total salinity).

The carbonate aquifer, characterized by an average chloride concentration of about 1,000 mg/L, is very vulnerable to pollution because of its high permeability due to fracturing and karstification. Collected data all indicate that the area of Ansedonia is the main point of seawater intrusion (Bianchi et al., 2006a,b; Nocchi and Salleolini, 2009). In the Albegna River plain (Barazzuoli et al., 2005, 2008), the water from wells screened in the lower aquifer layer (Pliocene gravel and sand) has the highest chloride concentrations; this layer therefore seems to be the one most affected by seawater intrusion. These wells are located in the sector facing the coast, where the piezometric depression is greatest, and their structure (with more screens) facilitates seawater intrusion within the aquifer system. The variation in the chloride content between July and February 2009 was about 100 mg/L, with peak values of between 100 and 400 mg/L near the coast; comparison with the results of previous investigations (Angelini et al., 2000; Bianchi et al., 2006a,b) revealed a temporal evolution characterized by the essential stability of chloride along the coastal strip, except in the south-east sector of Albinia, where salinity is constantly high due to greater withdrawals from public-supply wells.



Fig. 9: Chloride concentration contour map.

Isotope content

The environmental isotope (¹⁸O, ²H and ³H) content in groundwater was defined through analysis of water samples from 27 wells collected in the 2004-2009 period; the isotopic composition of local spring water and seawater was also analyzed (Bianchi et al., 2006a,b). The use of isotope techniques is particularly useful in this area where research has revealed the presence of coexisting flow systems of different rank, each governed by specific recharge/discharge relationships and with freshwater/saltwater interface in dynamic equilibrium with the groundwater hydraulic head, allowing the mixing of freshwater and saltwater, both superficial (recent) and deep (old), in various proportions.

The stable isotopic composition (Fig. 10) indicates that all groundwaters are highly correlated and plot near the reference meteoric water line. This suggests that the possible processes of evaporation during recharge and of isotope exchange between groundwater and the reservoir rock are insignificant. Furthermore, the succession of isotope values practically follows that of salinity values (Fig. 11), confirming that the chemistry of local groundwaters mainly derives from a process of mixing between seawater and groundwater in the cavernous limestone and the neo-autochthonous sediments; mixing between meteoric water and seawater produces intermediate products with increasing chloride concentrations and progressively more positive ¹⁸O values. In summary, the more negative δ ¹⁸O values are typical of less saline waters with relatively short flow paths and limited exchange with the mineral matrix of the aquifer (and therefore close to the meteoric origin); in contrast, δ^{18} O values greater than -5 ‰, or positive values, characterize waters derived through abundant mixing with seawater (n. V2, V5, C3 and TO), in some cases even assuming the characteristics of sea water (n. IT, C10). The only exception to this general trend is the Tricosto Spring (n. 120), which shows much lower δ ¹⁸O values with respect to other samples (of equal salinity), thereby indicating that it belongs to a different aquifer system.



Fig. 10: $\delta^2 H vs \delta^{18}O$ correlation plot: average values for 2004-2009. The red dashed line represents the meteoric water line identified by Longinelli and Selmo (2003) for central Italy



Fig. 11: $\delta^{18}O$ vs chloride correlation plot: average values for 2004-2009.

The plot in figure 12, which substantially compares the time (³H axis) and salinity (δ ¹⁸O axis) factors, identifies the following typologies (Bianchi et., 2006a,b): **a**) waters in which the contribution of saltwater does not exceed 10 %; these are distinguished for their tritium content and therefore for the time elapsed between infiltration and sampling. In particular, the coastal strip of the Albegna plain (wells n. 60 and 95) is characterized by groundwaters with very low tritium contents and therefore represents the meeting point of continental water and sea water with long residence times in the ground, as was found in the carbonate aquifer near the Orbetello Lagoon (n. 36, 112, 115 and 116). The other samples are mixtures of young and

old water in various proportions within the same aquifer systems; ε) waters pumped from most of the fish farm wells usually shows a marine contribution greater than 90 % and similar isotopic contents, with high δ ¹⁸O values and with sometimes very low ³H contents. They originated from a more or less deep flow of sea water with a medium-long residence time in the ground during its ascent along the freshwater/saltwater interface; δ) waters have intermediate characteristics and comprise the Osa thermomineral spring and some fish farm wells. The Tricosto Spring is confirmed to be a distinct typology linked to an extremely rapid circulation of water recently infiltrated into a different aquifer system.



