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Hydrogeochemical investigations for aquifers characterization  
and proposal of a new transmission protocol for the chemical  
and physical monitoring

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## Abstract

This dissertation presents the results of a hydrogeochemical study conducted on the Po River's floodplain aquifer, as a means for the detection and definition of the best placement of a new continuous monitoring system.

The chemical characteristics of the aquifers have been investigated through 343 chemical tests conducted on water samples of the mentioned area (253 from phreatic water sampling and 90 from the regional database collected during years from 2003 to 2015). Most of the waters have Ca-HCO<sub>3</sub> facies; fewer are of NaCl, CaCl and NaHCO<sub>3</sub> types. The application of Factorial Analysis to the chemical tests has allowed identifying three different groups of water: - Group 1: includes water samples affected by ion exchange processes; - Group 2: includes waters with low pH and enriched in heavy metals. - Group 3: includes samples with high concentration of HCO<sub>3</sub>. Climate changes such as increasing temperatures and decreasing precipitations are caused by climatic anomalies which are mirrored in groundwater's isotopic composition. These climatic changes can be validated by means of the presence of heavy isotopes in ground water (<sup>2</sup>H and <sup>18</sup>O). The heavy isotopes can bring to the enrichment or the impoverishment of waters. Hence, ground water's qualitative composition can be detected and studied by dint of these isotopic contributions and variations. Statistical interpretation of climate parameters data and a statistical- hydrogeochemical approach for the study of data about ground water are the adopted methods in this research.

A multidisciplinary approach is required to understand the alterations the waters are undergoing. The main effects of the climatic anomalies, which are reflected on ground water resources, are isotopic ratio depletion and increasing evaporation. They can be spotted in the isotopic ratio change and in the grade line comparing it to the North Meteoric Water Line (NMWL).

The isotope composition of the waters is in the range -10.75; -6.03 for  $\delta^{18}\text{O}$  and, -71, 3 - 43, 71 for  $\delta^2\text{H}$  and this suggest a meteoric origin for the recharging water. The combined approaches of hydrogeochemistry and climatology have enabled us to detect those climatic processes affecting ground water resources in a more accurate way, and these approaches will represent excellent assessment tools required for controlling water balance in future research.

Modelling has been used to better understand the geochemical reactions that take place and explain the groundwaters composition. The most evident alteration in the geochemical

composition can be attributed to changes in sediment's mineralogy and petrography: deep waters are characterized by a marked presence of  $\text{HCO}_3$  and low Mg, while phreatic water is characterized by an Mg marker. This is due to the fact that phreatic water, being in contact with clays minerals, receive the magnesium from the leaching of smectite/chlorite of the sediments It is also characterized by a crystalline structure due to a high cation exchange capacity (for Ca, Na and Mg).

Among the observed ongoing water reaction, role ion exchange between Ca and Na plays a key role and these kinds of water, which are rich in salt, can rise along faults and fractures by the ways of the decreasing of density due to the presence of  $\text{CH}_4$  in solution. The methane may arise in case of deep sources and locally presence of organic matter which is a key factor in water/soil cations exchange as highlighted by an increase of the CEC (cation exchange capacity).

The Bridge protocol allow the determination of the basic values and limit values for chemical and physical parameters which are helpful to insify the territory knowledge and understand the upper limit values for each parameters. A new monitoring transmission protocol have been create using the microcontroller ARDUINO to facilities the monitoring groundwaters practices. This card has been connect to a GSM aerial which sends data directly to a database in the cloud making possible to read real-time recorded data. The geochemical approach represent a method to identify the sites where it is interesting to place the continuously monitoring system in order to expand the existing one with the introduction of brand new technologies. The use of this low cost and easy management tool will allow an improvement in the water resource management.

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## Introduction

Over the last decades, the increasing massive abuse of water resources for industrial and agricultural purposes has put the spotlight on how to find a way for keeping groundwater's quality under control.

The complexity of this situation in addition to the E.U. legislative provisions on this specific field, have brought the scientific community to start taking action and to start studying and managing water resources, in order to be aware of their real status and to take care of the related issues, such as overexploitation, salinization and human pollution.

Geochemical studies, conducted over the past twenty years in Emilia Romagna, have revealed the presence of ancient water trapped in Pleistocene sediments which returns to the surface through deep structures such as rock fractures or cracks.

Besides, Hydrogeochemistry approach has reached a valuable knowledge of phenomena involving water processes. Such an important field makes it easier to understand groundwater flows, makes it possible to define the chemical composition of waters and, additionally, through the application of specific models, it allows to suppose the presence of potential waters or ongoing composition mixes.

The waters have undergone a progressive deterioration caused by the overexploitation and degradation of ground water brought on by the abuse of water resources in human activities such as massive irrigation.

Many studies have demonstrated that a mindful protection of the existing water resources could contribute to the preservation of the availability of fresh water (Martinelli et al. 1998; Cremonini et al 2000; Conti et al. 2000; Carminati et al. 2002, 2003; Zuppi et al. 2004; Ferronato 2006; Rapti-Caputo et al. 2006; Marcaccio et al. 2012).

The rain fall is one of the main climatic variables which has a great influence on groundwaters' turnover, on water resources in general, on river flows and on hydroelectricity production as well (Melo-Gonçalves et al. 2016).

Emilia Romagna is provided with a constant monitoring system for all bodies of groundwater. The legislative decree no. 30/2009, transposing the directive 2000/60 / EC and 2006/118 / EC, amending the previous 152/2006 on the matter of characterization and identification of groundwater bodies, it establishes quality standards and the specific thresholds for defining the chemical status of groundwater, setting criteria for quantitative monitoring and classifying

water bodies. Emilia Romagna has adopted the national legislation with the enactment of Law 17 of 4/11/2009 legislation.

The stations for chemical- monitoring are placed in 744 wells. Ferrara province is provided with 65 stations on different aquifer levels.

In this project, a constant monitoring network with seasonal control of chemical and physical parameters of phreatic waters has been realized, it has been based in a plain area.

Sampling points were set out in Mirabello (24), Sant'Agostino (6), Cento (11) Bondeno (7) and the resulting data have been compared with those coming from the WARBO project area, near Copparo (5). These sites have been selected in order to identify the bottom-up hazes which from depths water turn to the surface; it is therefore possible to identify the specific areas where these hazes are spotted.

Private citizens have ensured their availability on the occasion of studying and collecting samples, the monitoring system has thus collected data from their own wells too.

Required features for placing the monitoring system have been: phreatic wells with a maximum depth of 12 m.

The data resulting from the study of the aquifer A0 (unconfined aquifer, phreatic groundwater) have allowed us to determine the natural values and limits (Bridge Protocol) for waters stored in the deeper fractures (confined aquifer).

Based on the obtained results of the seasonal analysis conducted during the first two years of my PhD (2014-2015), on one hand, it had been possible to draw a clearer picture of the baseline characteristic of the studied area, on the other hand it was possible to create a monitoring prototype for a constant data acquisition.

Probes have been installed on 24 January 2016. These are the tools which allow the continuous measurement of temperature, electrical conductivity and piezometric parameters, and data is recorded every 10 minutes for each mentioned parameter. One probe has been installed in Mirabello and one in Sant'Agostino. Downloading data occur manually.

Further contributing features to the research have been the study of existing innovative technology possibilities, selection of the acquired data and transmission methods to realize a low cost system, which also provides an alternative way for monitoring the specific parameters and to storing them in a database.



In short, the purposes of this research have been:

- To increase the existing knowledge of the hydrogeochemical characteristics of the territory, by characterizing phreatic ground water from selected areas where geochemical signature of the aquifer level had been found;
- To use descriptive statistical for defining those samples to be selected as ultimate test pieces, whose analysis would let us understand the nature of mixing processes which underpin sodium-carbonate waters' composition identified in 2014-2015 sampling;
- To create correlation diagrams and to study the relationships between different groups of sampled waters by means of geochemical characterization of group A and through the study of a different marker, which could identify the various aquifer levels;
- To determine possible processes occurring in the mixing of water solutions selected on the basis of statistical analysis results of geochemical facies, which have been underlined in the piper diagram, with the use of a specific tool of PRHEEQC;
- To create representative synthetic solutions of possible mixes between two aqueous solutions belonging to the same level of A1 aquifer, in order to simulate the mixing water line in the composition Ca-HCO<sub>3</sub> and NaCl.
- To determine thresholds values characterizing the environment of the research area through the Bridge Protocol, which will be useful for future interpretation and management of data.
- To optimize the existing monitoring process through the use of technological information systems, with the aim of keeping costs at as a reasonable level as products on the market, this can be done by means of a new protocol for the constant monitoring system.

Recent innovations in the field of information management (such as sensor systems and knowledge of new technologies for the management of large data amounts), have opened new scenarios for the application of computer –aided systems to the environmental monitoring field.

The proposed system allows to obtaining data from the constant monitoring of chemical and physical parameters of the elements whose matrix are air, water and soil, in order to define the polluted status of the sites and to develop conceptual models, which future action plans will be based on.

The technological infrastructure on which this system has been built on is constituted by a series of sensors which measure specific parameters, managed and powered by an Arduino microcontroller that sends the data to an online database via a GSM aerial connected to the local network system. This monitoring proposal may be a useful solution for water resources management to come.

## Study area

### Geological setting

The Po Plain occurs in between the two mountain ranges and so it has been controlled in part by the Alps and in part by the Appennines. (Fig.1) However, its main geological structural features are buried, and the plain itself is characterized primarily by the meandering Po River and its large delta, and by tributaries flowing either from the Alps to its right (southern) bank. The course of the Po River is in some parts affected by buried Pliocene –Quaternary synclines, and overall it has tendency to shift toward the north (Dainelli 1975)

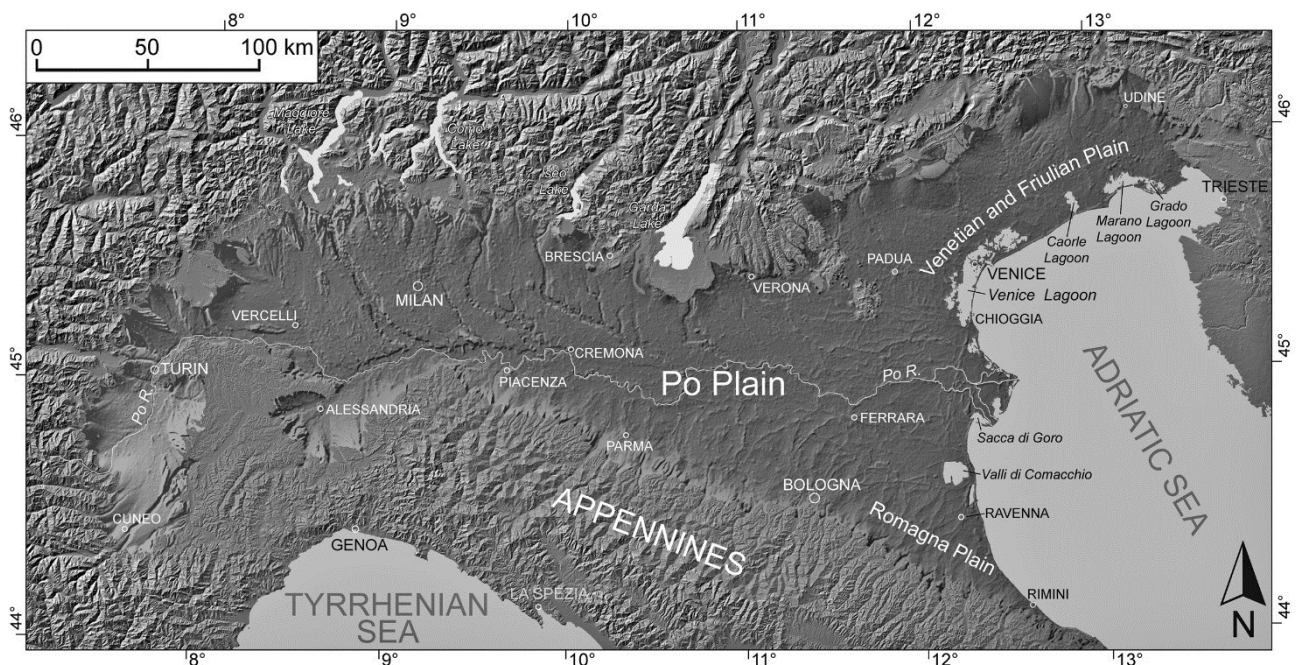


Fig.1 Study area is located in the Po Plain. Digital Elevation Model (DEM) of Italy derived by the SRTM (Shuttle Radar Topographic Mission) with location of the main alluvial plains. Elaboration by F. Ferrarese.

