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GROUNDWATER PLANNING AND PROTECTION: ASSESSMENT OF ENVIRONMENTAL INDEXES IN COMPLEX AQUIFER SYSTEMS. THE SOLOFRANA RIVER VALLEY CASE STUDY (SOUTH ITALY)

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ABSTRACT

Heterogeneity of natural systems governs the pathway of pollutant in the environment, mostly in groundwater resources. A large number of hydrogeological researches aim to parameterize and model these processes. Namely, the spatial variability of the hydrogeological properties of rocks may be defined from geologic observations and local measurements.

The Solofrana River Valley (South Italy) is a real natural laboratory to improve understanding of the behaviour and transfer of pollutants on large scale. The geological and structural complexity of the territory, due to the tectonic and morphological evolution of the carbonate platform domains, resulting in filling of the structural depressions by the quaternary deposits (volcanic, talus and alluvial sediments), is combined with a widespread agricultural activity and with the incidence of important industrial centres, among which stands out the Solofra's tanning pole.

A multidisciplinary approach was employed to delineate aquifer/aquitard unit and characterize scale-dependent heterogeneity by means of geological, hydrogeological and geochemical techniques.

This paper describes firstly the experience carried out in an area characterized by a high anthropic impact. Besides, it reports about relevant geological and hydrogeological aspects of the Solofrana River Valley and presents some interesting aspects related to field operations and characterization of pollutants flow and transport.

Existing data, combined with a specific geological survey and a monthly water level monitoring (July 2010; February 2011-October 2012), as well as a groundwater chemical-physical characterization based on a monthly EC, pH and temperature monitoring and on chemistry analyses involving 77 parameters (July 2010 - April-June 2012), provided to assess the groundwater composition indexes and the chief environmental indexes. So the improvement of the hydrostratigraphic architecture and the hydraulic continuity among aquifers, especially pushing up depths, derived from the assessment of equivalent parameters of hydrodynamic properties.

With regard to the hydrogeological and impact conditions, the results of multivariate statistical analyses proved the identification of a number of homogeneous zones even in such complex aquifer systems.

Key words: *groundwater quality, multivariate analysis, environmental indexes*

INTRODUCTION

The European Water Framework Directive (WFD 2000/60/EC) and the most recent European Groundwater Directive (2006/118/EC) provide criteria for delineating the groundwater protection policy.

Such directives introduce a new model of integrative water protection and changes in environmental governance. The topic of these rules is the characterization of the environmental status of water bodies in order to achieve good chemical and quantitative conditions by the end of 2015.

Water management has to be based on hydrological units. The central unit of such organization is the "River Basin Management", namely an "area of land and sea, made up of one or more neighbouring river basins together with their associated groundwaters and coastal" (art. 2.15 WFD 2000/60/EC).

In Italy, firstly the D.Lgs. 152/2006 and then the D.Lgs. 30/2009 recognized such European Directives.

With regard to the protection of groundwater against pollution, the assessment of the chemical status of groundwater is a key issue for the "sustainable development and territory management".

From a scientific perspective, the implementation of WFD and decision-making on groundwater protection policy need the improvement of studies and researches aimed at identifying hydrogeological properties, which control the behaviour and transfer of pollutants on large scale, by standardized procedures.

Heterogeneity of natural systems governs the pathway of pollutants in the enviroment, mostly in groundwater resources.

The relationship between a number of environmental pressures and the complex structure of groundwater flow systems generates many processes, which affect the behaviour and transport of contaminants. Such dynamic behaviour needs generally both geostatistical and fractal approaches (e.g. Felletti et alii, 2006; Galloway, 2010; Ouellon et alii, 2008).

It is difficult to apply such methods to parameterize and model flow systems in large areas, characterized by too sparse data set. As a result pollutant concentrations are not clearly defined in time and space. This consideration becomes increasingly concerned with analyses of sustainable development and territory management that require basin-wide investigations.

With regard to the wide variety of structural, volcanic and depositional processes which characterize the alluvial aquifer systems in the Campania Region (South Italy), this thesis describes a multidisciplinary approach to delineate aquifer/aquitard unit and recognizes scale-dependent heterogeneity by means of geological, hydrogeological, geochemical and geostatistical techniques.

In such complex hydrogeological structures special attention requires the recharge mechanism of confined or semiconfined aquifers, mainly of bedrock karst aquifers underlying heterogeneous deposits such as pyroclastic-alluvial successions (e.g. Foster, 1998; Griffiths et al., 2011; Shand et al., 2007). Just heterogeneity affects leakage in complex aquifer systems and increases hydrodispersion parameter uncertainty.

Namely this thesis identifies and analyses groundwater composition and heavy metals distribution in a suitable area to outline the basin scale indicators either of processes occurring within multi-layered aquifers or of natural attenuation potential. Each indicators describes a specific aspect of groundwater quality and their combination allows to define indexes of groundwater environmental state, due to natural and anthropogenic phenomena.

The sample area is the Solofrana River Valley, located in a Site of National Importance, the so-called "Hydrographic Basin of Sarno River" (L. 266/2005) just downgraded to Site of Regional Importance (D.M. 11/01/2013).

CHAPTER 1

EUROPEAN AND ITALIAN LEGISLATION ON WATER RESOURCES

1.1 - EUROPEAN WATER POLICY

Groundwater protection is a priority in European Union (EU) environmental policy for several reasons. First, once contaminated, groundwater is harder to clean than surface water and the consequences can last for decades. Groundwater is frequently used for the abstraction of drinking water, for industry and for agriculture, and its contamination can endanger human health and threaten those activities.

Groundwater provides the base flow for many rivers and can thus affect the quality of surface water systems; it also acts as a buffer through dry periods, and is essential for maintaining wetlands.

So the protection and management of water resources have become a focus of EU since the 1960ies.

Three distinct steps mark the evolution of EU water policy. The first step started in 1973 with the beginning of five-year Environmental Action Programmes (EAP), which laid down objectives and principles of the environmental policies of the European Commission (EC).

The basis for such innovative legal acts was the original European Community Treaty, whose article 174 lays down the achievement of a high quality environment in all Member States.

Since the end of the 1970s, several measures for the prevention and reduction of water pollution have been introduced in a number of Directives based mostly on a regulatory approach.

These Directives subdivided aquatic ecosystems into individual protected commodities and defined quality targets, each of which had to be followed or achieved through certain measures. In particular, in this time we had:

- ✓ Surface water directive (75/440/EEC);
- ✓ Bathing water directive (76/160/EEC);
- ✓ Fish water directive (78/659/EEC);
- ✓ Shellfish water directive (79/923/EEC);
- ✓ Drinking water directive (80/778/EEC).

The second step of the European water policy evolution occurred in 1990ies, as eutrophication of sea and fish waters increased and the general state of water resources decayed.

Consequently, two new legal instruments were adopted providing strict rules on the treatment of wastewater and on the use of nitrates in agriculture. Wastewater treatment (Directives 91/271/EEC and 98/15/EEC) became obligatory even in the smallest settlement and legally binding measures came into force to limit the use of animal fertiliser on fields (Nitrate Directive 91/676/EEC). With the implementation of the Directive concerning integrated pollution prevention and control (96/61/EC), a new rule for emissions control was formulated. Moreover, the guideline to control the dangers in the event of major accidents (96/82/EEC, the so-called Seveso II Directive) contains important aspects of water protection.

In spite of the numerous regulatory interventions on the community level, however, it was difficult to achieve an effective water protection policy in short time.

1.2 - WATER FRAMEWORK DIRECTIVE (2000/60/EC)

On the background of numerous unresolved problems that were encountered during the implementation and application of community water directives in the Member States, the European Council of Ministers asked for a reform of the water policy. The European Parliament and European Council adopted the Water Framework Directive (WFD) that represents the third step in the evolution of European water policy.

The new WFD, adopted in October 2000 and entered into force in December 2000, was designed in the view of integrated and more effective water management. So it outlines criteria to rationalise, standardise and improve the water protection legislation in European member states.

Such Directive concerns with aquatic systems, surface waters (rivers and lakes) as well as groundwater and coastal waters. Land ecosystems depending on groundwater are also included in the quantitative protection of groundwater.

The WFD has a number of objectives, such as preventing and reducing pollution, promoting sustainable water usage and environmental protection, improving aquatic ecosystems and mitigating the effects of floods and droughts. Yet the main target of this Directive is to achieve the "good status" of all surface, ground and coastal waters in the Community by 2015. Likewise it is possible to identify the ecological and chemical status of water. The basic thinking behind the term "good ecological status" is that humans can use water as long as the ecological function of the water body is not significantly impaired. The EU defines the ecological function for the different types of water. The "chemical water status" has to be determined by environmental quality standards for hazardous substances. From this, the WFD lays down that:

- "*Good surface water status*" means the status achieved by a surface water body when both its ecological (classified in accordance with Annex V of the WFD) and chemical status are at least "good".
- "*Good surface water chemical status*" means the chemical status required to meet the environmental objectives for surface waters established in Article 4(1)(a), that is the chemical status achieved by a body of surface water in which concentrations of pollutants do not exceed the environmental quality standards established in Annex IX and under Article 16(7) of the WFD, and under other relevant Community legislation setting environmental quality standards at Community level.

- "*Good groundwater status*" means the status achieved by a groundwater body when both its quantitative (defined in table 2.1.2 of Annex V of the WFD) and chemical status (see table 2.3.2 of Annex V of the WFD) are at least "good".

These objectives will be achieved through the implementation of River Basin Management Plans (RBMPs) for each river basin district (RBD) or international river basin district (IRBD). A river basin is the area of land from which all surface run-off flows through a sequence of streams, rivers and lakes into the sea at a single river mouth, estuary or delta (Fig. 1.1).

Each river basin must be assigned to a (I)RBD which is an area of land and sea identified as the main area for co-ordinated water management, made up of one or more neighbouring river basins together with their associated groundwater and coastal waters.

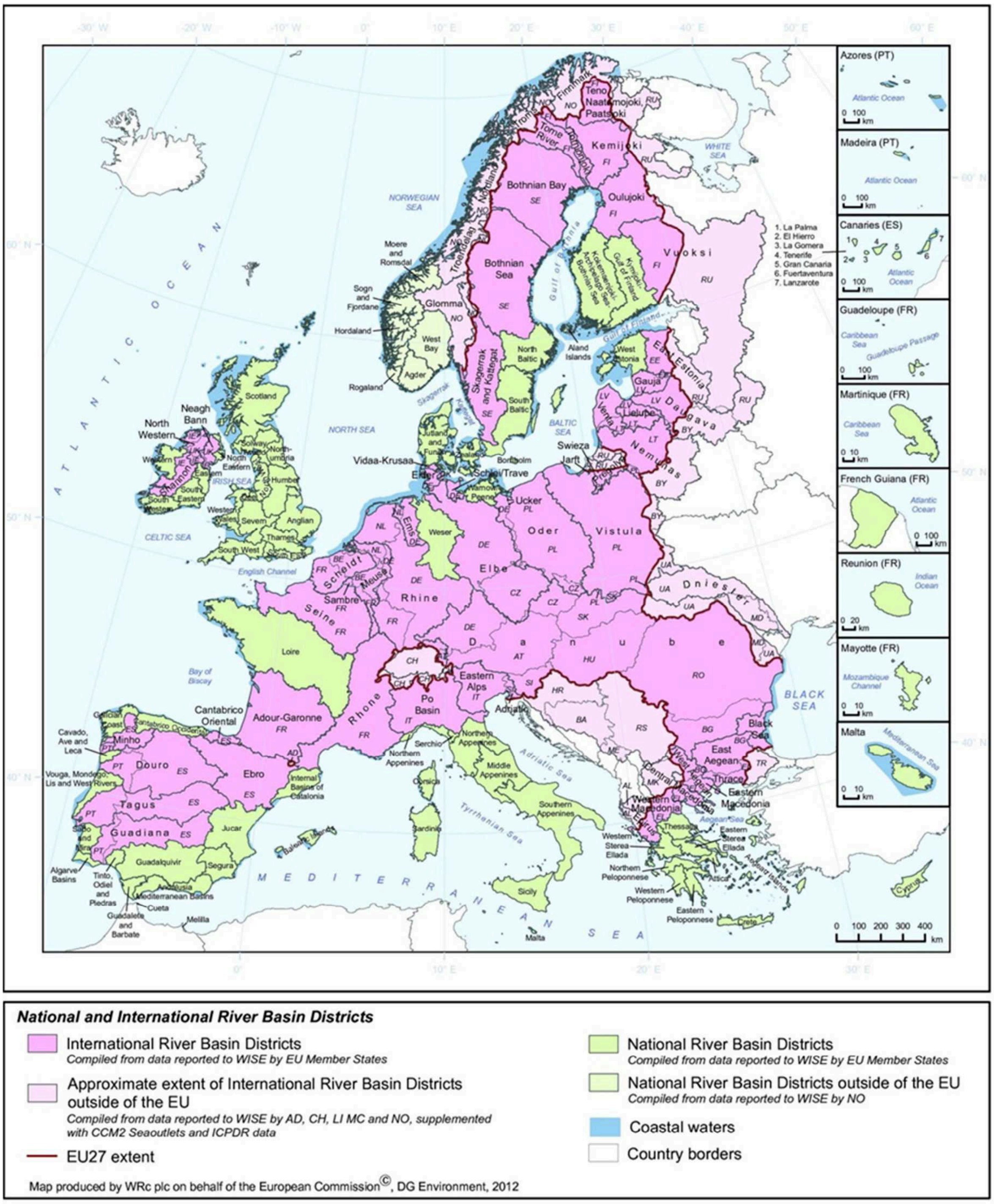
The RBMPs for each district identify the specific objectives and actions to be taken to achieve at least 'good status' for groundwater bodies by 2015. In particular they must aim to:

- ✓ prevent deterioration, enhance and restore bodies of surface water, achieve good chemical and ecological status of such water and to reduce pollution from discharges and emissions of hazardous substances,
- ✓ protect, enhance and restore the status of all bodies of groundwater, prevent the pollution and deterioration of groundwater, and ensure a balance between groundwater abstraction and replenishment,
- ✓ preserve protected areas.

These actions are known as Programmes of Measures (PoMs) and are established under Article 11 of the WFD.

Article 17 of the WFD requires Member States to adopt "specific measures to prevent and control groundwater pollution". It also required the European Commission to submit proposals for specific measures to prevent and control pollution with the aim of achieving the objective of good chemical status of groundwater. As a result on 12 December 2006, after six years of discussion, the

European Parliament finally agreed the Groundwater Directive which entered into force on 16 January 2007.



Map produced by WRc plc on behalf of the European Commission©, DG Environment, 2012

Fig. 1.1 - Map of National and International River Basin Districts (Version 29 October 2012).

1.3 - GROUNDWATER DIRECTIVE (2006/118/EC)

The Groundwater Directive (GwD), namely 2006/118/EC, is defined the Daughter Directives of the WFD.

Its main aims is to prevent pollution and deterioration of groundwater, Europe's main drinking resource, from agricultural residues such as pesticides and other harmful chemicals. This goal shall be pursued through specific measures finalised to ensure that groundwater quality is monitored and evaluated across Europe in an integrated way.

These measures include criteria for:

1. the definition of good chemical status
2. identifying significant and sustained upward trends in groundwater pollution levels, and for defining starting points for reversing these trends
3. preventing and limiting indirect discharges (after percolation through soil or subsoil) of pollutants into groundwater

These principles are enshrined in Article 1 of Daughter Directive and each one of them is the object of specific articles (i.e. articles 3, 4, 5, 6), while the technical procedures to be adopted are set out in Annexes I to IV which complete the text of the directive.

The GWD attaches great importance to the monitoring as an important tool for assessment of groundwater quality and also for choosing the most appropriate measures. According to the WFD, Member States are asked to use standardised methods for analysis and monitoring of water status and, where necessary, of guidelines on implementation including monitoring.

In other words, the use of statistical procedures, provided they comply with international standards and contribute to the comparability of results of monitoring between Member States over long periods is encouraged. This way allows a better coordination of activities in respect of monitoring, the setting of threshold values, and the identification of relevant hazardous substances, in order to ensure consistent protection of Member States sharing bodies of groundwater.

The Article 3 of GwD defined the Criteria for assessing groundwater chemical status. For this purposes, Member States are required to use the groundwater quality standards defined in Annex I and threshold values defined following application of the procedure and considerations set out in Annex II.

The groundwater quality standards involve the main groundwater pollutants, the nitrates, whose levels have not to exceed 50 mg/l, and pesticides, including their active substances, relevant metabolites, degradation and reaction products and biocidal product, for which levels have not to exceed 0,1 µg/l for each individual substance and 0,5 µg/l considering the total, namely the sum of all individual pesticides detected and quantified in the monitoring procedure.

The threshold values may be established by Member States, at the national, river basin district or groundwater body scales, for the pollutants, groups of pollutants and indicators of pollution which, within the territory of a Member State, have been identified as contributing to the characterisation of bodies or groups of bodies of groundwater as being at risk. In particular the potential impact on and interaction with, associated surface water bodies and directly dependent terrestrial ecosystems and wetlands should be taken into account.

The Annex II identifies (Part B) a minimum list of high-risk of pollutants and their indicators that must be considered when setting threshold values. This list include:

- substances or ions or indicators which may occur both naturally and/or as a result of human activities like, arsenic cadmium lead mercury ammonium chloride sulphate
- Man-made synthetic substances like, trichloroethylene and tetrachloroethylene
- Parameters indicative of saline or other intrusions like conductivity.

The threshold values defined for the purpose of determining whether a groundwater body is achieving good chemical status must be established by taking into account all of the requirements of good chemical status, as defined in Annex V (2.3.2) of the WFD.

As specified in Annex III, if a value set as a quality standard or a threshold value is exceeded, a detailed investigations have to be carried out to confirm, among other things, that this does not pose a significant environmental risk.

Member States must identify any significant and sustained upward trend in levels of pollutants found in bodies of groundwater. In order to do so, they must establish a monitoring programme in conformity with Annex IV to this Directive.

Taking account of Annex IV to the GwD, Member States must also define a starting point for reversing these upward trends. Trend reversals will focus on concentrations which pose a risk to associated aquatic ecosystems, dependent terrestrial ecosystems, human health or legitimate uses of the water environment.

Member States may amend the list of threshold values whenever new information on pollutants, groups of pollutants, or indicators of pollution indicates that a new threshold value is required to ensure that environmental objectives are being met (Article 3 - 6).

Analysing the GWD, the importance of monitoring as a key tool to assess the thresholds and level variation over time of the each contaminant in critical areas of water bodies is clear. Also, it is very important that the analytical procedures and those for statistical evaluation of data are standardized, for the purpose of mutual recognition of data within Europe.

1.4 - ITALIAN WATER POLICY

Italy has a long history of water legislation, which has evolved throughout the last century, until it aligns with the EU legislation in order to achieve the community environmental standards (Tab 1.1).

Through the decades, water policy in Italy has been characterized by a progressive increasing degree of complexity, aiming at broader and multiple water policy objectives (addressing quantitative and qualitative issues, and relating water to its environmental and health dimension), and towards a higher degree of decentralisation, characterised by an increasing number of actors involved in its management.

Years	Regime of concessions for water use	Regime of protection from water/hydraulic works	Regime of water quality and the environment
1865	**L. n.2248/1865**: definition of a regime to authorise water use	**L. n.2248/1865**: definition of a regime of water police, regulating hydraulic works and soil protection	Water quality issues are dealt with by sanitary laws
	R.D. n.1775/1933: organic revision of the previous regime	**R.D. n.1775/1933**: organic revision of the previous regime	
		L. n.129/1963: design of the General Regulatory Plan of Aqueducts, as a first organic attempt to plan in the water sector	
	1972: reform of the State with the transfer of State functions to the Regions, and a redistribution of roles and competence to authorise concessions for water use (through **L. n.616/1977**)	1972: reform of the State with the transfer of State functions to the Regions; minor hydraulic works are under the new responsibilities of the Regions Through **L. n.616/1977**, all functions regarding the aqueducts sector are explicitly transferred to the Regions	
			L. n.319/1976: this law mainly addresses the protection of water from pollution, focusing on waste water and on the planning of water use and protection. The law develops to adjust to the EU regulation, although its formulation is still rooted in health principles
		L. n.183/1989: first attempt to develop a structured water policy within a disciplinary action aimed at soil protection, through the introduction of the River Basin as the optimal area of intervention	**L. n.183/1989**: this law covers water quality issues and addresses water and environmental protection. First attempt to integrate water quality, water use and soil protection
	L. n.36/1994: definition of a new regime, through the creation of the integrated water service, administered by the ATOs [not yet fully implemented]		
1999	**D. lgs. n. 152/1999**: this law aims at the integration of environmental/ health/ economic and productive policies in the perspective of a global policy of water resources management. The law has been designed to integrate and implement EC directives on the subject.		

Tab. 1.1 - Main laws on water policy in Italy (GORIA & LUGARESI, 2004 modified)

The evolution of water policy can be described by a succession of four main stages (GORIA & LUGARESI, 2004).

The first one evolves between 1865 and 1933, ending with the promulgation of the 1933 Water Code (R.D. n.1775/1933). It focuses on the protection of land and population from water. This first stage was characterised by a simple water policy regime.

The second one evolves between 1933 and 1976 and focuses on the regulation of alternative uses of water (navigation, irrigation, productive or civil uses) which occurs through fragmented and separate laws. This stage may be considered as a step towards a more complex system of water management, because it considers the alternative uses of water with its fragmented and separated regulations.

The third stage, from 1976 to 2006, shows an increasing degree of complexity focusing on the protection of water resources, both from a qualitative and a quantitative perspective. During this stage, many regulations (Rana et alii, 2011) were promulgated, eg:

- L.n. 319/1976 (“Legge Merli”) on water quality,
- L.n. 183/1989 on water uses,
- L.n. 36/1994 (“Legge Galli”) on new water management system,
- D.lgs. n.152/1999, a global policy of water resources management.

The article 1 of L.n. 183/1989 establishes the need to enhance the “protection of lands, water rehabilitation, use and management of resources for a rational, economic and social development, and for the protection of the related environment”. Therefore, the law stated the need of planning at the hydrographical basin scale and created new public agencies: the River Basin Authorities (6 national River Basins and 18 inter-regional River Basin Authorities). The main objective of these authorities was to develop and apply the River Basin Management Plan.

With L.n. 36/1994 criteria of efficiency, effectiveness and economy were introduced through the creation of the integrated water service. Water supply, urban drainage and wastewater treatment systems were reorganised in Optimal Territorial Areas (ATO), leading to integrated and comprehensive management of water resources. Pollution control and environmental monitoring were assigned to the Regional Environmental Agencies.

It also states that water quality has to be seen in the context of ‘final use requirements’. In fact, the ‘the polluter pays’ principle was introduced. Moreover, the law also affirmed the concept of the public nature of all surface and groundwater and gave priority to water for human consumption.

The integration of the protection of water ecosystems into Italian legislation was introduced by D.lgs. n.152/1999. The primary goal of this decree was the protection of all waters (surface, marine and groundwater), anticipating some aspects of the WFD. The decree defines the general procedures to safeguard water, pursuing the objectives of:

- preventing and reducing pollution,
- reclaiming and improving the water status,
- protecting the water allocated to special uses,
- ensuring the sustainable use of the resources

- supporting well diversified animal and plant communities.

These objectives can be achieved through the application of proper water quality and quantity planning, represented in the Water Protection Plan within each hydro-graphical basin.

Therefore, this third stage was very important because it enabled the change from the culture of water protection to the culture of environmental improvement of water resources.

The fourth stage began in 2006 when the WFD was adopted in Italy by legislative decree n. 152.

1.5 - IMPLEMENTATION OF THE WFD IN ITALY (D.lgs 152/2006)

The WFD (2000/60/EC) has been implemented in Italy by Legislative Decree 152/2006. In the Part III of it - “Rules on soil conservation, desertification prevention, waters pollution protection and water resources management”, all pre-existing laws regarding water resources policies are enveloped and organized in a single framework.

The Decree aims to prevent, reduce and remediate pollution of contaminated water bodies; it pursues the protection of waters intended for special purposes, the sustainable yield of water resources and the subsistence of the natural self-depuration property of water bodies.

In order to implement both the Directive 2000/60/EC and the subsequent 2006/118/CE, the text of the law was updated. In particular, modifications mainly concern characterization and monitoring (Annex I, Part III). These updates are listed below:

- ✓ Decree n. 131, 16 June 2008: "*Regulations on the technical criteria about water bodies characterization (types, water bodies identification, pressure analysis) to modify technical rules of the Legislative Decree n. 152/2006*”.

- ✓ Decree n. 56, 14 April 2009: "*Technical criteria for water bodies monitoring and identification of reference conditions to modify the technical rules of the Legislative Decree n. 152/2006*".
- ✓ Decree n. 30, 16 March 2009: *"Application of Directive 2006/118/EC on the protection of groundwater against pollution and deterioration"*.
- ✓ Decree 17 July 2009: "*Territorial information identification and procedures for the collection, exchange and use of data concerning cognitive reports preparation about the implementation of European and national obligations on water policy*".

The decree n.152/2006 enabled the establishment of River basin districts and assigned to the District Authority the competence of the development of the River Basin Management Plan (RBMP). As showed in the figure 1.2, eight territorial districts were formed by aggregating territories previously belonging to existing authorities (the former River Basin Authorities).

Fig. 2 - Delimitation of Regions, River Basin Authorities territory and River Basin District territory in Italy. (Ministry of Environment, 2009).

In order to safeguard the protection and restoration of both surface water and groundwater, the Decree establishes the following qualitative standards:

- ➢ *Minimum environmental quality standard* for significant water bodies, as function of the ability to sustain natural self-purification processes and large and various communities and plants development.
- ➢ *Quality standards for intended use*, which identifies water quality levels for:
  - Fresh surface water and groundwater adopted as drinking water,
  - Bathing waters,
  - Fresh waters needing protection and improvement in order to support fish life,

- Water for permitting molluscs life.

Regions are entrusted with the task to identify for both surface water and groundwater bodies the matching quality standards, as stated in the Annex I, Part III. The quality of surface waters is assessed through the lowest ecological and chemical reached status, while for groundwater the assessment is related to chemical and quantitative one.

One of the main updates introduced by Legislative Decree 152/2006 is the definition of a contaminated site. According to the previous regulation, a polluted site, wherein remediation is compulsory, is an area in which coded thresholds limits were exceeded (or there was a real and actual hazard to be exceeded). Those thresholds were fixed by the Ministry Decree n. 471/99 in the Annex 1. Conversely the Decree 152/2006 distinguishes into:

- **Potentially contaminated sites**, as areas where one or more pollutants concentration values exceeds the coded thresholds values, called "Contamination Surveillance Concentrations (CSC)" (Annex 5, Article 240, paragraph 1, let. d);
- **Contaminated sites**, as areas where contamination thresholds are exceeded, called "Risk-Based Values Concentration (CSR)", to be determined executing a risk analysis (Article 240, paragraph 1, let. e).

CSC value represents the threshold beyond which the code establishes to carry out an investigation plan aimed at the environmental characterization preparatory for the site - specific risk analysis. Conversely, the remediation plan is carried out only in the case the CSR limit is exceeded.

The Decree 152/2006 strongly changes how dealing with contaminated sites and the intervention methodologies to adopt. In fact there is a switch from a tabular approach to a mixed criterion, in which the table values are part of a preliminary screening analysis.

Furthermore, art. 252 of such a Decree provides guidelines to identify Sites of National Importance (SIN), already established by Legislative Decree 22/97 (Ronchi Decree) and the Ministerial Decree 471/99.

Sites of National Importance are generally large-scale areas, in which the amount and/or type of pollutants poses a risk to the environment and human health, as well as prevent the development of areas of strategic importance for their prerogatives historic landscape, or to the development opportunities of the territory that would be achieved after their rehabilitation.

The institution of each SIN is carried out with a special Decree of the Minister of the Environment and Land and Sea Protection, in agreement with the concerned Regions. Sites of National Interest follow, therefore, different procedures than the other sites that could be considered of "local interest."

Campania Region, starting from 1998, identified with several legislation procedures the following six SINs:

- ✓ Eastern Naples - Law 426/98
- ✓ Domitian Phlaegrean Coast and Aversa Hinterland - Law 426/98
- ✓ Naples - Bagnoli - Coroglio - Law 388/00
- ✓ Vesuvius Coastal Areas - Law 179/02
- ✓ Hydrographic Basin of Sarno River - Law 266/05
- ✓ Pianura - M.D. 11/04/08

In particular the perimeter of Sarno river catchment area, in which our study area is included, was defined after the M. D 11 August 2006.

On January 11, 2013, with Protocol. 7, the Minister of the Environment and Land and Sea Protection has downgraded 18 SIN to Sites of Regional Importance (SIR), bringing them from 57 to 39. Among the Sites downgraded as SIR the Basin of Sarno River is present, together with Pianura, Domitian Phlegrean Coast and Aversa Hinterland and Vesuvius Coastal Areas.

The regulation lists and downgrades to Sites of Regional Importance, the ones that do not satisfy requirements given by Article 36 bis, Law 134 August 7, 2012:"Pressing measures for the Country's growth," amending the aforementioned Article 252 of the Decree. 152/2006.

So the responsibility for the necessary operations of checking the status and the possible remediation of SIR is entrusted to each concerned Region.

CHAPTER 2

ENVIRONMENTAL STATE OF GROUNDWATER RESOURCES IN COMPLEX AQUIFER SYSTEMS

The relationship between a number of environmental pressures and the complex structure of the flow system generates many processes, which affect pathways of pollutants. A dynamic behaviour needs generally both geostatistical and fractal approaches (Galloway, 2010). It is difficult to apply such methods to parameterize and model flow systems in large areas, likewise the Solofrana River Valley, characterized by too sparse data set. As a result pollutant concentrations are not clearly defined in time and space. This consideration becomes increasingly concerned with analyses of "sustainable development and territory management", which require basin-wide investigations.

Decisions on groundwater protection policy, according to European directives, may be based on the improvement of the concept of "aquifer analogue" (e.g. Anderson, 1989; Bersezio, 2007; Miall, 1996) to basin fills. It is useful to identify heterogeneity properties, which control the permeability distribution. So hydrostratigraphic architecture derives from equivalent parameters variability, which describes homogeneous media or hydrogeological units.

Such hydrogeological characterization of subsurface is mostly based on borehole data, but at basin scale it is difficult to identify the geometry of hydro-facies and connection among aquifers pushing up depths. Similarly to petroleum geology, a reliable definition of the spatial variability of hydrogeological parameters and the scale-dependent heterogeneity need procedures that involve and enhance the genetic, basin-scale geological process modelling.

An improvement in the conceptualization of hydrodynamics, especially in environmental key, has to take place gradually.

General implementation of such an approach requires a large number of investigations and a related financial effort. This is the reason why a methodology able to optimise the process and adapt the approach to areas with poor existing information is certainly of interest. In this way, an optimised aquifer analogue can be obtained through the joint inversion of existing and survey data as showed in figure 3.1.

In this line, the aquifer analogue can be associated to a set of indicators representative of the groundwater composition. Each indicator describes a specific aspect of groundwater quality and leads in combination with others to the definition of groundwater environmental index, due to natural and anthropogenic phenomena.

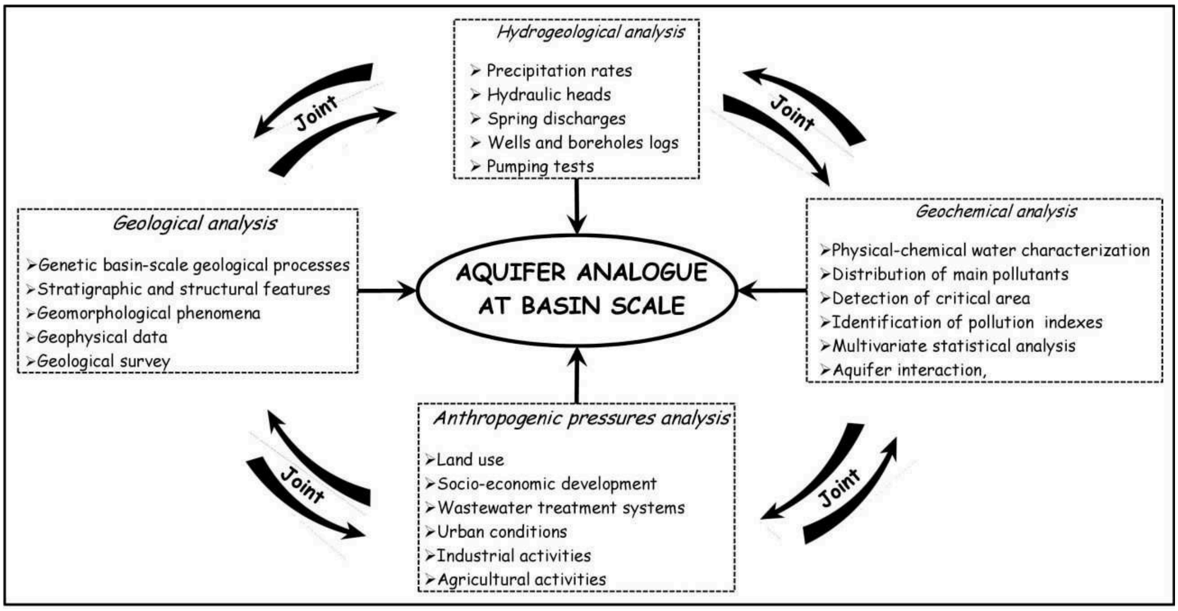


Fig. 2.1 - Multidisciplinary approach to define Aquifer analogue

Geologic evolution of the basin provides main lithological, stratigraphic, structural and morphological characteristics, which have to be correlated to borehole, geophysical and water well data. To investigate the hydrodynamic behaviour in the deepest zones of basin fills and to model aquifer analogues at basin-scale, it is necessary to combine knowledge of recognized hydrogeological parameters with geochemical groundwater characterization. At the same time, in wide regions this analysis enables to point out the more hazardous sites and leads the working scale and amount and typologies of investigations.

It is evident that boundaries conditions have to be defined as function of hydrodynamics as well as of distribution and typologies of source groundwater pollution.

In summary former geological data, derived from past works and researches, should be improved and processed taking into account the results of a suitable geochemical and hydrogeological survey, focusing on the socio-economic features of the territory that may induce pollution phenomena as well as perturbations of groundwater flow.

These joint activities lead to the definition of environmental indexes useful in the management and protection of groundwaters within a framework decision involving the "Hydrogeological scheme" and the "Spatial distribution of groundwater pollution indicators".

The identification and distribution of main groundwater indexes provides the spatial variability of aquifer complexes (hydrofacies) and so the most relevant heterogeneity at basin scale. Such indexes reveal the geometry and connectivity of aquifers even in the deepest zones of the basin fill.

CHAPTER 3

STUDY AREA

3.1 – GEOGRAPHICAL CONTEXT

The Solofrana River Valley, located in Campania Region (South Italy), is the inland portion of the Sarno River basin (Fig. 3.1).

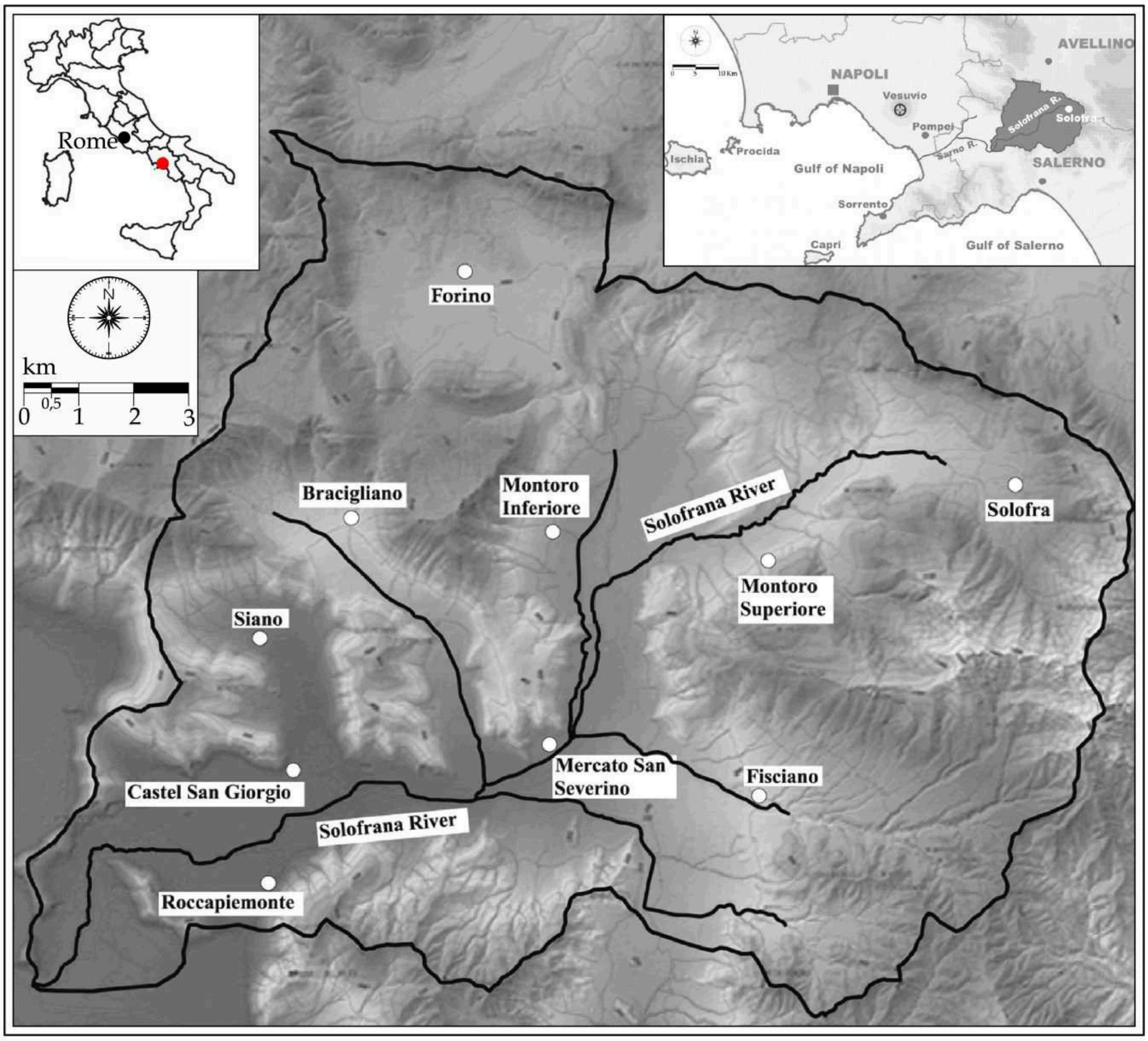


Fig. 3.1 - Location of the Solofrana River Valley

It stretchs for about 53 Km^2 and it is bounded by carbonate massifs. Namely, the Sarno Mountains to the North-West, the Lattari Mountains and Salerno Mountains to the South, the Picentini Mountains to the East and North-East.