Fig. 12: ³*H* vs δ ¹⁸*O* correlation plot: average values for 2004-2009. The plot also shows the average isotopic content of precipitation in central Italy. See the text for the definition of \mathbf{a} , $\boldsymbol{\varepsilon}$ and $\boldsymbol{\delta}$.

Aquifer monitoring and management

Expected scenarios

The medium- and long-term effects of land management policies are difficult to foresee due to interaction among numerous elements and variables of different nature, especially as far as seawater intrusion is concerned because many aspects of this problem are not completely understood (Custodio and Bruggeman, 1987; Custodio and Galofré; 1993; Bear et al., 1999; Cheng and Ouazar, 2004). Groundwater management therefore requires the use of numerical models to test present and alternative exploitation scenarios taking into account technical, economic, legal, social and political aspects (Wang and Anderson, 1982; Canuti and Giuliano, 1986; Bear and Verruijt, 1987; Emch and Yeh, 1998; van Dam, 1999; Maimone et al., 2004; Bear, 2004).

In recent years, conceptual and numerical models have been developed for simulating the hydrodynamics and hydrochemistry of the main aquifer systems in the study area. These models are still not completely reliable because of the incomplete knowledge of the systems and the few opportunities to fully check results; however, they can already provide important information on the general evolution of the systems under different stress conditions. In particular, the models can be used to quantitatively assess the impact of variations in the amount of water withdrawn and/or in the position of wells that could help remediate saltwater intrusion. Such general indications can no doubt be considered valid even in the sector south of the Melone Stream, although knowledge of this area is less complete. The numerical model developed for simulating the hydrodynamics of the Plio-Pleistocene aquifer of the Albegna River coastal plain (Barazzuoli et al., 2005, 2008) demonstrates that, at present, inflows and outflows appear to ensure the equilibrium of the aquifer system; however, seawater intrusion along the coastline is responsible for the substantial deterioration of the chemical quality of groundwater. The model helped establish that water withdrawal near the coast during the irrigation season is the main cause of seawater intrusion, especially in the Osa-Albegna sector; the inflow of sea water along the river at times infiltrates into the aquifer. The deterioration of groundwater quality therefore appears to be due to the way in which withdrawals are carried out (where and when) rather than to the considerable quantity of water being pumped (about 3·10⁶ m³/year).

The effects of hypothetical aquifer exploitations were assessed in terms of water budget and the evolution of hydraulic head starting from February 2003; these forecasts concern the next 10 years and take into consideration local climate trends. In particular, two exploitation scenarios were examined: scenario E considers the relocation of all coastal wells to at least 3 km inland from the shore and maintenance of the current total withdrawal; in contrast, scenario B considers halving withdrawal from all wells in the plain but no relocation. The results of these simulations were compared with those obtained maintaining unchanged current aquifer exploitation, i.e. scenario A (Fig. 13). Analysis of water budget variations



Fig. 13: Water budget in scenarios A, B and E for the February 2012 - February 2013 period (Barazzuoli et al., 2008): positive values are inflows into the aquifer system, negative values are outflows. Albegna: upstream = from La Marsiliana to the confluence with the Magione-Radicata stream; downstream = from the confluence with the Magione-Radicata stream to the mouth. Mare: Osa-Albegna sector = from the mouth of the Osa R. to the mouth of the Albegna R.; opposite lagoon = from the mouth of the Albegna R. to the southern end of the model. See the text for the definition of scenarios.