The most important structural aspects of the Po Basin, however, are buried under the blanket sedimentary and the first knowledge of the subsoil are derived from geophysical studies that developed in especially starting from the late seventies and the purpose of seeking water and hydrocarbons (AGIP Mining 1959; AGIP 1977). These studies, based mainly on the interpretation of seismic sections, have been integrated to date with insights from several different purposes, which have highlighted the structural characteristics of the Po Basin and its sedimentary filling. The synthesis of these jobs permit to define the Po Valley as a foreland basin evolving formed for progressive migration of the African plate towards that European

resulting in subduction of the "microplate" Po-Adriatic from Cretaceous. (Pieri and Groppi 1975, 1981; Cremonini and Ricci Lucchi 1982; Pieri 1983; Boccaletti et al. 1987,1990; Gelati et al. 1989; Bigi et al. 1990; Castaldini and Panizza, 1991; Doglioni 1993; Anelli et al. 1996; Farabegoli et al. 1997; Regione Emilia-Romagna and ENI-AGIP 1998; Amorosi et al. 1999; Mariotti and Doglioni 2000; Castiglioni and Pellegrini 2001; Vai and Martini 2001; Lombardy region and ENI AGIP Division 2002; Bello and Fantoni 2002; Amorosi and Colalongo 2005; Molinari et al. 2007; Amorosi 2008). Which constitutes the offshoot northern most of the Apennines the overriding north on the Po-Venetian platform (Doglioni et al. 1996; Barchi et al. 2001; Vai and Martini 2001; Argnani et al. 2003; Boccaletti et al. 2004). This structure shows a trend NW-SE parallel to the adjacent chain and it has been formed on the inside of four structural arches, which extend for hundreds of kilometers, which have been called Monferrato Arc, Arco Folds of Emiliano-Romagna, Arc of Folds Ferraresi and Adriatico Arc. These arches are symmetrical and similar to each other: in the west are made up of west-verging thrust belt systems, while further east are characterized by a set of folds and thrust faults NE-verging (Costa 2003). In the Padano Adriatic Basin are identified numerous Quaternary discontinuity surfaces (Ricci Lucchi et al 1982) these were selected four main sequence limits that represent significant steps in the evolution of the basin (Fig.2). These surfaces are dated unconformity in outcrop; which subdivide the Po succession in four depositional sequences (defined informally Aquifer Group A, B, C and D above) (Fig.3).

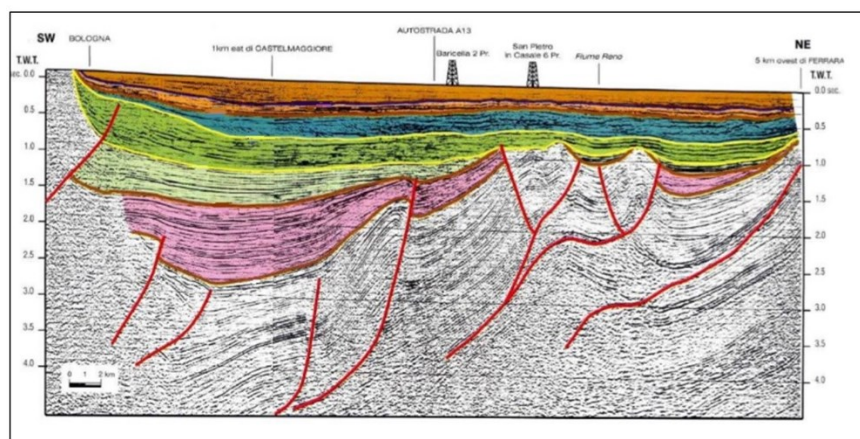


Fig. 2 Seismic section illustrating the subsoil stratigraphy Po (by Regione Emilia-Romagna & Eni- AGIP, 1998).

Apennine chain formation during Oligocene leads to the development of reservoirs and deep foredeep subsidence, characterized by the accumulation of powerful turbidite sequences and shallow-marine marginal deposits basins modest extension (Ricci Lucchi et al. 2002).

In order to standardize the knowledge of the basin scale, Region Emilia-Romagna & ENI-AGIP (1998) and Lombardy & ENI-AGIP Division (2002) have produced, in the national geological mapping project (Project CARG) a multidisciplinary study aimed at the reconstruction of the sedimentary evolution of the Po subsoil and the definition of its hydrogeologic characteristics. This study has been conducted both north and south of the Po and produced a breakdown of the Po succession, through correlation of well data, in four depositional sequences (Mitchum et al. 1977).

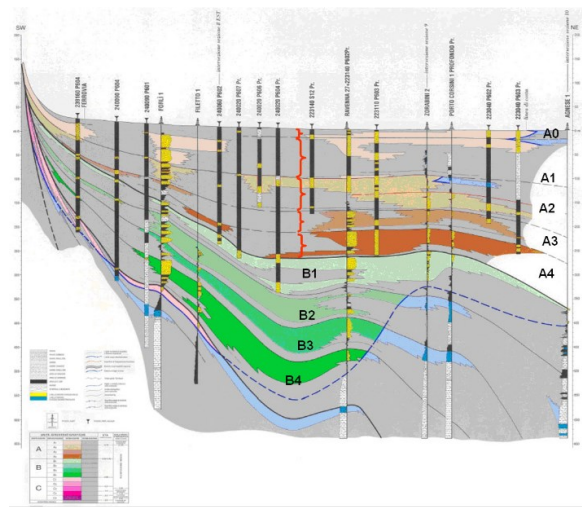


Fig.3 The section shows the breakdown in the underground aquifers of different groups and the respective distinction of the various complexes aquifers. The aquifers complexes are hydrostratigraphic unit and as such represent a depositional sequence characterized by a very continuous basal aquitard, which has been followed by a finer sedimentation, which then becomes very coarse in the terminal portion of the sequence. The figure has been taken from ER Environment Emilia Romagna (Lombardy Region & Eni- AGIP Division, 2002). The legend in the lower left shown summarizes the correspondence relative to the colors that will be explained in detail in the section of classification hydrostratigraphic.

In the proposed sequence in Figure 3 are the thicknesses of about 200-250 meters and present depositional cyclicity, with an alternation of coarse deposits consisting of gravel and sand and fine deposits represented by silts and clays. At the edge of the basin, there is a drastic reduction of the space available for the sedimentation where there are gravelly bodies of heavily amalgamated and fluvial channel. In the central areas of the seismic discontinuity surface tend to diverge and alternate depositions of gravelly bodies and then sandy channel river that demonstrate a tabular geometry type and a lateral extension also of some tens of kilometers. The thickness of these cycles is approximately 50-60 meters and are referred to as potential aquifers.

Po Valley during Oligocene becomes an active margin related to the formation of the Alps and the Apennines domain. (Astori et al 2002)

In the end Messinian almost completely tectonic movements related to the structuring of the building tectonic Alpine (Region Lombardi and ENI Agip Division 2002).

In Messinian -Tortoniano the Po foreland has been connect to the movement of accretion of the Northern Apennines and the opening movements of the Tyrrhenian Sea, sedimentation during this period has been characterize by cyclic deposition of organic carbonate successions. In this period, it originated an acceleration phase of tectonic deformation with lifting of the Apennines and outward migration of the deformation front. The Apennine chain for the first time emerges generating an Apennine drainage system, which feeds the foreland basin, and contemporary are interrupted earlier supply routes in the Alps (Ricci Lucchi et al. 2002)

With the Messinian, sedimentary cycle ends a complex that is also a result of the approach of the African plate and the European one. This closer reduces the width of the basin (Vai and Ricci Lucchi 1977; Gelati et al. 1989; Butler et al. 1995). The sedimentary evolution of the Po Basin exhibits an overall 'regressive' trend, punctuated by minor fluctuations, from Pliocene open marine facies to Quaternary marginal marine and then alluvial deposits (Amorosi 1996). Begins a regression of the basinal with the onset of evaporite sequence which replaces the open sea (Dondi et al. 1982)

In the central part of the basin continues the deposition of clastic turbidite sequences and there has been a general decrease in the salinity of the water and to a generalized transgression. (Castellarin et al 1985).

The Apennines emerged provides abundant detritus mostly terrigenous. In Messinian begins a turbidite sedimentation, brackish basins separated by structural highs. With the Pliocene, brackish basins has been report in marine conditions after the rapid ascent of the sea.

The tectonic phases of the Pliocene lead surfaced some foredeep Po sections (Dondi and D'Andrea 1986).

In Tertiary and Quaternary era the Po Basin, receive a considerable detrital contribution that determines the progressive filling and the passage in the continental places. In the Quaternary and in detail in the Middle-Upper Pleistocene deposits has been characterize by the basin scale accumulations in large waves identifiable as filling the remaining depressions of basinal Pliocenic system.

The evolution of the Pliocene-Quaternary basin recorded a downward trend identified at the Apennine margin Ricci Lucchi et al. (1982) who studied marine deposits gradually shallower environments to continental deposits. The recognition of an unconformity surface of regional significance has been use for the first stratigraphic Quaternary succession interpretation.

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The unconformity separating the marine sedimentary cycle (QM) and Continental (QC) was subsequently studied leading to the distinction of depositional sequences of lower rank in the two sedimentary cycles QM and QC (Marabini et al. 1985; Farabegoli and Onorevoli 1991; Di Dio et al. 1997; Amorosi et al. 1998).

The Qm cycle is characterized by prevailing fine particle size, remarkable continuity of sedimentation, lack of terracing phenomena and is dominated by marine deposits; thickness in the range from 50 to 1200 m, based in continuity on Pliocene deposits and marked by a clear roof area of inconformity on which rest alluvial deposits belonging to Qc cycle. Within QM, recognize two main lithostratigraphic units:

- Clays Blue (Colalongo et al. 1982; Vai 1988; Barchi et al. 2001);
- Sands of Imola or Yellow Sands of Imola or depositional sequence QM4 (Ruggieri 1962, 1995; Farabegoli 1985; Vai 1994; Marabini et al. 1995; Amorosi et al. 1998). The most recent term of marine succession.

The cycle QC is characterized by coarser deposits compared to the previous cycle and is composed of alluvial terraces and continental environments of age comprised between the middle Pleistocene and the current (Francavilla et al 1980)

A Pleistocene sedimentary succession in the subsurface of the Po Valley characterized by various facies architecture (Amorosi et al. 1999) is typical of postglacial sedimentation.

It is recorded a developed transgressive-regression cycle in a relatively distal sites in the basement of this coastal plain (Comacchio and Ravenna). In those areas, the transgressive deposits consist of coastal plains and back-reef, rich organic sludge is separated from the overlying transport reef sands from a chin area ravine- clearly recognizable (RS). These deposits record the migration to the land of a reef System-Lagoon estuary in the early Holocene.

The peak of this transgression records a shift of the line thing about 20 km from its current location. (Amorosi et al 2002). The stratigraphy of coastal deposits logs all phases of higstand and lowstand of recent cycle's trasgressivoregressivi Pleistocene and Holocene.