The river pattern outlines the major structural features of the area. So in the valley it is possible to recognize three sectors with different directions. The Solofrana river flows from the E-NE to the W-SW, but in the Montoro plain suddenly turns southwards.

The area has a Mediterranean climate regime, with average annual temperature of 15,68 °C and average annual rainfall of 1400 mm (Protezione Civile Regione Campania, 2000-2012)

3.2 - GEOLOGICAL SETTING

The Solofrana river valley is the South-East part of a peri-tyrrheneian depression, the so-called "Campanian Plain" (e.g. D'Erasmo, 1931; Ippolito et alii., 1973; Brancaccio et alii., 1995; Bellucci, 1994; Aprile et alii., 2004; Milia & Torrente, 2011) that dates back to the Plio-Pleistocene (Brancaccio et al., 1991; Cinque et al., 1993). Its current structural and geo-morphological architecture derives from the palaeogeographical changes occurred during the late Early and the Middle Pleistocene with the definitive rise of the Apennine chain (Santangelo et al., 2012). Accordingly, in the frame of the regional geological features the study area is related to the Southern Apennine chain history (e.g. D'Argenio et al, 1973; Ippolito et al., 1975; Mostardini and Merlini, 1986; Cello and Mazzoli, 1999; Patacca and Scandone, 2007; Bonardi et al, 2009), and more precisely to the geodynamics of the Mediterranean domain (Patacca et al., 1990; Hippolyte et al., 1995; Ascione and Romano, 1999; Caiazzo et al, 2006; Milia and Torrente 2011).

So the structural setting is due to the combination of mainly compressive tectonic events, attributed to the rollback of the subducting Adria plate, and the extensional tectonics related to the opening of the Tyrrhenian basin (Malinverno and Ryan, 1986; Patacca and Scandone, 1989; Doglioni, 1991). The Southern

Apennine recognizes a deep-seated carbonate duplex system tectonically overlain by NE-verging rootless nappes derived from basin and platform domains (Patacca and Scandone, 1989; 2007). Along the Thyrrenin margin of the Campania, the late Tertiary/Quaternary tectonic events produced wide grabens and the onset of magmatic activity in the so-called Campanian Volcanic Zone (Ippolito et al., 1973; Bigi et al., 1983; Brancaccio et al., 1991; Brocchini et al., 2001, Rolandi et al, 2003; Casciello et al, 2006, Milia and Torrente, 2011). These morphostructural units, characterized by complex patterns of subsidence and uplift, have been filled by Pliocene-Quaternary deposits of up to 3 km thick (Cinque et al., 2000; Caiazzo et al., 2006).

The fault pattern responsible of the configuration of horst-and-graben with NE–SW trend along the Tyrrhenian slope is related to many fault systems. Namely, the E-W strike-slip regime that took place in the Late Miocene-Earliest Pliocene, the N-S to NW-SE extensional trending faults occurred until the Early Pleistocene and the NE-SW extensional regime that happened in the Middle-Late Pleistocene (Caiazzo et al., 2006).

As a result the morphostructural depression of Solofrana River valley, the inner part of the southern “Campanian plain”, consists of Mesozoic platform carbonates of the Lattari– Picentini Mountains unit (AA.VV., 2009).

In the south-eastern ridge (Cuculo Mt., Papariello Mt.) outcrop the massive and well-bedded dolomites of the Triassic carbonate series; in the northern and south-western ones (San Michele Mt., Sarno Mt., Salto Mt.) are widespread the Jurassic and Cretaceous deposits, mainly limestones and dolomitic limestones. Along the northeastern margin of the Picentini Mountains and so in the northeastern part of the Solofrana basin, the siliciclastic deposits of the Castelvetere formation (Pescatore et al., 1969) unconformably overlies the Cretaceous carbonates of the Lattari-Picentini Mountains unit. These wildflysch deposits (Upper Tortonian-Early Messinian) consist mostly of disorganized coarse-grained sandstones and polygenic conglomerates, containing olistholiths of platform-derived carbonates and olistostromes and slides of Sicilide-derived materials (e.g. Critelli and Le Pera, 1995; Patacca and Scandone 1989, 2007; Bonardi et al., 2009) (Fig. 3.2).

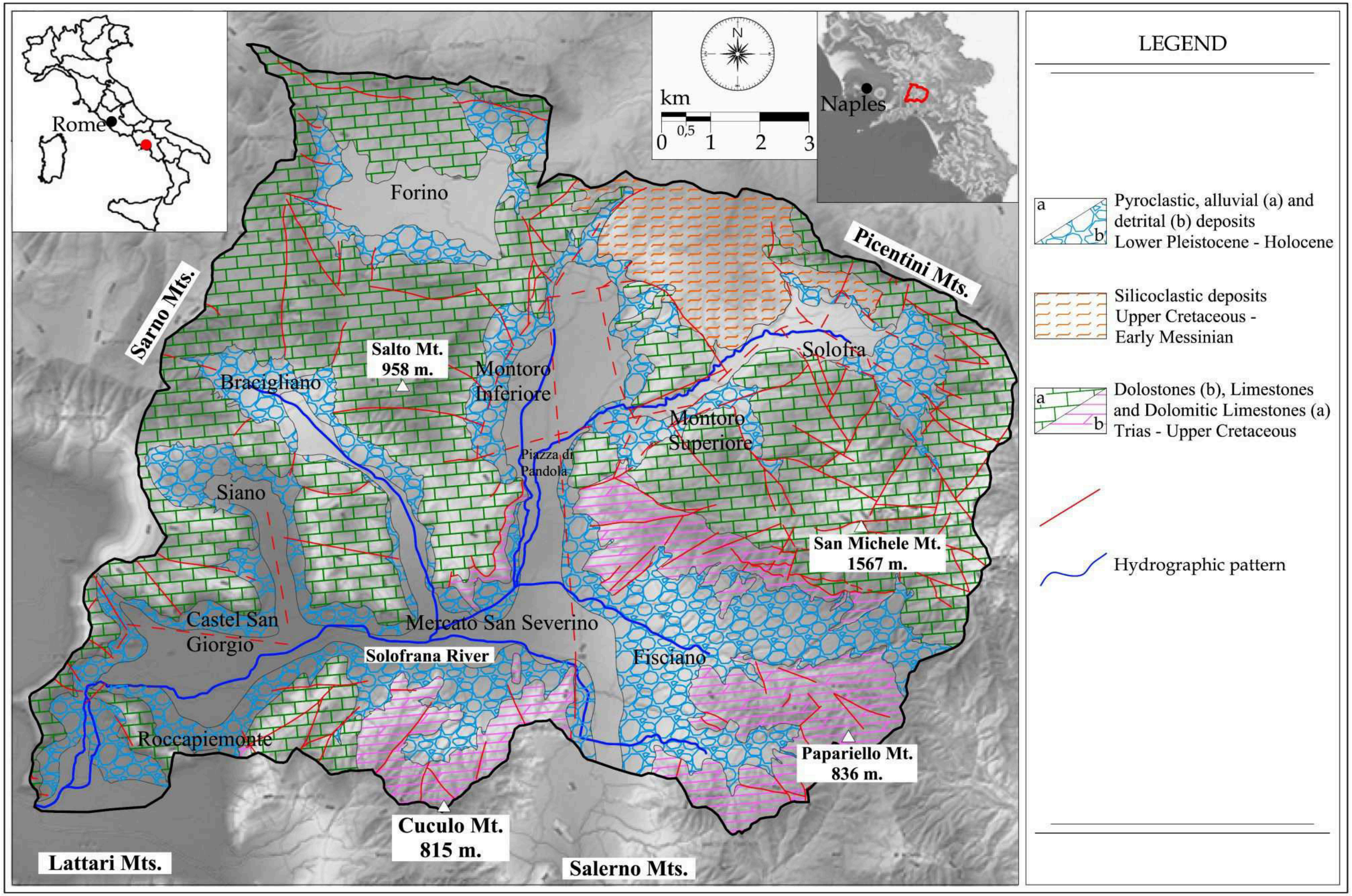


Fig. 3.2 - Geological and structural sketch of the Solofrana River Valley

Moreover, the overthrust of the basinal and torbiditic deposits of the "Argille variegate" and of the Corleto-Perticara (Upper Cretaceous- Early Miocene) formations (AA.VV., 2009, Di Nocera et al., 2006) on the Mesozoic carbonate platform in the same area shows its structural complexity and the migration in the space and time of transgressive units. Namely the "Argille variegate" consist of calcilutites, marls, siliciclastic calcarenites with intercalations of clays and marly clays, whereas the Corleto Perticara formation is characterized mostly by marly limestones, calcareous marls and white calcilutites with thin intercalations of clays (Patacca and Scandone 1989, 2007; Di Nocera et al., 2006; Bonardi et al., 2009) (Fig. 3.3).

Fig. 3.3 - Argille Variegate next to Solofra town.

Many stratigraphic, geomorphological and vulcanological studies outline the characteristic of the composite Plio-Quaternary depositional sequences, which fill the Solofrana Valley (e.g. Brancaccio et al., 1994; Bellucci, 1994; Rolandi et al., 2003). Alluvial and lacustrine sediments interbedded with volcanoclastic ones unconformably overlie the Mesozoic basement. The geomorphological analysis of the carbonate basin and gravimetric survey point out a multicyclic evolution of the valley and a subaerial erosion of the carbonate substratum with fluvial and karstic morphological evidences (Brancaccio et al., 1994). With regard to the depth of the bedrock and the stratigraphic architecture of the quaternary deposits previous studies give discontinuous reconstruction, albeit they show their main features. The thickness of the fill is at least about 150 m (De Riso and Ducci, 1992; Brancaccio et al, 1994) and geophysical surveys recognize the carbonate basement at depth of about 330 m (Celico et al., 1991) in the north-eastern sector of the valley and variable from 100 to about 300 m in the western one (Brancaccio et al., 1994). The sedimentation in the valley was firstly lacustrine, such as evident in the western part of the study area, and then fluvial and volcanoclastic. Foothills consist of coarse detrital deposits of colluvial or fluvial origin. The major alluvial fans are located along the lower course of the Solofrana River, more precisely along the southern boundary of the valley from Fisciano to Castel S. Giorgio (Fig. 3.1 and Fig. 3.2).

The most important event of the volcanoclastic aggradation produced a significant stratigraphical and geochronological marker. This key formation is due to the violent explosive Campanian Ignimbrite (CI) eruption occurred about 39 ka ago (e.g. Di Girolamo, 1968; De Vivo et al, 2001; Rolandi et al., 2003). These tephra deposits (CI) covered uniformly the Campanian Plain and in the study area is interbedded in Plio-Pleistocene deposits with ticks up to 40 m. The lower CI unit is characterized by the so-called "Campanian Grey Tuff" (Di Girolamo, 1968) , which overlies the "basal pumice" (Di Girolamo et al., 1973). In the western area of the Solofrana River Valley it is possible to identify the yellow tuff of the older Taurano Ignimbrite beneath a paleosol and the CI basal pumice (Rolandi et al., 2003).

3.3 - HYDROGEOLOGICAL SETTING

Hydrogeological features of the Solofrana River Valley derive from a number of studies that was carried out in the early nineties (e.g. Celico et al., 1991; De Riso and Ducci, 1992; Celico and Piscopo, 1995; Celico et al, 1995).

With regard to the hydrogeological properties of the lithotype present in the study area, the following five principal hydrogeological complexes (Carta Idrogeologica dell'Italia Meridionale, 2007) may be recognized (Fig. 3.4):

- *Dolomitic complex*: It consists of massive dolomites, marls, bituminous shales and thin bedded dolomites. This complex, in stratigraphic contact with the overlying calcareous complex, forms a permeability boundary, which can influence the groundwater flow of the hydrogeological calcareous units, in relation to the local structural settings. It has a medium high permeability (Lower Triassic – Upper Triassic).
- *Calcareous complex*: made up of dolomitic limestones, calcarenites, and back reef calcilutites. It is the more higher-yielding aquifer of the study area because of its high fracture and karst permeability (Jurassic – Upper Cretaceous).
- *Flysch complex*: is made up of proximal turbiditic series. In this complex the groundwater flow is active in the upper part because pelitic intercalation are less present than the lower one. It has a low intrinsic and fracture permeability so it's possible consider this complex as an aquiclude (Middle Miocene – Upper Miocene).
- *Detrital complex*: it consists of clastic deposits, frequently cemented, related to gravitational and/or short range hydraulic transport. It forms active and relict talus slope and stream fan deposits. Generally it is an aquifer with a moderate transmissivity, even if heterogeneous and anisotropic. It may be considered an yielding aquifer when hydraulic groundwater feeding from adjacent carbonate units occurs. The complex is characterized by a medium high intrinsic permeability.
- *Alluvial – pyroclastic complex*: it is made up of incoherent clastic deposits of variable grain size. It is a porous aquifer, heterogeneous and anisotropic, with a groundwater flow that locally can be multilayer, but at large scale can be considered unique. This complex has a medium intrinsic permeability.

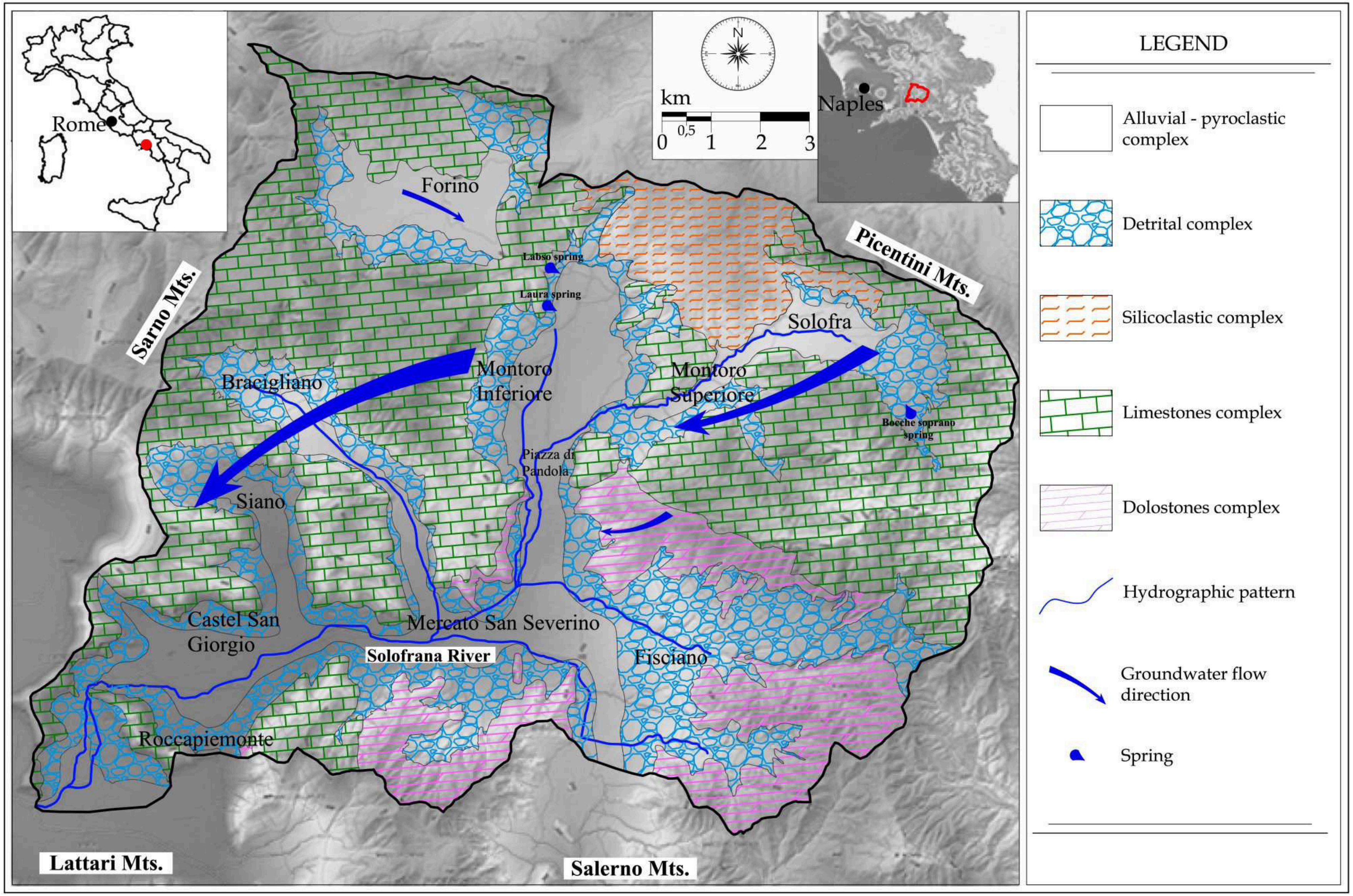


Fig. 3.4 - Hydrogeological sketch of Solofrana River Valley.

The geological and geomorphological evolution of the study area outlines its main hydrodynamic features at basin scale.

The structure of the pyroclastic-alluvial deposits in the plain is very intricate due to the spatial variations in granulometry or more precisely to the variable alternations of sandy, gravel and pelitic intervals. So locally more overlying groundwater flows may be recognized. Nevertheless, the intercalation of an extensive aquitard, like the "Campanian Grey Tuff", identifies at basin scale two groundwater flows, recharged by precipitations and indirect intake from carbonate bordering hydro-structures. The deeper flow may be confined or semiconfined and leakage phenomena between two overlying aquifers take place with a downward flow in natural conditions (De Riso and Ducci, 1992; Celico and Piscopo, 1995; Celico et al, 1995).

Accordingly, even as the well completion at multiple depths that involve the two distinct aquifers, it is reasonable to detect at large scale only one groundwater flow in the plain aquifer. In other words, a simplified hydrogeological framework of the plain, based on the available water table maps concerning the recharge period of the year 1987 and 1991 (Celico et al, 1991; De Riso and Ducci, 1992), reflects the morphology of the valley and recognizes the main groundwater drainage line along the course of the Solofrana river (Fig. 3.5). Albeit, the hydraulic relationships between the aquifer and the river are limited because the riverbed is practically clogged.

Clearly the carbonate substratum identifies the deepest aquifer of the plain. It is hydraulically connected to the bordering carbonate unit and groundwaters generally flow southwestward. Hydraulic connections between carbonate aquifer and basin-fill aquifers may occur through aquifer boundaries and downward leakage, locally advanced through buried swallow holes (Celico et al, 1991).

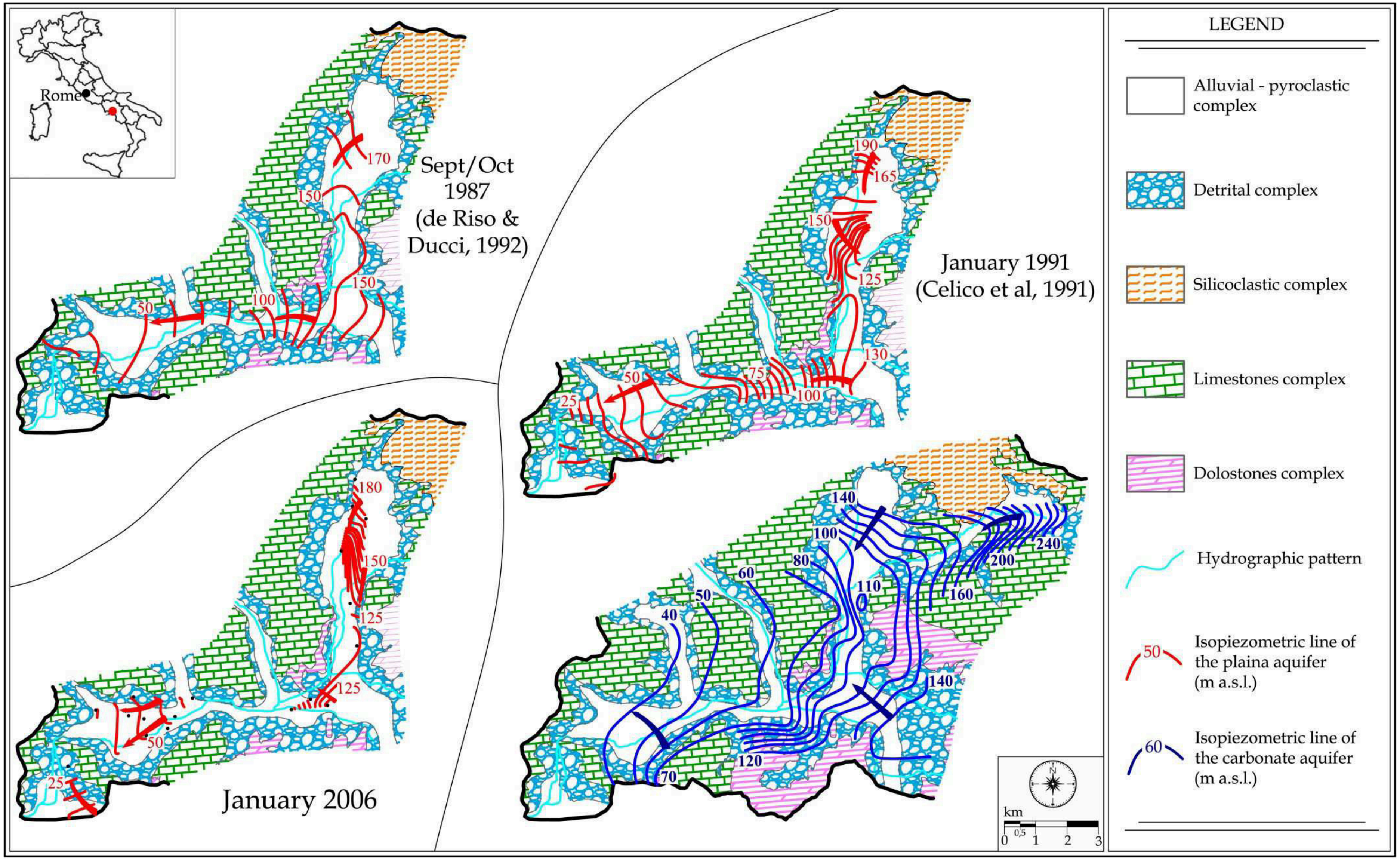


Fig. 3.5 - Historical water table maps.

3.4 - SOCIO-ECONOMIC SETTLEMENT

Copious groundwater supplies (about 41 x 106 m3/y the withdrawal evaluated in Celico et al., 1991) has considerably improved the socio-economic development and the urbanization of this territory, as well as many plain areas in South Italy.

The Solofrana River crosses seven towns (Fig. 3.1) (Castel San Giorgio, Roccapiemonte, Mercato San Severino, Fisciano, Montoro Inferiore, Montoro Superiore and Solofra) where live about 89948 people. In the last 10 years the population density has increased by 75 persons per km^2 reaching the value of 648 persons per km^2, as regard to the analysis of the Italian National Institute of Statistics (ISTAT, 2011).

Fig. 3.6 - Agricultural area in Montoro plain

Agriculture is still an important component of the economy in the Solofrana River Valley, even though characterized by a steady increase in use of fertilizers and pesticides to achieve and sustain higher yields. Horticultural cropping system is widespread and involves plants for food (fruits, vegetables, culinary herbs) and nonfood crops propagated or in greenhouse. More precisely in the central sector of the valley (the so-called Montoro plain) firstly was very extensive the tobacco cultivation, while since the early 2000 relevant are floriculture practices (flowers and ornamental plants) (Fig. 3.6)

Well-developed large corporations as well as smaller, family-run industries characterize the industry sector. These activities involve agricultural and food processing, chemical, mechanical and plastic manufacturing, as metalwork, woodwork, leatherwork and paper milling.

The most important industrial centres are the Solofra tanning pole and the industrial area of Fisciano-Mercato San Severino. The district of Solofra represents one of the leading areas in Italy for the tanning of sheep and goat skins. As a result, about 40% of Italian production of clothing-leather and footwear are made here (Sarno River Basin Authority, 2004; Distretto Conciario Solofra, 2011), (Fig. 3.7).

Fig. 3.7 - Solofra tanning pole

The wastewater treatment occurs in two joint plants. A centralized chemical-physical and biological treatment plant collecting tanning wastewater of the Solofra pole is located in the north-eastern part of the study area. The process of refining effluents takes place in the southern sector of the valley, in the Mercato San Severino wastewater treatment plant (Fig. 3.8). Here urban sewages and industrial effluents are collected. This treatment system goes back to the early nineties, but for many technical problems it became rather efficient only in the last years (Loda, 2001; Galasso and Raimo, 2006).

Fig. 3.8 - Outflow of Mercato San Severino treatment system (photo taken on August 2011)

It is argued that agricultural nonpoint source pollution may be the leading source of water quality impacts and the major contributor to groundwater contamination, such as point sources of water pollution include sewage treatment plant discharges and industrial plant discharges (Fig. 3.9).

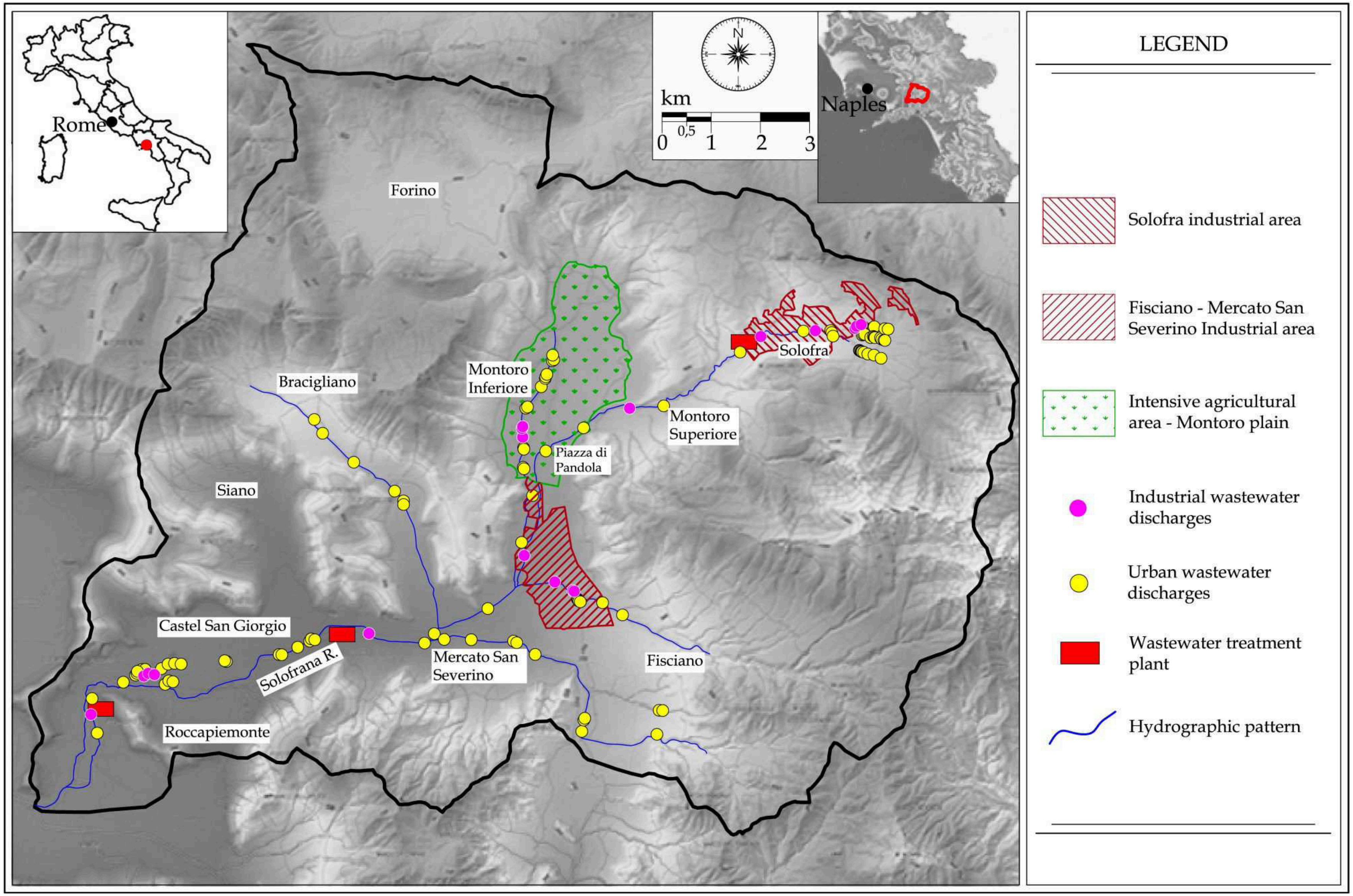


Fig. 3.9 - Main potential pollution sources in the sample area (Sarno River Basin Authority, 2004, modified)

CHAPTER 4

DATA AND METHODS

4.1 – DATA COLLECTION AND INVESTIGATION PLAN

About 285 stratigraphic and well-logs, with depths variable from 20 to over 250 m, have been collected (e.g. de Riso et al., 1992, as public authorities, municipalities, Land Reclamation Authority, Basin Authority, private enterprise) (Fig. 4.1).

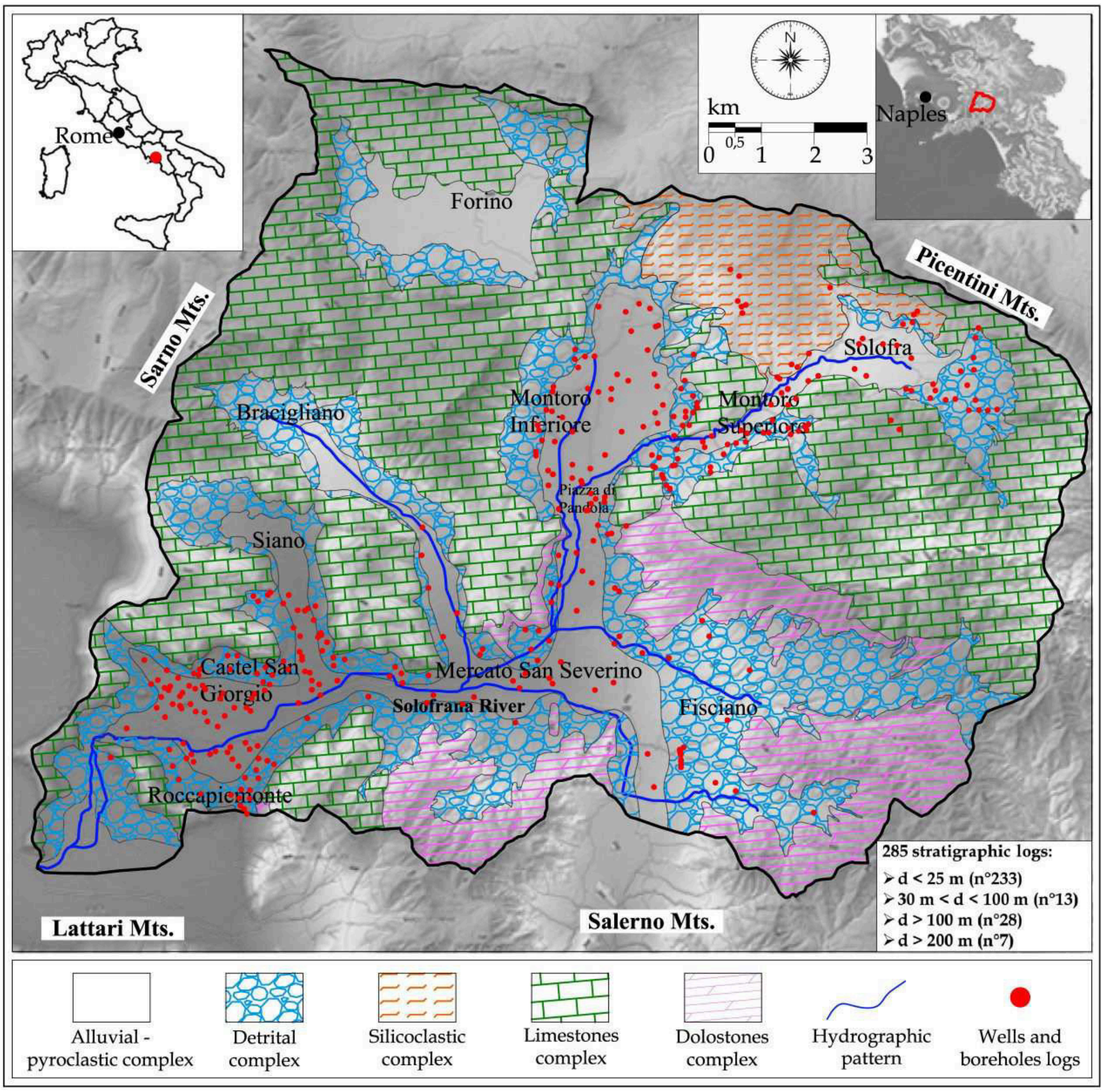


Fig. 4.1 - Spatial distribution of stratigraphic logs

These data, combined with geological map information and a specific geological survey, were used to reconstruct the hydrostratigraphy of the area.

Available water table maps were collected in order to define the hydrogeological setting and the hydrodynamic evolution of the same area. Existing piezometric data were used to reconstruct the water table maps since the 1987. The figure 3.5 shows the hydrodynamic setting with reference to the period of interest:

- September and October 1987, only for the plain aquifer (de Riso & Ducci, 1992)
- January 1991, for both plain and carbonate aquifers (Celico et al,1991)
- January 2006, only for plain aquifer (Del Gaudio, 2007).

Background hydro-chemical information were derived from a hydrogeological study about bordering carbonate units (Celico et al., 1991) and from a groundwater protection plan of the Sarno River Basin Authority, the so-called "Piano Stralcio di Tutela delle Acque", which dates back to the years 2003 and 2004.

In the study area 10 water well and 2 spring water samples were collected and analyzed on May and November 2003 (Fig. 4.2).

Namely, on May groundwater chemical characterization was restricted to the assessment of only major ion constituents, while on November analyses involved measure concentrations of most widespread heavy metals (Cr VI, total Cr, Ni, Cu, Zn, Cd and Pb) too.

On February 2004 the groundwater analyses had been carried out on only four sampling points of the above-mentioned monitoring network. Groundwater analyses had performed in ARPA Campania Laboratories (Regional Agency for Environmental Protection in the Campania Region, Napoli, Italy).