tion (February 2013), and its variations with respect to calculated values in scenarios B and E; scenario B produces a rather uniform

increase in the piezometric level (the balance of the aquifer system

increases by over $2 \cdot 10^5$ m³), whereas scenario E leads to a decrease in the piezometric level in the northern sector and an increase in the

southern sector near the lagoon (the amount of water in the aquifer decreases by about $3.5 \cdot 10^4$ m³). In conclusion, a considerable de-

crease in extraction from the aquifer would lead to the reactivation

of net groundwater discharge to the sea and especially to the Al-

begna River. When wells are only relocated, with no significant de-

crease in water extraction, there is a decrease in seawater intrusion



Fig. 14: Piezometric results at the end of the simulation (Barazzuoli et al., 2008): a) Simulated groundwater level contour map for February 2013 (scenario A); b) Piezometric difference between scenarios B and A for February 2013; c) Piezometric difference between scenarios E and A for February 2013. See the text for the definition of scenarios

reveals that halving the discharge (scenario B) determines both an increase in the quantity of water drained by the river and a decrease in the quantity of water from the river, for an overall decrease of about $9 \cdot 10^5$ m³ in the flow of water from the Albegna River to the aquifer; the quantity of water which infiltrates into the saline portion of the river decreases by nearly $6 \cdot 10^4$ m³. The opposite effect is obtained by relocating the coastal wells further inland (scenario E). As for the coastal limit, in both scenarios there is an increase in aquifer discharge to the sea, especially in the Osa-Albegna sector, where extraction is greatest. The relocation of coastal wells therefore determines a decrease in saltwater intrusion, and can effectively contrast the degradation of groundwater quality.

Figure 14 shows the piezometric surface at the end of the simula-

The numerical model developed for simulating the hydrodynamics and hydrochemistry of the carbonate aquifer east of the Orbetello Lagoon (Bianchi et al., 2006b; Nocchi and Salleolini, 2007, 2009) demonstrates that the freshwater budget is negative (almost $9 \cdot 10^6 \text{ m}^3$) even in a period characterized by above-average meteoric recharge (+ 37 %); this indicates that the aquifer is overexploited due to the quantity of freshwater drawn along with seawater (about 12.5 $\cdot 10^6$ m³, 26 % of the total) by fish farms in the Ansedonia area.

The effects of hypothetical aquifer exploitations were assessed in terms of hydraulic head and salinity evolution starting from October 2005; these forecasts concern the next 10 years and take into consideration local climate trends. In particular, two exploitation scenarios were examined: exploitation of the aquifer continues under the present conditions (W_{const}); withdrawal decreases by 50 % ($W_{-50\%}$). The impact of the climate trend is represented by the plot in figure 15a. Note that the piezometric level decreases significantly with respect to level in the hypothesis of constant recharge, whereas the chloride content always increases by the same amount (about 10 %), confirming that the current state of exploitation would in any case lead to degradation of the chemical quality of water. Figure 15b shows the evolution over time, calculated considering the negative trend in meteoric recharge, in the hypothesis of reduction of withdrawal. Note that the greatest impact on the evolution of the hydraulic head is determined by pumping by fish farms; although there are some uncertainties in the estimated solute transport, the chloride content increases regardless, indicating that the system would be overexploited even with a 50 % reduction in withdrawals

Monitoring

The acquired hydrogeological and hydrogeochemical data on the study area and the specific problem of the degrading chemical quality of groundwater suggested the importance of quality and quantity monitoring of aquifers using both existing wells and additional observation wells. The proposed monitoring network not only takes into account the results of this study, information reported in AR-PAT (2005) and the guidelines in Legislative decree n. 152/99 (as amended) but is also readily practicable.