The sequential method used by Ricci et Lucchi in 1982 for the Regional geological framework has been taken as the basis for further processing in the work Region Emilia Romagna ENI-AGIP (1998) in which the main sedimentary cycles Qm and Qc (defined as SUPERSINTEMA EMILIANO ROMAGNOLO). Units below in which has been divide the sedimentary cycles represent the basic unit at the regional scale where is organize coverage of the Po Valley deposits.

The Supersistema Emiliano Romagnolo is the stratigraphic unit that includes the set of quaternary continental origin deposits outcropping at the Apennine margin Po cycle QC by Ricci Lucchi et al. (1982). This has been divided into lower AEI SINTEMA ROMAGNOLO and higher AES SINTEMA ROMAGNOLO. These two units have a match on aquifers Groups B and A (respectively).

Subsequent work carried out in this direction has the subsystems divided into 8 parts: B4 to A1 and later in the work of Molinari et al. (2007) was also introduced the A0 level.

These sedimentary cycles have been considered the product of the fourth order Climate-eustatic elementary cyclical nature of the history of the Quaternary (Region Emilia Romagna and ENI-AGIP 1998).

Based on the transgressive-regressive cycles of recognized characters in the underground, their temporary duration of their extension to the regional scale, these deposits have been considered as the product of the elementary cyclical climate-eustatic fourth order that characterizes the evolution of the Quaternary period.

The waters better exploited for drinking water purposes in northern aquifers are contained in the Pliocene-Quaternary continental and marine deposits Po. This great important and valuable aquifer reservoir was the subject of extensive research over the past 20 years. Numerous studies have investigated the stratigraphic characteristics of the Po Basin (Amorosi and Colalongo 2005; Zuppi and Sacchi 2004; Civita et al. 2007).

The compaction of the Plio-Quaternary sediments has been affected by a differential evolution, which has produced different degrees of subsidence. (Amorosi et al. 2002) Holocene subsidence values recorded intervals between 1.0 and 2.0 mm/year (Bitelli et al. 2000) for compaction of alluvial deposits. The arrival of human-induced subsidence due to heavy urbanization, the reclamation of land and the extraction of methane in the underground have also increased this tendency to tectonic subsidence.

### **Hydrogeological setting**

Emilia Romagna plain aquifers consist mainly of alluvial deposits in the most superficial part of the plain, for a thickness of about 400-500 m from marginal marine deposits.

On the basis of the stratigraphy made available by ENI-Agip (Regione Emilia Romagna and Eni-Agip deposit 1998) for hydrocarbons investigations three aquifers groups were identified and referred as A, B and C. The first two groups have been allocated in the Quaternary deposits.



The geological studies carried out over time by the Regional Geological Survey allowed to identify the thickness of these aquifers, including at local level. These studies have shown that the first confined aquifer in the area of Po has been hydraulically separate from the aquifers of the alluvial fans of the Apennines, for the presence of a substantial thickness of predominantly fine sediments that belong to the floodplain of the Apennine Rivers (Emilia-Romagna Region 2010). The distribution of the sedimentary formations at the subsurface has been schematical show in a diffuse cross-section with south-north direction, or from the Apennine margin, which separates the mountain aquifers from those of the plains, the River Po (Fig.5).

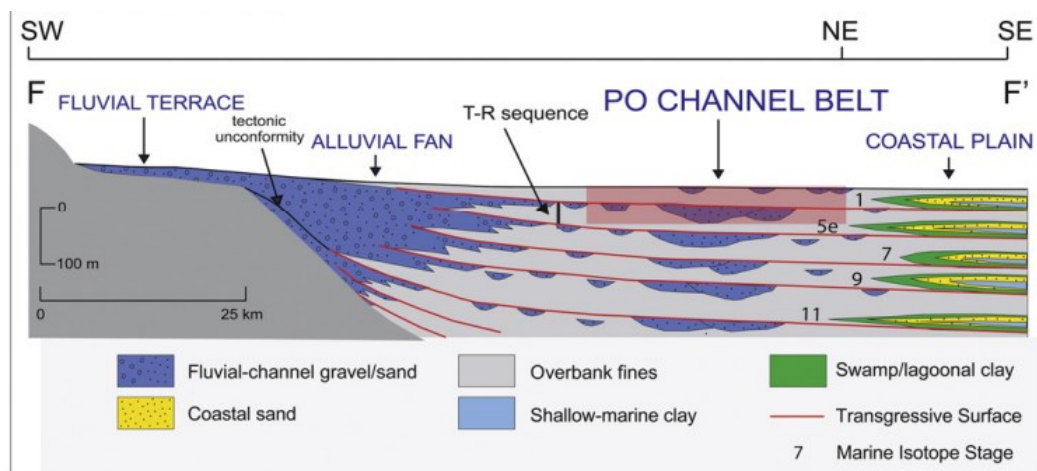


Fig. 5 Scheme of correlation of transgressive-regressive (T-R) cycles in the padano subsoil (from Amorosi 2008).

In the section, the sedimentary bodies from south to north in sequence (Fig.5):

- Alluvial fans;
- Floodplain Apennine;
- Coastal plain.

The alluvial fans have been form by sediments brought by rivers at the time of energy loss. Proximal area at the mouth of the river, where there is initial loss of energy in the proximal alluvial fan, coarse gravels prevail. Proceeding towards the plain finer deposits are more abundant, always alternated with gravel (distal cone area).

The alluvial fans represent the seat of the main aquifer of the Emilia Romagna plains since they consist of very permeable and thick deposits.

The proximal alluvial fans support the unconfined aquifer of the plain, which has been recharge by surface and rainwater. The cones are distal seat of the multilayer complex aquifer system, with aquifers confined, some with leakage.

Proceeding from south to north, the alluvial fans follows the floodplain Apennine. This plain has been formed by fine sediments deposited by rivers over long distances. These sediments have been formed by an alternation of more or less clayey silts and silty sands. The alluvial plain begins where the gravelly sediments give way to sand representing the channel fill deposits and proximal levee.

These deposits include rich peat horizons of organic matter, which are the testimony of alternation of marine transgression events that have affected the coastal area of Emilia Romagna in the Pliocene. These organic horizons have been interpreted as real driving levels of these sequences. This depositional environment is not attractive as hydrogeological resources.

In the western part of the region, these sand deposits become alluvial, which represent the parts of the Po delta that have been formed in the Pliocene. Sandy layers have been alternated with fine sediments formed by more or less clayey silt, clay and silty sands. This formation, very extensive and permeable, is very interesting because it supports the main confined aquifer (Fig. 6). The shallow multilayer aquifer has been recharged through the riverbed, while the deeper aquifer receives water in part from the Po River in a remote area and in part by the Apennine and Alpine regions

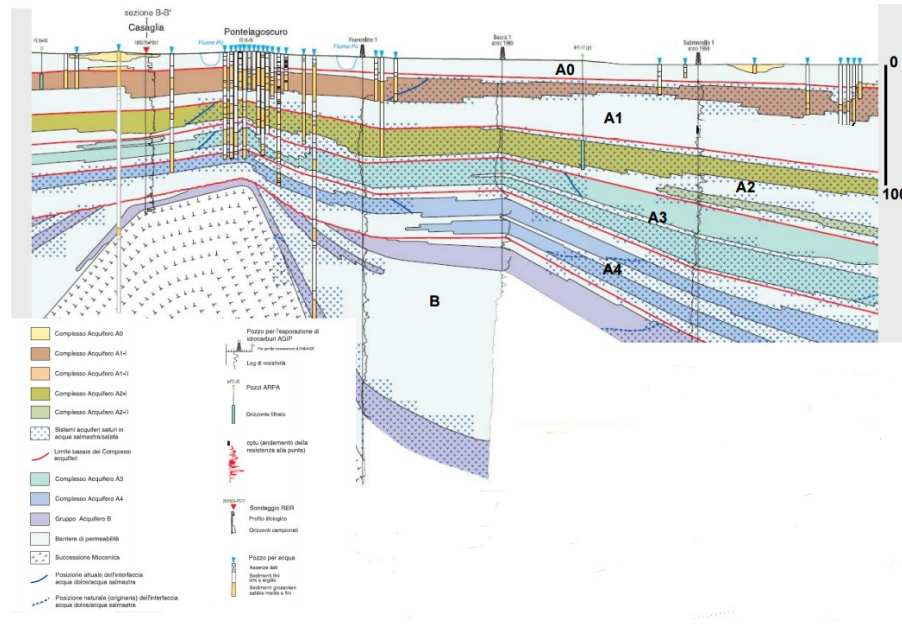


Fig.6 Schematic distribution of the aquifer system in the Po Valley (Region Emilia Romagna and ENI Agip)

The phreatic aquifer of the plain A0 is formed mainly by a thin layer of fine sediments that continues north across the plains. These sediments have been formed by fluvial channel deposits, bank and flood plains in direct contact with surface water and depends from

ecosystems, as well as with all human activities. This aquifer has a thickness of about 10 meters and is developed in the hydrostratigraphic unit A0. The maximum thickness may also exceed 10 meters in areas where the subsidence of the formation is higher, and in some places, the bottom of the A0 unit can have some confinement. The bottom of the A0 unit consists of clay sediments, enriched in organic matter. The top of A0 is alternate from fine sediments (silty and clay sediments). These sediments appear to be representative of fluvial channel deposits. The wells in this aquifer have been drill in the sandy sediments, and are not used for water exploitation because of its low productivity, but they are used to irrigate small fields and domestic use. Aquifers are developed in alluvial terraces, which generally have a flat topography and consist of gravel and river channel sand, topped by thin layers of finer materials. They are very thin phreatic aquifers, recharged by rain and runoff. According the last decree 100/2016 should be get the quality standards for requalification and artificial recharge of groundwater.

The Geological Service, Seismic and Soil Survey of Emilia - Romagna has proposed a new valid stratigraphy at the basin level for alluvial and marginal marine deposits, in the first few hundred meters (Fig.7). This study began in CARG project development, subsequent to the publication of Water Resources of the Plain (1998).

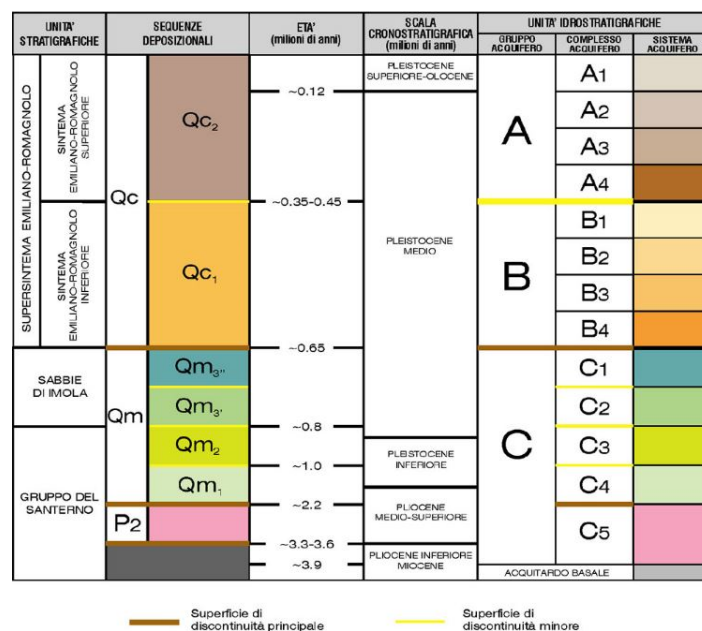


Fig. 7. Summary diagram proposed by the Geological, Seismic and Soil Survey of Emilia - Romagna for a new valid stratigraphy at the basin level for alluvial and marginal marine deposits in the first few hundred meters of the underground

The deposits of the plain have been divided into three stratigraphic units, aquifers Groups A, B and C: the Aquifer Group A is the most recent and it has an age that goes from up to 350,000 to 450,000 years the Aquifer Group B, intermediate, ranging from 350,000 to 450,000 years up to about 650,000. The Group C Aquifer is the oldest and ranges from 650,000 to over 3 million years (Fig.7).