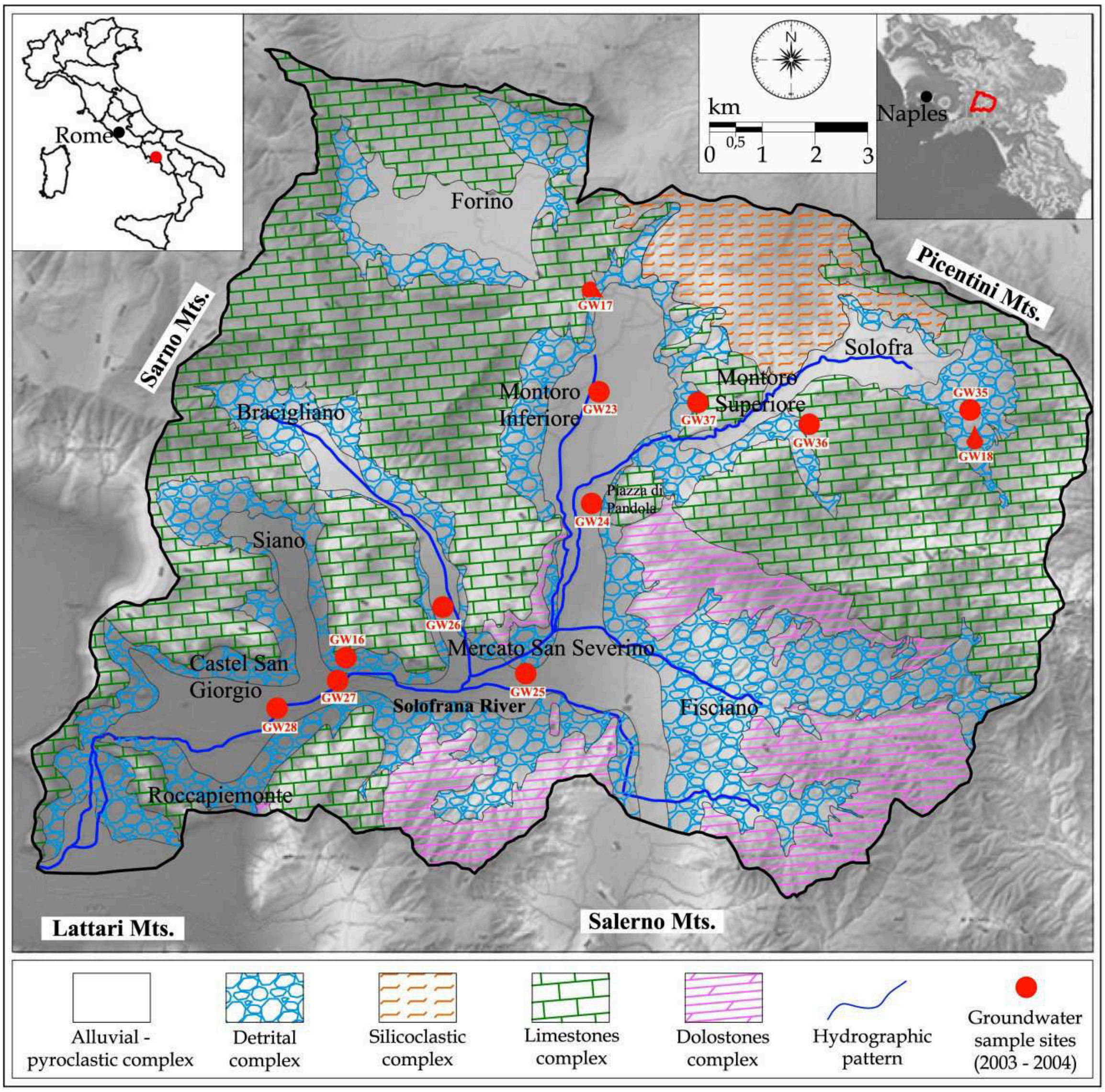


Fig. 4.2 - Groundwater samples distribution (2003 - 2004)

The reliable elaboration and interpretation of available geological, hydrogeological and hydrochemical data led experimental investigations.

Groundwater level and groundwater quality monitoring networks were developed. These are composed of about 90 groundwater points, including 4 springs. Monitoring activities were carried out as to this timetable:

July 2010: firstly, groundwater level measurements involved 43 water points, whereas groundwater sampling and analyses only a select 30 points (Fig. 4.3). Measurements of groundwater electrical conductivity (EC), pH and temperature (T) were carried out in situ, collecting samples for chemistry analyses under low flow conditions. Analyses concerned 77 parameters, including main 6 anions (Br^-,

Cl^-, NO_3^-, NO_2^{--}, PO_4^-, SO_4^{--}) and most common heavy metals (Cr, Ni, Cu, Zn, Cd and Pb) were carried out by Acme Analytical Laboratories Ltd. (Vancouver, Canada).

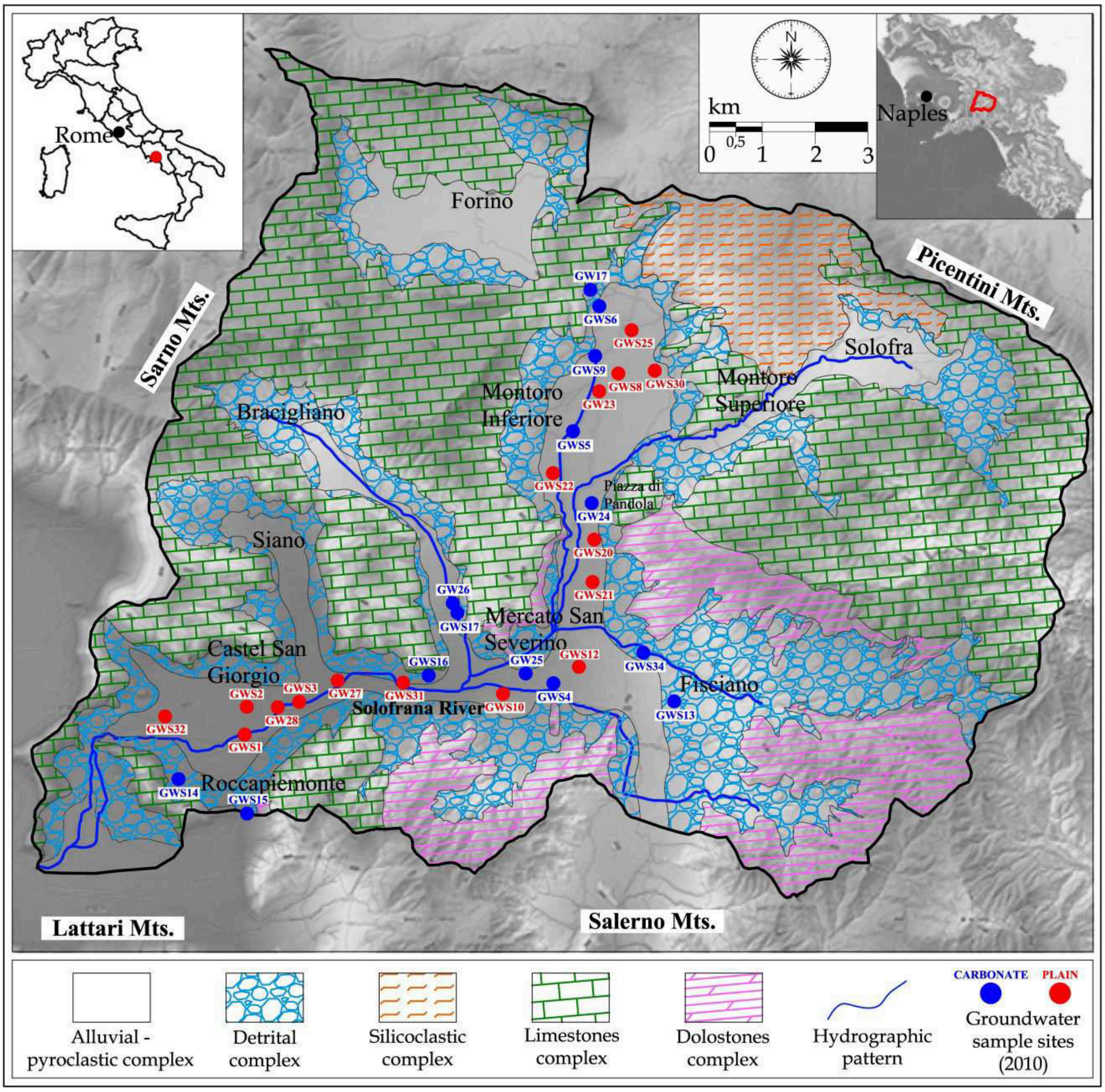


Fig. 4.3 - Groundwater samples distribution (July 2010)

February 2011 – October 2012: a monthly water level monitoring involved 90 groundwater points, including 4 springs (Fig. 4.4). In the same time in field parameters (EC, pH and T) were recorded, such as spring discharges. On April 2012 and June 2012 groundwater sampling and analyses only a select 17 points (Fig. 4.5) were carried out. Such analyses concerned 34 parameters, including main

6 anions (Br^-, Cl^-, NO_3^-, NO_2^{--}, PO_4^-, SO_4^{--}) and most common heavy metals (Cr, Ni, Cu, Zn, Cd and Pb).

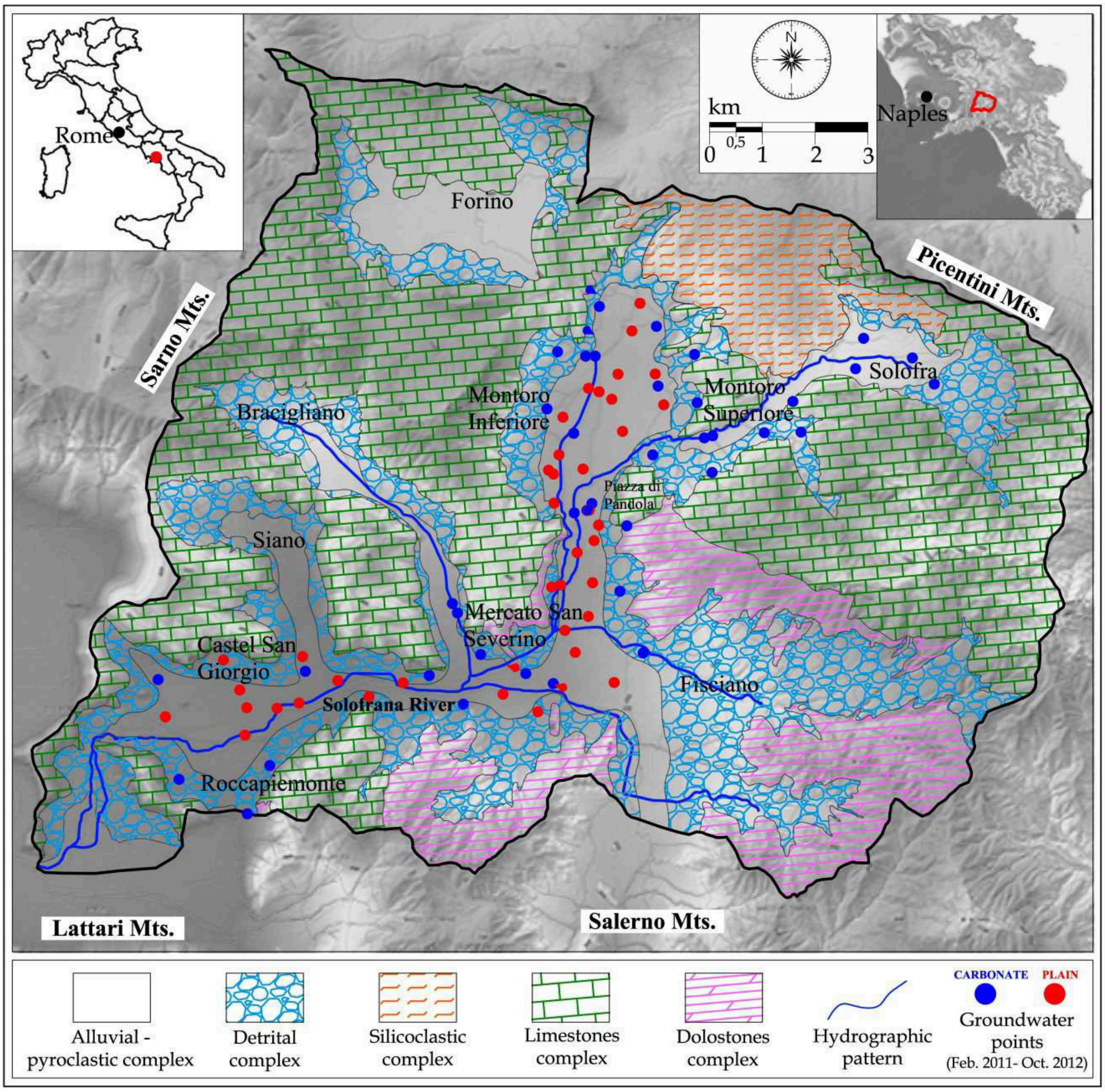


Fig. 4.4 - Groundwater monitoring network (February 2011 – October 2012)

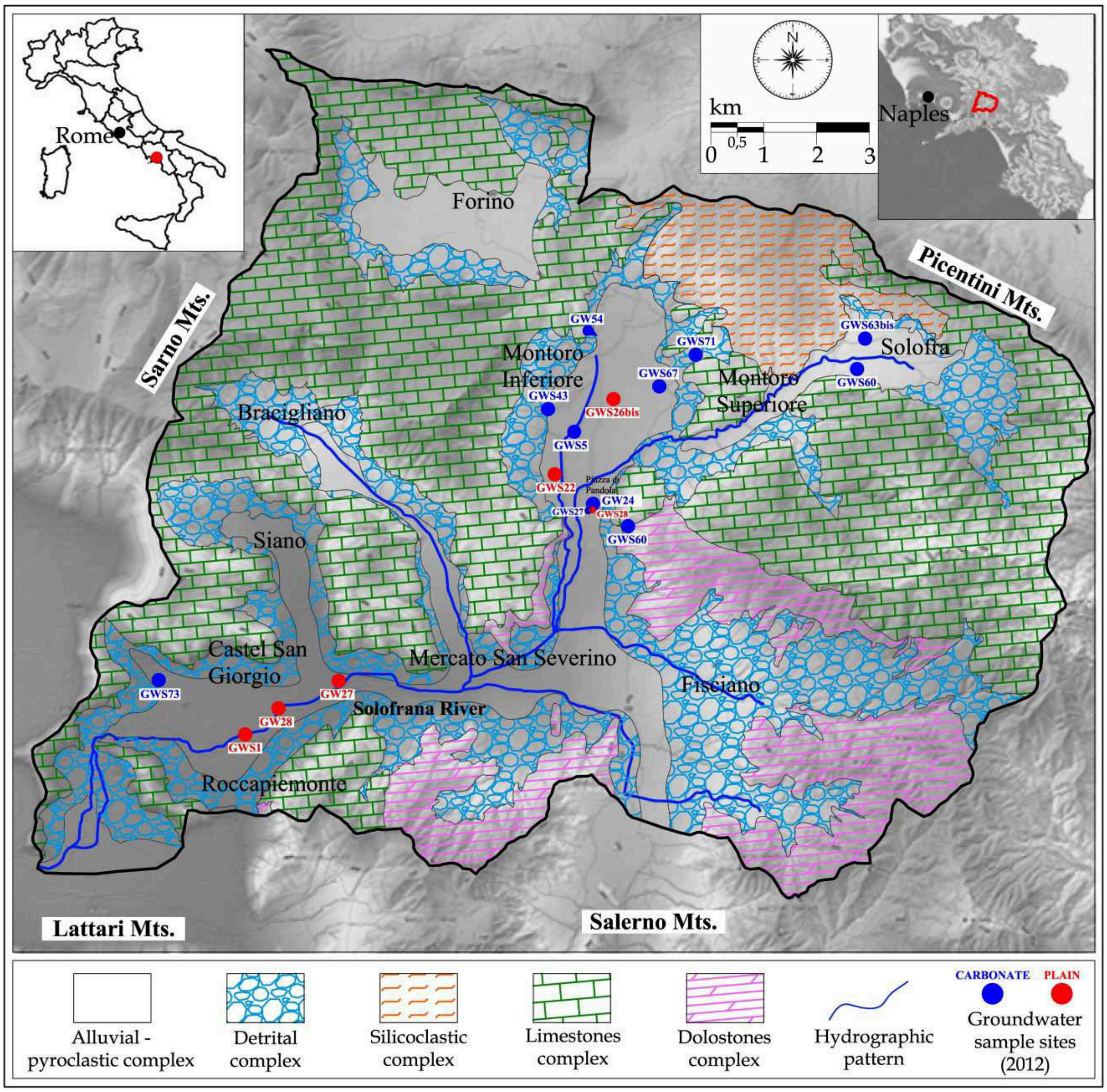


Fig. 4.5 - Groundwater samples distribution (July 2010)

The rainfall data were obtained from the "Protezione Civile" of the Campania Region with reference to the period 2000-2012. The geographical coordinates and altitude of each pluviometer are summarized in the table 4.1.

Pluviometer	Latitude	Longitude	Elevation
	WGS84		(m. a.s.l.)
Baronissi	40° 45' 04,6"	14° 45' 58,6"	226
Bracigliano	40° 49' 29,3"	14° 42' 40,2"	349
Cetronico	40° 48' 34,6"	14° 42' 30,3"	265
Forino	40° 51' 36,2"	14° 44' 44,9"	399
Mercato S.Severino	40° 46' 42,3"	14° 45' 10,4"	141
Piani di Prato	40° 50' 05,6"	14° 38' 55,4"	840
Pizzolano	40° 47' 06,1"	14° 47' 11,9"	244
Ponte Camerelle	40° 44' 03,3"	14° 41' 05,4"	97
S.Pietro	40° 49' 06,5"	14° 47' 13,1"	209
Solofra	40° 49' 25,2"	14° 51' 18,4"	534

Tab. 4.1 - Pluviometer network

4.2 – CLUSTER ANALYSIS

Cluster Analysis, a term first used by Tryon in 1939, is a multivariate methods which aims to divide a sample of objects into homogeneous and distinct groups, clusters, on the basis of a set of measured variables. In this way, objects within each cluster are similar to one another with respect to considered variables, and the groups themselves stand apart from one another.

The clustering can be carried out in many ways depending on the criterion used to measure similarity or distance between data, or the clustering techniques. Distance is a measure of how far apart two objects are, while similarity measures how similar two objects are. For cases that are alike, distance measures are small and similarity measures are large.

The variables used in cluster analysis can be numerical or categorical data. A mixture of different types of variable will make the analysis more complicated. This is because the type of measure used will depend on data type.

A number of different measures have been proposed to measure 'distance' for numerical and categorical data. For the first ones, the most common distance measure used is the Euclidean distance.

In general, if you have p variables X_1,X_2, . . . ,X_p measured on a sample of n objects, the observed data for object i can be denoted by x_{i1}, x_{i2}, . . . , xi_p and the observed data for object j by x_{j1}, x_{j2}, . . . , x_{jp}. The Euclidean distance between these two objects is given by:

$$d_{ij} = \sqrt{\sum_{k=1}^{p} (x_{ik} - x_{jk})^2}$$

All distances between objects are usually expressed by means of a *distance matrix*. In this distance matrix, the non-diagonal elements express the distances between pairs of objects and zeros on the diagonal is the distance from each object to itself (of course 0). As the distance between two objects, A and B is the same as between B and A, the distance matrix is symmetrical (Tab. 4.2)

Objects	A	B	C
A	0	130320,53	114294,93
B	130320,53	0	46300,876
C	114294,93	46300,876	0

Tab. 4.2 - Euclidean distance matrix

Other types of distance measure are: *squared Euclidean distance, city block distance, Minkowski distance, cosine distance, Pearson correlation distance.*

In the assessment of the distance between objects, the scale of measurement of the variables may be an issue, as changing the scale will obviously effect the distance between objects. In addition, if one variable has a much wider range than others then this variable will tend to dominate. To get around this problem each variable can be standardised (converted to z-scores). However, this in itself presents a problem as it tends to reduce the variability (distance) between clusters. This happens because if a particular variable separates objects well then, by definition, it will have a large variance (as the between cluster variability will be high). If this variable is standardised then the separation between clusters will become less.

Once decided how to measure the distance between the data, a "strategy" (method) for classification has to be selected.

Classification can be *hierarchical* or *non-hierarchical* (often known as *k-means clustering methods*).

4.2.1 – HIERARCHICAL METHODS

Hierarchical clustering is the most straightforward methods in which clusters can be formed. The term "*hierarchical*" is used because all clusters formed by these methods consist of mergers of previously formed clusters.

It can be either:

- *Agglomerative*, in which subjects start in their own separate cluster. The two 'closest' (most similar) clusters are then combined and this is done repeatedly until all subjects are in one cluster. At the end, the optimum number of clusters is then chosen out of all cluster solutions.

- *Divisive*, in which all subjects start in the same cluster and the above strategy is applied in reverse until every subject is in a separate cluster

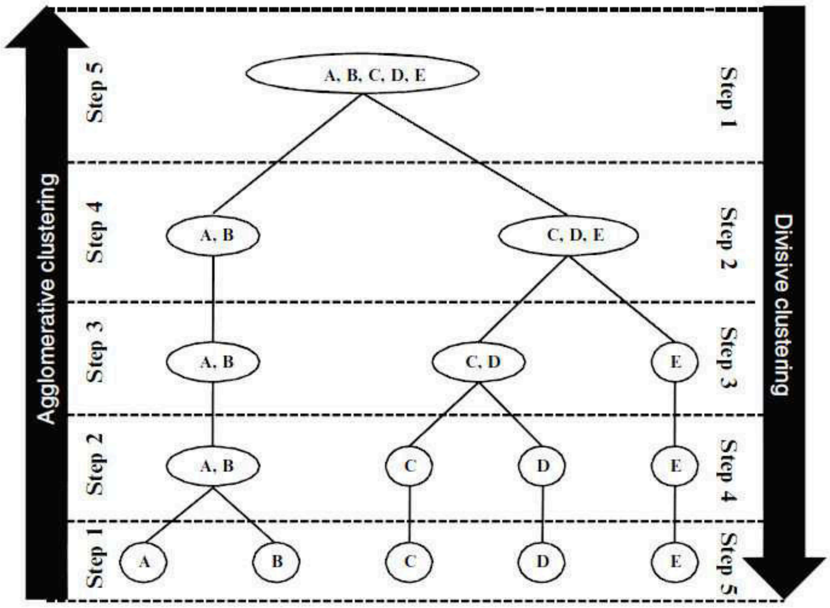


Fig. 4.6 - Agglomerative and divisive clustering (Mooi & Sarstedt, 2011)

In Figure 4.6 this concept is illustrated. In both agglomerative and divisive clustering, a cluster on a higher level of the hierarchy always encompasses all clusters from a lower level. This means that if an object is assigned to a certain cluster, there is no possibility of reassigning this object to another cluster. This is an important distinction between these types of clustering and k-means methods.

Agglomerative clustering methods are generally used in statistical analysis.

Within this approach to cluster analysis there are a number of different methods used to determine which clusters should be joined at each stage. The main methods are summarised below:

✓ *Single linkage* (nearest neighbour): The distance between two clusters corresponds to the shortest distance between any two members in the two clusters.

- ✓ *Complete linkage* (furthest neighbour): The oppositional approach to single linkage assumes that the distance between two clusters is based on the longest distance between any two members in the two clusters.
- ✓ *Average linkage*: The distance between two clusters is defined as the average distance between all pairs of the two clusters' members.
- ✓ *Centroid*: In this approach, the geometric center (centroid) of each cluster is computed first. The distance between the two clusters equals the distance between the two centroids.
- ✓ *Ward's methods:* This approach does not combine the two most similar objects successively. Instead those objects, whose merger increases the overall within-cluster variance to the smallest possible degree, are combined. This method tends to produce clusters of approximately equal size, which is not always desirable. It is also quite sensitive to outliers. Despite this, it is one of the most popular methods, along with the average linkage method.

When carrying out a hierarchical cluster analysis, the process can be represented on a diagram known as a dendrogram (Fig. 4.7). This diagram illustrates which clusters have been joined at each stage of the analysis and the distance between clusters at the time of joining.

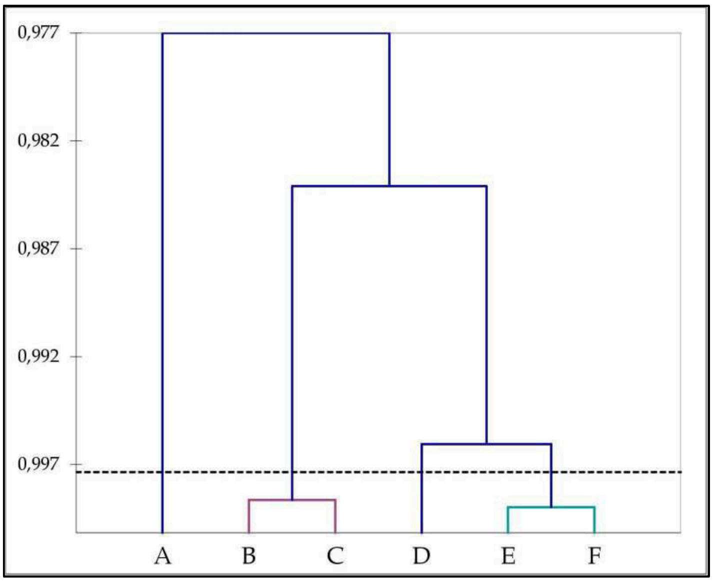


Fig. 4.7 - Example of dendrogram

4.2.2 - NON-HIERARCHICAL METHODS

Another important group of clustering procedures are non-hierarchical methods, often known as *partitioning* or *k-means clustering methods*.

The k-means algorithm follows an entirely different concept than the hierarchical methods discussed before. This algorithm is not based on distance measures such as Euclidean distance or city-block distance, but uses the within-cluster variation as a measure to form homogenous clusters. Specifically, the procedure aims at segmenting the data in such a way that the within-cluster variation is minimised. Consequently, a distance measure is not required in the first step of the analysis.

The clustering process starts by randomly assigning objects to a number of clusters. The objects are then successively reassigned to other clusters to minimize the within-cluster variation, which is basically the (squared) distance from each observation to the centre of the associated cluster. If the reallocation of an object to another cluster decreases the within-cluster variation, this object is reassigned to that cluster.

With the hierarchical methods, an object remains in a cluster once it is assigned to it, but with k-means, cluster affiliations can change in the course of the clustering process. Consequently, k-means does not build a hierarchy as described before, and this is the reason because the approach is also frequently known as non-hierarchical method.

One problem associated with the application of k-means relates to the fact that the operator has to pre-select the number of clusters to retain from the data, but it is often difficult to know how many clusters you are likely to have and therefore the analysis may have to be repeated several times.

This makes k-means less attractive and still hinders its routine application in practice.

4.3 – ASSESSMENT OF CLUSTER NUMBER

Güler and others (2002) described hierarchical cluster analysis as "an efficient means to recognize groups of samples that have similar chemical and physical characteristics".

An important question is how to define the number of clusters to retain from the data, in other words what is the "best cluster solution" that represents my data set? Unfortunately, hierarchical methods provide only very limited guidance for making this decision. The only meaningful indicator relates to the distances at which the objects are combined. This is easier to understand by actually looking at a dendrogram. As stated above, this diagram illustrates the distance between clusters at the time of joining. If there is a large jump in the distance between clusters from one stage to another then this suggests that at one stage clusters that are relatively close together were joined whereas, at the following stage, the clusters that were joined were relatively far apart. This implies that the optimum number of clusters may be the number present just before that large jump in distance.

In complex aquifer system, like the one in the study area, this approach to find the number of clusters may not be efficient. The risk is to overestimate or underestimate the number of clusters and, therefore, also the number of samples grouped in the same cluster. In other words waters with some similarity could be grouped even if they have different hydrochemical facies.

Therefore, in areas where it is difficult to identify the geometry of hydro-facies and connection among aquifers, especially pushing up depths, the definition of the clusters number resulting from an hierarchical cluster analysis needs to be refined through the identification of the most significant water composition indexes.

4.4 – COMPOSITION INDEXES APPROACH

In the Solofrana River Valley, the structural complexity of the area affect the groundwater chemical composition and induces mixing phenomena between carbonate aquifer groundwater and those of the plain aquifer. In addition, the anthropogenic pressures, locally or even at basin scale, may alter the chemical-physical characteristics of groundwater due to the introduction in the environment of components associated to human activities.

In this framework, the definition of homogeneous groundwater groups by hierarchical cluster analysis has to be performed in according to:

- ✓ natural mixing phenomena;
- ✓ anthropogenic pressures.

Therefore it's necessary to identify parameters that should describe both natural and anthropogenic phenomena that influence the groundwater chemical evolution. So for every sample it is possible to define an overall feature (natural + anthropogenic); as a result, the grouping in homogeneous clusters of waters belonging to the same hydrofacies is more significant and reliable.

An important step is the identification of the end-member, both for carbonate and plain aquifer. In other words, in the data set two key samples are needed, one representative of the chemical composition of carbonate groundwater and the other representative of plain groundwater; so we can define the first like "Substratum End-Member" (*S.E*.M.), the second " Plain End-Member"(*P.E.M*).

According to the parameters describing the overall feature, each sample can be compared with both *S.E.M.* and *P.E.M.*. The result is that each sample will have a couple of indexes; one associated to *S.E.M.* the other to *P.E.M.* that expresses the whole of components (natural and anthropogenic) leading to that specific chemical composition.

A vector algebra procedure has been implemented in order to get quantitative results. Each sample is considered a vector in the space and every feature index is a component of the vector:

$$\text{Sample} = \left| \begin{matrix} I_1 \\ I_2 \\ I_3 \\ I_4 \\ \ldots \end{matrix} \right|$$

Written the vectors for *S.E.M.* and *P.E.M.*, the following formula may be applied:

$$\text{G.I.} = \frac{\left| \begin{bmatrix} S\\U\\B\\S\\T\\R\\A\\T\\U\\M \end{bmatrix} \cdot \begin{bmatrix} P\\L\\A\\I\\N \end{bmatrix} \right|^2}{\left| \begin{bmatrix} S\\U\\B\\S\\T\\R\\A\\T\\U\\M \end{bmatrix} \cdot \begin{bmatrix} S\\U\\B\\S\\T\\R\\A\\T\\U\\M \end{bmatrix} \right| \cdot \left| \begin{bmatrix} P\\L\\A\\I\\N \end{bmatrix} \cdot \begin{bmatrix} P\\L\\A\\I\\N \end{bmatrix} \right|} \qquad (1)$$

The formula (1) give a value, that we can define global index (G.I.), variable from 0 to 1. G.I. equal to 1 means that the two vectors are the same, 0 means that the two vectors are completely different. In our applications if G.I. is equal to 1 means that the "End-Member " have the same composition while if it is equal to 0, the "End-Member" are chemically different. For this reason it's important that the G.I. is closer to 0 than 1.

A G.I. close to 0 indicates that the choice of *S.E.M.* and *P.E.M.* is correct and that the used composition indexes are truly representative of the hydrochemical features. This is an iterative procedure; in other words the goal is to obtain the lowest value of GI. This is possible by acting on the type of indexes, on their number and on the choice of the end-member, always in total according with the hydrogeological conceptual model of the study area.

Since the reference scale varies from 0 to 1, it is recommended to choose indexes expressed in the same scale; therefore their values have to be normalized to the maximum value.

Achieved the best solution for the GI, with the same indexes configuration, the following formulas can be applied:

$$\mathbf{S.I.} = \frac{\left|\begin{Bmatrix}S\\E\\M\end{Bmatrix}\cdot\begin{Bmatrix}S\\A\\M\\P\\L\\E\end{Bmatrix}\right|^{2}}{\left|\begin{Bmatrix}S\\E\\M\end{Bmatrix}\cdot\begin{Bmatrix}S\\E\\M\end{Bmatrix}\right|\cdot\left|\begin{Bmatrix}S\\A\\M\\P\\L\\E\end{Bmatrix}\cdot\begin{Bmatrix}S\\A\\M\\P\\L\\E\end{Bmatrix}\right|} \quad (2) \qquad \mathbf{P.I.} = \frac{\left|\begin{Bmatrix}P\\E\\M\end{Bmatrix}\cdot\begin{Bmatrix}S\\A\\M\\P\\L\\E\end{Bmatrix}\right|^{2}}{\left|\begin{Bmatrix}P\\E\\M\end{Bmatrix}\cdot\begin{Bmatrix}P\\E\\M\end{Bmatrix}\right|\cdot\left|\begin{Bmatrix}S\\A\\M\\P\\L\\E\end{Bmatrix}\cdot\begin{Bmatrix}S\\A\\M\\P\\L\\E\end{Bmatrix}\right|} \quad (3)$$

Each sample has to be multiplied with S.E.M. (2) and P.E.M. (3). As stated above, every sample has a couple of indexes, “Substratum indexes” (S.I.) from (2) and “Plain indexes” (P.I.) from (3).

As for the G.I., the values of S.I. and P.I. may vary from 0 to 1 with the same meaning. For example, if a sample has S.I. close to 1, its composition is comparable with S.E.M., instead if it is close to 0 is very different. The same is true for P.I. in relation to the P.E.M.. Such composition indexes can also be considered to assess the mixing degree of groundwater for each sample.

A scatter plot (Fig. 4.8) based on S.I. and P.I. values obtained for each sample, is useful to visualize the distribution of points in relation to “End-Members”.

A careful analysis of the scatter plot highlights the number of samples clusters. At this stage, a K-means clustering analysis may be performed imposing as number of clusters (k), the number of groups revealed in the scatter plot. The variables to be use in K-means are the composition indexes above illustrated.

If the K-means returns a samples distribution compatible with the hydrogeological model of the study area, it means that the scatter plot provides a reliable scenario of the similarity of the analysed samples. In other words, the k used in K-means clustering analysis, represents the "best cluster solution".

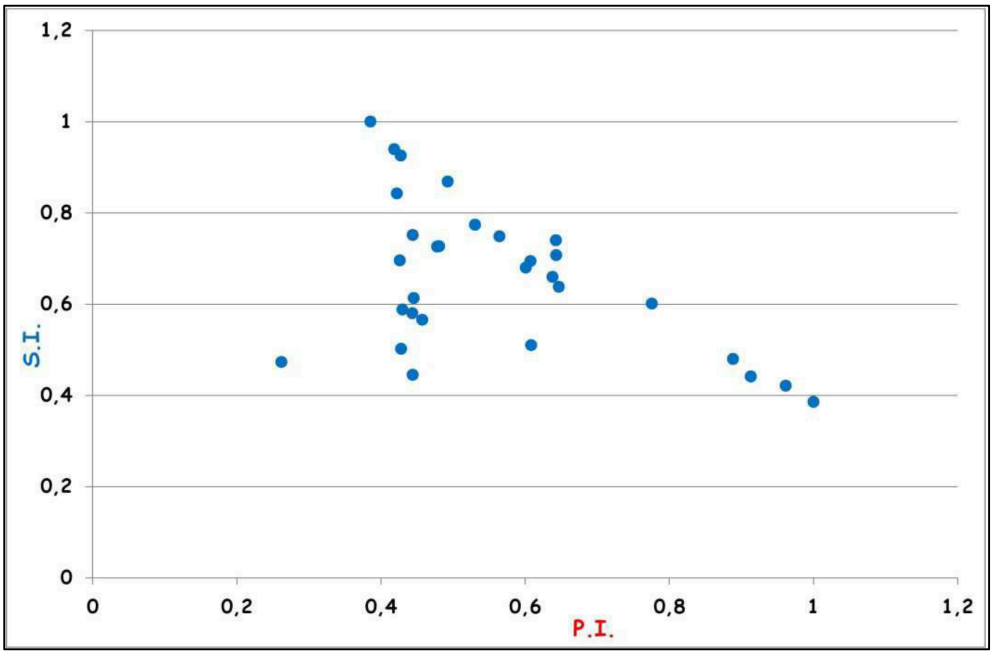


Fig. 4.8 - Example of scatter plot based on S.I. and P.I. values

The final step of this procedure is to perform a Hierarchical Agglomerative Cluster Analysis considering the entire data set of the chemical composition of the samples. The produced dendrogram will be "cut" in order to show the same number of clusters considered as the "best solution".

In this way the number of clusters is chosen by an analytical way, however considering the similarity of features between groundwater samples.

The application of this procedure is showed in the paragraph 5.3. It shows as a useful clustering analysis was so refined and improved, allowing the identification of hydrofacies connection at basin scale.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 - HYDRO-STRATIGRAPHIC ARCHITECTURE

The analyses of above mentioned 285 stratigraphic and well logs data and the geological survey allowed the reconstruction of a geo-structural model represented in a number of significant cross-sections (Fig. 5.1 – 5.2). A complex geological structure results.

The lower CI unit (Rolandi et al., 2003), interbedded in Plio-Quaternary deposits, is rather continuous in the valley. Its average thickness is about 20-25 m and reaches maximum values (about 60 m) in the southern sector. Locally, it seems to be missing or to have smaller thickness because of mining exploitation. In addition, as a result of diagenetic processes, the top of the so-called "Campanian Grey Tuff" often becomes incoherent. The thickness of CI gradually decreases towards foothills, where it may overlie carbonate bedrock. As for the *"basal pumice"*, it has generally a thickness of about 2 m.

The layer of overlying pyroclastic and alluvial deposits has a variable thickness (about 20-40 m) including primary and reworked facies, more or less consolidated, with silty-clayey and silty-sandy texture. As poorly consolidated pumices and locally gravel and coarse sands are recognizable too.

Conglomeratic sequences deposited by sediment-gravity flows characterize the north-eastern sector of the valley. So main alluvial fans provide a detailed record of denudation slope processes and give a detailed picture of rift-basin alluvial sedimentation.