Existing wells were selected so as to obtain a homogeneous distri-

bution of measurement points in the area while ensuring the ability to carry out piezometric survey and sample water for physical-chemical analyses; furthermore, all selected wells are characterized by accessibility, reproducibility and significativity (Canter et al., 1987; Zavatti, 1988). The position of selected wells is shown in figure 16. As for analytical determinations, the temperature and electrical conductivity of groundwater will be measured *in situ*; samples will be taken from wells of particular significance for the laboratory analysis of Na, K, Ca, Mg, HCO₃, Cl, SO₄, NO₃ and Br ion concentrations. As for the frequency of measurements, piezometric survey will be carried out every three months; at the same time, the temperature and electrical conductivity of groundwater will be measured. Samples for laboratory analysis will be collected every six months.

Assuming the availability of funds, the proposed monitoring network will be integrated with new observation wells in which to carry out the same operations as in the existing wells. These additional measurement points, which should be positioned as shown in figure 16, were identified with the following aims: *a*) to reduce the most significant gaps in the network of existing wells, i.e. those in the outcrops of cavernous limestone in the central sector of the study area. In the selected areas, observation wells will have to extend well below sea level, so that their maximum depth will be of the order of 300 m; *b*) to obtain essential information for monitoring seawater intrusion, in particular electrical conductivity measurements at various depths along the coastal strip to identify the freshwater/saltwater mixing zone. In the selected areas, water will therefore be sampled at different depths.

Management

Remedial actions for contrasting the advance inland of the saltwater intrusion are truly effective only if they balance the freshwater deficit which is responsible for the degradation of the groundwater quality; partial solutions, which merely aim to block seawater intrusion, lead to other inconveniences typical of aquifer overexploitation (depletion of water resources and reserves, progressive degradation of the chemical quality of water, etc.). The only reasonable and feasible solution appears to be the integrated management of groundwater and surface water resources, taking into account the required quantity and quality of water for various purposes (Custodio and



Fig. 15: Model forecasts under constant conditions (a) and for a 50 % decrease (b) in current withdrawals (Nocchi and Salleolini, 2009, modified): average values for the entire aquifer.



Fig. 16: Proposed distribution of measurement points for quality and quantity monitoring of aquifers. Wells in the monitoring network: A) hydraulic head; B) hydraulic head, temperature and electrical conductivity; C) hydraulic head, temperature and electrical conductivity, chemical analysis. Additional observation wells: 1) piezometric survey and groundwater sampling; 2) vertical distribution of salinity

Galofré, 1993; Emch and Yeh, 1998; van Dam, 1999; Maimone et al., 2004; Bear, 2004); however, in Italy much remains to be done in terms of land-use planning and mitigation of conflicts among different users (Barrocu, 2003).

In general, all ways of directly and/or indirectly improving the water budget of aquifers should be considered: for example, the reuse of treated wastewater, the creation of reservoirs and of channels for diverting streams, etc.. However, these measures entail great financial expenditure and should therefore be enacted only after careful hydraulic and hydrogeological studies which confirm their feasibility and effectiveness. Even the necessary repair of obsolete sections of the water supply network would allow the recovery of water resources, thereby improving the balance of the water budget.

The degradation of the chemical quality of groundwater in the multi-aquifer system of the Albegna plain is essentially linked to abundant withdrawals, mostly for agricultural purposes and concentrated in the irrigation season, which draw sea water especially into the Osa-Albegna sector. In this case, the most appropriate solution seems to be replacement of the amount withdrawn by treated wastewater and/or surface water stored in reservoirs; another possible solution is the creation of systems for artificially recharging the aquifer using injection wells or infiltration basins containing treated wastewater and/or infiltration channels which divert the flood water of streams. Obviously, mixed solutions may be taken into consideration.