The Aquifer Group A and Group B have been mainly formed by alluvial deposits and in particular by the gravels of alluvial fans, by fine deposits of alluvial plain and the sands of the plain of the Po River. The aquifer group C has been mainly formed by coastal and marine marginal deposits and by bundles of sands alternating with finer sediments. Close to major outlets, the aquifer C Group also contains gravels intercalated to sands, which make up the alluvial fan deltas of the Apennine Rivers during the Lower and Middle Pleistocene.

There is an agreement between the aquifers Groups (defined as Hydrostratigraphic Unit) and Stratigraphic Units used in the Geological Map of Italy.

The Aquifer Group A matches Sistema Emiliano-Romagnolo Superiore (AES), the aquifer Group B to Sistema Emiliano-Romagnolo Lower (AEI), the Aquifer Group C in different units outcropping in the Apennines, the most recent of which is the formation of Yellow sands of Imola (IMO).

The hydrostratigraphic units are formed from one or more depositional sequences characterized by cyclic alternations of fine deposits (at the base) and coarse (the roof) very thick. At the base of each sequence is a very constant level to low permeability that acts as aquiclude identified between the different units.

Within each group are then distinguished complexes Aquifers, hierarchically inferior units Aquifer are complexes Unit hydrostratigraphic and represent a depositional sequence characterized by a very continuous basal aquitard, which has been followed by a finer sedimentation. Aquifer within the Group A of the Underground Water Reserves have been identified five main UIS named Complex Aquifers: respectively from bottom to top Complex Aquifer A4, A3, A2, A1 and A0 phreatic aquifer (Fig.6; Fig.7).

The phreatic aquifer of the plain (called A0) is formed mainly by a layer of fine sediments that continues north across the plains, these sediments are formed by fluvial channel deposits, bank and flood-plains in direct contact with the waterways surface and the ecosystems that depend on them, as well as with all human activities.

At the base of the A0 consists of clay sediments, are enriched levels of organic substance. The waters of this area have been influenced by reduction reactions by the widespread presence of organic matter. Organic matter deposits in Po delta has been found even a few tens of meters

deep, these deposits chemical and physical conditions will decompose and produce gases, especially methane. (Martinelli et al. 1998; Sciarra et al. 2013)

There are alternate fine sediments alternating silty clay sediments in various proportions. These sediments appear to be representative of fluvial channel deposits. Wells belonging to this aquifer level are mostly in sandy sediments, they are not exploited as water resource because of poor ability, but they are used to irrigate small fields and to domestic use.

In complex aquifer A0 base is a detectable organic clays level, made from some meters of dark clays. The presence and extent of this clay layer is attributable to the rising sea levels that altered the shape of the alluvial plain during Pleistocene end. The change in the shoreline position causes an interruption in the course of some rivers, dark clays due to waterlogging phenomena arising from the response of the fluvial sedimentation to environmental change.

Some features recognizable in the hydrological structure of the Emilia Romagna aquifer are:

- All aquifers have been separate from the underlying structures by powerful and continuous fine deposits and so have the characters confined aquifers.
- A1 have been formed by sand deposits that tend to create ribbon-like deposits; on the contrary, the A2 group tends to form tabular deposits. Proceeding from the Po to Bologna, these stores give way to the Apennine sourced deposits. Charging the A2 group it could be identified with more orinetal areas and belonging to the northern areas of the Po Valley.
- Of the group B does not have a lot of information and do not know the charging point.

The water mass flowing in the complex aquifer A has been analyzed in its various sublevels (Dugoni et al. 2007), the hydrogeochemical composition of the A1 level is mainly Ca-HCO<sub>3</sub>, area west of the city of Ferrara exhibition of water points Na-Cl composition. The values of E.C. are of 400 µS/ cm. Iron and manganese have high values (up to 490 µg/l Fe) and are derived from the interaction between water and sediments (Dugoni et al. 2007).

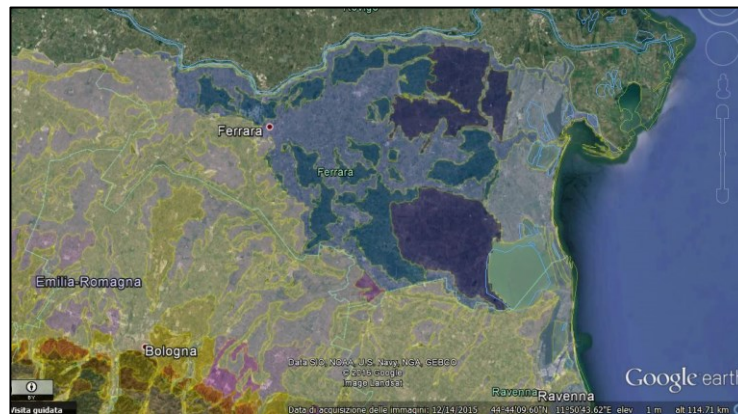
The hydrogeochemical A2 show E.C. of 1000 µS/ cm and southeast with values of 1500 µS/cm with water passing from Ca-HCO<sub>3</sub> to Na-HCO<sub>3</sub>. Increased compared to the upper level of Fe and Mg values which rose from 490 µg/ l A1 to 3690 µg/ l Fe of the A2. A3 water Ca-HCO<sub>3</sub> with a E.C. 1000 µS/ cm.

### **Geological and hydrogeological setting of the sampling area**

The area in which was decided to carry out the selection wells for ground water monitoring falls in Late Quaternary floodplain deposits.

The particularly flood plain is characterized by morphologies characterized by large depressed areas separated by reliefs and bumps of convex shape, which are related to the evolution of ancient riverbeds.

Deposit forms have been modified by human intervention, so the streams do not show the trend and the grating of the past. Current geomorphological structure is therefore to be attributed to the interaction between the natural evolution of the alluvial plain and human activity. Currently the altitude of the province still preserves traces of the most recent fluvial ridges because very often the oldest were leveled, both from the natural action of erosion, both from anthropogenic. Also subsidence, tectonic and/or geotechnical, led to the complete burial of the oldest.



- 1A Soils in the deltaic plain with hydromorphic shallow, peaty horizons, salinity, frequent sulphate acidification.
- 1B Soils in the deltaic plain with hydromorphic shallow, in contrasting texture (end of media), various internal reorganization evidence of carbonates and shrinking and swelling clays.
- 1C Soils in the delta plain, with hydromorphy shallow, medium texture, biochemical alterations, several internal reorganization evidence of carbonates.
- 1D in the coastal soils, with hydromorphy shallow flat, mainly coarse texture, low differentiated profile.
- 2A Soils in morphological depressions of the floodplain, with contraction phenomena and clay swelling, weak reorganization evidence of carbonates, desalination of surface horizons, frequently gypsum accumulation in the substrate.
- 3A Soils in morphologically detected areas of the flood plain, to biochemical alteration, moderate differentiated profile, very weak evidence of internal reorganization of the carbonates.

Fig.8 Image of the province of Ferrara taken by Charter of the Emilia Romagna soils 1: 500,000, is the new ER.

The Emilia Romagna Geological Survey maps (Fig.8) show different environments at the regional level ([geo.regione.emilia-romagna.it](http://geo.regione.emilia-romagna.it) website). The predominant environmental Ferrara province is the deltaic plain.

The dominant environment that affects the central and western part of the delta plain is characterized by complex bumps. The texture of soils ranging from medium to moderately fine. The soils are made up of fine sediments whose deposition took place in several stages.

The remaining area of the province southwest of the city of Ferrara is characterized by depression of varying amplitude and recent land reclamation, usually between bumps of Apennine streams; the surfaces do not have steep climbs and are crossed by a network of channel, the drainage of surface runoff.

The soils of this unit are flat cartographic fine texture, a moderate content of oxygen, limestone, moderately alkaline. They are also frequently saline or saline-sodic in the deep horizons.

The area of the selected wells for monitoring falls in the latter described environment. This area is also known as: High Ferrarese.

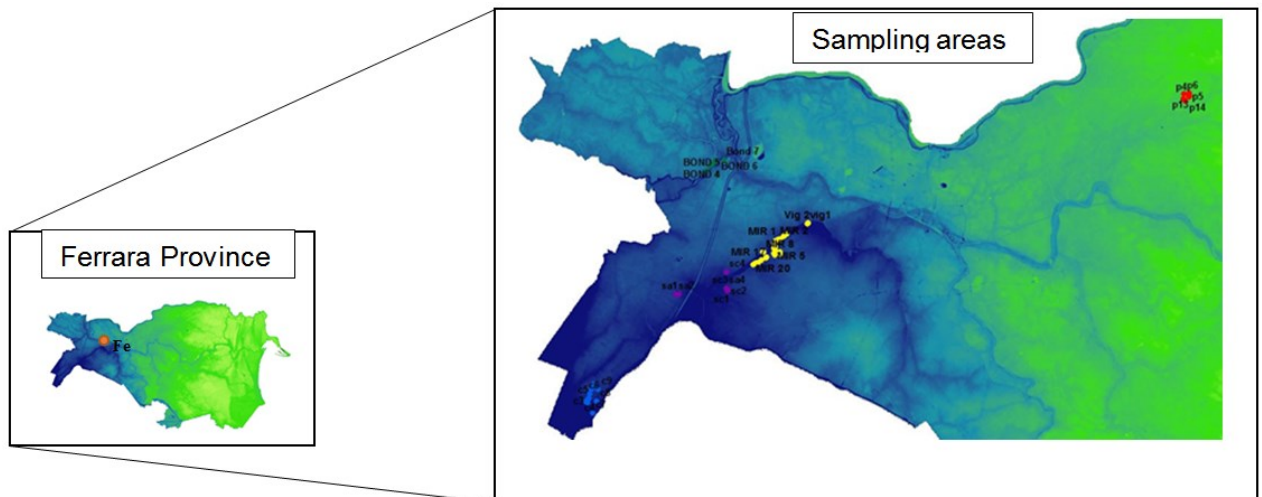
The High Ferrarese territory occupies the western part of the Ferrara Province.

The southern boundary, which separates the High Ferrarese by the Province of Bologna, is constituted by the River Reno; the northern limit corresponds in part to the province of Mantua (Lombardy) and in part in the course of the Po River, the border between the provinces of Ferrara and Rovigo (Veneto). The High Ferrarese altitude is between a maximum of 23.35 m s.l.m. (In the Municipality of Cento) and a minimum of 4.4 m s.l.m. (In the municipality of Bondeno) (Fioravante V. 2008). The elevation gain for the whole territory of the High Ferrarese is approximately 19 meters and, except for the southern portion of the municipality of Cento, that is estimated at no more than 10 meters. On the elevation elaboration is easily read the ancient courses of the main rivers which have sailed these lands, now expressed as paleo riverbeds and well recognize. In particular, it is evident the course of Paleo-Reno in Cento territory headed towards the riverbed of the Ferrara Po, the paleo-Reno area of present digression near the town of Sant'Agostino and the bumps due to paleoriver from different eras (Poazzo and Po di Ferrara) that grow in the area where now runs the Panaro River. On elevation map, are visibile also depression areas (Fig.9). The most important are the area of Diamantina the border between the municipalities of Bondeno and Vigarano Mainarda and the area of Sammartina the eastern end of the town of Poggio Renatico.

The geomorphology of the area still retains the paleo-channel signals that once crossed this area. The ancient paleo channels were flattened by the action both natural erosion, from antropic effects and by the action of subsidence that led to the burial of the oldest channels.

The present geomorphology was classified in the work by Castiglioni and Pilgrims (2001), among them are counted the bumps paleo channels, no bumps paleo channels, fans and route

channels, basins interfluvial, some forms exclusively as anthropogenic effect, artificial stretches of the riverbed, current channels and abandoned channels.