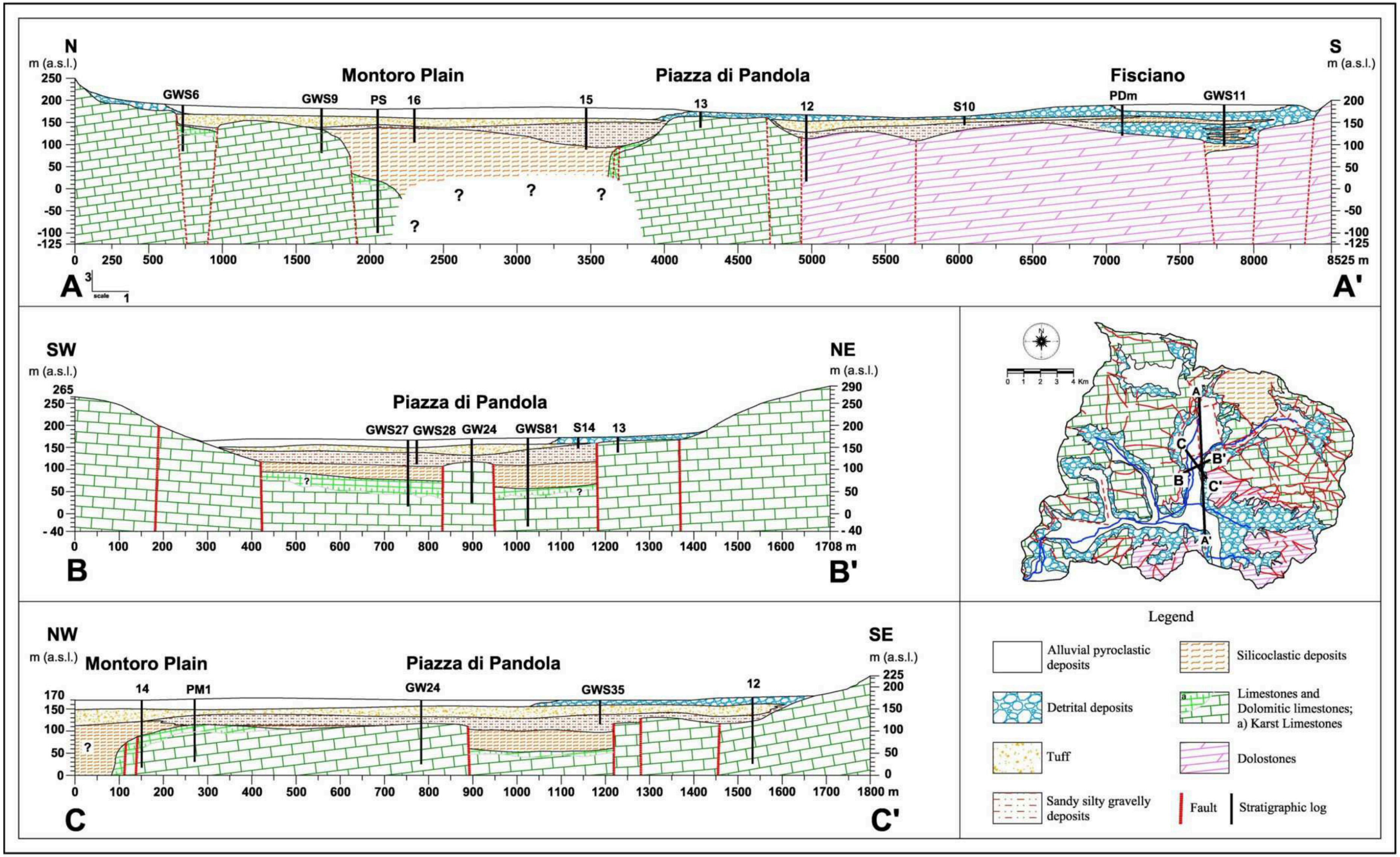


Fig. 5.1 - Cross section of the central sector

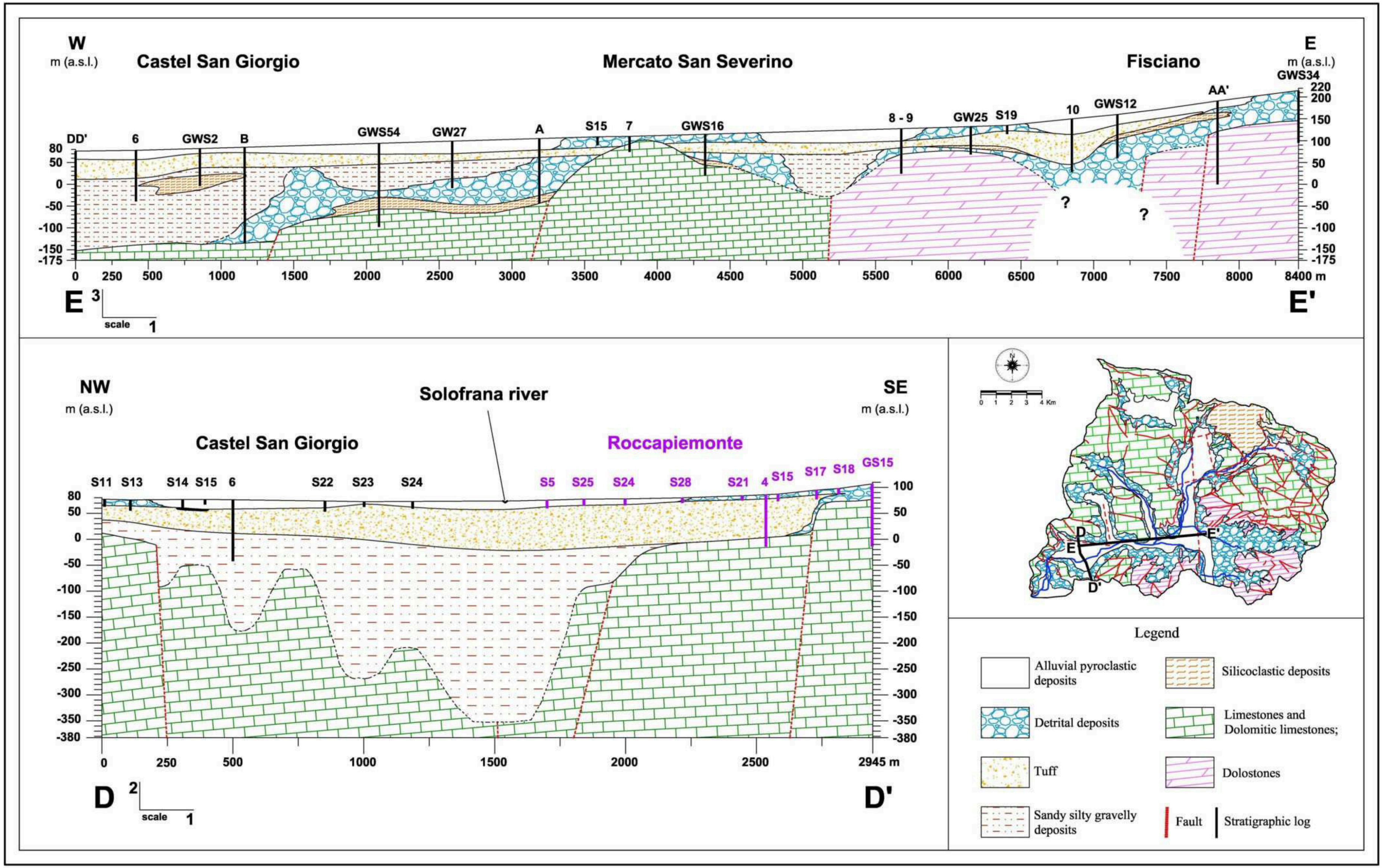


Fig. 5.2 - Cross section of the southern sector

The stratigraphic reconstruction of the Montoro plain and its morphological features point out particular paleogeographical and paleoenvironmental conditions of the area. According to the multicyclic evolution of the valley and to the subaerial erosion of the carbonate substratum (Brancaccio et al., 1994), well logs data of the Montoro Plain confirms its origin, i.e., an endorheic and karst basin closed by cyclic conglomeratic incoming due to the weathering and erosion of reliefs.

The carbonate substratum underlies these karst breccias (Fig. 5.3) and is at depth at least 150 m. Just in the Piazza di Pandola area, where took place the outlet of the basin, it is recognizable at about 52 m of depth (Fig. 5.1 – cross section BB').

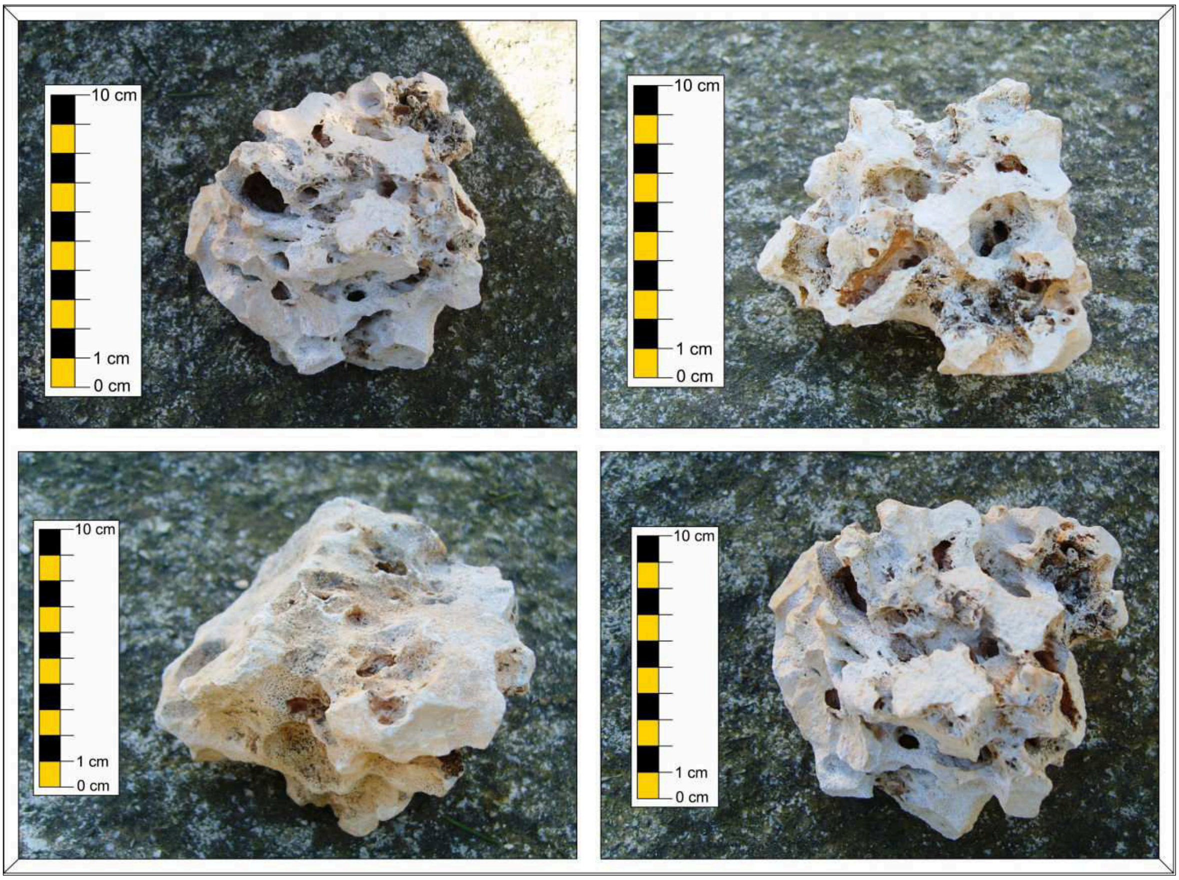


Fig. 5.3 - Karst breccias extracted during the drilling of deeper wells of the Plain of Montoro

Deposits of the "Argille variegate" overthrust these limestones and underlie directly the CI in the northern sector of Montoro plain, whereas alluvial and pyroclastic deposits in the southern one and at foothills. As regard to quaternary deposits at the bottom of CI, they have a thickness of about 30 m and are mainly gravels and breccias.

5.2 – HYDRODYNAMIC CONDITIONS

In Figure 3.5 water table level reconstructions from 1987 to 2006 are shown. Most recent water table reconstructions were based on the monthly measurements of groundwater levels carried out between February 2011 and October 2012 (Fig. 5.4 to 5.9) and provide the upgrading of the conceptual hydrogeological model in order to characterize the heterogeneity of the plain aquifer system and to identify the relationship between this plain aquifer and the deepest carbonate one.

The reconstruction of the water table maps and so of the "Hydrogeological Scheme" as for plain aquifer as for carbonate bedrock (Fig. 5.4 to 5.9) points out the most critical conditions, which affect the groundwater flow pathways and velocity.

Even though historical records of water levels are space-time discontinuous (Fig. 3.5), the distribution and allocation of the monitored wells in the period 2011-2012 (Fig. 4.4) improve the assessment of the temporal and spatial evolution of groundwater dynamics due to as natural as human behaviour. Comparing these maps there are no considerable changes in the flow directions both in the pyroclastic-alluvial aquifer and in the carbonate aquifer.

From the comparison of the maps significant variations in hydraulic head of the two overlapped aquifers result. In the first period (1987-1991) it is possible to observe a general lowering of the water table in the plain aquifer, even if with different range of values in various sectors.

At the end of the '80s, as a result of the big lowering (about 20 m) in wide areas located between Montoro Inferiore and Mercato San Severino, the Mercato San Severino springs (Q_{av}= 200-300 l/s) missed.

In the early of the 2000s even the Laura spring, one of the outflows of the contiguous carbonate aquifer, failed (Sarno River Basin Authority, 2004).

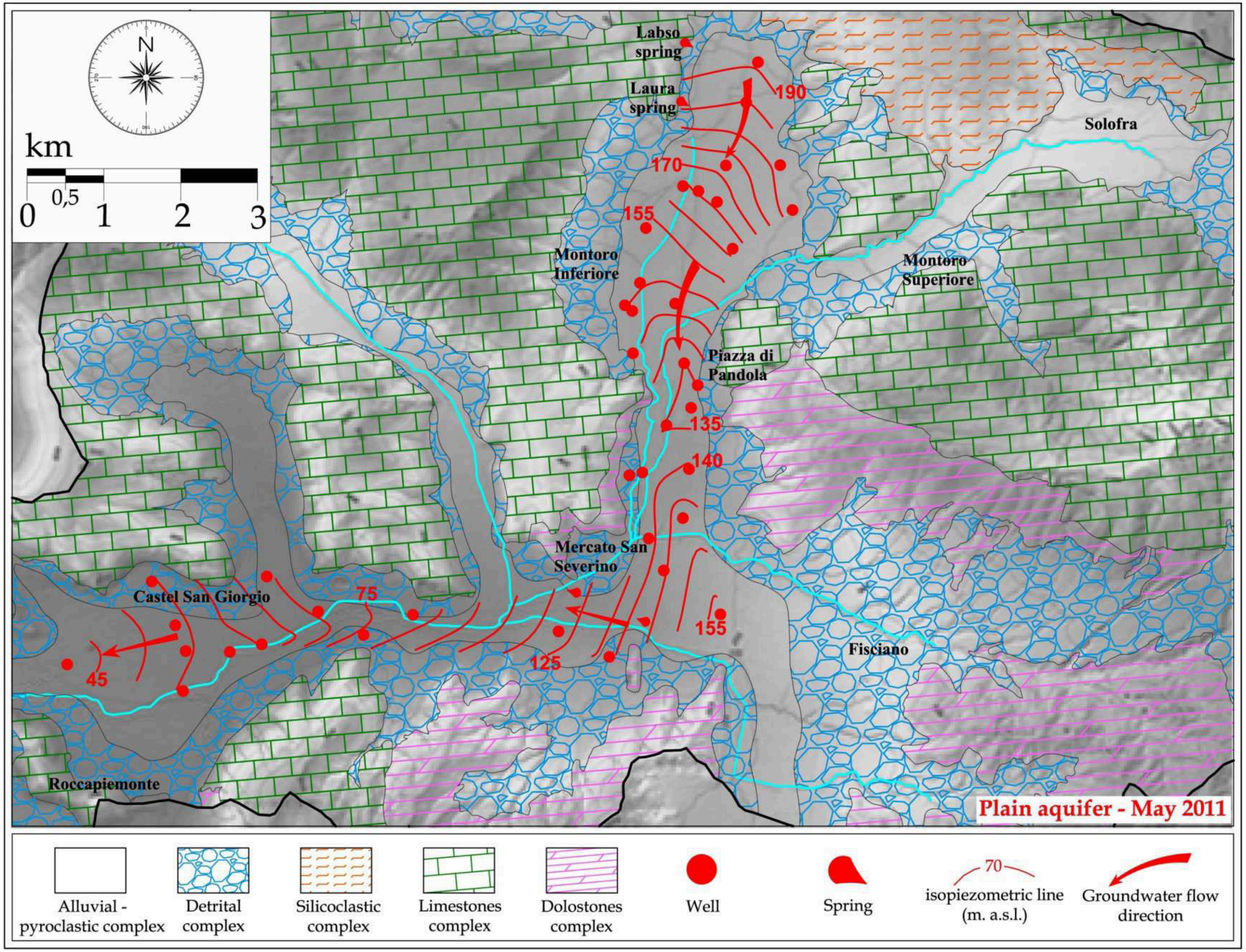


Fig. 5.4 - Water table map of Plain aquifer (May 2011)

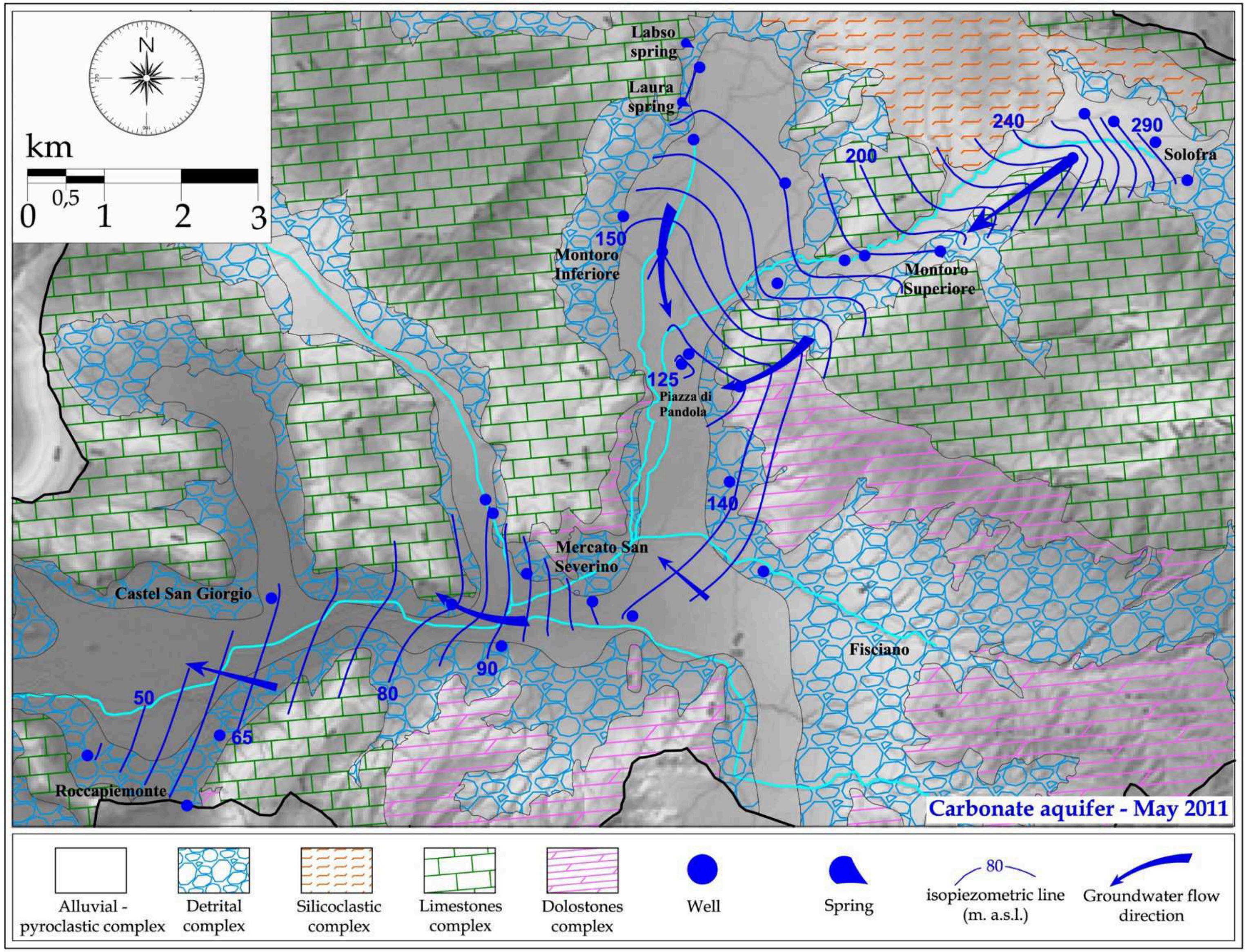


Fig. 5.5 - Water table map of Carbonate aquifer (May 2011)

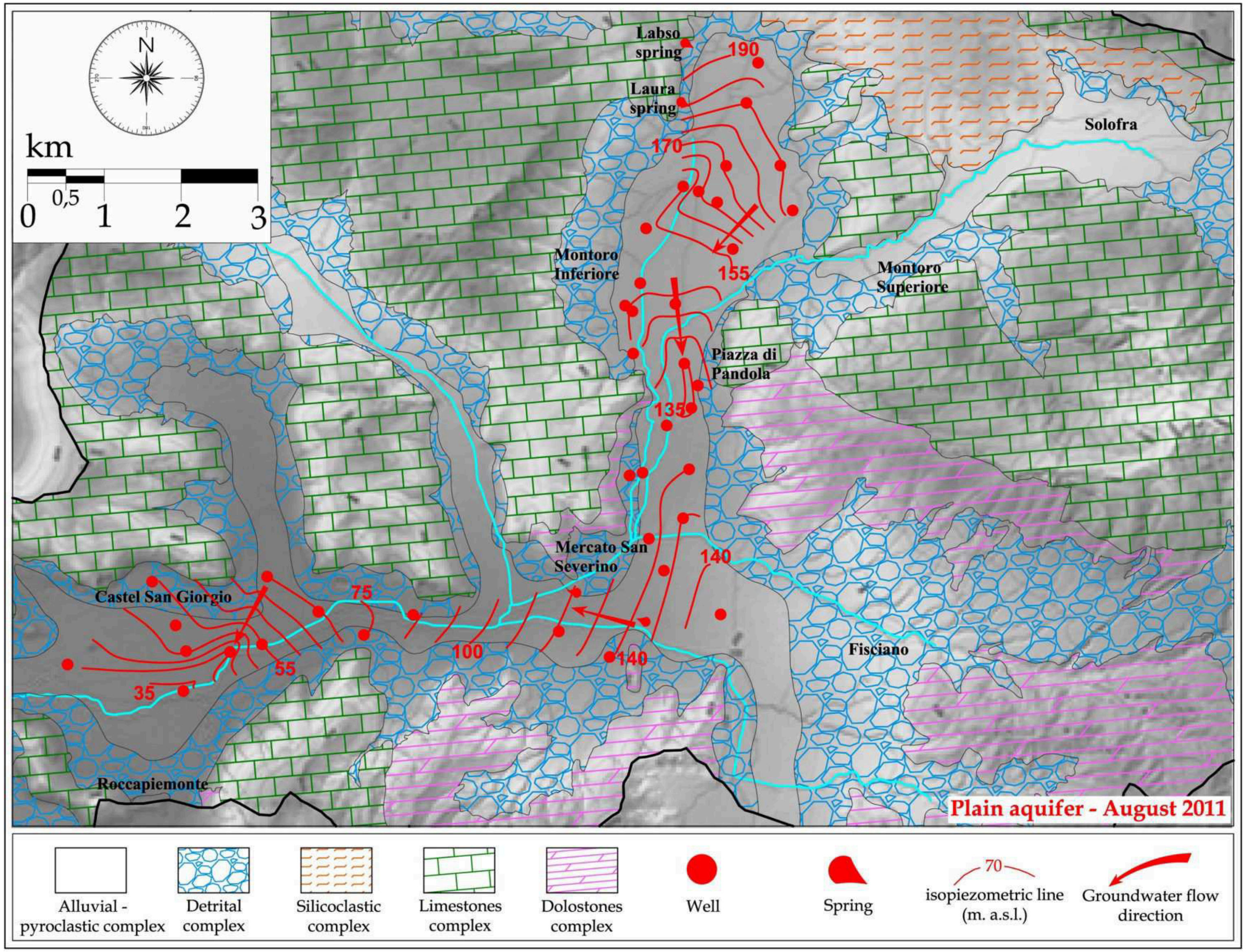


Fig. 5.6 - Water table map of Plain aquifer (August 2011)

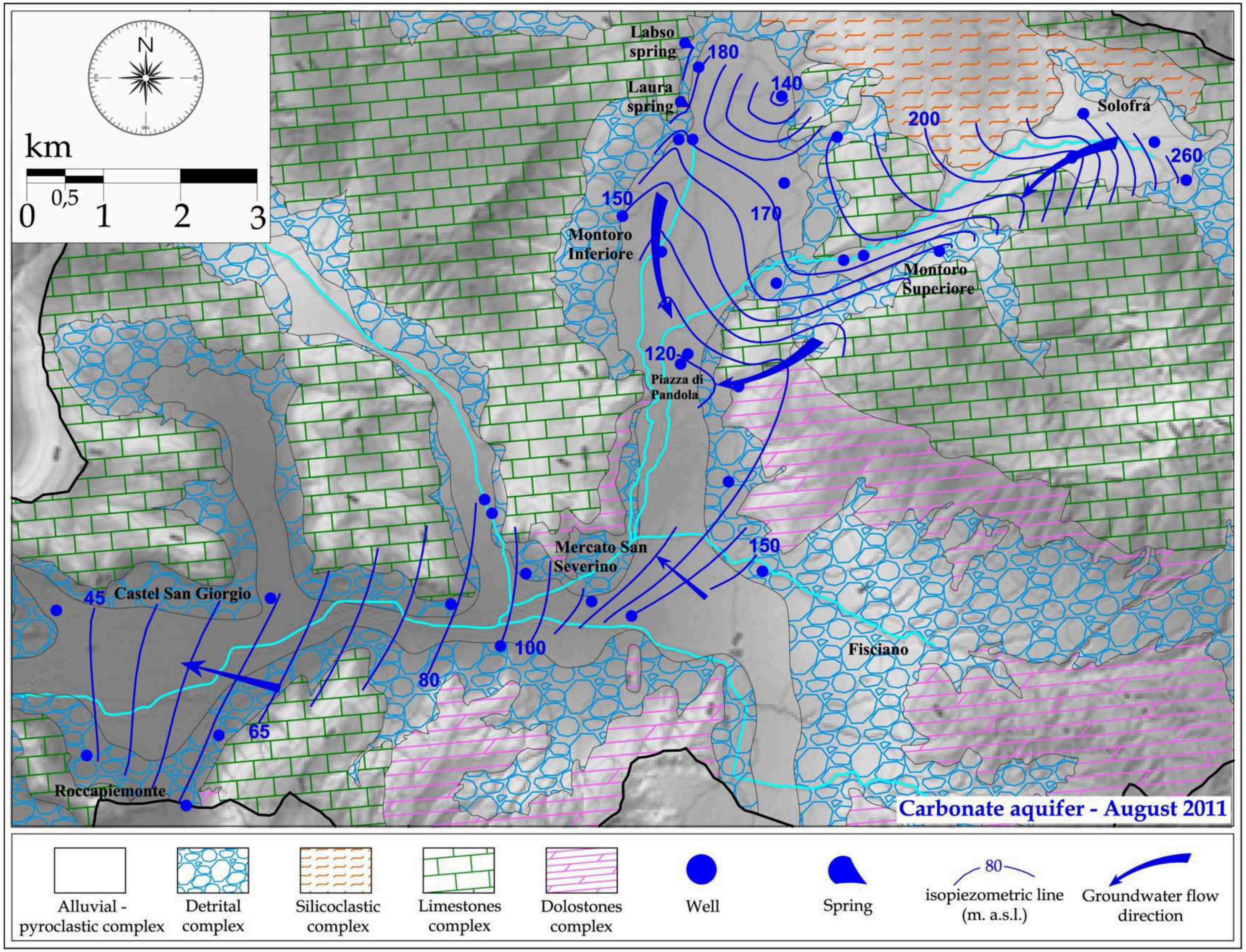


Fig. 5.7 - Water table map of Carbonate aquifer (August 2011)

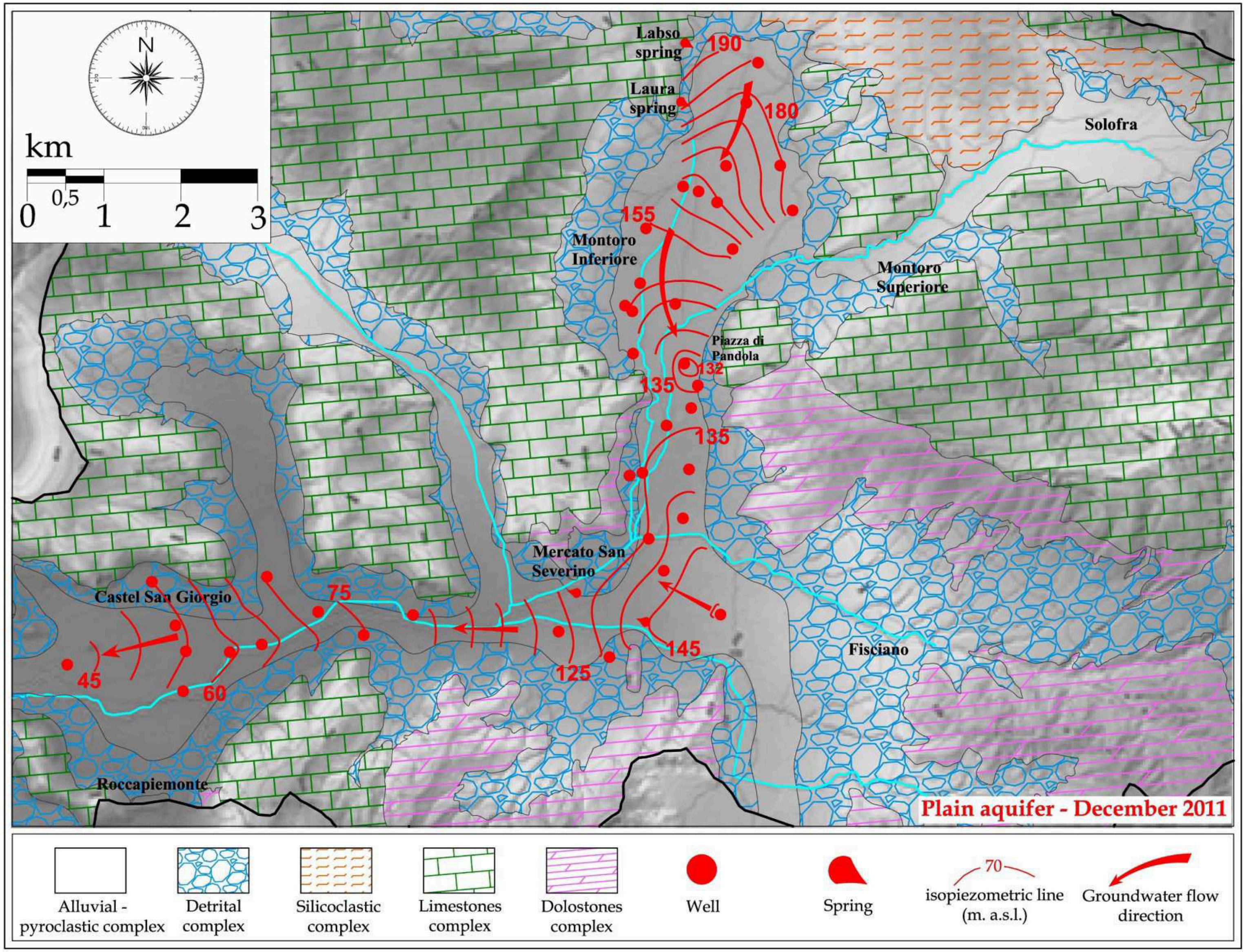


Fig. 5.8 - Water table map of Plain aquifer (December 2011)

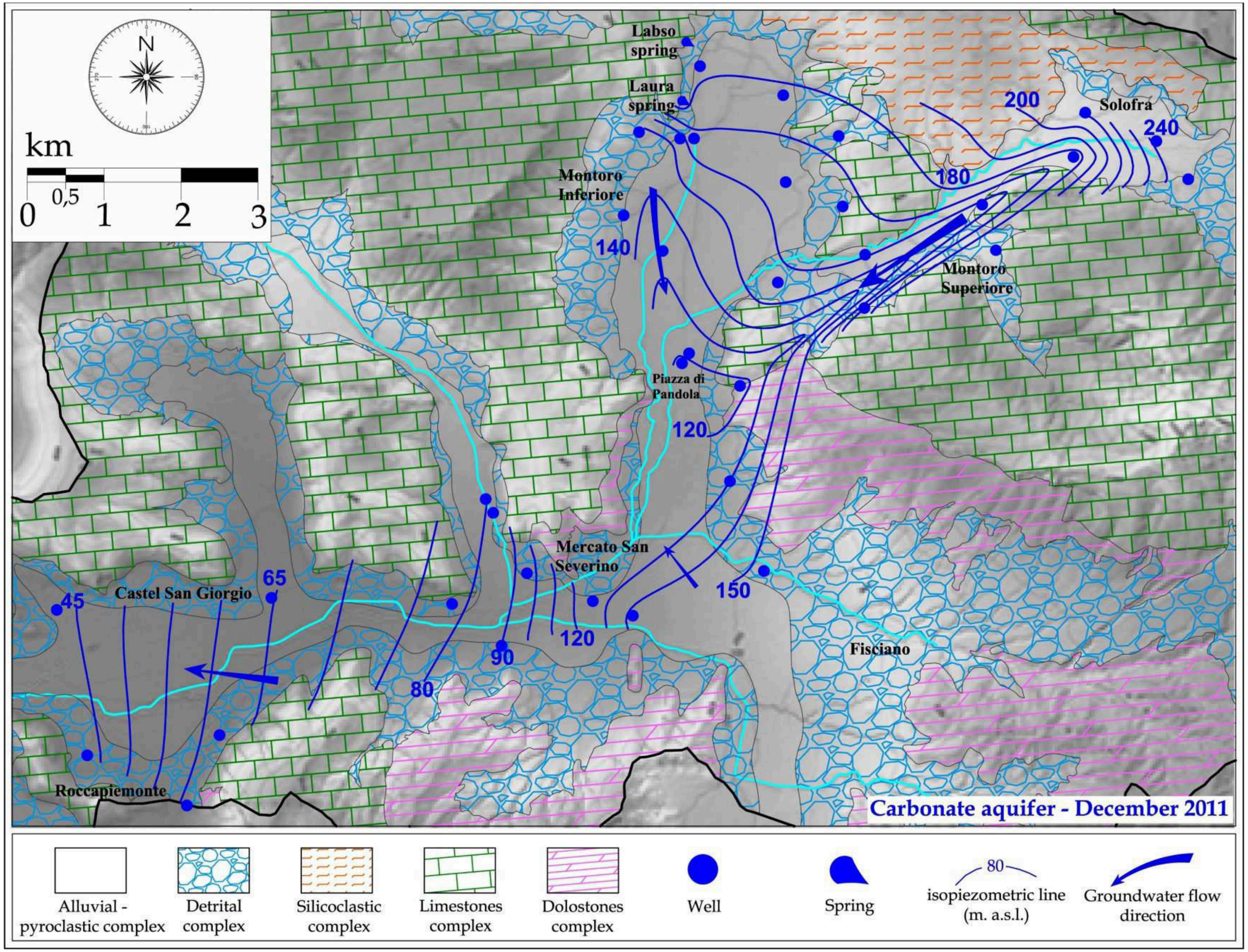


Fig. 5.9 - Water table map of Carbonate aquifer (December 2011)

During the period 1991-2006 the hydrodynamics of the aquifers did not show significant changes in flow directions, but localized water table lowering took place in the areas where major human activities are located. In particular, this circumstance is confirmed by the comparison between the maximum water table lowering in the Montoro Plain (20-30 m range) and the level rising in the Fisciano-Mercato San Severino (10-15 m range). Similarly in the Castel San Giorgio area, lowering of about 2 meters are observed together with 4 m rising.

The rainfall in the last 10 years is reported in the following figures (Fig. 5.10 to 5.12). After a dry period observed until 2002-2003 (De Vita and Fabbrocino, 2007), it is observed that a gradual increase in the Solofrana Basin occurred since 2004 up to 2010, when in the study area the rainfall is more than 50% of the average value, with a peak of 67% recorded by Solofra pluviometer.