Overexploitation of the carbonate aquifer east of the Orbetello Lagoon is caused above all by withdrawal of large quantities of freshwater for fish farming, which should instead use only seawater in order to guarantee the continuity and quality of marine fish production (1.7·10³ tons for sales of 17·10⁶ Euro in 2003). Modelling results suggest that fish farm wells should be extended to deeper portions of the aquifer stably occupied by marine waters alone (Nocchi and Salleolini, 2007, 2009) in such a way as to form an efficient extraction barrier controlling seawater intrusion into the aquifer (Driscoll, 1986; Sherif and Hamza 2001; Kacimov et al. 2009); this solution, which is being implemented, will also increase knowledge of aquifer characteristics and zone mixing. Furthermore, even in this case, the groundwater pumped for irrigation purposes (about $2 \cdot 10^6$ m³/year) should be replaced with treated wastewater and/or surface water stored in reservoirs; the permeability of the aquifer material (cavernous limestone) and the altitude of outcrops are such that the artificial recharge of the aquifer through injection wells or infiltration basins containing treated wastewater and/or infiltration channels which divert the flood water of streams is not advisable. Lastly, another remedial action involves redesign the network of wells in the water supply system so as to obtain a more regular layout, further away from the coast and with a better distribution of quantity withdrawn (besides the necessary repair of obsolete sections of the water supply network).

Conclusions

In many coastal areas the growth of human settlements, together with the development of agricultural, industrial and tourist activities, has led to the overexploitation of aquifers. Such overexploitation induces a rise in the freshwater-saltwater interface (seawater intrusion) and thus the degradation of the chemical quality of groundwater; the problem will be aggravated by the expected rise in sea level associated with global warming. The choice of indicators able to reveal the process in time for the implementation of remedial actions, the development of methods of study able to suggest techniques for monitoring and prevention, and the identification of management strategies most suited to the control of saltwater intrusions are major objectives in the sustainable development of coastal water resources (Custodio and Bruggeman, 1987; Custodio and Galofré; 1993; FAO, 1997; Bear et al., 1999; Cheng and Ouazar, 2004). In Italy, unfortunately, the general lack of knowledge on the hydrogeology and hydrogeochemistry of the involved aquifers is such that one risks enacting measures that are either ineffective or else too restrictive for the development of local economic activity.

Investigation of the coastal strip between the Osa River and Chiarone Stream (southern Tuscany) reveals the presence of coexisting flow systems of different rank which allow mixing of freshwater and saltwater, both superficial (recent) and deep (old), in various proportions. Hydraulic head measurements show that withdrawals strongly affect groundwater, causing areas of negative hydraulic head at the site of the most intensely exploited wells (water supply systems, fish farms); geochemical interpretation reveals that the evolution of the chemical composition of groundwater is mainly controlled by mixing of sea water with water circulating in the cavernous limestone and in neo-autochthonous sediments (and by related ionic exchange reactions).

Acquired data allowed the definition of conceptual models for the aquifers; these models serve as a basis for developing numerical models that simulate the general hydrodynamic and hydrochemical evolution of the systems under different stress conditions. Schemes to counteract seawater intrusion, in the context of the integrated management of surface water and groundwater resources, were also identified: i) in general, repair of the obsolete sections of the water supply network and replacement of the quantity withdrawn for irrigation purposes with treated wastewater and/or superficial water stored in reservoirs; ii) for the multi-aquifer system of the Albegna plain, creation of systems for artificially recharging the aquifer through injection wells or infiltration basins containing treated wastewater and/or infiltration channels which divert the flood water of streams; iii) for the carbonate aquifer, requalification of the pumping systems of fish farms and redesign of the network of wells in the public water system.

Lastly, this study proposes a network for quality and quantity monitoring of aquifers based on existing wells and additional observation wells; the periodic control of hydraulic head and of the main physical-chemical parameters is a prerequisite for the rational management of the aquifers. The hoped for leap forward in understanding of the aquifer systems can only be achieved through the careful organizational and economic planning of the authorities managing territorial resources, above all water resources.

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