**S1: Copparo 21 Samples;**  
**S2: Mirabello 116 samples**  
**S3: Bondeno 34 Samples**  
**S4: Sant'Agostino 31 Samples**  
**S5: Cento 42 Samples**  
**S6: Diamantina 2 samples**  
**S7: Diamantina surface water 2 samples**

Fig.9 DTM portion of the province of Ferrara in which the research is carried out. From the map is possible to see the paths of paleo channels that still mark the geomorphological characteristics of the area today. The colored dots represent the sampling areas that will be explained in the next chapter.

The territory is completely flat and in a geological context of this type is easy to read the province DTM, where are particularly evident the area levees (Fig.9).

Bumps riverbeds are not particularly easy to spot on maps. The fans and route channels also have a difficult recognition because their slope decreases with increasing distance from the river.

One of the fans is certainly the most evident in area Scortichino (Bondeno) then there are fans of flooding of the Reno near Poggio Renatico and several broken channels of the Reno in the southernmost portion of Cento.

Closely connected to the geomorphology surface is the structural setting. Compressive tectonic generated folds groups and a system of faults with NNW-SSE, WNW-ESE and N-S resulting subdivision of the Po Valley in areas located by paleofaults. (CNR 2002)

Lowland sector soils have been modified in the Pliocene in which was notice a marked bending and increased erosion.



The tectonic phases that have followed have generated geographical paleo features variables in temporal succession. These stages have generated an alternation of marine depositional environments, coastal deltaic and lagoon.

The tectonic structure placed under the blanket of alluvial sediments resulted in both folds trending NW-SE; the presence of faults with NNW-SSE, WNW-ESE and NS contributed to the Po area subdivision, that have determined the basin sedimentation and different evolution.

The Ferrara Romagna arch is the most important structural element of the Northern Apennines and is bounded externally by a group of reverse faults and thrust faults (Fig.10). It is these thrust faults that separate the Ferrara Romagna arc and monoclinal Alpine as well as from the axis Berici-Euganei and the Adriatic monoclinal (Pieri and Groppi 1981).

The Romagna Ferrara arc can be divided into 3 groups of minor folds which are: the outer Ferrara folds, the inner Romagna folds and Adriatic which present a strong disharmony between clastic and carbonate sediments.

Between the ferrarese folds the dominant unit is the structure known as "Dorsal Ferrarese" consists of pleats, folds and faults and tilted fault WNW-ESE, which already in the Pliocene had high structural function. At the sides of the ridge instead are located areas of subsidence.

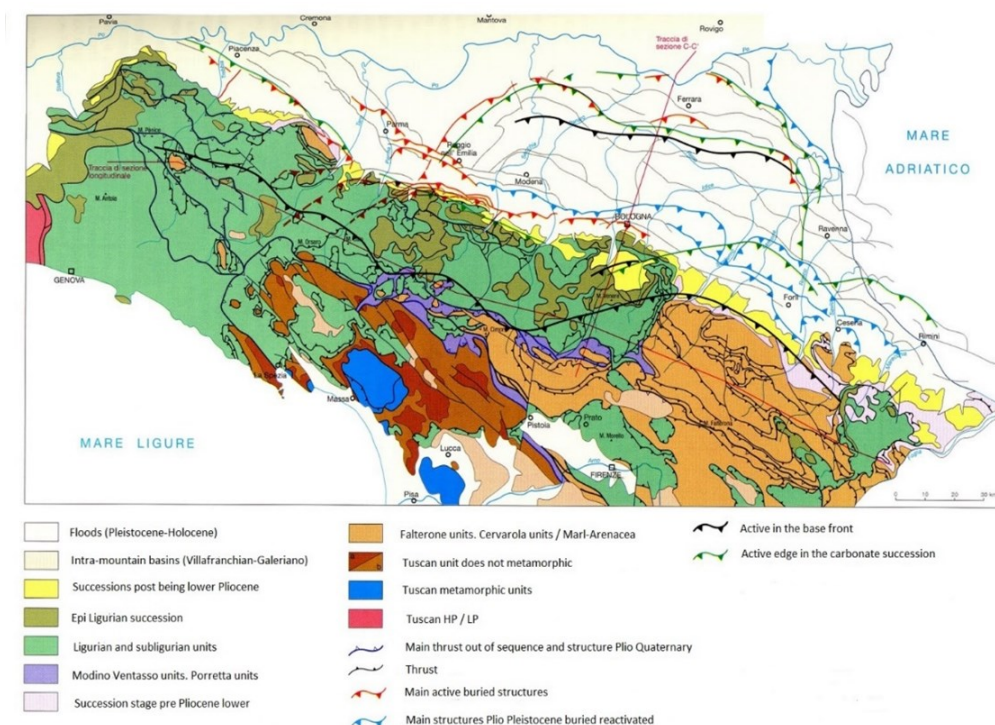


Fig 10 - Geological and structural diagram Emilia Romagna (Boccaletti 2004).

Dislocations in damage confirms that the subsoil has been affected by tectonic compression, identified as thrust faults in the Northeast and fault to the South-West.

From observations of stratigraphic logs collected nowadays, in the ViDEPI project site of the province of Ferrara, can be observed the succession of the units in depth. The deepest unit is characterized by sandstone and calcareous marl of Oligocene. In this period occurred processes of emergence which is accentuated in the lower Miocene. The emergence of the Alps and Apennines generated erosion and settling of loosed material transported by rivers. The deep units are characterized by sandstone and marl Oligocene calcareous marl. In this age occur processes of emergence which is accentuated in the lower Miocene. The emergence of the Alps and Apennines generates a grave marked by perhaps settling of loose material transported by rivers and erosion of material coming in emerging chains. This pit is also characterized by a strong subsidence that continues in the Middle Miocene. In the lower Miocene sedimentation contributed to the formation of marl, sandstone and marl sandstones. They created so the structural high areas, among them began bordering structures to define a system of folds measured in arc between Comacchio and the Modena Apennines representing Dorsal Ferrarese. In the upper Miocene stops the subsidence and it was establishing a hypersaline lagoon environment, with formation of evaporite deposits. In the period of transition between the Miocene and Pliocene there was phenomena of bending, due to a further tectonic phase. In Pliocene took place a clastic sedimentation in depressions and a smaller particle size dominance of sedimentation on the submerged ridges. The Pliocene is characterized by very porous blue clays, interbedded with layers of sand (Martinetto et al. 2015).

The Pliocene sedimentation influenced the course of the Pleistocene sedimentation, that occurs corrugated convergence of sedimentation in the south-east as they follow the structural arches immersed Pliocene.

The quaternary sediments are based on those of the upper Pliocene. In the upper Pleistocene alternate lagoon marine and continental facies, sedimentary deposits are mainly characterized by clay and peat layers.

The brackish lagoon facies are characterized by abundant plant remains and continental facies with swamps with peat levels. Clays, sandy with the local presence of peat lenses also dominate the Holocene sedimentation. The dominant and characterizing event regarding the sedimentation of the lower Quaternary are, obviously, the eustatic sea level variations, caused by glaciations which induce a type of continental sedimentation that covers the previous one marine. The sedimentation of recent alluvial deposits, which we find in the upper part of the

succession, are dominated by a wavy pattern and indicative of the presence of a variation in the sedimentation power. These characteristics of undulations may be due to the presence of the riverbeds. Most surface sediments have an age of two thousand years and are part of the post-evaporite sequence of the Po and the Adriatic margin resulting from the presence of the hydrographic network. The change in the sea level, climate and hydrographic network are the components that have most influenced the amount of transported sediment, the geomorphology of the delta, and the coast. The land surface of the sequence is grouped in Supersintema Emiliano Romagnolo, divided in Inferior and Superior Supersintema Emiliano Romagnolo, as previously explained in the section on geological arrangement (RER ENIAGIP 1998).

The areas chosen as sites for the creation of monitoring networks fall in the western area of the Po valley, known as high Ferrara. The municipality of *Copparo* has been chosen because already chosen for a wells monitoring network used as part of a European project in which a team from the University of Ferrara was involved. This area and the previous data have been made available for the realization of this thesis. The chosen areas fall, for the most part, in flood plain areas of fluvial channel deposits and embankments. In correspondence of the riverbeds are sandy sediments (principally silty sand and clayey sand) alternating with soils formed from mixtures of silt and silty clay. In morphological depressions instead topsoil consists from clay materials, composed by sandy clay, silty clay and clay. The first group of samples (Fig.11) is the one belonging to the area of the municipality of Copparo, indicated by the abbreviation S1.

S1 is located in an area in which dominate in the first layers of the soil layers of silt and clay low permeability through which a relatively permeable sandy riverbed in which is identified a semiconfined aquifer (Vincenzi 2013, Comerlati et al 2013). The water table is very shallow and has a depth of 2-2.5 m from ground level.

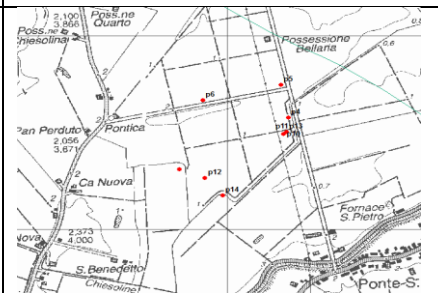
The second group of samples (Fig.11), indicated by the abbreviation S2, was sampled in the municipality of *Mirabello*, where the predominant lithology is given by ternary mixtures of sand silt clay; in the eastern part of the territory it passes to terms clayey silt. The main street in Mirabello, Corso Italia, is oriented in the direction SW-NE and retraces the old bed of the Reno River. The soil can be divided into three depositional units described from top to bottom. The first unit is important from the geomorphological point of view as there are two elements morphodepositional detected that match Paleo levees (Argine Postale left and the Argine Vecchio on the right). These paleo river beds are made, in the most proximal area, of fine sand alternating with sandy silt that pass laterally to sandy and clayey silt. In the central part of the

depression of the two paleo channel, there is a paleo river bed filled with lenticular sand bodies. Below the fluvial sands there are clays and silts with a major fraction of organic matter and levels of peats. This unit shows the presence of marshy areas. The thin layers of silty fine sand can be interpreted as distal deposits and river route. The base corresponds to step Pleistocene Holocene. The lower stratigraphic unit is composed by an alternation of sandy silts and silty sands, and form the flat Pleistocene alluvial.

*Bondeno* is the S3 sampling site (Fig.11), the western part of the area is primarily occupied by clayey silt sediments, here there are also ternary mixtures of silt and sandy clay. The riverbed of the river is a filled depression of sandy clay sediments. In the northern central portion of the municipal area are also recognizable silty sediments. The site of the sample S4 is the area of San Carlo and *Sant'Agostino* (Fig.11). Nearly the whole territory consists of ternary mixtures of clay silt sand northward pass to sandy clay sediments. The town is crossed by paleo river bed that Vigarano Mainarda reaches the level of Cento.

The last municipality in which is realized the monitoring network is in the town of *Cento*, the samples were marked with the initials S5 (Fig.11). Southern part of the town is occupied by clay sediment silt and sand, alternating with argillaceous sediments silty in the central area of the municipality.

In Emilia Romagna were explored 517 onshore wells for hydrocarbons research; 63 in Ferrara province. In 1949, at the end of exploitation in the locality Diamantina, Ferrara, it was drilled an exploration well (with the coordinates: 00°57'21,00"W, 44°53'03,00 "N, Monte Mario) to 618 m depth. The well have been " capped " because it was considered unproductive, not producing enough gas to allow production. This same well, on 21 May of 2014, was reactivated; it produced bubbling deep water. The water samples (S6) taken from this well were used in the present study, as well two samples collected in a channel few tens meters from S6 site, to compare the chemistry of the deep water and shallow water.