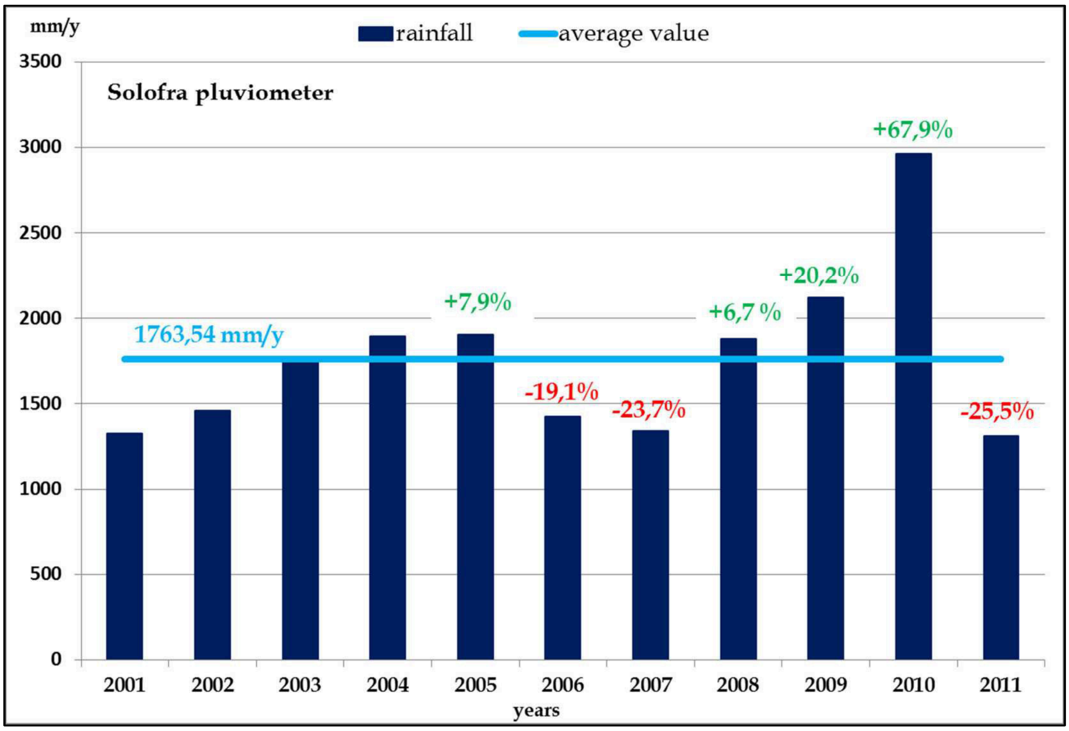


Fig. 5.10 - Rainfall recorded by Solofra pluviometer

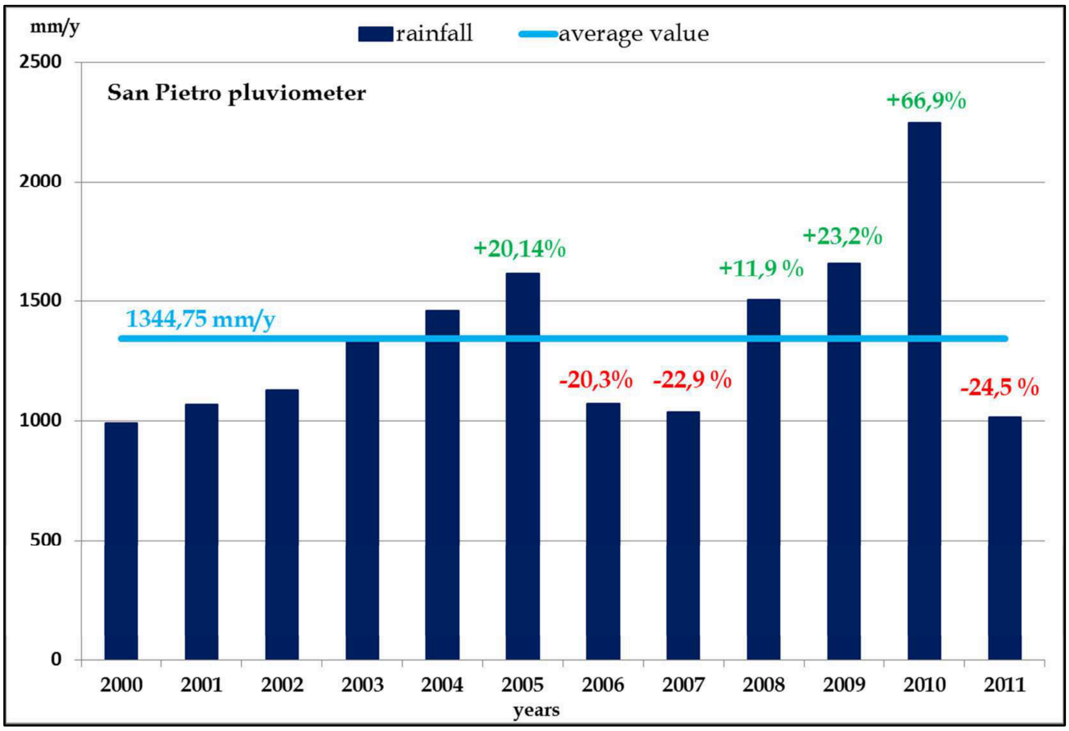


Fig. 5.11 - Rainfall recorded by San Pietro pluviometer

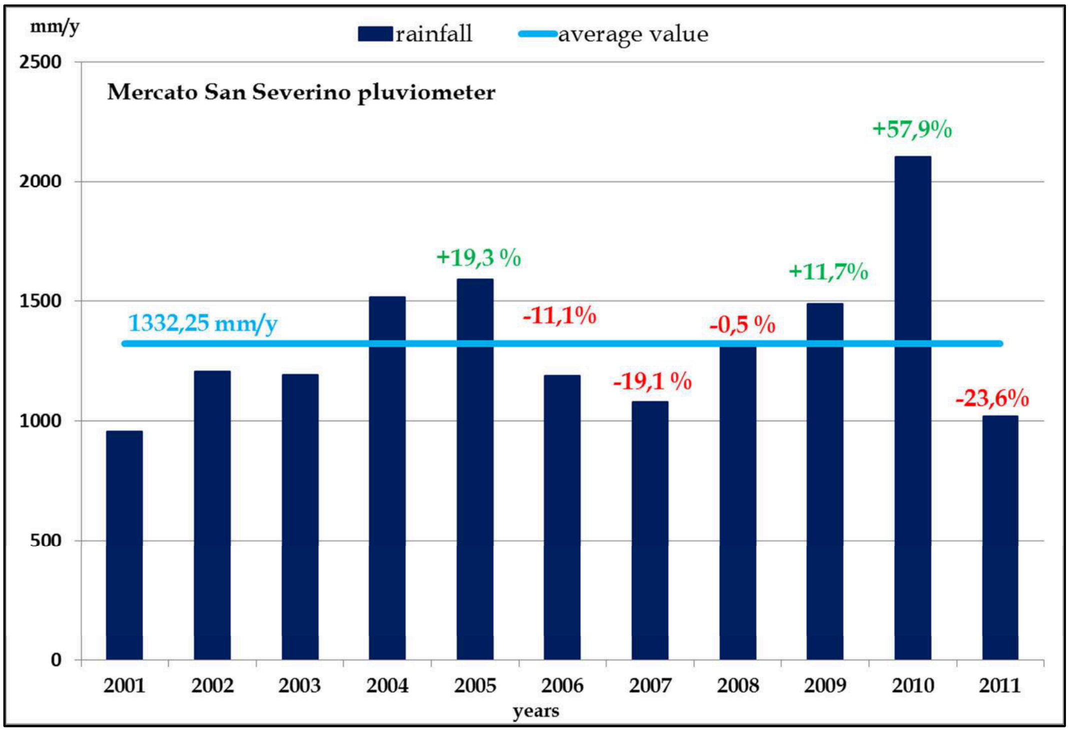


Fig. 5.12 - Rainfall recorded by Mercato San Severino pluviometer

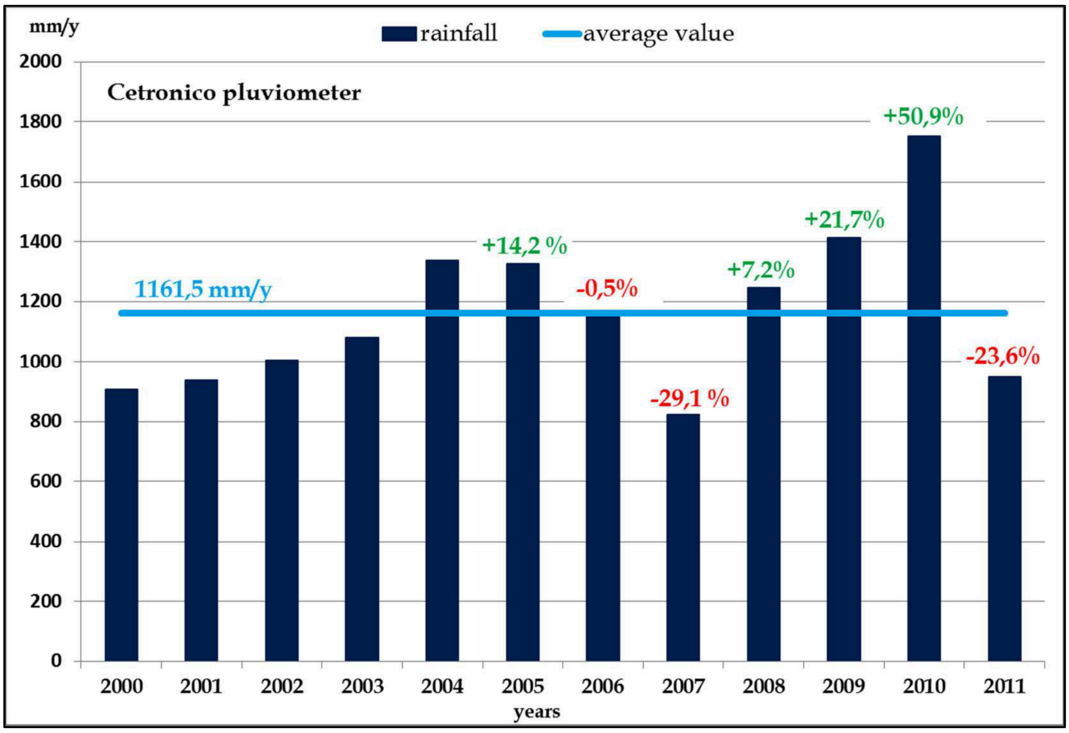


Fig. 5.13 - Rainfall recorded by Cetronico pluviometer

As from 2006 a gradual rise of piezometric heads takes places (Tab. 5.1) and in the end of 2011 the Mercato San Severino springs occurred again, reaching a discharge of 10-30 l/s (November 2011-February 2012).

Well	2005/2006 m (a.s.l.)	2011/2012 m (a.s.l.)	Δh m
GWS1	52,38	56,48	4,10
GWS2	51,54	53,90	2,36
GWS3	56,19	61,40	5,21
GWS4	132,07	142,80	10,74
GW25	117,36	129,26	11,90
GW24	129,08	124,70	-4,39
GWS5	114,19	134,45	20,27
GW23	157,48	164,04	6,56
GWS6	179,72	180,52	0,80
GW27	64,56	73,53	8,98
GWS8	166,17	168,40	2,24
GWS9	168,67	170,36	1,68
GWS10	104,83	117,27	12,45
GWS46bis	50,21	54,61	4,40

Tab. 1 - Rise of piezometric heads since 2005/2006 to 2011/2012 (in red wells in plain aquifer, in blue wells in carbonate aquifer)

Data collected up to 2012 made possible a distinction between the ground water flow in the carbonate aquifer and the flow active in the plain aquifer and the characterization of the main aspects of their interactions.

The flow in the plain aquifer is confined with hydraulic gradients of about 1,6%. Its hydraulic head is placed above or within the Campanian Ignimbrite.

The Mercato San Severino area is affected by a different hydraulic pattern. It is on average about 2,3% due to the reduced draining section and to the leakage from the Fisciano alluvial fan. On the analogy, increased gradients are observed in the areas where more relevant is the water withdrawal.

This circumstance is confirmed by the observed fluctuations of the water table and of the piezometric regimes; the figure from 5.14 to 5.17 show the well piezometric regime associated with rainfall.

Maximum piezometric levels are recorded in the period May-June 2011 and show a constant decrease all over the year until June 2012. Different trends are shown by the wells located in the West sector of Montoro Inferiore, which increase the level up to November/December 2012.

The only data referring to the well GWS42 show a recession period ranges between March 2011 and January 2012. Response time of the aquifer is three/four months on average.

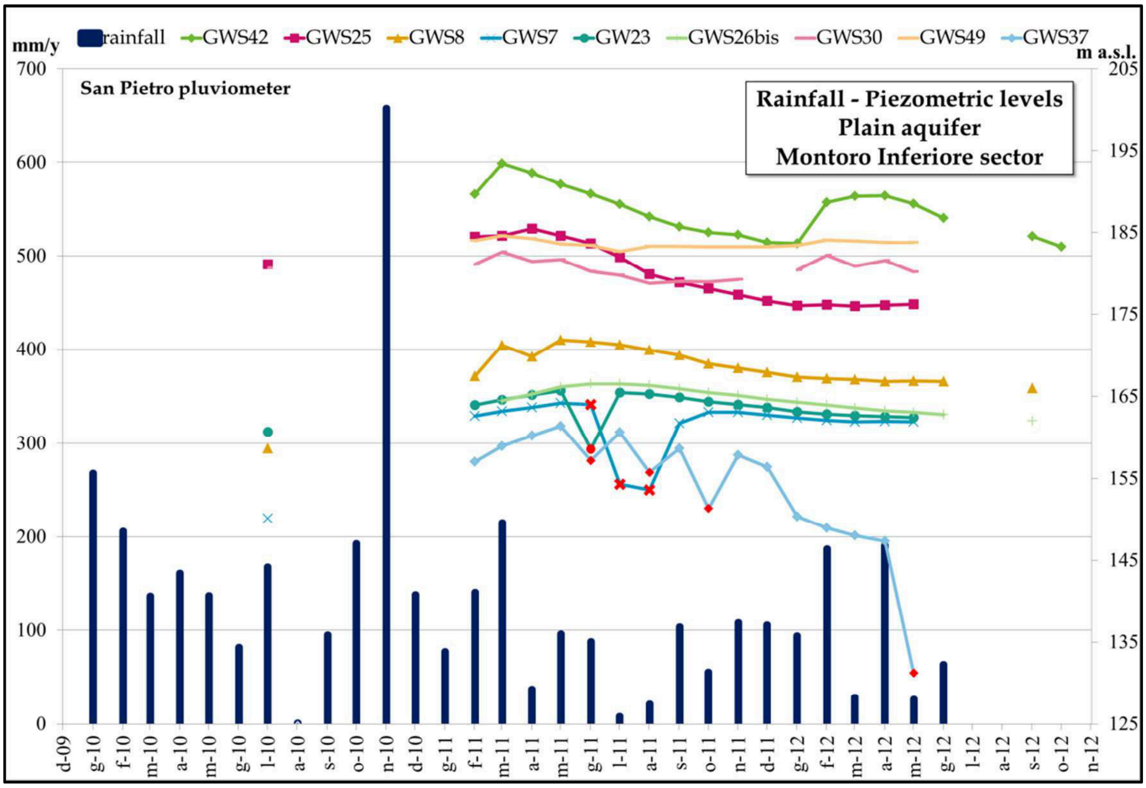


Fig. 5.14 - Rainfall and piezometric levels of plain aquifer in Montoro Inferiore sector

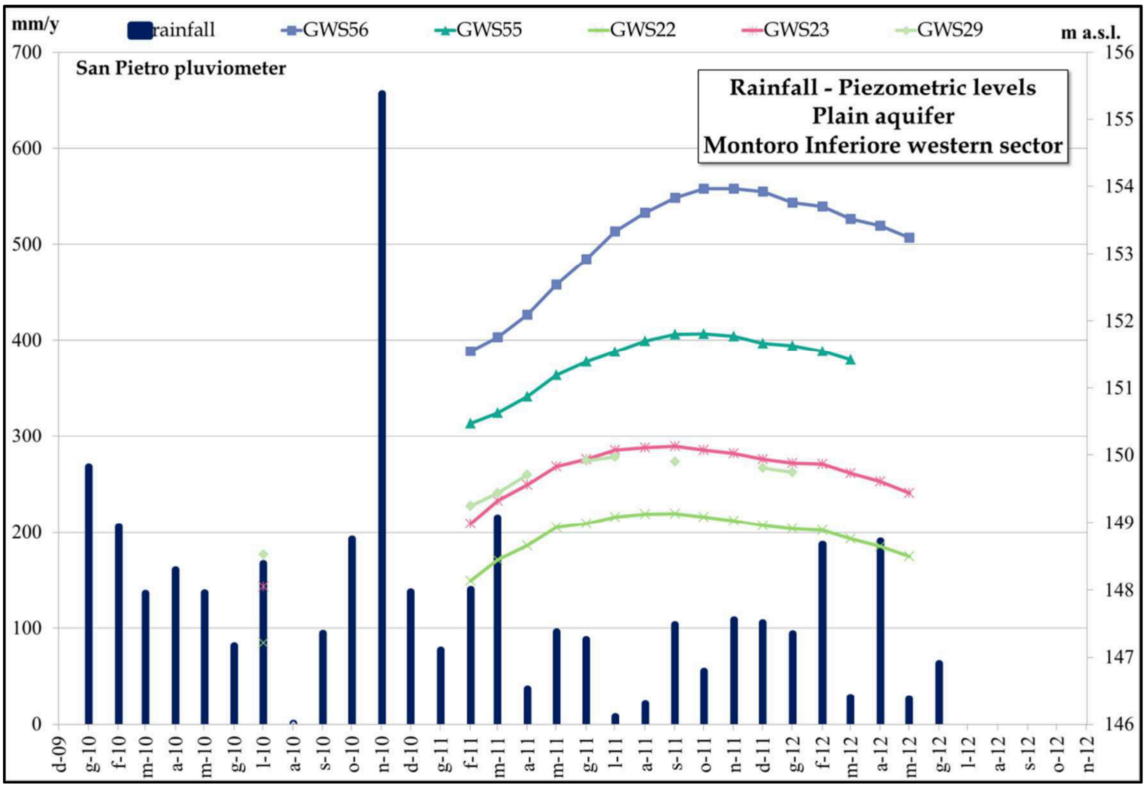


Fig. 5.15 - Rainfall and piezometric levels of plain aquifer in Montoro Inferiore wester sector

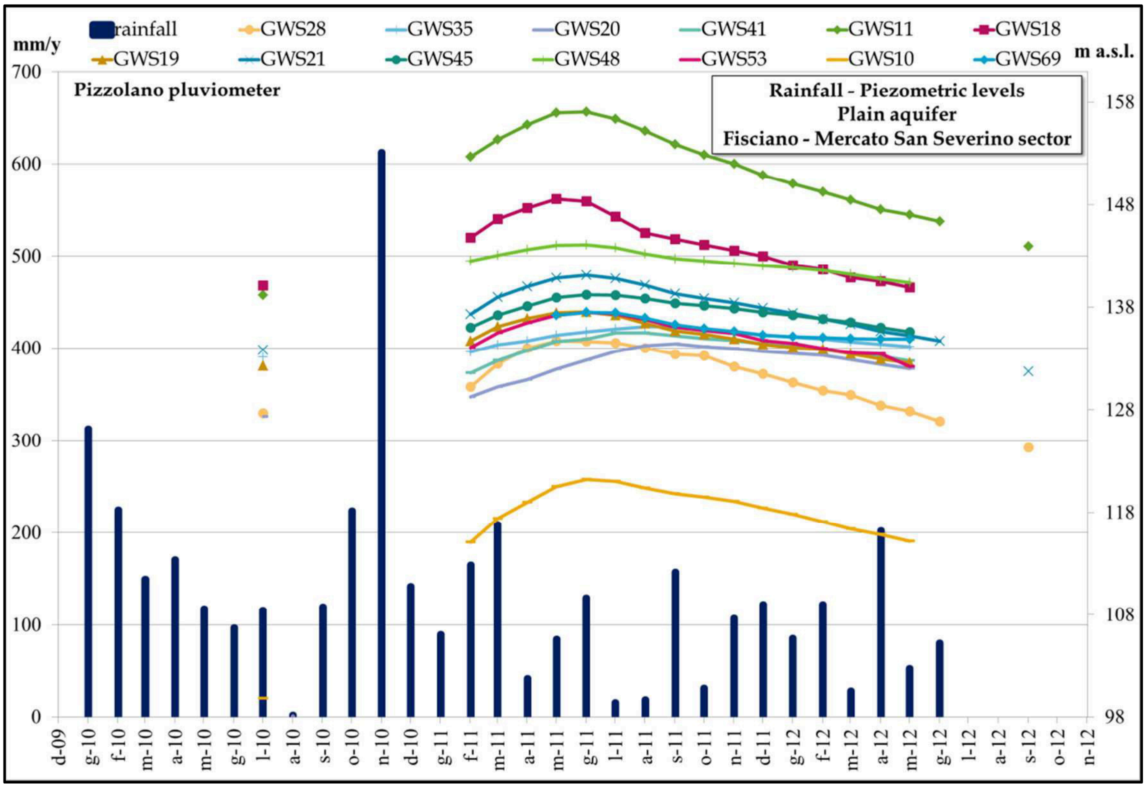


Fig. 5.16 - Rainfall and piezometric levels of plain aquifer in Fisciano – Mercato San Severino sector

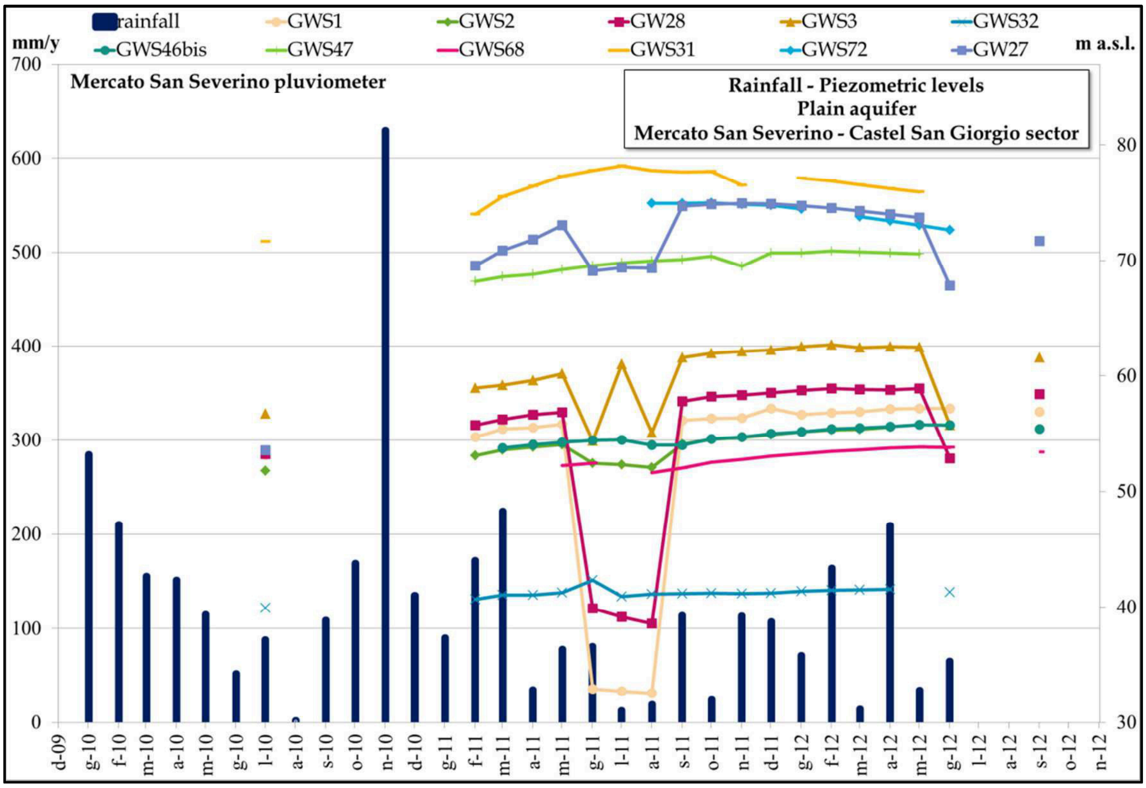


Fig. 5.17 - Rainfall and piezometric levels of plain aquifer in Mercato San Severino – Castel San Giorgio sector

On the other hand, the carbonate aquifer during the period 1991-2011 was characterized by rising of water table. Namely water table levels increase of about ten meters in the area of Solofra; of about 30 meters in the sector of Fisciano-Mercato San Severino and of about 20 meters in the sector of Castel San Giorgio.

With reference to the period of measurements (February 2011- October 2012) hydrodynamic conditions and main flow directions are constant. Change in groundwater flow directions took place in the northern part of Montoro plain only in August 2011 due to the strong water withdrawal.

The flow in the carbonate aquifer is confined with hydraulic gradients of about 0,7-0,8%.

The Solofra and Montoro Inferiore-Mercato San Severino areas seem to be affected by a different hydraulic pattern. They are respectively on average about 6% and 2-3% due to the structural setting and to limited groundwater withdrawal.

This circumstance is confirmed by the observed fluctuations of the water table and of the piezometric regimes; the figure from 5.18 to 5.21 show the well piezometric regime associated with rainfall.

Maximum piezometric levels are recorded in the period March-April 2011 and show a constant decrease until December 2011-January 2012. Different trends are shown by the wells located in the sector of Montoro Inferiore and Castel S. Giorgio, whose well piezometric regime is comparable with the behaviour of the aquifer plain.

Response time of the aquifer is four/five months on average but in some cases it is possible to observe an instantaneous effect of rainfall on groundwater levels.

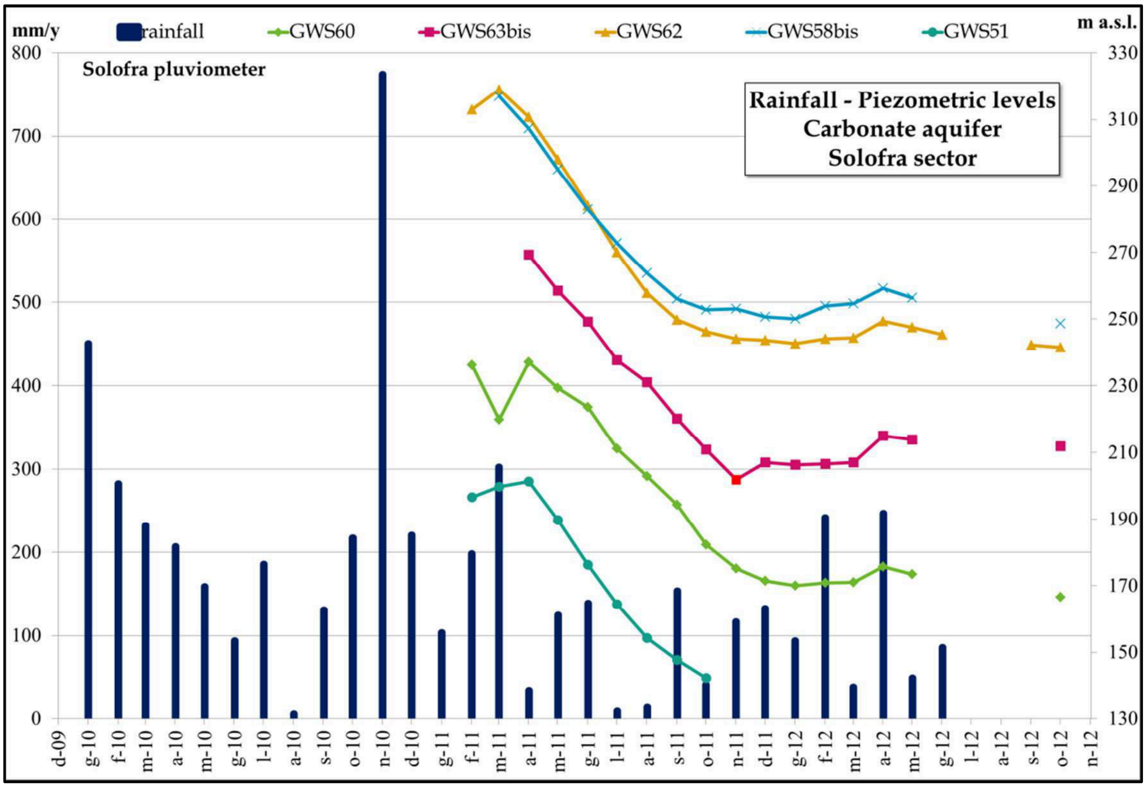


Fig. 5.18 - Rainfall and piezometric levels of carbonate aquifer in Solofra sector

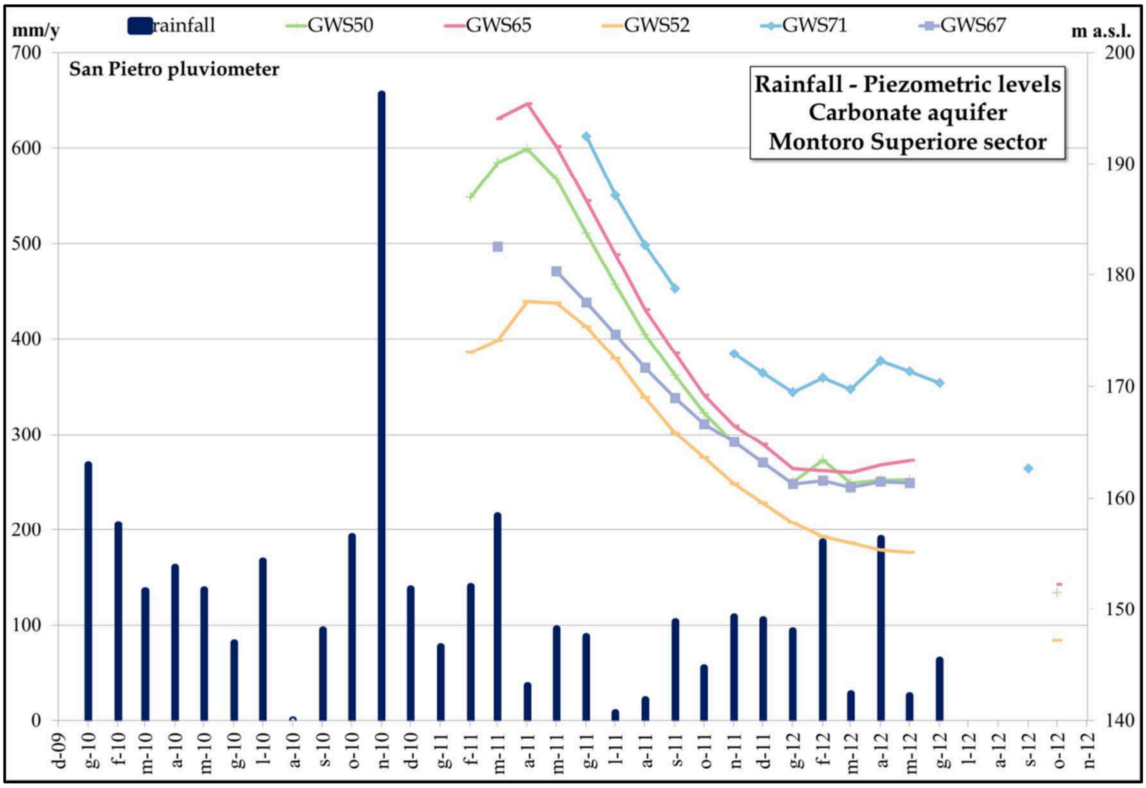


Fig. 5.19 - Rainfall and piezometric levels of carbonate aquifer in Montoro Superiore sector

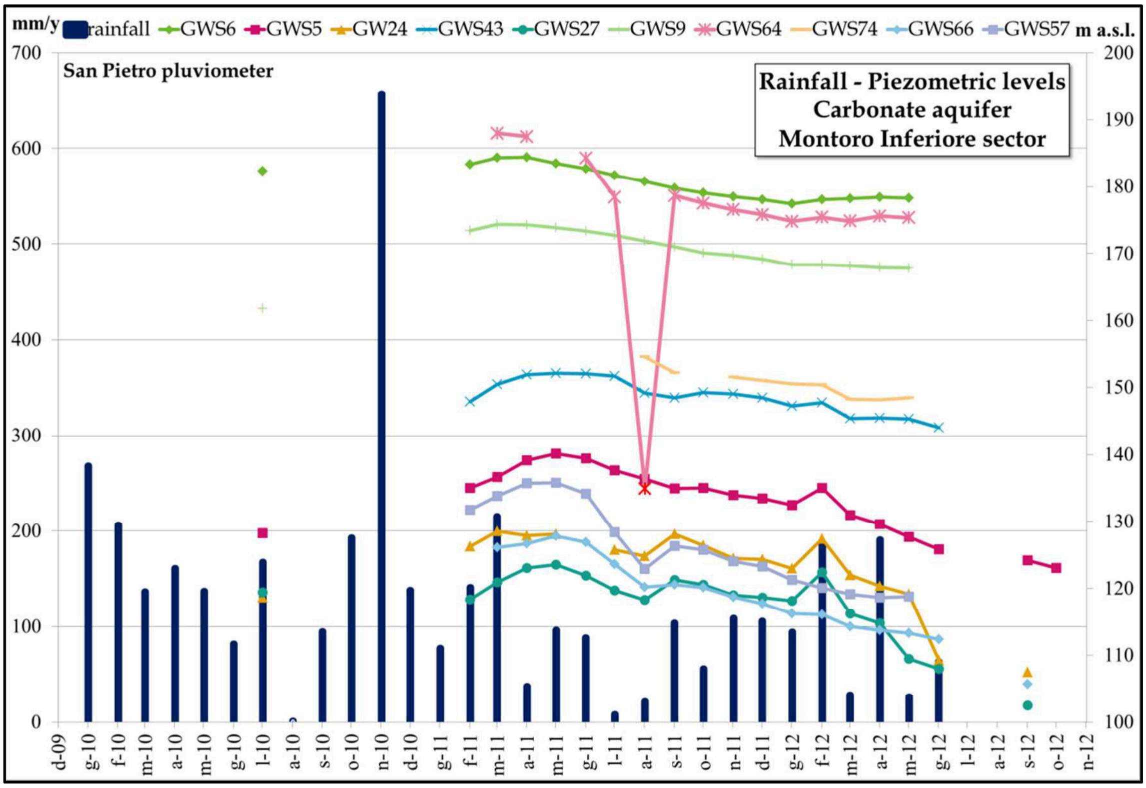


Fig. 20 - Rainfall and piezometric levels of carbonate aquifer in Montoro Inferiore sector

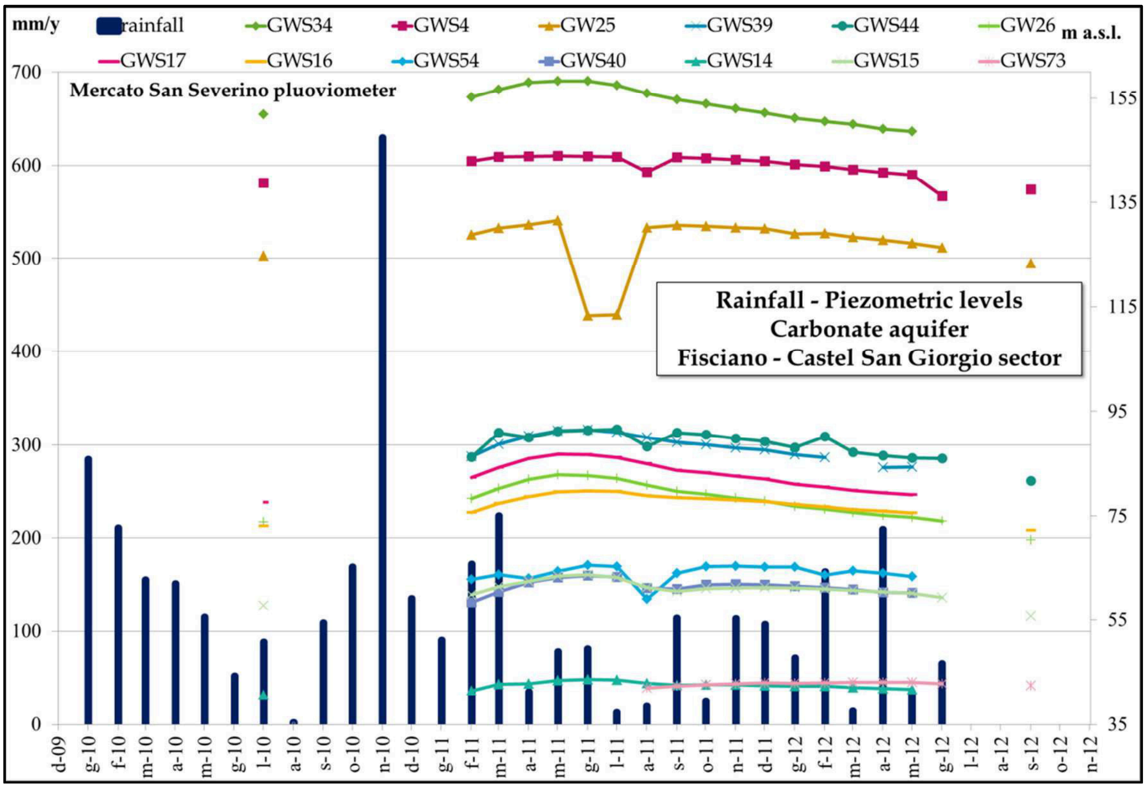


Fig. 5.21 - Rainfall and piezometric levels of carbonate aquifer in Fisciano - Castel San Giorgio sector

The recession constants for carbonate aquifer and plain aquifer have been identified (Fig. 5.22 to 5.25).