Sample id	City	Soil composition	Samples localization
S1	Copparo	Soil layers of silt and clay low permeability through which a relatively permeable sandy riverbed	

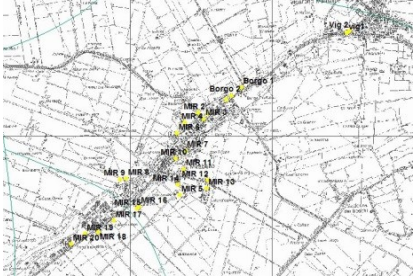



<p>S2</p>	<p>Mirabello</p>	<p>Sand and silt clay; in the eastern part of the territory it passes to clayey silt. The main street in Mirabello, Corso Italia, is oriented in the direction SW-NE and retraces the old bed of the Rhine River.</p>	
<p>S3</p>	<p>Bondeno</p>	<p>Clay silt sediments, here there are also mixtures of silt and sandy clay.</p>	
<p>S4</p>	<p>Sant'Agostino</p>	<p>Clay silt sand northward pass to sandy clay sediments. The town is crossed by paleo river bed that Vigarano Mainarda reaches the level of Cento.</p>	
<p>S5</p>	<p>Cento</p>	<p>Clay sediment silt and sand, alternating with silty sediments in the central area of the municipality.</p>	

Fig.11 Samples point localization. a) S1-Copparo:9 samples; b) S2-Mirabello:24;c) S3-Bondeno:7; d) S4-Sant'Agostino:6;e) S5-Cento:11.

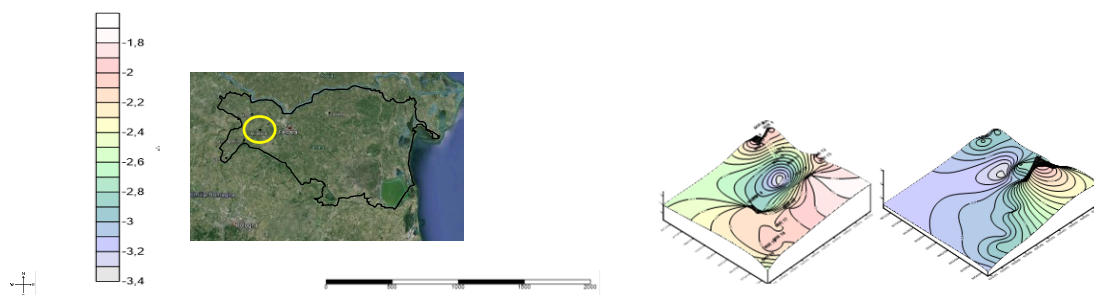


Fig 12 Piezometric level in the monitoring wells. The first picture a) is the representation of piezometric level during summer 2014, the second picture b) is the representation of the piezometric level measure during autumn 2014. The measurements are referred to the ground level.

The phreatic aquifer of the plain is the most shallow aquifer, the piezometric surface follows the topography, flowing regularly from the higher areas of the banks of the ancient Reno course to the more depressed area. The piezometry which have been misure in the Mirabello area, in the summer and autumn 2014 follow the geomorphology line of the ancient riverbed (Fig.12).

Based on available data, it is assumed that the maximum annual variation of the water level is about two meters, and always in strong dependence on the precipitation. To outline the effect of meteoric recharge of the shallow aquifer, the climatic characteristics of the studied area were analyzed.

### *Climate*

Climatically the territory is part of the dynamic segment of the Upper Adriatic which is attributable to the geographic location area called subcostiera. It extends from the sea for about thirty kilometers inland. In proximity of the sea, the area shows climate characteristics tending to continental.

The research has been conducted in wells situated in the area around the towns of Bondeno, Cento, Copparo, Mirabello and Sant'Agostino in the region of Emilia Romagna, north-east of Italy (Fig.11). In order to obtain a wider and more general climatic observation, temperature variations of the region from 1935 to the present days have been taken into account (Fig.13).

It can be seen that from 1935 to 1949 there has been a strong climate variability and from 1950 to 1980 there has been a strong tendency to negative anomalies reaching a peak in 1975. Since 1980, however, there has been a climate change with a first positive anomaly in 1994, which has been followed by a greater one higher than the average values considered during the year 2014, which appears to be a positive anomaly with a long-term average variation.

As far as temperatures are involved, an increase in the regional level has been registered, especially in recent years. As regards the percentages of rainfall over the same time interval, a positive anomaly has been recorded in 2010, a year characterized by one of the highest percentages of rainfall ever recorded since 1935, dry years such as 2011 and 2012 have followed, turning to a slight growth over the last three years (Fig.13 b).

The method of climatic type definition can be described as “outer Padanian type” characterized by scarce rainfalls yet well distributed throughout the year, whose most wet season is autumn, while the driest is winter.

The recorded rainfall average is quite coherent throughout the country, nevertheless it is considered to be underneath the Italian annual average of about 35% (640 vs 990 mm/ year). The station of Codigoro (in the province of Ferrara) has been selected as representative sample on the basis of the parameters in the observation period (1950-2016).

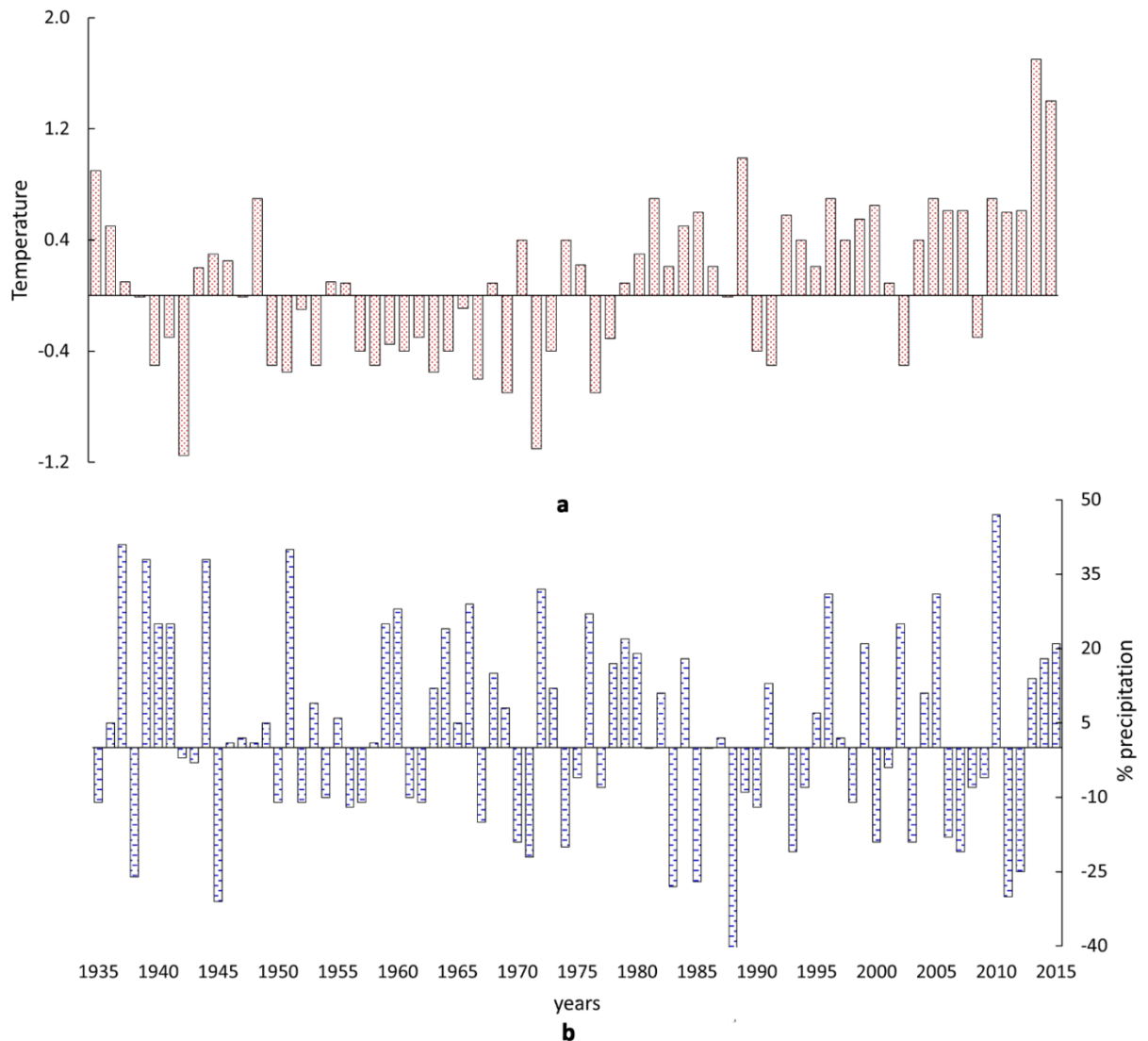


Fig. 13 a.Trend Of regional average temperatures from 1950 to 2015. Trend b. trend of the % rainfall on the Emilia Romagna region from 1950 to 2015. Chart Source: Annals hydrological, ARPA-ISCM networks and ASMER.

In the station of Copparo the percentage of rainfalls and temperature measurements (during the sampling years 2014-2015) have been more thoroughly analysed because of the considerable amount of available data.

In Codigoro it has been analysed that the distribution of short and intense rainfalls within 1 hour and within 3 hours demonstrate a greater concentration of weather events during summer

months as far as precipitation within 1 hour is concerned, while precipitations within 3 hours are better apportioned from February to November, with a higher concentration always in summer months. Winter would thus seem to be the driest season (Fig. 14). Figure 15 show the relation between the intensity of the most intense phenomena, to 3h and 1h, were actually prevailed short phenomena or if they had prevailed those from passages of storm lines (to 3h). Even in this case, the signal does not show significant variations; clear sign that the atmospheric dynamics that determines storm conditions is absolutely not varied.

Rainfall observations in Copparo have shown changes from 757 mm / year in 2014 to 625 mm / year in 2015, this assessment is the result of combined temperatures anomalies (in 2014 and 2015 Copparo station passes from an average of 9.89 ° C to 8.21 ° C with an increasing maximum of 20.2 ° C and 23.3 ° C during the two years respectively).

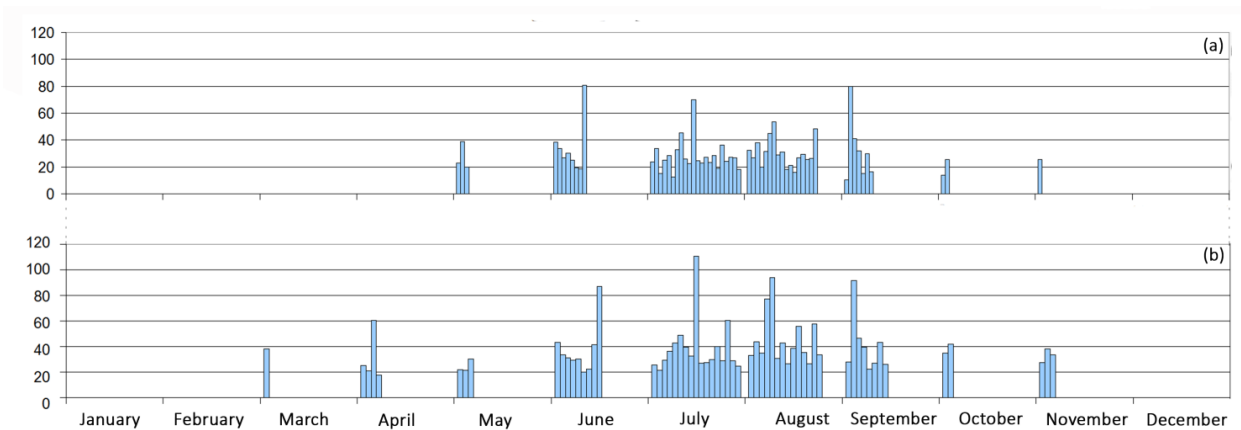


Fig 14. Monthly trend of short and intense rainfall in 1 hour and b) 3 h in the station Codigoro.