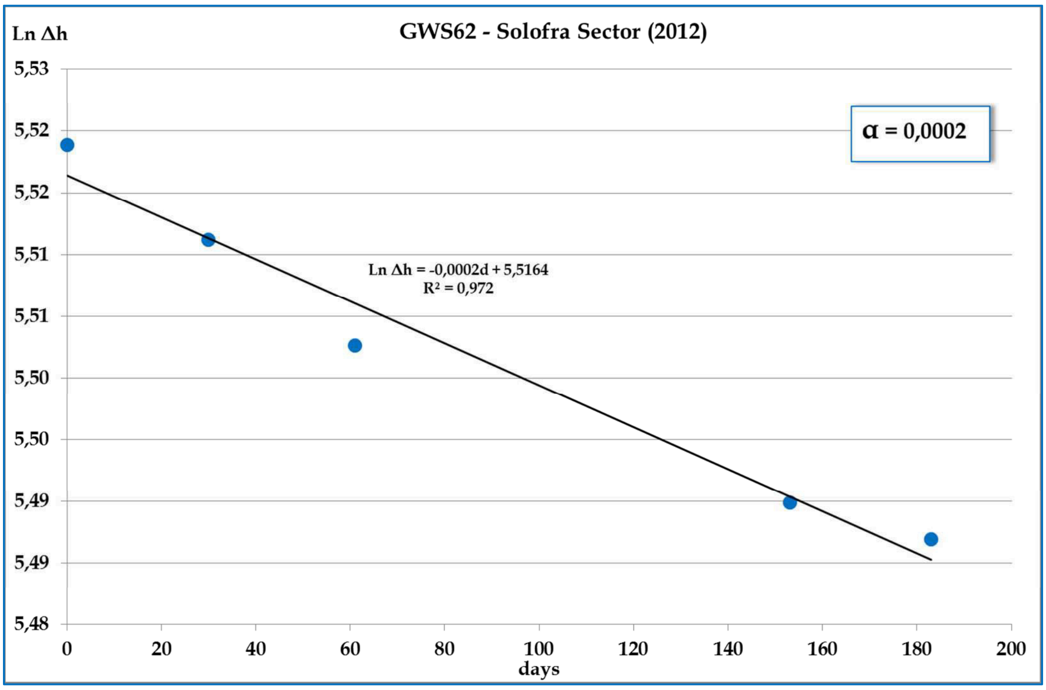


Fig. 5.22 - Recession constant of carbonate aquifer in Solofra sector

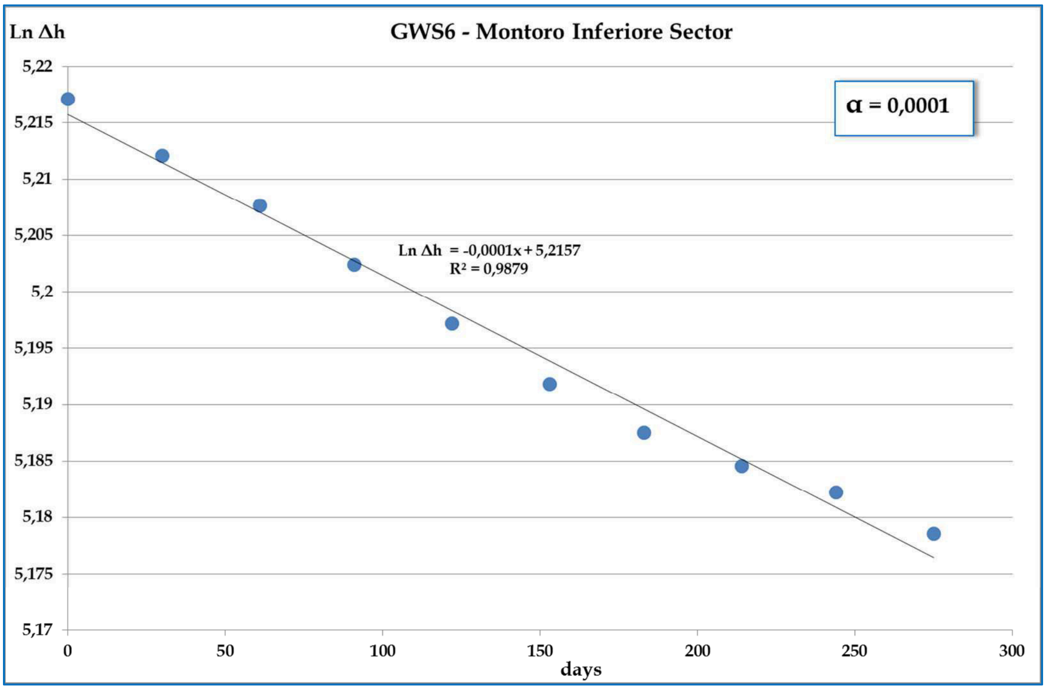


Fig. 5.23 - Recession constant of carbonate aquifer in Montoro Inferiore sector

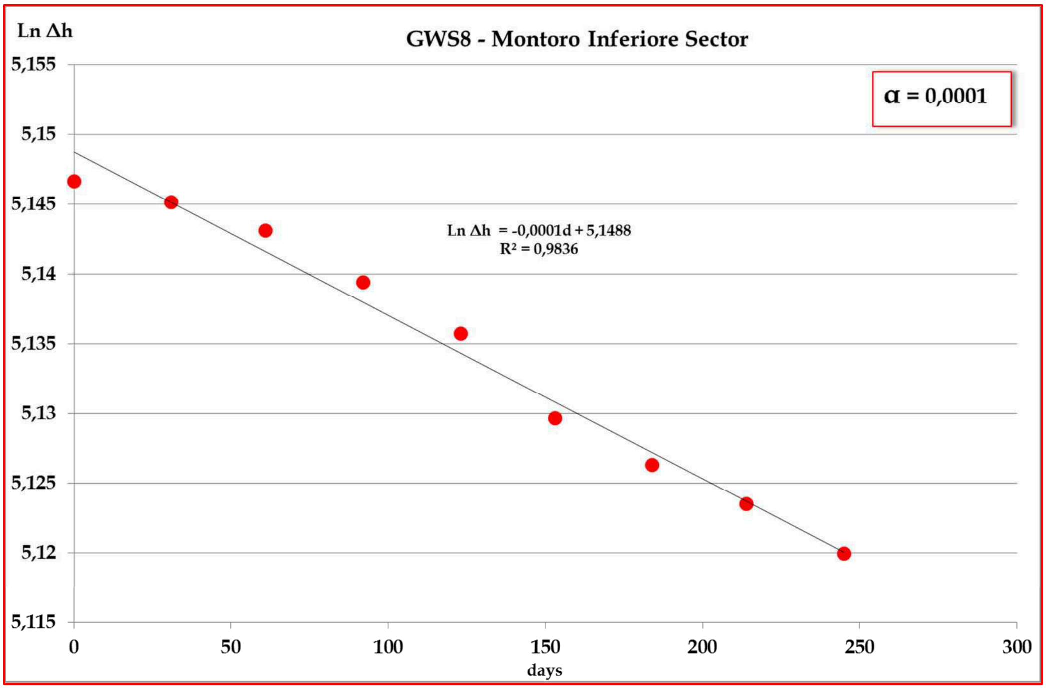


Fig. 5.24 - Recession constant of plain aquifer in Montoro Inferiore sector

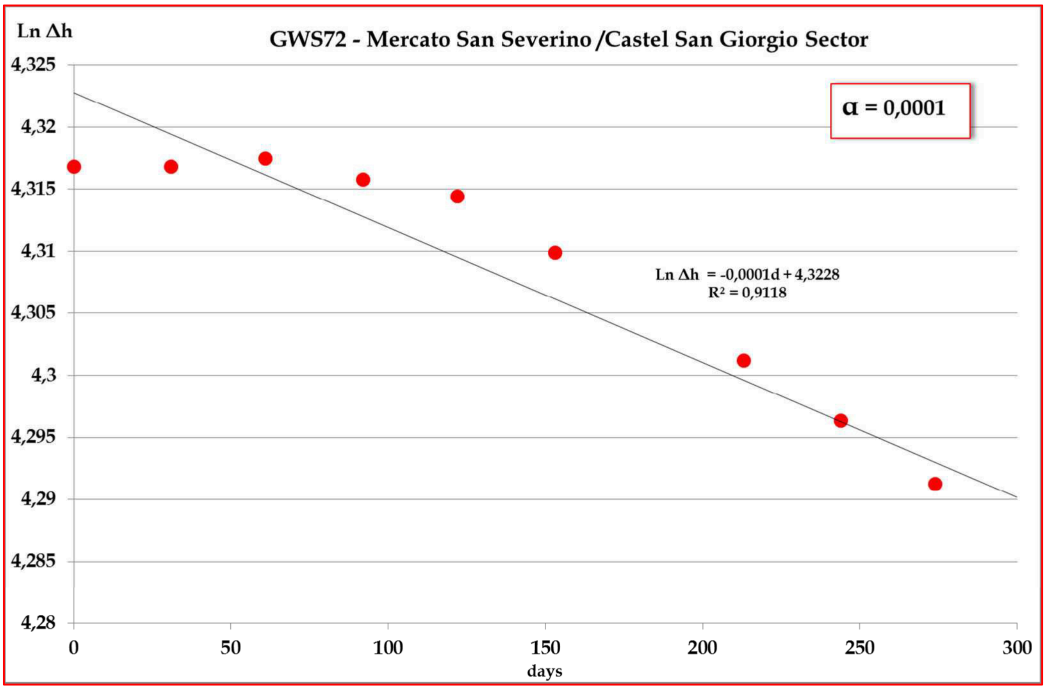


Fig. 5.25 - Recession constant of plain aquifer in Mercato San Severino-Castel San Giorgio sector

Recession constants of the plain aquifer do not change all over the plain; a common value to all the areas can be identified as 1-2 10^{-3} d^{-1}.

Lower values are found in the West sector of Montoro, where the piezometric rising phenomenon is observed.

The transmissivity of the plain aquifer derived from the existing pumping tests is estimated in 10^{-5} m^2/sec in the Montoro sector, where the Argille Variegate are located below the Campanian Ignimbrite; it increases up to 10^{-3} m^2/sec in the area of Pandola and Castel San Giorgio, where the aquifer becomes coarser and its thickness is much larger.

Similarly, recession constants of the carbonate aquifer do not change all over the plain; a common value to all the areas can be identified as 10^{-4} d^{-1}.

Higher values (1,2-1,4 10^{-3} d^{-1}) are found in the sector of Solofra, where in the year 2011 the piezometric rising phenomenon probably involved more carsified carbonate (Fig. 5.25). In the year 2012 the recession constant became comparable with the above mentioned values (10^{-4} d^{-1}).

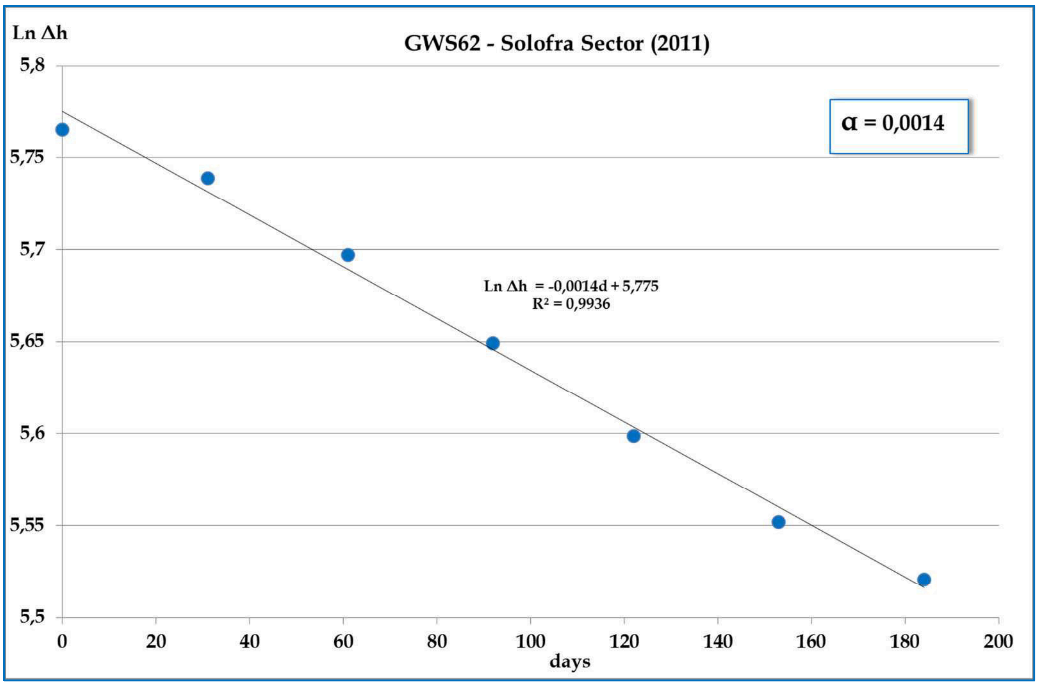


Fig. 5.26 - Recession constant of carbonate aquifer in Solofra sector on 2011

The transmissivity of the carbonate aquifer, derived from the existing pumping tests, is estimated in 10^{-3}-10^{-4} m^2/sec, but such aquifer is characterized by a strong heterogeneity. So the most permeable and carsified areas show a transmissivity of about 10^{-2} m^2/sec.

The seasonal fluctuations for the plain as for the carbonate aquifer were assessed, for the range May 2011 – August 2011, August 2011 – December 2011, May 2011 – December 2011 (Fig. 5.27 to 5.32)

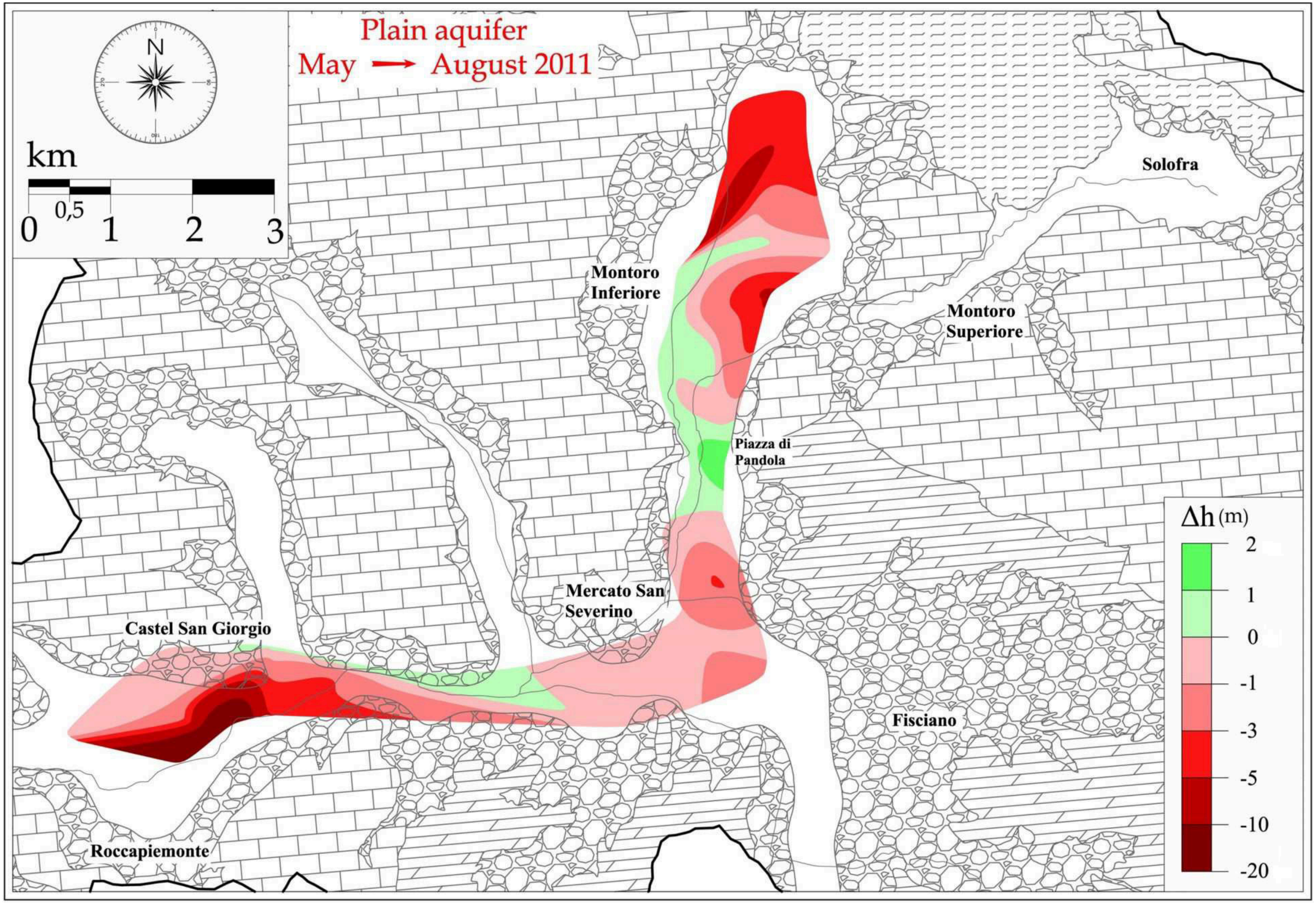


Fig. 5.27 - Seasonal fluctuation of plain aquifer (May - August 2011)

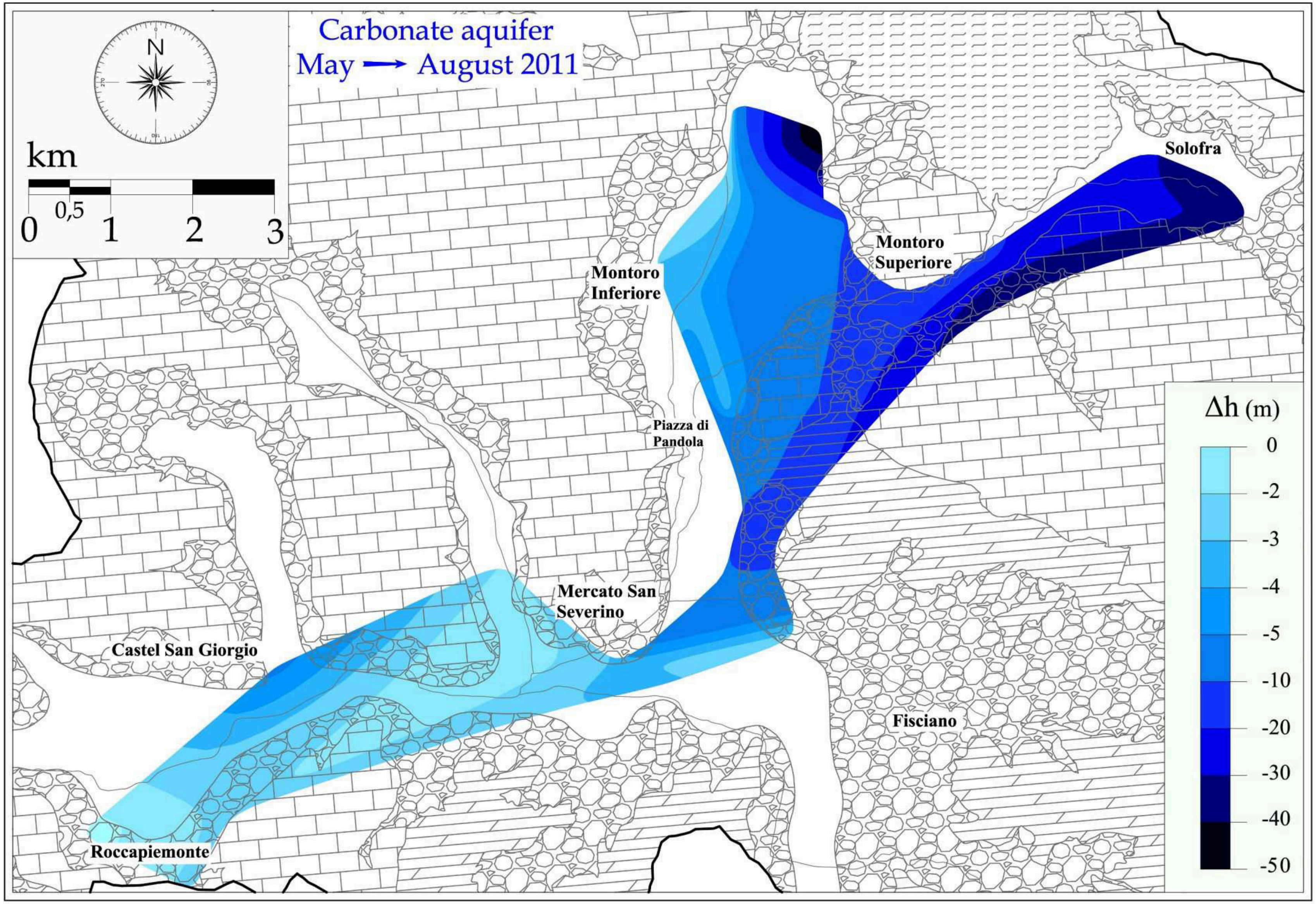


Fig. 5.28 - Seasonal fluctuation of carbonate aquifer (May - August 2011)

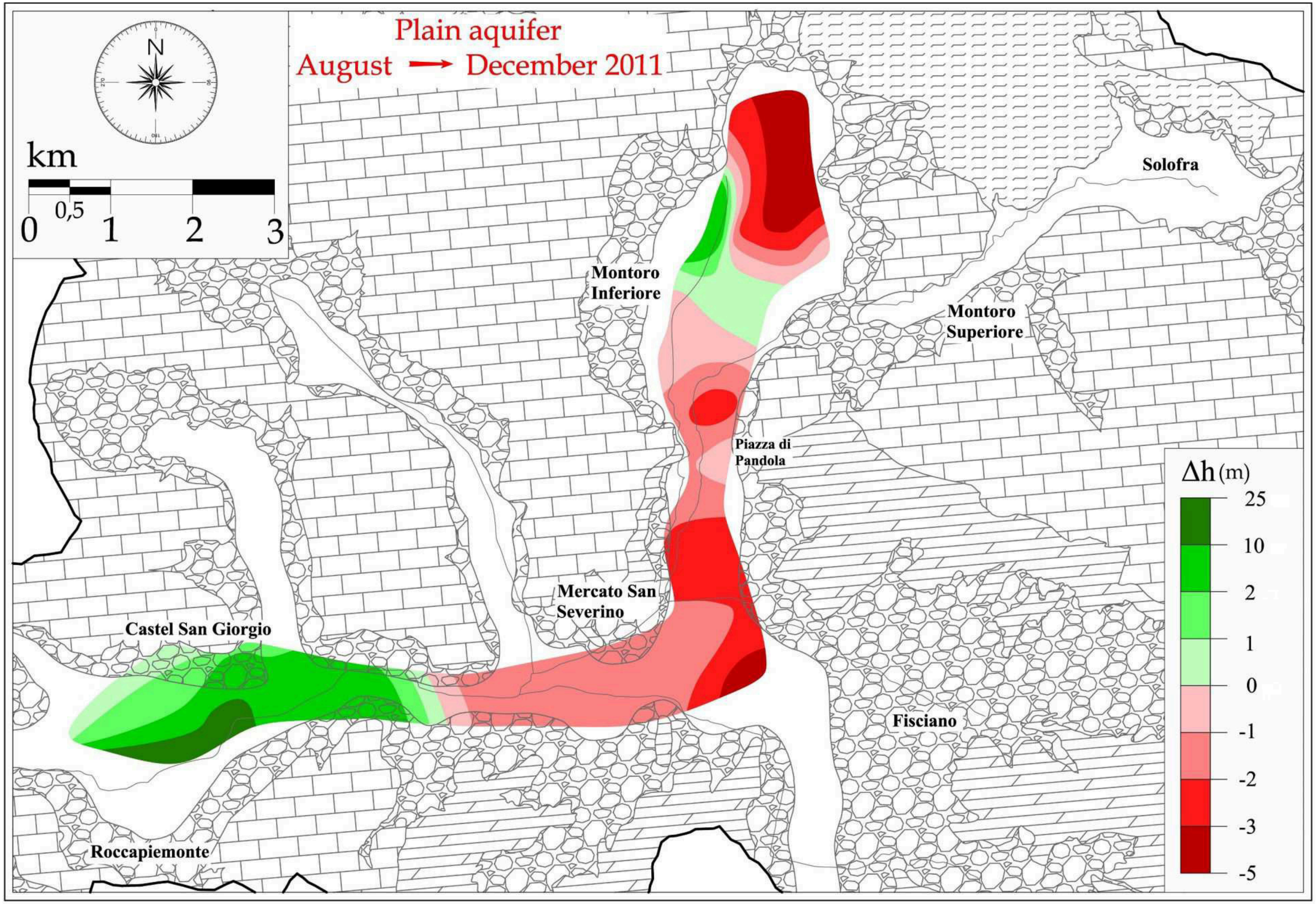


Fig. 5.29 - Seasonal fluctuation of plain aquifer (August - December 2011)

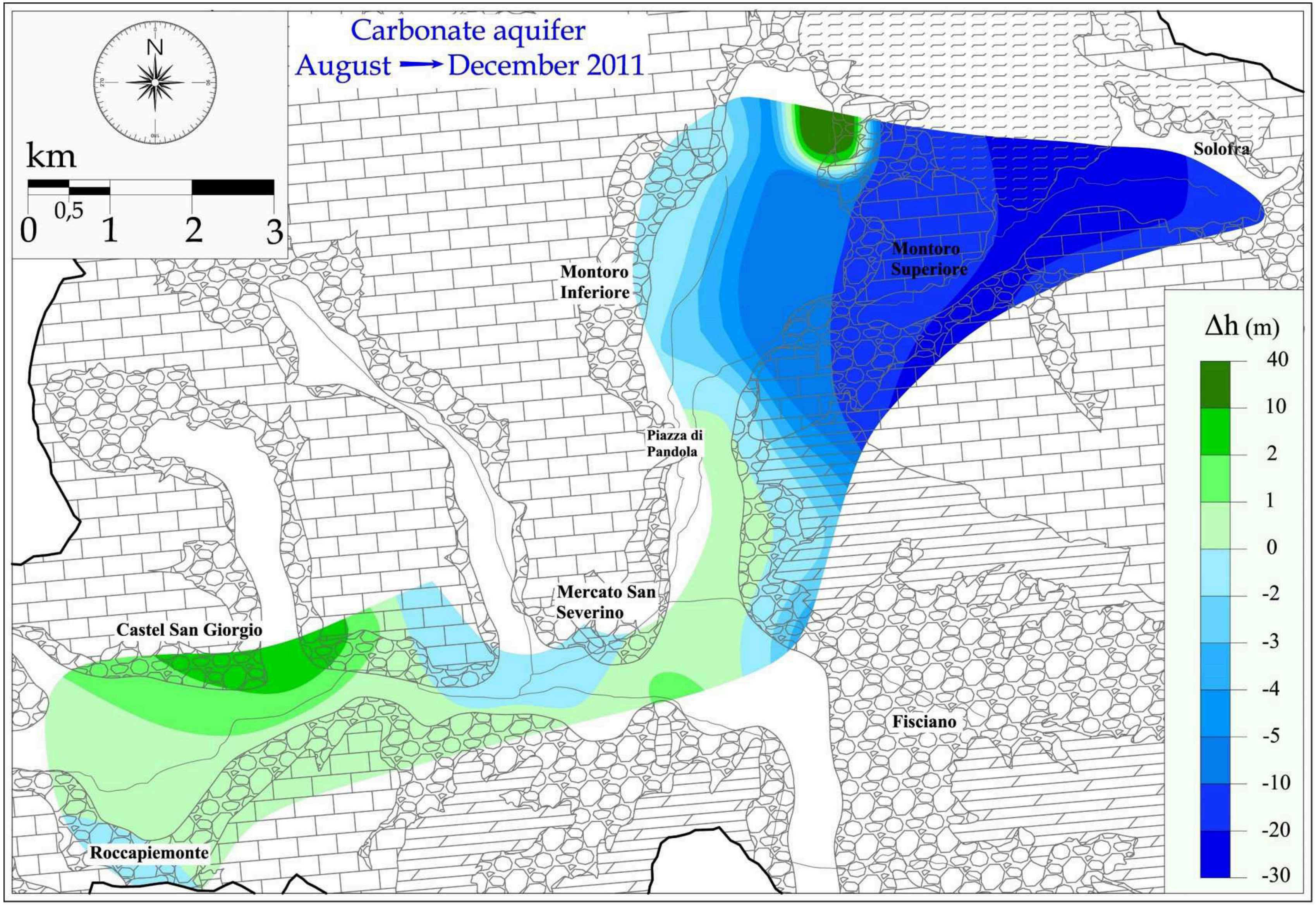


Fig. 5.30 - Seasonal fluctuation of carbonate aquifer (August - December 2011)

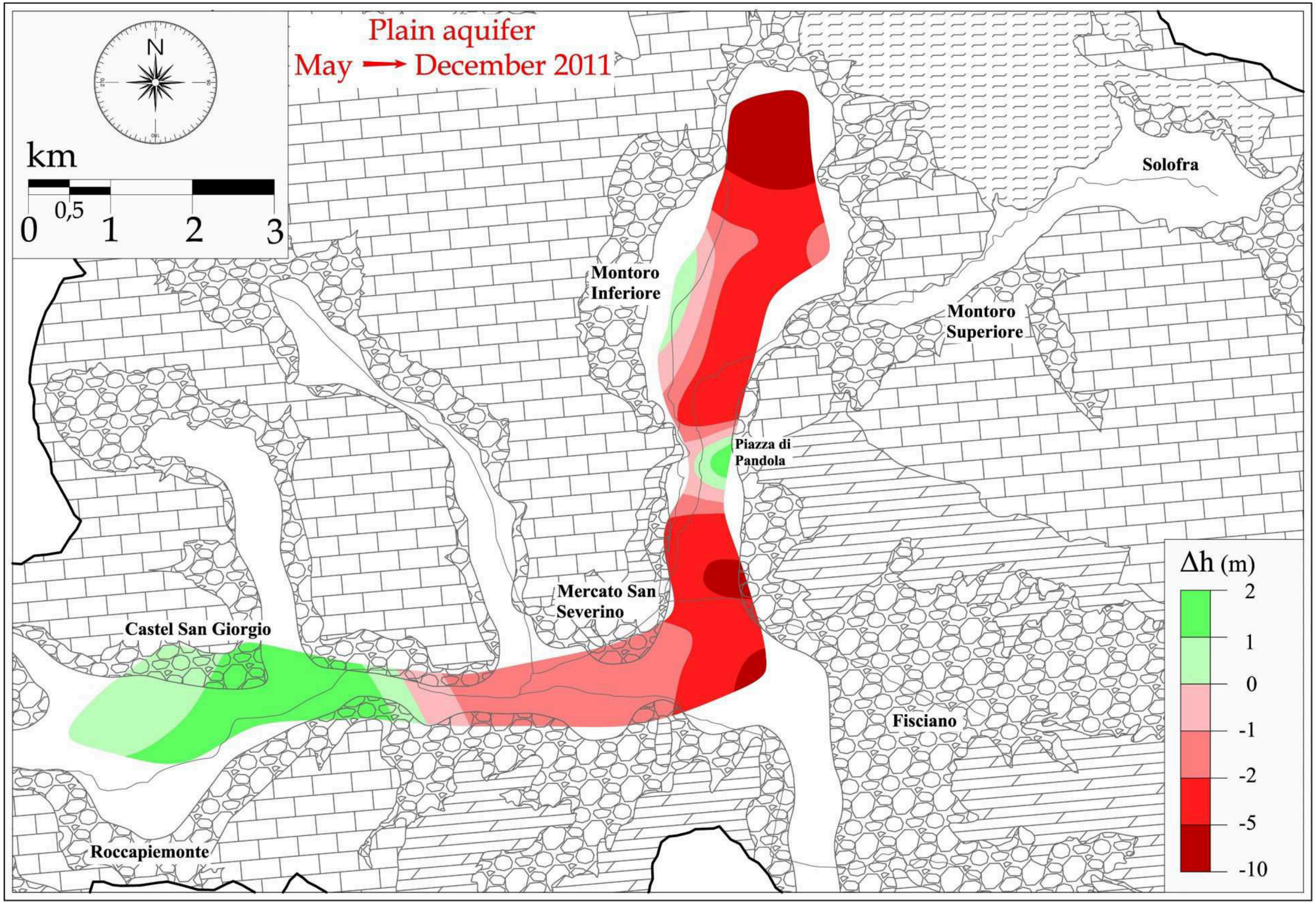


Fig. 5.31 - Seasonal fluctuation of plain aquifer (May - December 2011)

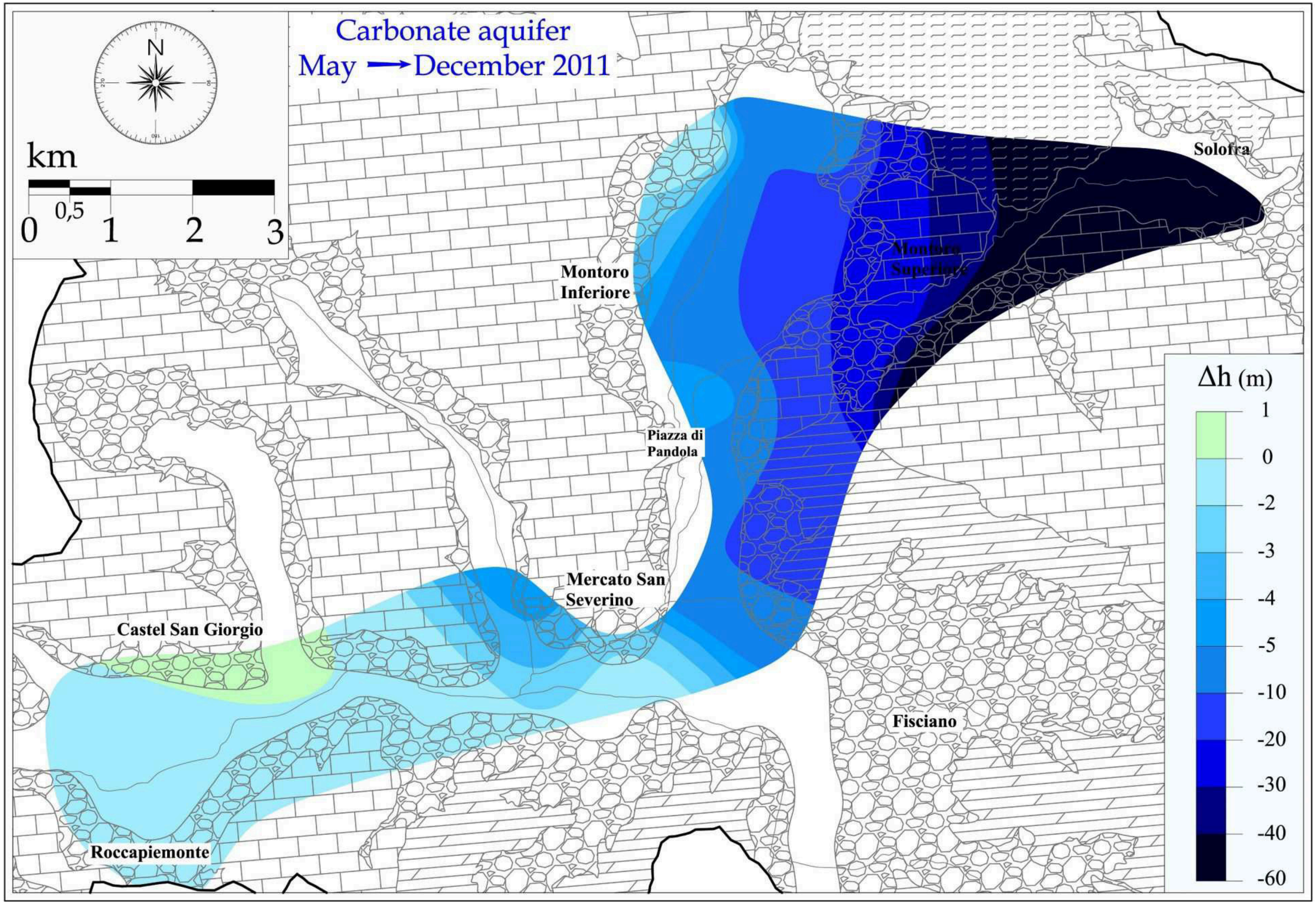


Fig. 5.32 - Seasonal fluctuation of carbonate aquifer (May - Decembere 2011)

The analysis of the piezometric regime provides the control of groundwater resources utilization on seasonal fluctuations as for the plain as for the carbonate aquifer, such as identifies the distribution of the main production sites.

In fact, in selected areas the maximum rising between May and December 2011 or between August and December 2011 corresponds to the maximum lowering between May and August 2011.

Moreover three sectors of the plain characterized by homogeneous hydrodynamic conditions can be set in accordance with specific natural and human states.

The most critical features of hydrogeological setting can be found in the central sector of the plain, where the presence of the main groundwater flow direction remarks the leakage to carbonate aquifer (hydraulic heads of aquifer plain are about 15 m higher than the carbonate one) and reveals, in the so-called Piazza di Pandola area, the outlet of the paleo-endorheic and karst basin (cf. 5.1). Piazza di Pandola and the Fisciano-Mercato San Severino sector are characterised by a similar hydro-stratigraphic architecture that can be associated to an interaction of the two overlapped aquifers. However an inversion of such leakage phenomena may occur due to overpumping in the upper aquifer.

5.3 – GROUNDWATER QUALITY

The elaboration of existing hydrochemical information, which dates back to the period 2003-2004, leads to the improvement of the hydrogeological model and to the detection of the aquifer interactions such as of the critical sites boundary.

According to the hydrogeological scheme, groundwater of the Solofrana River Valley are classified as bicarbonate–calcium, but a complex combination of natural and human processes (dissolution, mixing of different waters, complexation reactions, flow conditions) operates at many levels by establishing broad trends to chloride–sulfate–calcium-sodium-magnesium facies (Fig. 5.33). So there are considerable variations in many parameters, such as electrical conductivity.

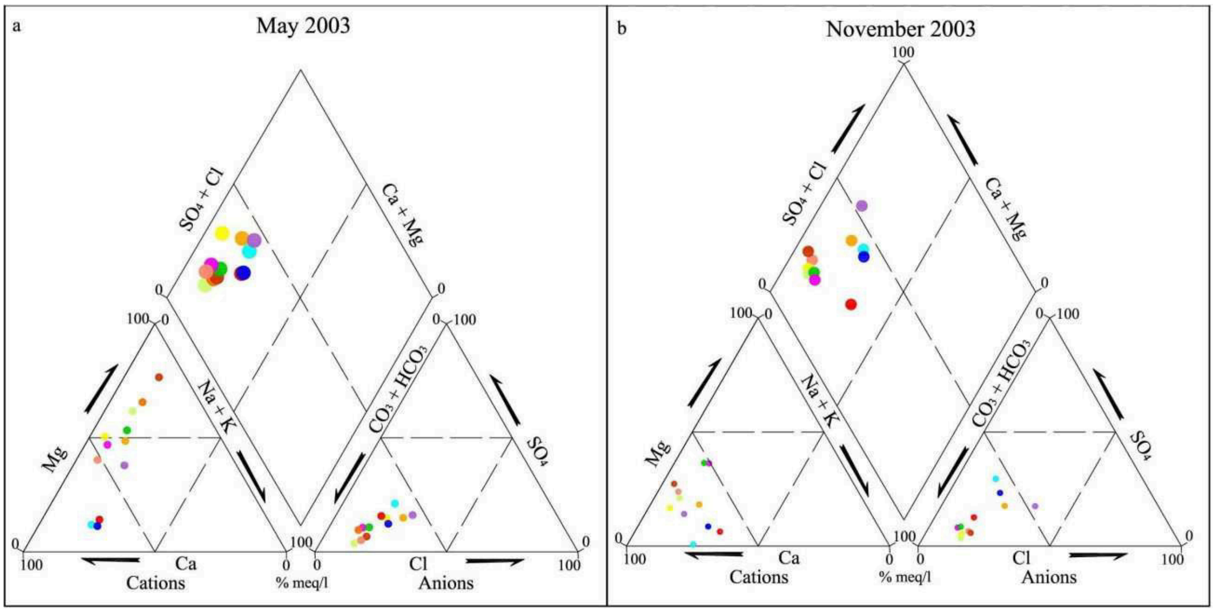


Fig. 5.33 - Piper diagram (2003)

The Schoeller Berkaloff diagrams (Fig. 5.33) describe the main features of the groundwater composition.

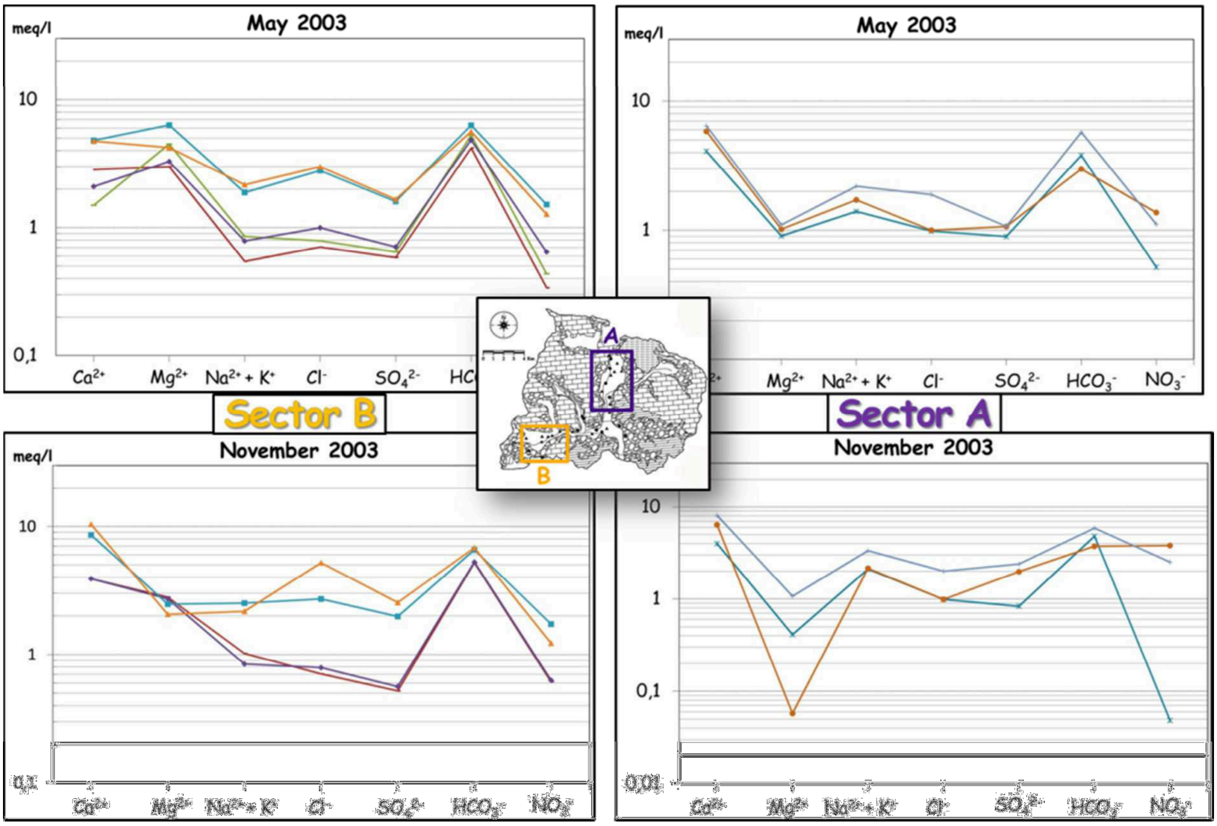


Fig. 34 - Schoeller Berkaloff diagram (2003)

As might be expected the concentrations of major ions are clearly comparable. The apparent anomalies are due to specific flow conditions and human impact. The groundwater samples from the central sector of the valley (A) have high concentrations of Ca^{2+}, whereas the groundwater from the western part of the southern sector (A) are more mineralized and have higher concentrations of Cl^{-} and SO_4^{2-} such as the zinc concentration exceeds the Italian regulation thresholds (D.Lgs. n°152/2006). Hence groundwater samples, for completion of wells at multiple depths, are mainly made up of mixtures of carbonate and plain waters, especially in the central sector of the valley. The analysis of the groundwater hydrochemical profiles in the southern part of the valley, conversely, identifies localized contaminations and potential interactions with surface waters due to the degradation of artificial banks and to periodic river floodings (Adamo et al., 2003). Just in this area, localized downstream of a water treatment system, on July 2010 and November 2010 significant Solofrana river flood events have been recorded (Fig.5.35).

Fig. 5.35 – Photos taken two day after river flood events on July 2010

Groundwater sampling and analyses carried out on July 2010 confirm such hydrochemical framework (Tab. 5.2, Fig. 5.36).

Element	Unit	Detection Limit	Minimum	Maximum	Mean	Standard deviation
T	(°C)		11,00	19,90	15,83	1,87
pH			7,69	8,73	8,05	0,25
E.C.	(µS/cm)		500,00	1495,00	846,00	254,43
HCO_3^-	mg/l	1	248,15	549,70	405,59	74,85
Cl^-	mg/l	0,5	11,00	160,00	39,73	39,68
NO_3	mg/l	2	3,00	44,00	15,08	10,00
NO_2	mg/l	0,5	0,00	0,00	0,00	0,00
SO_4	mg/l	0,5	11,00	130,00	56,57	29,17
PO_4	mg/l	0,005	0,01	0,01	0,01	0,00
Br^-	mg/l	0,04	0,40	1,30	0,73	0,29
Ag	µg/l	0,05	0,05	0,05	0,05	
Al	µg/l	1	1,00	9,00	2,70	2,67
As	µg/l	0,5	0,70	4,40	2,22	0,77
Au	µg/l	0,05	0,07	0,09	0,08	0,01
B	µg/l	5	23,00	119,00	60,07	27,18
Ba	µg/l	0,05	3,04	130,18	28,76	25,56
Be	µg/l	0,05	0,06	0,20	0,11	0,05
Bi	µg/l	0,05	0,00	0,00	0,00	0,00
Br	µg/l	5	20,00	248,00	109,27	56,83
Ca	mg/l	0,05	68,27	182,17	112,24	30,80
Cd	µg/l	0,05	0,09	0,09	0,09	
Ce	µg/l	0,01	0,00	0,00	0,00	0,00
Cl	mg/l	1	13,00	205,00	45,40	49,17
Co	µg/l	0,02	0,02	0,49	0,15	0,15
Cr	µg/l	0,5	9,60	60,00	18,00	9,50
Cs	µg/l	0,01	0,11	2,58	0,68	0,55
Cu	µg/l	0,1	0,30	5,30	1,10	1,00
Dy	µg/l	0,01	0,00	0,00	0,00	0,00
Er	µg/l	0,01	0,01	0,01	0,01	0,00
Eu	µg/l	0,01	0,00	0,00	0,00	0,00
Fe	µg/l	10	0,00	0,00	0,00	0,00
Ga	µg/l	0,05	0,00	0,00	0,00	0,00
Gd	µg/l	0,01	0,01	0,01	0,01	0,00
Ge	µg/l	0,05	0,09	0,09	0,09	
Hf	µg/l	0,02	0,00	0,00	0,00	0,00
Hg	µg/l	0,1	0,00	0,00	0,00	0,00
Ho	µg/l	0,01	0,00	0,00	0,00	0,00
In	µg/l	0,01	0,00	0,00	0,00	0,00
K	mg/l	0,05	5,54	33,05	19,58	8,79
La	µg/l	0,01	0,01	0,07	0,03	0,03
Li	µg/l	0,1	0,60	6,00	2,58	1,40

Element	Unit	Detection Limit	Minimum	Maximum	Mean	Standard deviation
Lu	µg/l	0,01	0,02	0,02	0,02	
Mg	mg/l	0,05	7,90	59,78	29,72	15,43
Mn	µg/l	0,05	0,08	1,65	0,48	0,49
Mo	µg/l	0,1	0,70	14,40	2,83	2,35
Na	mg/l	0,05	10,03	113,75	31,39	20,34
Nb	µg/l	0,01	0,01	0,08	0,03	0,02
Nd	µg/l	0,01	0,04	0,04	0,04	
Ni	µg/l	0,2	0,60	283,40	71,40	141,33
P	µg/l	20	23,00	36,00	29,50	9,19
Pb	µg/l	0,1	0,40	1,80	0,78	0,52
Pd	µg/l	0,2	0,00	0,00	0,00	0,00
Pr	µg/l	0,01	0,00	0,00	0,00	0,00
Pt	µg/l	0,01	0,00	0,00	0,00	0,00
Rb	µg/l	0,01	14,20	90,07	45,08	20,26
Re	µg/l	0,01	0,00	0,00	0,00	0,00
Rh	µg/l	0,01	0,01	0,03	0,01	0,01
Ru	µg/l	0,05	0,00	0,00	0,00	0,00
S	mg/l	1	4,00	54,00	23,17	12,23
Sb	µg/l	0,05	0,07	0,25	0,13	0,04
Sc	µg/l	1	0,00	0,00	0,00	0,00
Se	µg/l	0,5	0,60	2,20	1,21	0,39
Si	µg/l	40	9432,00	31086,00	21449,10	6031,13
Sm	µg/l	0,02	0,00	0,00	0,00	0,00
Sn	µg/l	0,05	0,00	0,00	0,00	0,00
Sr	µg/l	0,01	111,55	1007,51	426,02	175,26
Ta	µg/l	0,02	0,00	0,00	0,00	0,00
Tb	µg/l	0,01	0,00	0,00	0,00	0,00
Te	µg/l	0,05	0,00	0,00	0,00	0,00
Th	µg/l	0,05	0,00	0,00	0,00	0,00
Ti	µg/l	10	0,00	0,00	0,00	0,00
Tl	µg/l	0,01	0,03	0,18	0,08	0,04
Tm	µg/l	0,01	0,00	0,00	0,00	0,00
U	µg/l	0,02	0,49	11,82	3,95	3,14
V	µg/l	0,2	1,90	6,20	4,07	1,29
W	µg/l	0,02	0,03	0,56	0,19	0,12
Y	µg/l	0,01	0,01	0,13	0,05	0,03
Yb	µg/l	0,01	0,01	0,03	0,02	0,01
Zn	µg/l	0,5	0,50	738,10	60,35	147,95
Zr	µg/l	0,02	0,02	0,10	0,04	0,02

Tab. 5.2 - Hydrochemical composition assessed on July 2010

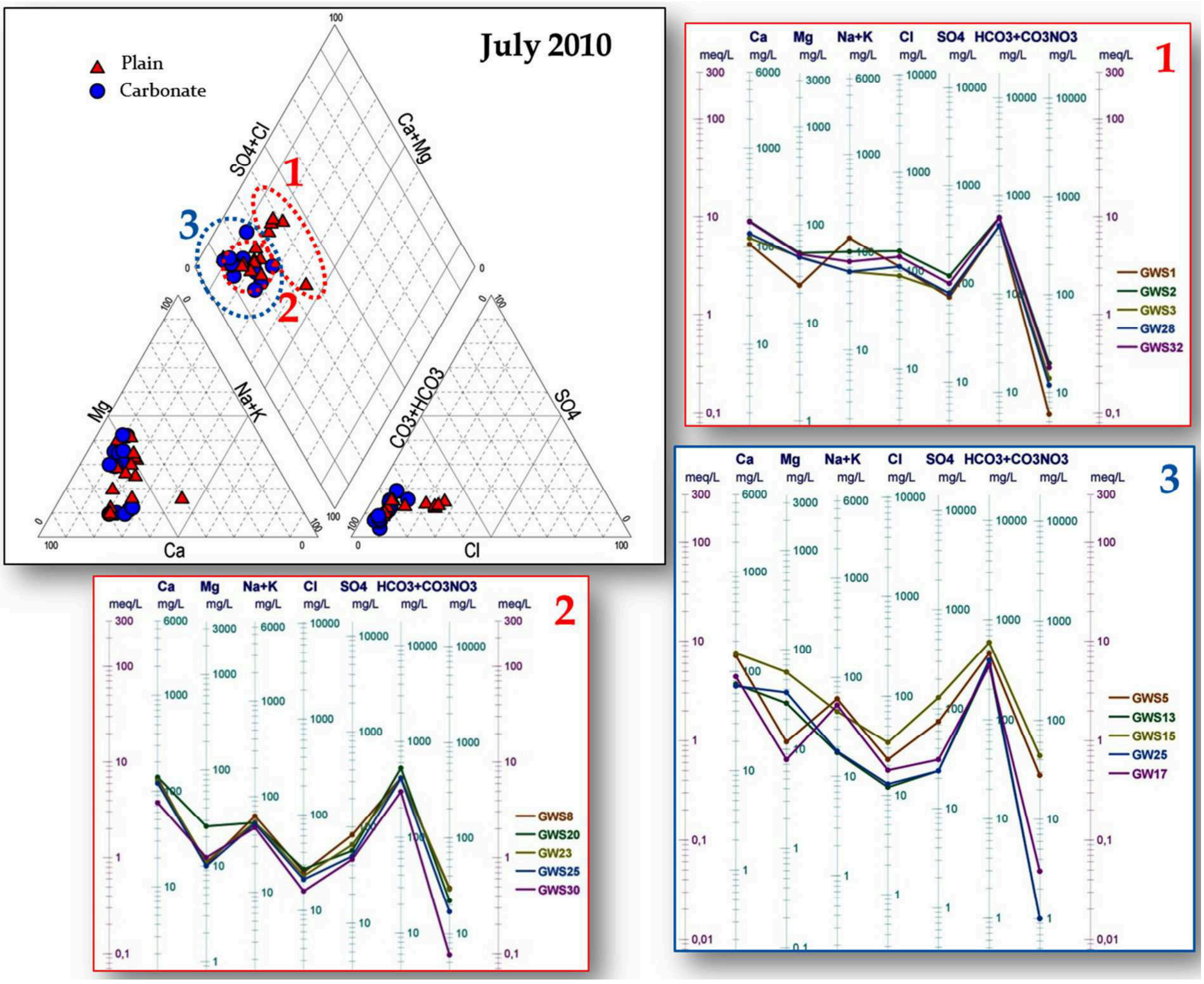


Fig. 5.36 - Piper e Schoeller Berkaloff diagrams (July 2010)

With regard to the Italian regulation thresholds the environmental state of groundwater resources of the Solofrana River Valley was not worring, except for Cr and Ni in the southern sector, corresponding to the river flooding areas.

But at basin scale two homogenous zones, characterized by different impact on carbonate aquifer and on plain aquifer were recognized according to the hydrodynamic setting and to main characteristics of the potential sources of contamination (Tab. 5.3).

Sample		T (°C)	Ph	E.C. (µS/cm)	Cl$^-$ mg/l	NO$_3^-$ mg/l	SO$_4^{2-}$ mg/l	As µg/l	B µg/l	Be µg/l	Cd µg/l	Co µg/l	Cr µg/l	Cu µg/l	Mn µg/l	Na mg/l	Ni µg/l	Pb µg/l	Zn µg/l
*					200	50	250	10	1000	4	5	50	50	1000	50	200	20	10	3000
Plain Aquifer	GWS1	19,9	7,98	1107	110	6	73	2,9	119	<0.05	<0.05	0,49	60	5,3	0,5	113,75	<0.2	<0.1	35,2
	GWS2	14,3	7,7	1495	160	20	120	3,5	79	0,06	<0.05	0,07	30,8	0,6	<0.05	69,3	<0.2	<0.1	11,8
	GWS3	14,5	7,99	1113	88	14	81	2,8	62	<0.05	<0.05	0,08	23,8	0,7	0,6	43,12	<0.2	<0.1	1,1
	GWS8	17,9	8,02	848	25	30	83	1,1	67	<0.05	<0.05	<0.02	9,6	2	<0.05	29,62	<0.2	<0.1	63,8
	GWS10	14,6	7,99	705	18	9	32	1,3	46	<0.05	<0.05	<0.02	15,1	0,9	<0.05	18,96	<0.2	<0.1	2,9
	GWS12	13,9	8,45	560	11	<2	24	2,3	24	<0.05	<0.05	<0.02	13,5	0,9	1,38	10,03	0,9	<0.1	8,5
	GWS20	17,4	7,99	917	27	22	57	2,1	67	0,11	<0.05	<0.02	15,7	0,7	0,09	27,5	<0.2	0,4	7,8
	GWS21	17,9	8,03	783	25	9	40	1,6	45	<0.05	<0.05	<0.02	18,1	0,6	0,4	25,32	<0.2	0,8	54,4
	GWS22	16	7,95	893	27	25	71	2,6	101	<0.05	<0.05	<0.02	13,1	0,5	<0.05	29,51	<0.2	<0.1	6
	GW23	17,8	8,09	819	23	29	66	2,1	67	<0.05	<0.05	<0.02	10,4	0,6	<0.05	28,27	<0.2	<0.1	2,2
	GWS25	16,7	7,98	764	21	17	50	1,9	73	0,12	<0.05	<0.02	12,5	2,6	0,08	26,84	<0.2	0,6	1,4
	GW27	16,5	7,87	980	49	13	65	2,6	58	0,07	<0.05	0,02	20,4	0,7	<0.05	33,97	<0.2	<0.1	<0.5
	GW28	13,8	7,98	1170	110	12	79	3,1	57	<0.05	<0.05	0,1	22,4	1,5	0,1	44,66	283,4	<0.1	13,4
	GWS30	17,1	7,85	580	16	6	46	0,7	48	<0.05	<0.05	<0.02	11,3	1	0,18	23,69	<0.2	1,8	20
	GWS31	15,9	8,27	794	24	10	44	2,6	62	<0.05	<0.05	<0.02	18,5	1,2	<0.05	27,18	<0.2	<0.1	0,8
	GWS32	17,4	7,95	1441	140	18	100	4,4	115	<0.05	<0.05	0,13	26,7	1,5	0,09	47,97	<0.2	<0.1	15,3
Carbonate Aquifer	GWS4	11	7,95	685	16	8	28	1,6	34	<0.05	<0.05	<0.02	14,8	0,4	<0.05	15,03	<0.2	<0.1	0,5
	GWS5	16,2	7,69	852	23	28	75	2,3	87	0,07	0,09	<0.02	12,2	2,9	0,28	31,6	0,6	<0.1	64,2
	GWS6	15,9	7,74	622	22	9	46	2,7	84	0,2	<0.05	<0.02	12,3	0,6	<0.05	31,29	<0.2	<0.1	50,3
	GWS9	18,1	7,75	740	20	17	58	1,7	68	<0.05	<0.05	<0.02	10,3	0,4	<0.05	29,06	<0.2	<0.1	5,7
	GWS13	14,2	8,49	556	12	<2	24	2,4	28	<0.05	<0.05	<0.02	13,8	0,3	<0.05	11,44	0,7	<0.1	7,8
	GWS14	15,1	8,73	500	19	<2	11	1,3	27	<0.05	<0.05	<0.02	13,3	0,8	<0.05	17,45	<0.2	<0.1	62,3
	GWS15	17,4	7,98	1187	34	44	130	1,1	37	<0.05	<0.05	<0.02	15,9	0,9	0,47	25,02	<0.2	<0.1	3,8
	GWS16	16,9	7,96	908	32	14	60	2,5	60	<0.05	<0.05	0,03	20,5	0,9	0,45	31,95	<0.2	0,5	738,1
	GWS17	14,8	8,45	720	23	3	29	2,2	33	<0.05	<0.05	0,15	17,6	1,1	1,65	20,71	<0.2	<0.1	307,9
	GW17	12,6	7,85	570	18	3	31	2,7	64	<0.05	<0.05	<0.02	13,1	0,5	<0.05	26,59	<0.2	<0.1	1,2
	GW24	14	7,93	1059	50	17	83	2,5	106	<0.05	<0.05	0,29	25,9	0,6	<0.05	55,35	<0.2	<0.1	0,7
	GW25	16,4	8,16	615	13	<2	24	2,1	23	<0.05	<0.05	<0.02	13,6	0,7	<0.05	11,76	<0.2	<0.1	<0.5
	GW26	15	8,25	685	19	3	30	1,7	27	<0.05	<0.05	<0.02	16,6	1	<0.05	18,54	<0.2	<0.1	21,4
	GWS34	15,7	8,35	712	17	6	37	2,2	34	<0.05	<0.05	<0.02	18,1	0,7	<0.05	16,08	<0.2	0,6	181,4

Tab. 5.3 - Environmental state of groundwater resouces
(*Italian regulation thresholds - Dlgs 152/2006 - Dlgs 31/2001)

The identification of the most significant indicators of chemical groundwater characteristics that may be related to human activities leads to a better definition of both agricultural and industrial impact on groundwater resources.

The correlation and the combination of such indicators point out the indexes that are representative of the chief hydrochemical imprint due to agricultural or industrial activities. For the examined aquifer system the correlation between NO_3^- and E.C. as well as between NO_3^- and sulfate/chloride ratio is very effective. These correlations identify two different trends (Fig. 5.37) according to the characteristics of the potential sources of contamination:

1. in the central sector, it was observed a direct correlation between NO_3^- and sulfate/chloride ratio. In this area, corresponding to the so-called Piazza di Pandola, agricultural activities are widespread. In this site, historically devoted to tobacco cultivation, floriculture practices are very important;
2. in the southern sector, it was observed an inverse correlation between the same indexes. In this area are localized the main sewage and industrial plants.

These two sectors differ for the correlation between NO_3^- and E.C. too.

As for the carbonate aquifer the consequent values of such specific indexes (Fig. 5.29) validate the above mentioned hydrostratigraphic architecture and hydrodynamic conditions, that is to say the natural attenuation due to the plain aquifer.

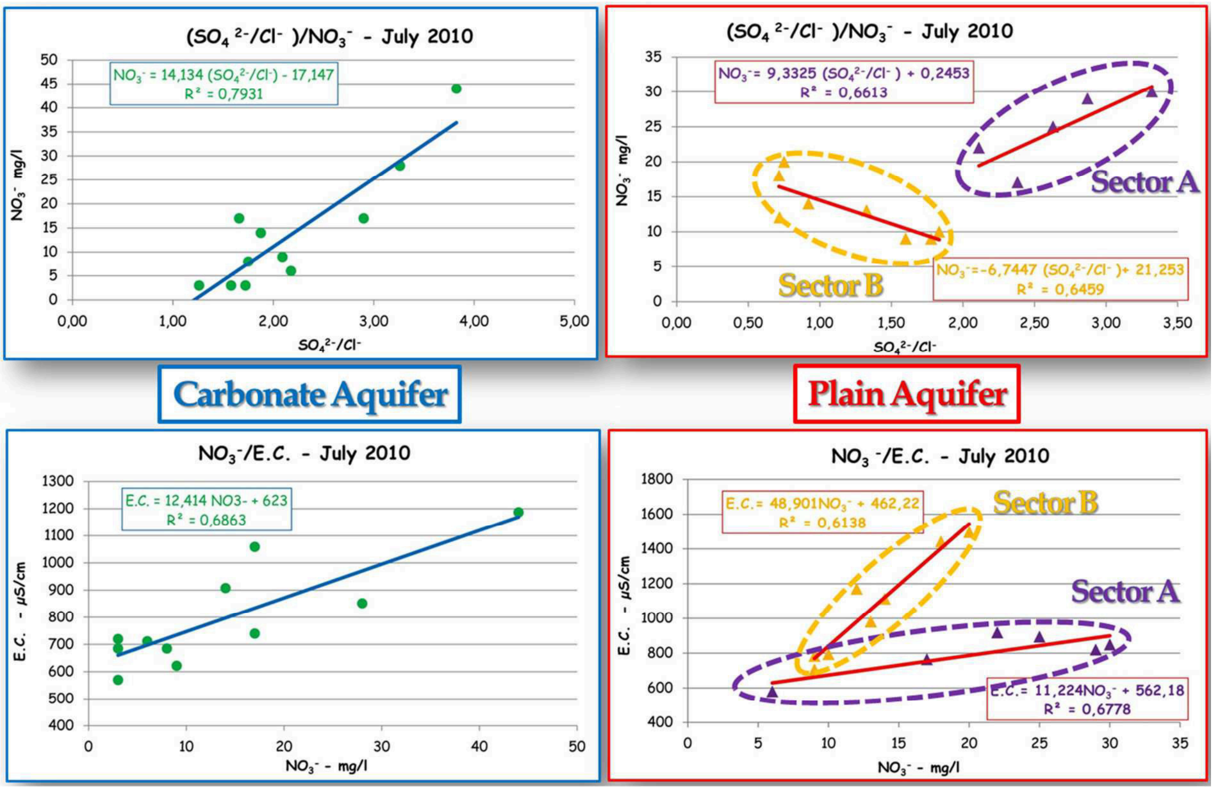


Fig. 5.37 - Correlation between main composition indexes

In figures 5.38 and 5.39 are shown the most relevant indexes of groundwater composition due to human activities, which confirm and exemplify the different impact on carbonate aquifer and on plain aquifer in the two recognized sectors of the plain.

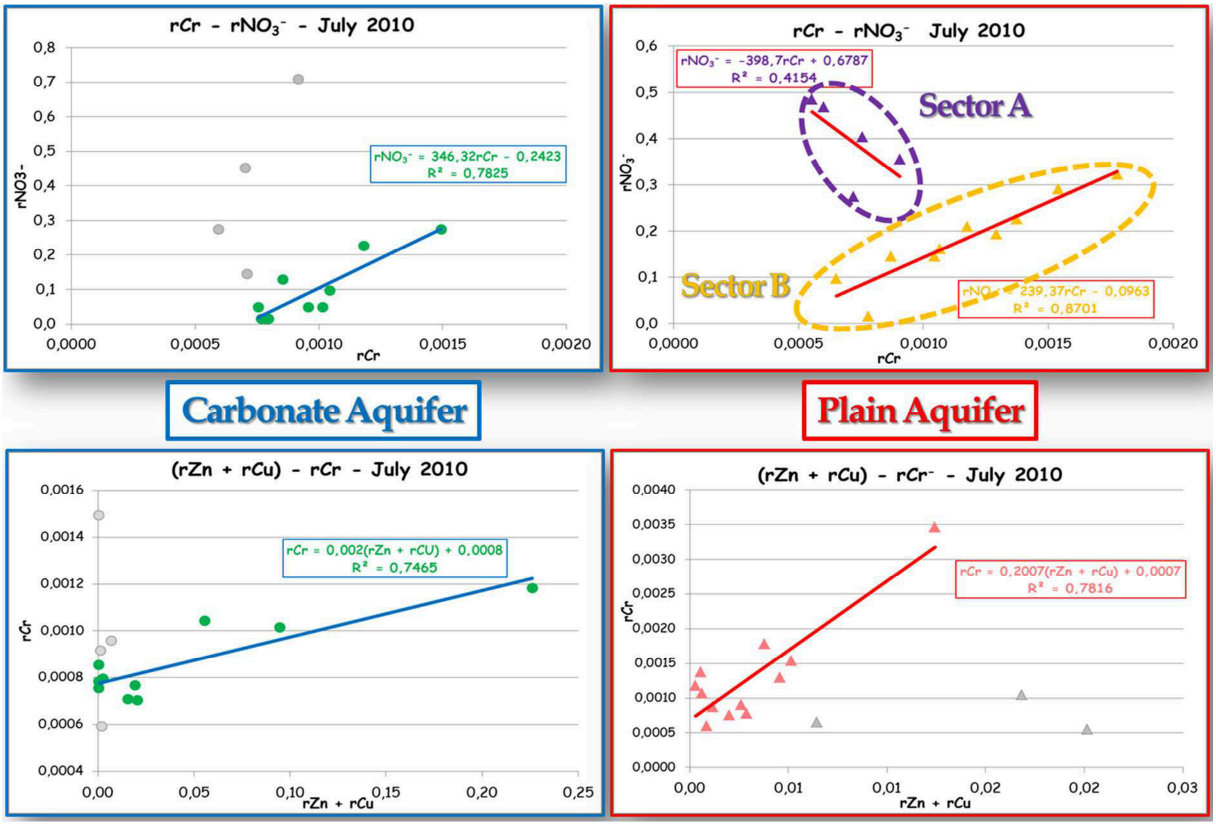


Fig. 5.38 - Composition indexes

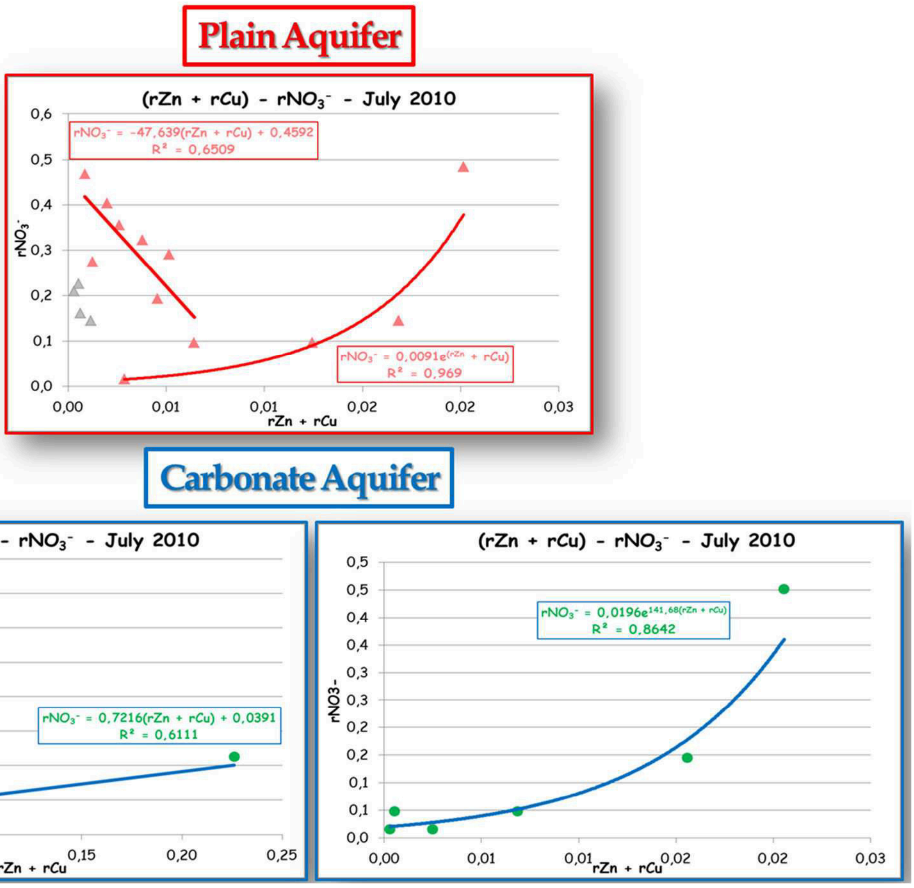


Fig. 5.39 - Composition indexes

Instead the "Spatial distribution of the groundwater composition indicators", namely copper and zinc for agricultural practices and chromium for industrial activities, proves that the most hazardous areas correspond just to the same above mentioned two sectors of the valley. In the southern sector the high risk of contamination of plain aquifer is mainly due to the anthropogenic impact, so the higher concentrations of toxic elements (e.g. Cr) were recorded. As for the carbonate aquifer a different natural attenuation capacity was assessed. Especially in the Piazza di Pandola area the bad completions of many wells locally increases the carbonate aquifer vulnerability.

At basin scale the results of the multivariate statistical analysis improved the identification of a number of homogeneous zone, characterized by different natural and/or anthropogenic conditions, even in such complex aquifer systems.

The statistical procedure described in paragraph 4.4 was applied.

The hydrogeological and hydrostratigraphic conceptual model led the choice of the groundwater sample representative either of the "Substratum End-Member" (*S.E.M.*) or of the "Plain End-Member"(*P.E.M.*). Both hydrodynamic and socio-economic conditions recommended the composition indexes, which had to be used in the vector algebra.

According to the Piper (picture X) and Schoeller Berkaloff diagrams (fig.XX), the sample GW17 was selected as S.E.M.. This groundwater sample derives from the Labso Spring, the carbonate spring located in the Montoro Inferiore area. The sample GWS32 was selected as P.E.M.; this groundwater sample derives from a well located in the Castel San Giorgio area.

The table 5.4 shows the groundwater composition indexes, representative both natural and anthropogenic features, used in vector algebra procedure. The indexes named "natural" depend mostly on natural phenomena that affect the groundwater chemical evolution (i.e. dissolution, mixing of different waters, complexation reactions).

Groundwater composition indexes	
Natural	*Anthropogenic*
rSO_4/rCl	NO_3/E.C.
rMg/rCa	rCr/rNO_3
rK/rNa	(rCu+rZn)/rCr
rNa/rCa	$(rCu+rZn)/rNO_3$
rBr/rCl	rB/rLi
(rCa+rMg)/(rNa+rK)	
(rNa + rK)/rCl	
$(rSO_4/rCl)/rNO_3$	
Idca	
$rHCO_3/(rCl + rSO_4)$	

Tab. 5.4 - Grondwater composition indexes combined in the vector algebra procedure

The indexes named "anthropogenic" depend mostly on human activities and derive from a specific correlation analysis (i.e. Fig. 5.37 – 5.38 – 5.39).

The table 5.5 shows the values of such composition indexes for each sample collected on July 2010.