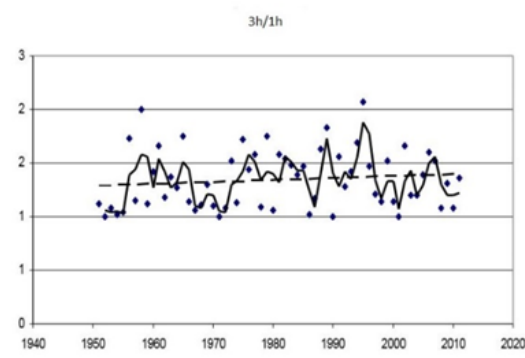


Fig 14 Precipitation ratio 3h / 1h. in Codigoro station



**Subsident phenomena**

The high consumption levels due to the great exploitation of water resources have generated land subsidence phenomena of 10–40 mm/year in main towns (Carminati and Martinelli 2002) this overfishing have generates marked subsidence and deterioration of groundwater quality. Over 20% of groundwater is used for agriculture (Dadomo et al. 2013). Phreatic aquifer is characterized by a depth water in the range 1–12 m while the average yearly excursion is around 1.2 m. Monitoring surveys allowed to establish that recharge of phreatic aquifer is mainly due to local rainfalls while rivers and a dense channels network drain phreatic aquifer. The geologically active areas in the subsurface of the Po Valley are conditioned by Ferrara folds which affect the distribution of ground regional subsidence. The rate of subsidence affect the provincial qualitative status of groundwater and conditions the changes in the water chemistry and in particular the variation in the salinity determines electrochemical phenomena capable of inducing the decrease of volume of clay minerals (Pignone et al. 2008). The most critical situations occurring in part in the coastal area, there where the average subsidence values were measured around 5-10 mm/year. Topography is low with many sectors below the sea level, the phenomenon is a risk factor that can lead to consequences of deterioration of water quality by encouraging the marine ingression.

**State of monitoring action on the territory**

The Water Protection Plan PTA, in accordance with the provisions of Legislative Decree no. 152/99 and the European Directive 2000/60 (WFD) are the regional instrument to achieve the environmental quality objectives in water and coastal region. The Regional Council has approved the preliminary document of the PTA in November 2003, after a work done in collaboration with the provinces and the Basin Authority and the technical and scientific support of Region (ARPA provincial) experts and specialists in various sectors, and coordinated by the competent regional department in collaboration with other regional areas. Following approval of the preliminary document, were held by Planning Conferences and by the provinces.

The Water Protection Plan was finally approved by Resolution no. 40 of the Legislative Assembly on 21 December 2005. On BUR - Part Two No. 14 of February 1, 2006 has been

given notice of its approval, while the BUR n. 20 of 13 February 2006 was published the Resolution of approval and standards (<http://ambiente.regione.emilia-romagna.it/acque/temi/piano-di-tutela-delleacque>).

According to Article 5 and Attachment 4 of the Legislative Decree 152/99, the PTA shall establish the measures necessary for the maintenance or achievement by 12.31.2016 on the environmental quality objectives for significant bodies in view the objectives defined by the Authority. As the PTA is a dynamic tool, is needed a constant monitoring and assessment of effects and spin offs of management policies and actions which could enable to adjust managements modes of the water cycle and changing scenarios, in view of the attainment of targets or the identification of difficulties or critical issues. LR 3/99 has attributed to Provinces relevant competences in water policies both concerning knowledge based aspect (monitoring of qualitative and quantitative features of water via ARPAE). The co-responsability in the choice made through the PTA the tool definition and the attribution of autonomous planning choices. Arpae manages 20 monitoring networks for continuous monitoring of the main environmental matrices (water, air and atmosphere, soil) in region. Through use automated equipment, manuals and specific measures campaigns are acquired data and indicators to analyze and evaluate the state of the environment. Arpae adopted a quality management system based on the UNI EN ISO 9001: 2008

The groundwater monitoring includes two types of monitoring quality network:

- Regional network of environmental state monitoring of groundwater;
- Regional network of groundwater automatic monitoring.

Regards continuous monitoring of physical parameters, as part of the project-related activities for the seismic verification of embankments on the right bank the River Po from Boretto (RE) to Ro (FE) have been put in place 40 piezometers equipped with sensors for level hourly reading, temperature and electrical conductivity. This probes have been distribute in 10 stations in the river area (Severi et al 2012). Four of these stations have been place in the town of Bondeno (Ferrara province) to test the effects generated by the Po River on the confined and unconfined aquifers.

Each monitoring station consists of 10 m deep wells for control of unconfined aquifer and 50 m for the confined aquifer, positioned near the river and a few kilometers to the south.

This monitoring conducted by the Region estimated that there is a direct influence of the river on the first confined aquifer level at a distance of 1-1.5 meters from the river.

Instead aquifer further away from the river, considering for example a distance of 2.5 kilometers are affected only by the river during floods more.

The water table shows seasonal fluctuations, with highs usually late spring and minimum usually late summer or autumn. The maximum variations were recorded from 2 to 2.5 m due to influence of local rains. As regards instead the confined aquifer monitoring, it was noted that this follows the course of the river but nevertheless always lower to it. The trend of the aquifer shows a certain seasonality strongly influenced by the presence of the river Po (with maximum spring or late winter and summer minimum). The multiparameter probes (temperature, level, and electrical conductivity) were installed by the Region to conduct this continuous monitoring project with STS automatic probes Environmental monitoring associated with a GPRS data transmission module that communicates with a base station (laptop) with a remotely communication connection.

After evaluating state of provincial monitoring network has been established that the geographical areas in which set the new monitoring surveys point and continuous monitoring network would be Bondeno, Cento, Mirabello and Sant'Agostino. Moreover, the municipalities of Copparo was included, being only out area from the called High Ferrarese zone. This last was selected because affected by presence of paleochannel relatively permeable sand (Vincenzi 2013).

These location points have been selected in order to obtain representative data for an homogeneous area of the monitoring parameters. In this work it was decided to create a phreatic aquifer monitoring network in area poorly covered by the provincial monitoring network, in order to evaluate eventually existing shuffles between the deep and surface water corresponding to deep structures. The data from the sampling of the network created specifically for this work were compared with data collected by the provincial database. The possibility of comparing the phreatic monitoring data with the data belonging to the deeper aquifer levels was made possible thanks to a collaboration with the Emilia Romagna Region in particular with the Geological Survey of the Region and with dr. Paolo Severi.

## **Materials and methods**

### **Available data set**

The data used come from:

- Physico Chemical data and depth to from ARPA Network Monitoring (2002-2015)
- Physico Chemical data from the monitoring network in the areas of high Ferrara (2014-2015)

For the construction of the monitoring network were taken into account:

- wells/ piezometers not abandoned and privately owned
- depth of wells / piezometers no more than 10-12 m.

Hydrochemical data series selected for the provincial aquifer levels analysis have been collected from the data managed by databases Regional Agency for Prevention and Environment of Emilia Romagna. The data collected in the wells were collected prior to a file for synthesizing the structural characteristics, after by affiliation level and year.

Samples collected for the groundwater definition:

55 samples to represent and classify A1;

16 samples A2;

19 samples A3;

the useful samples to represent A4 are 6, statistically insufficient to represent the aquifer level.

Data collected added to the data of the new monitoring network made in the areas subject of this thesis: 26 samples in the S1, 116 S2, S3 in 34, 31 in S4, S5 42, S6 2 samples, S7 2 samples for a total of 253 samples (Fig.16) . The water wells that have been analyzed are of ancient construction, have a diameter of 1 meter and have been built when the excavation wall is sustained by briks while their depth goes from 7 to 10 m.

### **Sampling area and tratament method for analysis**

The work concerning the hydrogeochemical characterization of groundwater and trend of salinization / freshening processes, has been divide according the following steps:

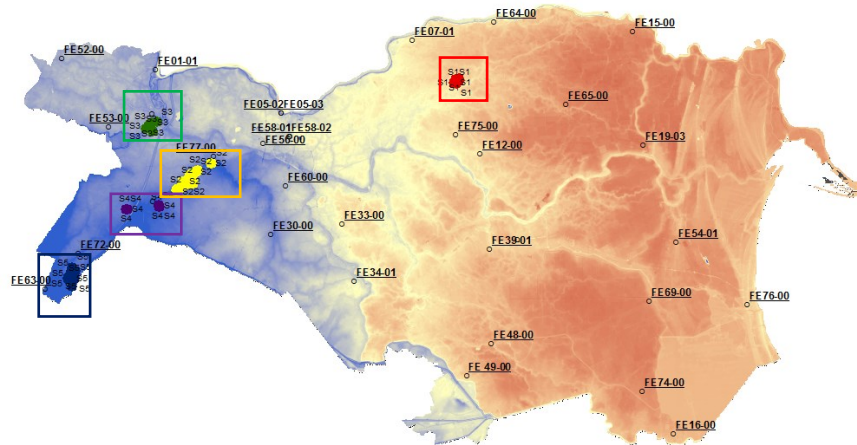


Fig.16 The figure shows the DTM the province of Ferrara and the collected data points. The points black are part of the data collected in the ARPA Ferrara relations, in red are represented the points championships in Copparo S1, yellow wells sampled in Mirabello S2, in Green points championships in Bondeno S3, in purple sampled wells Sant'Agostino S4 and blue wells sampled in Cento S5

- a) Analysis of the territory on a map (DTM, CTR) and digital (Google Earth) for the identification of the most appropriate sampling points and direct recognition in the country ;
- b) Collection of water samples from the surface of the first unconfined aquifer, according the disponibility of citizen private wells;
- c) Laboratory analysis;
- d)Hydrogeochemical interpretation of characteristics of each aquifer levels and identification of specific chemical markers;
- e)Application of geochemical models indicative of the tendency of the processes which take in place.

Three aliquots were collected for each sample point, the waters were stored in polyethylene bottles and filtered with a 0,45 micron filter. The samples for the measurement of minor and trace elements were acidified with  $\text{HNO}_3$  diluted (1:10 or 1:20 depending on the E.C.). The temperature, pH, electrical conductivity and TDS were measured in situ using a multiparametric probe of Hanna instrument (HI 9828).

Precautions consist of measuring sensitive components in the field or the conservation of samples for later analysis in the laboratory. Conservation is in most cases done by adding  $\text{HNO}_3$  acid to the samples. Acidification stops most bacterial growth, blocks oxidation reactions, and prevents adsorption or precipitation of cations.

The  $\text{HCO}_3^-$  has been measure in situ with the Alkalinity Test Kit Hanna instrument (HI3811). This method measures the total alkalinity by using a drop of Bromophenol blue indicator in 5 ml of sample in addition then using a titration solution until the solution becomes yellow (Fig.17).

The accuracy of the analysis for major ions can be estimated from the electrical balance (E.B.) since the sum of positive and negative charges in the water should be equal:

$$\text{Electrical Balance (E.B., \%)} = \frac{(\text{Sum cations} + \text{Sum anions})}{(\text{Sum cations} - \text{Sum anions})} \times 100$$

where cations and anions are expressed as meq/L and inserted with their charge sign. The sums are taken over the cations  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , and anions  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ .

All water samples were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo Electron Corporation X series spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts) An internal element standard composed of Rh and Re was added to each solution to a final concentration of 100 ppm. As standard reference materials, SCP-Science were employed.

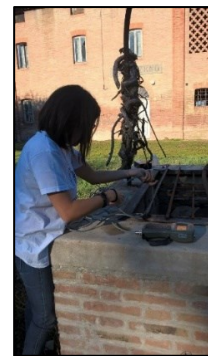


Fig 17 The figure shows examples of private wells in which was conducted the sampling. In the middle photo it is visible to the sampling kit and analysis of bicarbonates. The sampling sites are for the most part located in country farms in which the well water is used to irrigate the surrounding fields.