Indexes	GWS1	GWS2	GWS3	GWS4	GWS5	GWS6	GWS8	GWS9	GWS10	GWS12	GWS13	GWS14	GWS15	GWS16	GWS17
rSO_4/rCl	0,490	0,554	0,680	1,292	2,407	1,544	2,451	2,141	1,313	1,611	1,477	0,427	2,823	1,384	0,931
rMg/rCa	0,381	0,474	0,651	0,885	0,135	0,180	0,125	0,149	0,886	0,762	0,639	0,569	0,644	0,569	0,505
rK/rNa	0,134	0,270	0,284	0,391	0,546	0,533	0,656	0,553	0,367	0,325	0,306	0,330	0,483	0,268	0,319
rNa/rCa	0,942	0,331	0,309	0,167	0,192	0,284	0,191	0,221	0,199	0,124	0,133	0,223	0,143	0,228	0,170
rBr/rCl	0,003	0,004	0,004	0,006	0,004	0,004	0,004	0,004	0,005	0,008	0,007	0,005	0,007	0,007	0,004
(rCa+rMg)/(rNa+rK)	1,293	3,502	4,162	8,095	3,832	2,710	3,564	3,348	6,928	10,755	9,410	5,295	7,779	5,418	6,730
(rNa + rK)/rCl	1,808	0,848	0,970	2,015	3,275	3,362	3,026	3,478	2,220	1,863	1,920	1,883	1,683	1,951	1,831
NO_3/E.C.	0,005	0,013	0,013	0,012	0,033	0,014	0,035	0,023	0,013	0,002	0,002	0,002	0,037	0,015	0,004
$(rSO_4/rCl)/rNO_3$	5,063	1,716	3,009	10,013	5,331	10,634	5,065	7,808	9,041	99,866	91,543	26,499	3,977	6,130	19,237
Idca	-0,280	0,155	0,034	-0,062	-0,170	-0,243	-0,176	-0,201	-0,080	-0,043	-0,051	-0,090	-0,053	-0,088	-0,067
rCr/rNO_3	0,036	0,006	0,006	0,007	0,002	0,005	0,001	0,002	0,006	0,048	0,049	0,048	0,001	0,005	0,021
(rCu+rZn)/rCr	3,5934	2,1381	0,4056	0,3267	29,2054	21,9541	36,3825	3,1468	1,3438	3,7030	3,1162	25,1705	1,5764	191,1878	93,1204
$(rCu+rZn)/rNO_3$	0,1285	0,0118	0,0025	0,0022	0,0455	0,1073	0,0416	0,0068	0,0081	0,1788	0,1538	1,1971	0,0020	1,0011	1,9536
$rHCO_3/(rCl + rSO_4)$	1,578	1,285	1,744	6,379	3,003	3,117	2,412	3,076	5,905	6,985	6,651	6,558	2,414	3,828	5,853
rB/rLi	47,742	44,745	36,181	54,563	44,089	64,705	26,880	27,862	73,820	57,772	89,868	51,995	27,405	27,511	45,393

Indexes	GW17	GWS20	GWS21	GWS22	GW23	GW24	GWS25	GW25	GW26	GW27	GW28	GWS30	GWS31	GWS32	GWS34
rSO_4/rCl	1,272	1,559	1,181	1,941	2,119	1,226	1,758	1,363	1,166	0,979	0,530	2,123	1,354	0,527	1,607
rMg/rCa	0,147	0,305	0,490	0,173	0,142	0,200	0,136	0,864	0,686	0,665	0,573	0,269	0,707	0,469	0,502
rK/rNa	0,568	0,550	0,248	0,547	0,530	0,290	0,552	0,320	0,316	0,308	0,244	0,598	0,355	0,393	0,332
rNa/rCa	0,261	0,172	0,194	0,190	0,192	0,357	0,195	0,143	0,185	0,280	0,286	0,274	0,257	0,234	0,133
rBr/rCl	0,005	0,013	0,007	0,003	0,004	0,004	0,004	0,007	0,005	0,005	0,004	0,006	0,004	0,003	0,005
(rCa+rMg)/(rNa+rK)	2,804	4,895	6,151	4,002	3,889	2,607	3,762	9,848	6,917	4,541	4,426	2,895	4,908	4,507	8,452
(rNa + rK)/rCl	3,570	2,434	1,949	2,607	2,899	2,202	3,059	1,841	1,980	1,398	0,779	3,647	2,366	0,736	1,943
NO_3/E.C.	0,005	0,024	0,011	0,028	0,035	0,016	0,022	0,002	0,004	0,013	0,010	0,010	0,013	0,012	0,008
$(rSO_4/rCl)/rNO_3$	26,276	4,392	8,137	4,815	4,529	4,469	6,411	84,502	24,090	4,671	2,739	21,932	8,391	1,816	16,603
Idca	-0,237	-0,117	-0,077	-0,149	-0,161	-0,189	-0,171	-0,046	-0,071	-0,063	0,075	-0,233	-0,115	0,267	-0,057
rCr/rNO_3	0,016	0,003	0,007	0,002	0,001	0,005	0,003	0,049	0,020	0,006	0,007	0,007	0,007	0,005	0,011
(rCu+rZn)/rCr	0,6941	2,8781	16,1204	2,6373	1,4367	0,2698	1,7292	0,3784	7,1657	0,2523	3,5380	9,8695	0,5833	3,3456	53,3623
$(rCu+rZn)/rNO_3$	0,0108	0,0073	0,1159	0,0049	0,0018	0,0015	0,0045	0,0184	0,1418	0,0014	0,0236	0,0665	0,0039	0,0177	0,5756
$rHCO_3/(rCl + rSO_4)$	4,159	3,965	4,946	2,818	2,855	2,208	3,548	6,997	5,730	2,565	1,569	2,887	4,338	1,449	5,580
rB/rLi	47,403	64,512	50,976	62,742	56,098	92,786	43,931	44,292	39,996	30,187	49,894	44,017	44,221	36,910	72,750

Tab. 5.5 - Values of Natural and Anthropogenic groundwater composition indexes

The value of the G.I. (see the section 4.4) is **0.38574,** as shown in the following table:

S.E.M = GW17 **P.E.M. = GWS32**

Indexes	GW17	GWS32	n°	G.I.
rSO4/rCl	0,450	0,187		
rMg/rCa	0,165	0,529	2 >	0,40644
rK/rNa	0,865	0,599	3 >	0,72165
rNa/rCa	0,277	0,248	4 >	0,74144
rBr/rCl	0,379	0,268	5 >	0,76443
(rCa+rMg)/(rNa+rK)	0,261	0,419	6 >	0,75469
(rNa + rK)/rCl	0,979	0,202	7 >	0,59785
NO3/C.E.	0,142	0,338	8 >	0,57789
(rSO4/rCl)/rNO3	0,263	0,018	9 >	0,56487
Idca	0,079	1,000	10 >	0,3399
rCr/rNO3	0,511	0,398	11 >	0,38048
(rCu+rZn)/rCr	0,004	0,017	12 >	0,38046
(rCu+rZn)/rNO3	0,006	0,009	13 >	0,38047
rHCO3/(rCl + rSO4)	0,594	0,207	14 >	0,38459
rB/rLi	0,319	0,108	15 >	0,38574

Tab. 5.6 - Output table of formula (1)

PLAIN			**SUBSTRATUM**		
	S.I.	**P.I.**		**S.I.**	**P.I.**
GWS1	0,472964	0,26184832	GWS4	0,638173	0,647043
GWS2	0,421059	0,961785631	GWS5	0,751877	0,444359
GWS3	0,479869	0,8885579	GWS6	0,925605	0,427673
GWS8	0,695676	0,426233741	GWS9	0,842451	0,422088
GWS10	0,659471	0,638179964	GWS13	0,613075	0,445461
GWS12	0,579813	0,443888648	GWS14	0,587838	0,429894
GWS20	0,748619	0,564512251	GWS15	0,509988	0,608385
GWS21	0,707402	0,643274154	GWS16	0,444706	0,444416
GWS22	0,77372	0,530626074	GWS17	0,502241	0,428089
GW23	0,725964	0,478093382	GW17	1	0,385744
GWS25	0,868463	0,492704678	GW24	0,72682	0,48094
GW27	0,60105	0,776201367	GW25	0,565846	0,457382
GW28	0,441427	0,913438787	GW26	0,694767	0,607651
GWS30	0,939391	0,418725398	GWS34	0,679959	0,601274
GWS31	0,739806	0,642966753			
GWS32	0,385744	1			

Tab. 7 - S.I. and P.I. for each groundwater sample. In red are shown the samples of the aquifer plain; in blue are the samples of the carbonate aquifer.

For each sample the S.I. and the P.I. were estimated, as shown in table 5.7.

The associated scatter plot (Fig. 5.40) points out three groups of groundwater samples.

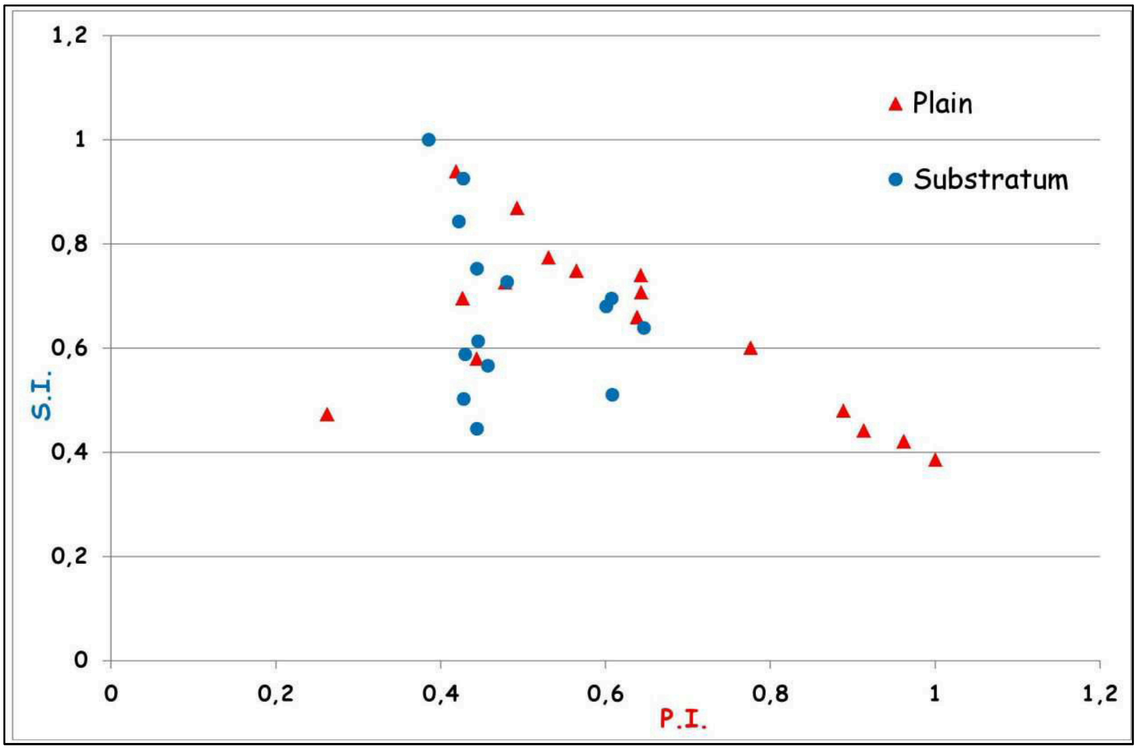


Fig. 5.40 - Distribution of sample based on S.I. and P.I

Therefore, a K-means clustering analysis was performed to identify 3 clusters. The table 5.8 shows the distribution of all samples in the three recognized clusters and the distance of each sample from the centre of the cluster.

Cluster Membership

Sample	Cluster	Distance
GWS1	1	,272
GWS2	2	,061
GWS3	2	,025
GWS4	1	,128
GWS5	1	,113
GWS6	3	,011
GWS8	1	,092
GWS9	3	,080
GWS10	1	,121
GWS12	1	,094
GWS13	1	,080
GWS14	1	,075
GWS15	1	,165
GWS16	1	,196
GWS17	1	,140
GW17	3	,100
GWS20	1	,096
GWS21	1	,148
GWS22	1	,118
GW23	1	,074
GW24	1	,096
GWS25	3	,079
GW25	1	,091
GW26	1	,121
GW27	2	,174
GW28	2	,019
GWS30	3	,033
GWS31	1	,170
GWS32	2	,122
GWS34	1	,092

Tab. 5.8 - K-means clustering

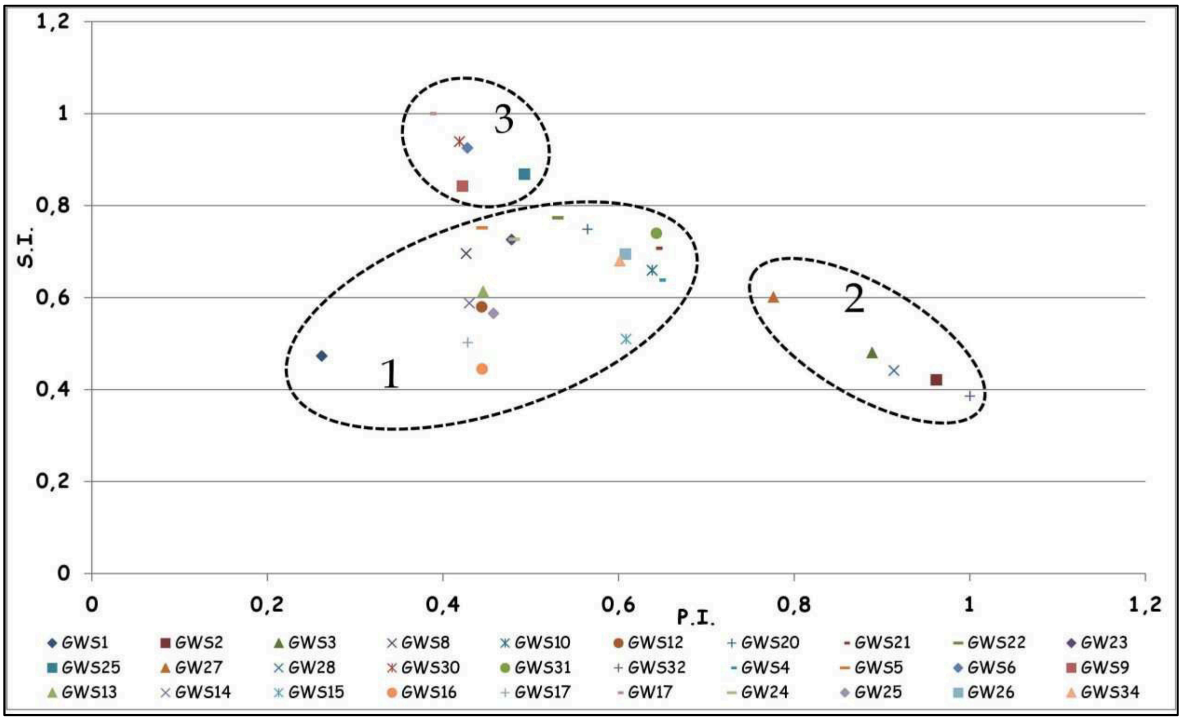


Fig. 5.41 - Scatter plot with cluster recognized by the k-means analysis

The Fig. 5.41 shows the scatter plot and the clusters recognized by the K-means analysis. The cluster 2 involves groundwater samples comparable with the plain end-member; the cluster 3 includes groundwater samples comparable with the substratum end-member; the cluster 1 involves groundwater samples representative of dynamic mixtures of the recognized end members. This clusters configuration outlines a homogeneous territorial spreading too. The wells associated to the cluster 2 are located in the Castel San Giorgio area; the wells associated to the cluster 1 are located in the Mercato San Severino-Fisciano area; finally, the wells related to the cluster 3 are located in the Montoro Inferiore area.

Then a hierarchical agglomerative cluster analysis was performed by using the complete chemical-physical data set, which is summarized in the table 5.2.

The related dendrogram was cut to highlight three clusters (Fig. 5.42)

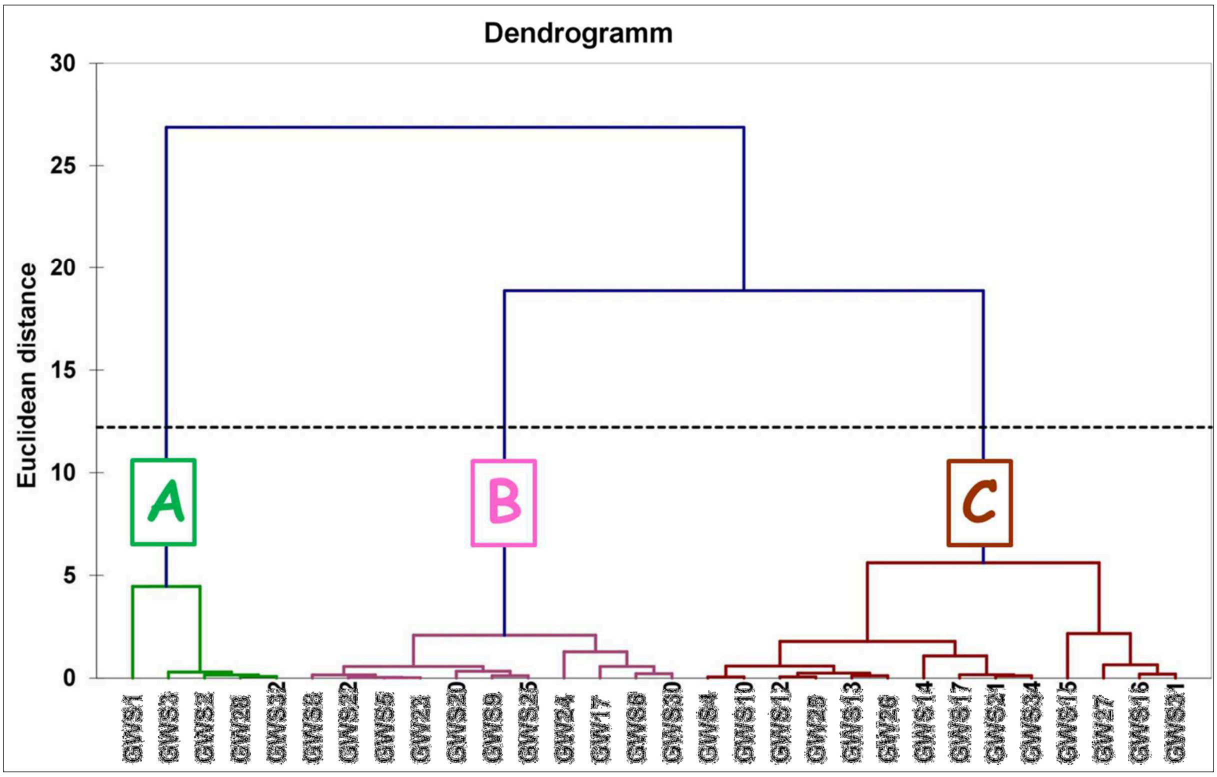


Fig. 42 - Dendrogram by Hierarchical agglomerative cluster analysis that shows the 3 recognized groups

Such analysis was performed to group groundwater samples according to chemical similarities by adopting the Euclidean distance and the Ward's method. The figure 5.35 shows the areal distribution of the 3 recognized clusters in Solofrana River Valley and the boundary of three homogeneous sectors in terms of geological and hydrodynamic features as well as of impact conditions.

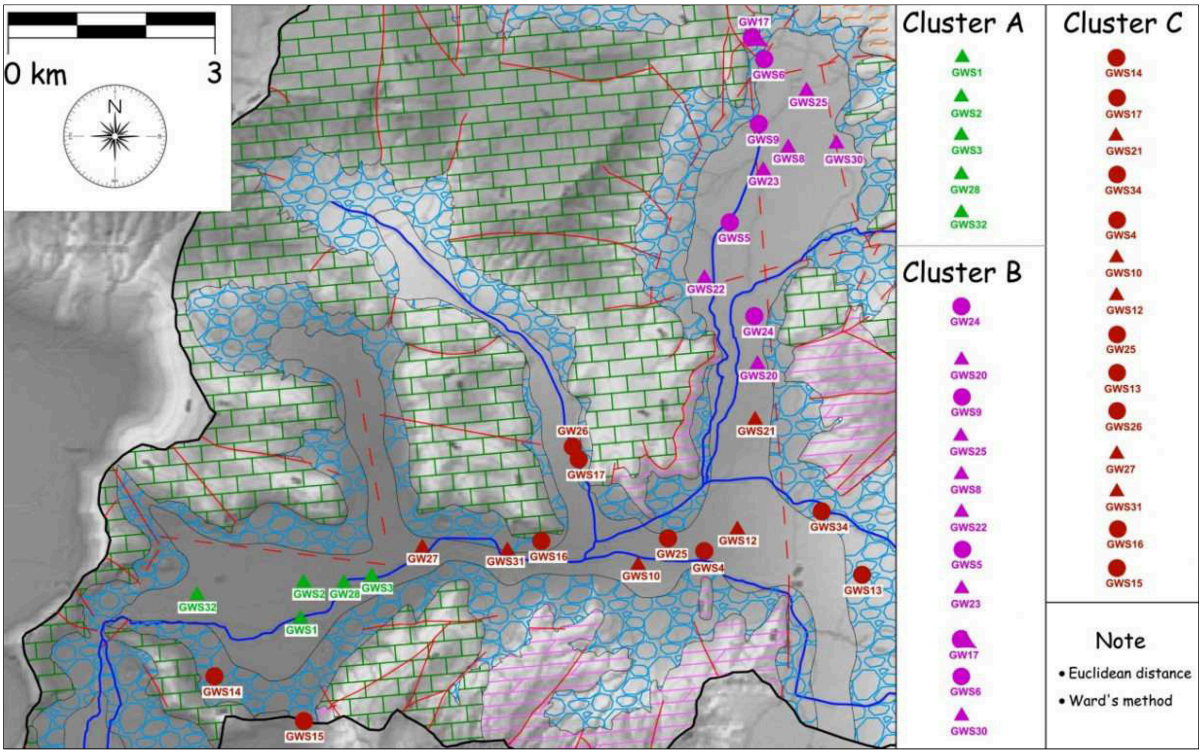


Fig. 5.43 - Spatial distribution of clusters. Triangles = Plain, Circles = Carbonate

The recognized clusters represent a specific chemical evolution of groundwater, according to the hydrochemical facies shown in the Piper diagram (fig.5.36).

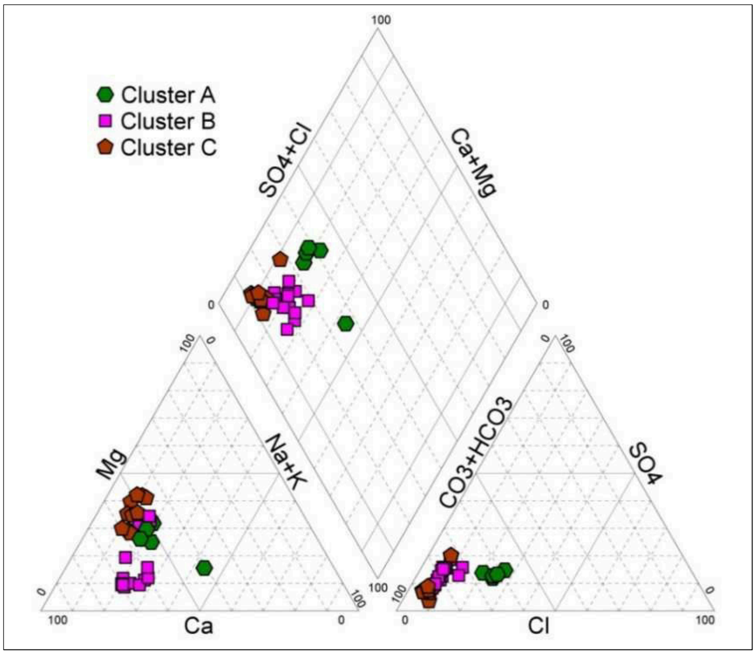


Fig. 5.44 - Piper diagram with cluster recognized

This circumstance is confirmed by the multivariate statistical analysis of data collected on April-June 2012, that proved the critical sites boundaries and the great influence of the industrial activities on groundwater composition in the Castel San Giorgio sector (Fig.5.45, 5.46, 5.47.).

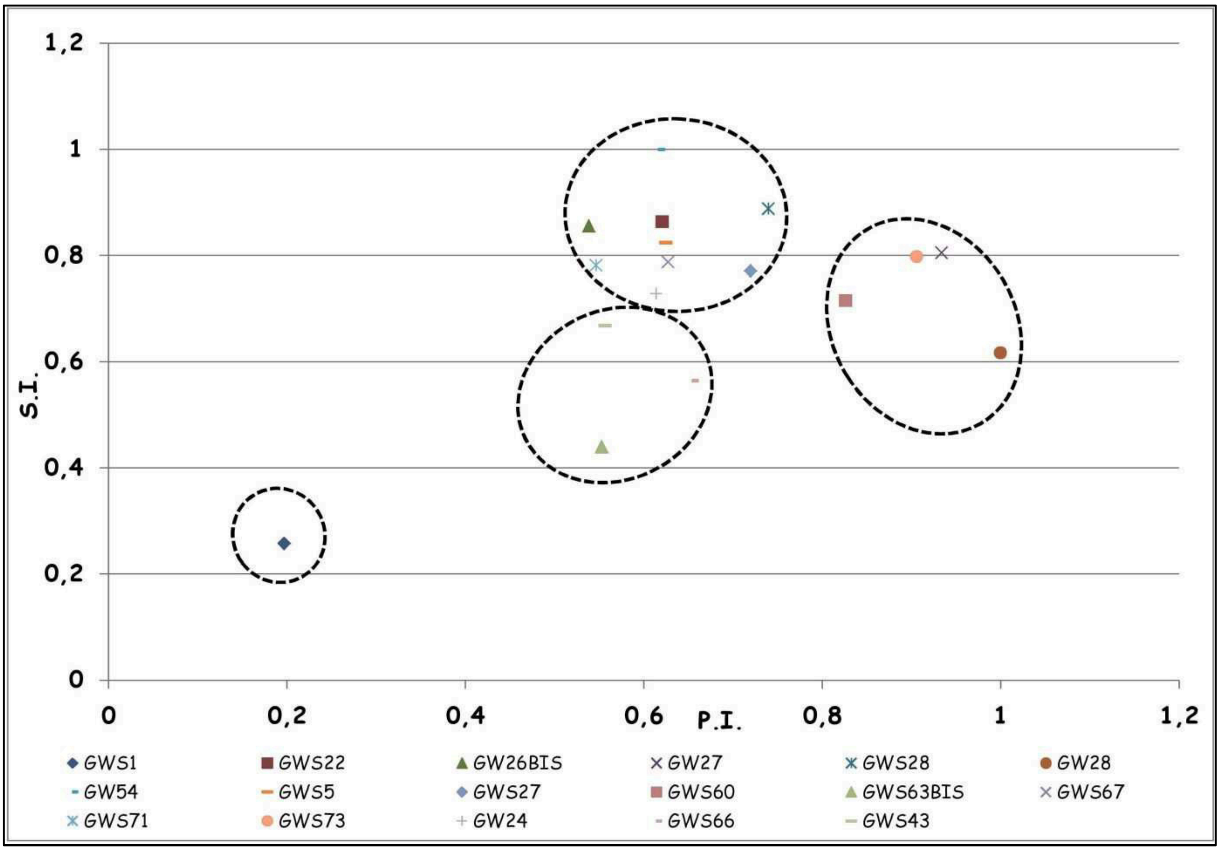


Fig. 5.45 - Scatter plot with cluster recognized by the k-means analysis (2012)

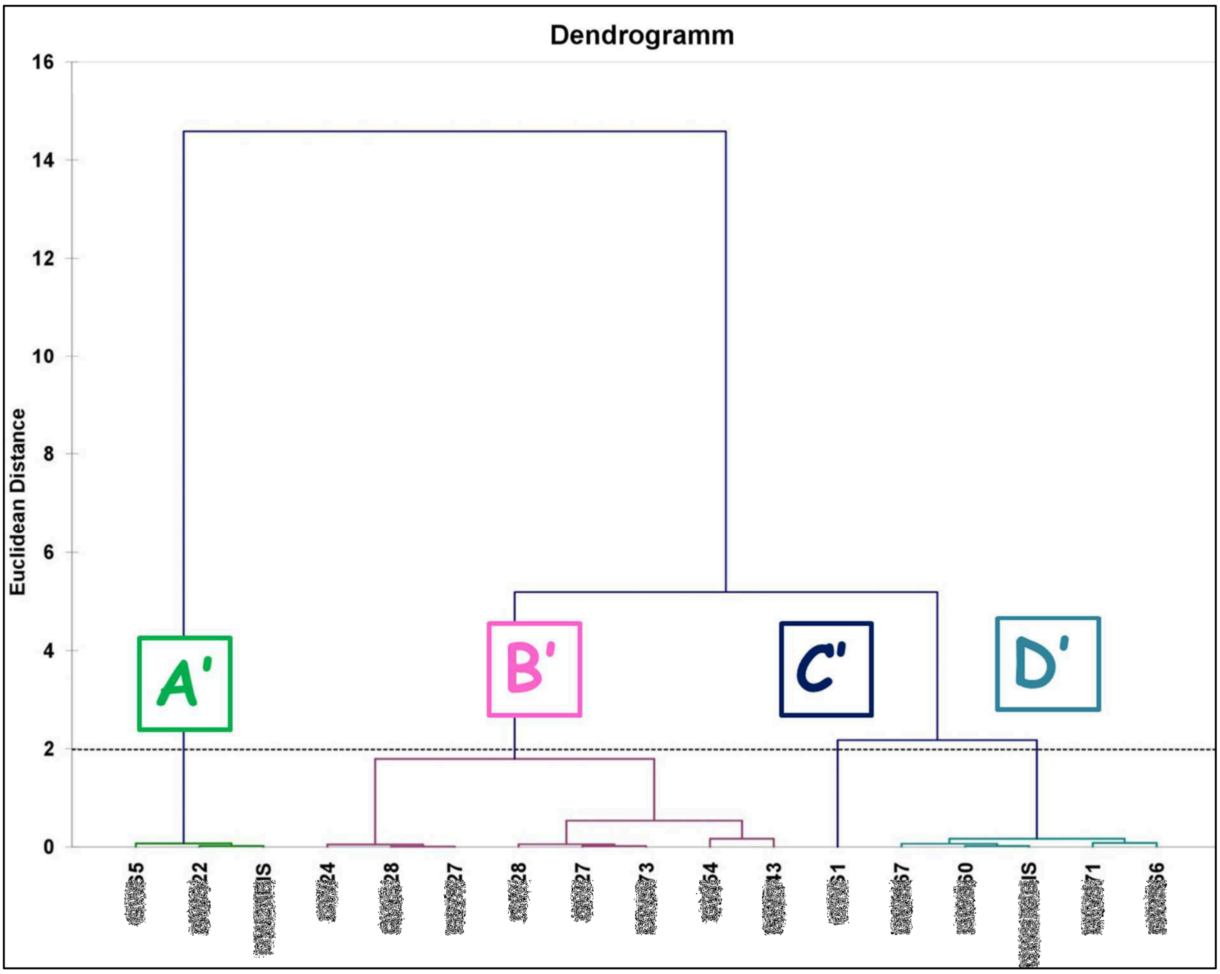


Fig. 5.46 - Dendrogram by Hierarchical agglomerative cluster analysis that shows the 4 recognized groups

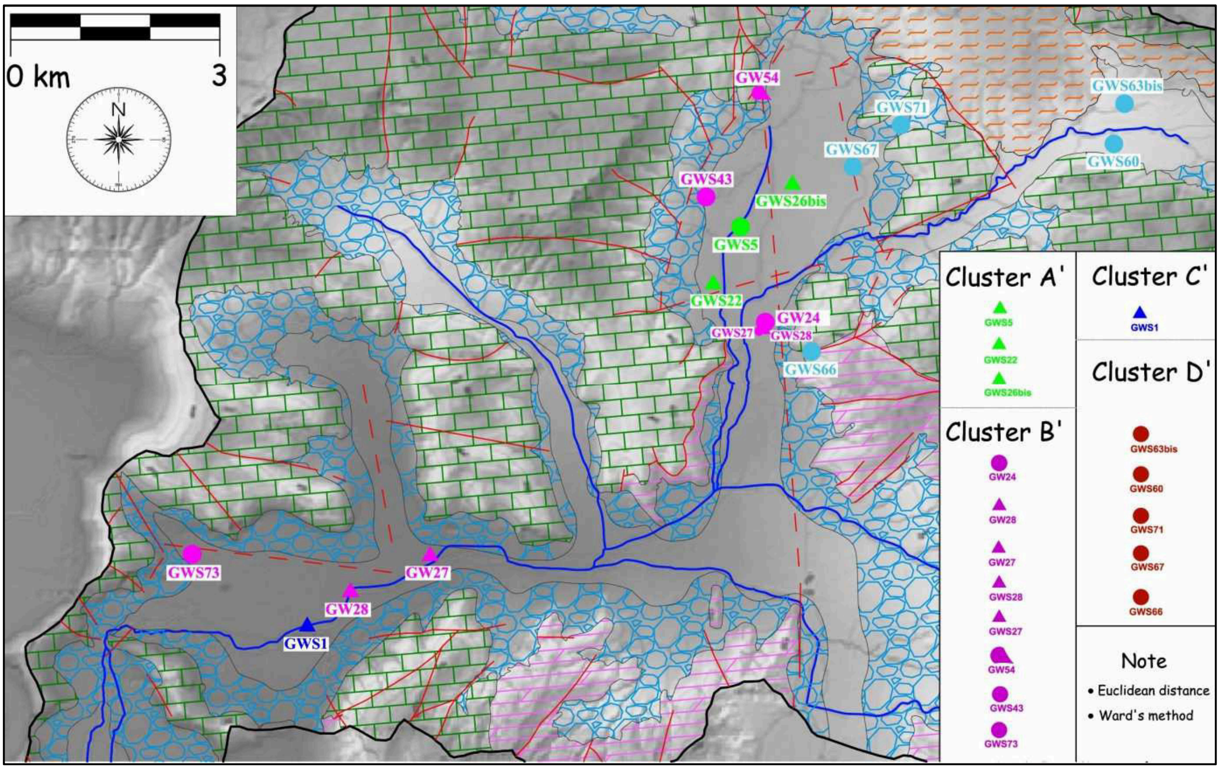


Fig. 5.47 - Spatial distribution of clusters (2012). Triangles = Plain, Circles = Carbonate

CHAPTER 6

CONCLUSIONS

The sustainable development and territory management aimed at the groundwater protection and remediation needs a multidisciplinary approach.

With regard to complex aquifer systems the focus is the identification of the geometry of hydrofacies and the connection among aquifers to incorporate heterogeneities in quantification-modelling-prediction of flow systems and processes across a range of spatial scales.

This study describes the criteria and procedure for identifying heterogeneity properties, which control the permeability distribution. At the scale of basin fill the hydrostratigraphic architecture was improved by means of equivalent parameters variability that describes homogeneous media or hydrogeological units.

As the interdisciplinary approach usually requires both general and discipline-specific science, the heterogeneity, the anisotropy and so the spatial variability of hydrogeological parameters was dealt with by observing geologic features and making local measurements.

The uncertainty due to the lack of competent information, especially increasing depths, was minimized by involving the identification of basin scale indicators of both processes occurring within multi-layer aquifers and natural attenuation potential. Each indicator depicts a specific aspect of groundwater quality and their combination allows to define indexes of groundwater environmental state, due to natural and anthropogenic phenomena.

This work gives an outline of the main groundwater environmental indexes and the most critical questions about groundwater protection policy in the

Solofrana River Valley (South Italy), located in a Site of National Importance just downgraded to Site of Regional Importance (D.M. 11/01/2013).

With regard to the Italian regulation thresholds the environmental state of groundwater resources of the Solofrana River Valley was not worring, except for Cr and Ni in the southern sector, corresponding to the river flooding areas. At basin scale at least two homogeneous zones, characterized by different impact on carbonate aquifer as well as on plain aquifer, were recognized according to the hydrodynamic setting and to characteristics of the potential sources of contamination. In the central sector agricultural activities are widespread; in the southern sector are localized the main sewage and industrial plants.

Groundwater were classified as bicarbonate-calcium, but a complex combination of natural and human processes operates at many levels by establishing broad trends to chloride-sulfate-calcium-sodium-magnesium facies. The identification of the most significant indicators of chemical groundwater characteristics that may be related to human activities, i.e. copper and zinc for agricultural practices and chromium for industrial ones, and the results of multivariate statistical analyses proved the groundwater environmental indexes and critical sites boundaries as well as the poor attenuation due to the aquifer plain.

The most critical hydrodynamic conditions were recognized in the central sector of the plain, where the coupled inversion of data was able to reveal the outlet of a paleo-endorheic and karst basin. So, just where the main groundwater flow direction remarks the leakage to carbonate aquifer, the carbonate substratum underlies karst breccias and is recognizable at about 52 m of depth.

The study provides the potential of the groundwater composition to constrain hydrodynamic parameters if combined with geological and hydrogeological techniques as with an anthropogenic pressures analysis.

The socio-economic development and the urbanization of the study basin, as well as many plain areas in South Italy, provide a particular picture of the groundwater quality. Human activities lead the chemical-physical characteristics of groundwater in complex multilayered aquifer systems, like pyroclastic-alluvial aquifer. Furthermore, wells become local vehicles for transporting pollutants in deeper confined or semiconfined aquifers, like carbonate ones, and modify or increase the risk of groundwater pollution.

So in plain multi-layered aquifers, in order to manage and protect groundwater, it is necessary to involve within the framework decision the "Hydrogeological scheme" and the "Spatial distribution of groundwater composition indicators". The identification of main groundwater environmental indexes arises the spatial variability of aquifer complexes (hydrofacies) and the most relevant heterogeneity at basin scale.

In conclusion a reliable assessment and application of groundwater environmental indexes allows to point out homogeneous sectors, useful for planning technical and procedural solutions, which may support the protection and requalification of widespread areas.

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