Ion chromatography 883 Basic IC plus was used at the Department of Earth Sciences of Technical University of Darmstadt (Germany) (Fig.18) to obtained anions values of ( $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  mg/L). The samples were prepared by dilutions of suitably calculated on the basis of the electrical conductivity of the samples.

In Department of Earth Sciences of Darmstadt have been analyze heavy isotopes of water samples by the instrument Picarro L2140 which analyzes  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ ,  $\delta\text{D}$  and  $^{17}\text{O}$ -excess liquids and  $\delta^2\text{H}$  (Fig.19).

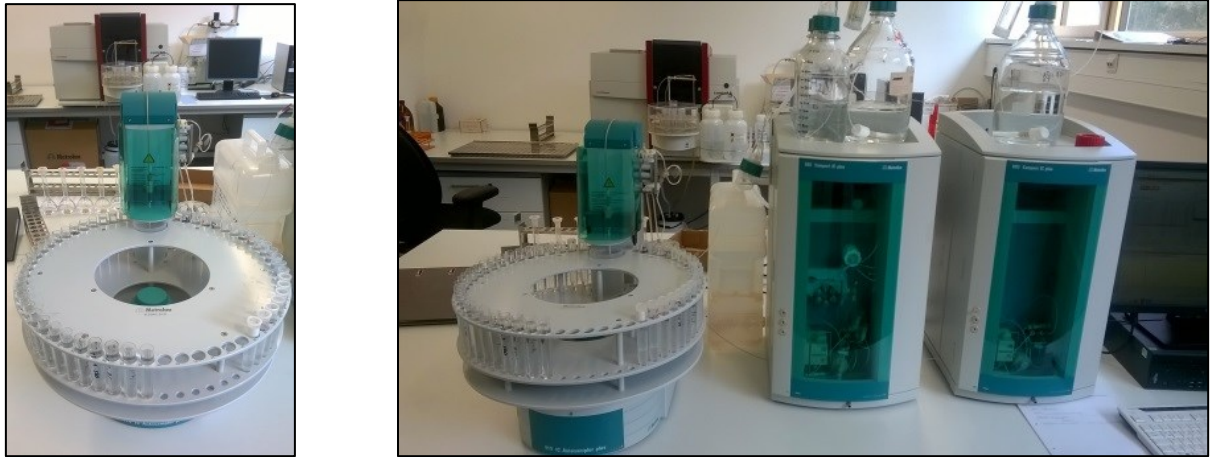


Fig. 18 Ionocromatography used at TU Darmstadt.



Fig.19 Instrument Picarro L2140, used in TU Darmstadt, automatic sampling device.

The spectroscopy Picarro laser is constituted by: Vaporizer: cylindrical chamber equipped with a temperature control system maintained at 140°C to allow the complete and instantaneous vaporization of the injected sample, which is then mixed with gaseous nitrogen or dry air (gases with functions of extender and carrier) and then sent to the analyzer Data Acquisition System - DAS:

All samples were analysed by accredited laboratories of universities, using standard practices. Groundwater's geochemical compositions is mainly influenced by the evaporation of surface water, which produces a high concentration of salts during low-rainfall seasons when the water recharge is less than during the rest of the year. If there is no evaporation no exchange

with rocks or dissolved gases, the stable isotopes are retained and it can be reflected the mixture of ground water's turnover and origin. The abundance of stable isotopes in water's molecules, has allowed us to track the hydro-climatic history of aquifers.

The isotopic abundance which leads to a specific signature of the ground water, is influenced by environmental conditions ( $T^{\circ}\text{C}$ ) and by the depth of the turnover (Mook 2001; Negrel et al. 2017).  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of precipitation could be a first-approximation way to reconstruct vapor-mass sources and air-humidity. The use of the d-excess value has allowed to track the kinetic effects due to air masses evaporation.

Several studies have shown that high d-excess values in precipitation are typical of higher moisture recycling along air masses trajectories over the continent, while low values indicate evaporative losses (Craig 1961; Dansgaard 1964; Merlivat and Jouzel 1979; Jouzel and Merlivat 1984; Johnsen et al. 1989; Rozanski et al. 1993).

According Oberhänsli (2009), hydrogeological investigation should start from the knowledge of the hydrogeochemical characteristics of the surface water and ground water, whose sources are represented by rain water.

The variations of these parameters in natural waters are attributable to the different properties of the water's light and heavy molecules, during the evaporation-condensation processes, previously described by Fritz and Fontes (1980) in terms of kinetic effects and isotopic exchange in equilibrium reactions. The vertical and horizontal movements of air masses involve the progressive isotope residual water depletion (Dansgaard 1964; Craig 1961).

In this work, the isotopic technique has been used to identify any compositional alteration due to climate change using heavy isotopes as phreatic aquifer tracers in specific sites of the province of Ferrara (Emilia Romagna, Italy).

The quality of data for each water sample has been verified by means of electronic budget; all the samples that presented an estimated error rate of above 10% have been rejected.

The two-way Analysis of Variance (ANOVA) was used to verify the differences among groups on all data collected during water analyses. All data analyses were carried out by means of the XLSTAT software (Addinsoft, Paris, France). Data elaboration was made with GW\_Chart (Version 1.29.0.0 U.S. Geological Survey, Reston).



**Bex index**

To check if ion exchange occurred with waters of marine origin, there are a series of indices that compare the ratio between the most present ions in fresh waters (Ca, Mg) and the ions that characterize the composition of the sea (Na, Cl). In this project has been chosen the bex index in which is used the equation:

$$\text{BEX} = [\text{Na}^+ + \text{K}^+ + \text{Mg}^{2+}] \text{ measured} - 1.0716 * \text{Cl} [\text{measured}]$$

The BEX index is expressed in meq/l and the 1.0716 factor is equal to the average ratio of cations and anions typically marine oceans (Skirrow and Riley 1975).

The index use BEX, however, provides the following assumptions:

- the cations  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  are mainly derived from marine origin;
- chlorine always maintains a conservative behavior;
- the three typical sea water cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ) all contribute to the exchange with the  $\text{Ca}^{2+}$ .

The first of the above assumptions is particularly important, since the main mineral carriers of Na and Mg are halite and dolomite, respectively, which in fact may be constituents of the solid matrix of the aquifer, in 2008 the same author (Stuyzand 2008) proposed a new cation exchange index in which magnesium does not appear to be used when it notes that the presence of dolomite aquifer

$$\text{BEX} = [\text{Na}^+ + \text{K}^+] \text{ measured} - 0.8768 * \text{Cl}^- [\text{measured}]$$

Respecting the conditions listed above, depending on the values assumed by the BEX index it possible interpret the trend of the on going processes in the aquifer:

BEX > 0 softening trend

BEX = 0 substantial balance

BEX < 0 tendency to salinization

**Adsorption cationic process**

The cation exchange capacity is the amount of exchangeable cations, expressed in milliequivalents per 100 gr (meq/100g), that a said exchanger material, provided with adsorption properties, can retain ion exchange.

The adsorption or cation exchange is a reversible process that develops in the interface of the surface of separation between a solid material, provided with exchange properties, and a solution of salts. These cations are held by the negatively charged clay and organic matter particles in the soil through electrostatic forces (negative soil particles attract the positive cations). The cations on the CEC of the soil particles are easily exchangeable with other cations and they are plant available. The CEC of a soil represents the total amount of that the soil exchangeable cations can adsorb. Soil pH is important for CEC because as pH increases (becomes less acid), the number of negative charges on the colloids increase, thereby increasing CEC.

In the soil, the heat exchanger is depicted by the solid particles that have a size less than 0.1  $\mu$ m, able to behave as hydrophilic colloids electronegative; these particles are in clay particle size and are represented for the most part from the humus and clay minerals from the properly said (montmorillonites, vermiculites, illiti, etc.). At high pH values behave as colloids also electronegative iron hydroxides and aluminum (gibbsite) and clay minerals of the kaolinite group, but in these minerals ordinary conditions have a very low cationic exchange capacity and behave as colloids electropositive. The total area developed by electronegative colloids is generically called "exchange complex". The salts in the soil solution is represented by the water that occupies the interstices of the soil and the mineral salts dissolved in its. The CEC depends in a first approximation by the grain size of the sediments, and from the specific surface area of all the particles, as well as by their chemical-mineralogical composition. Clays for example have a large surface area with a provision of areal electronegative charges, while the organic colloids can present to their surface is negative charges than positive.

So considering the arrangement of charges on the surface it's possible deduce that the more extended is the colloidal surface, the greater adsorption capacity of the ions from the soil. The adsorbed ions are in dynamic equilibrium with those present in solution and can be exchanged with the latter becoming available to plants. The release with which it can be exchanged for a cation depends, in addition to the characteristics of the heat exchanger, also by the characteristics of the adsorbed ion (number of charges, ionic radius, hydration, etc.), by the presence of other cationic species in solution in contact and their concentration. The ions that

would normally go to neutralize the negative sites constituting the CEC are calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), potassium ( $\text{K}^+$ ), sodium ( $\text{Na}^+$ ), hydrogen ( $\text{H}_3\text{O}^+$ ) and Aluminum ( $\text{Al}^{3+}$ ). The last two are acidifying ions. The cations calcium, magnesium, potassium and sodium together form the basis of exchange. The relationship between the bases of exchange and the CEC indicates the degree of base saturation (GSB).

In soil, the presence of particles provided with exchange properties is concentrated almost exclusively in the fraction clay. In these conditions the CEC is determined not only by the nature of the exchanger and on the pH but also from the content in the clay fraction. The CEC show relatively high values in clay soils of temperate zones, especially if soil is rich in minerals of vermiculite and montmorillonite groups. The highest values of the cationic exchange capacity are found in any way in the organic substance-rich soils, with extremely high levels in peat soils. In general, relatively high values, including between 15 - 50 meq/100g are found in rich clay soils of high exchange capacity colloids, while in soils with a high content in organic matter can also exceed 100 meq / 100g. An empirical formula that binds the CEC to the percentage of clay and the organic carbon content in next to neutrality pH conditions (Breeuwsma et al. 1986) is as follows:

$$\text{CEC (meq / kg)} = 7 * (\% \text{ clay}) + 35 * (\% \text{ C})$$

The table 1 reports the CEC of the common soil constituents. From this table it is evident what was said before and that is, as the CEC depends on the mineralogical structure of the sediments and the surface area accessible to water (Appelo et al. 2005).

<b>Mineral components of common soil CEC</b>	<b>CEC</b>
Kaolinite	30 – 150
Halloysite	50 - 100
Montmorillonite	800 – 1200
Vermiculite	1000 – 2000
Glaucinite	50 – 400
Illite	200 – 500
Clorite	100 – 400
Allophane	Up to 1000

Tab.1 CEC values of mineral components of common soils (from Appelo et al., 2005)

The determination of the Cationic Exchange Capacity is based on the ability of the basic residue of an electrolyte to remove the bases of adsorbed exchange. The soil sample is subjected to the action of a solution containing a specific electrolyte; in this phase are adopt

standard procedures which provide for example the buffering of the pH to a reference value, the mechanical treatment (agitation, centrifugation). During the treatment the basic residue, represented by a cation, replacing the cations adsorbed that pass into solution. It is possible to make specific analyzes to allow trace the value of the exchange capacity. The most commonly used methods for the extraction of the bases of adsorbed exchange (Ca, Mg, Na, K) use of solutions of Ammonium Acetate, chloride Barium and Silver-Thiourea.

Most common methodologies applied for the cation exchange determinations are:

- *Extraction with ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>):* The upside of this method is the availability of a substantial database against which to check your own results. This method is well suited to run in testing laboratories and offers a good repeatability of the results, with an error margin of 10%. Moreover, the extract can subsequently be used for the quantitative determination of the exchange bases (Ca, K, Mg and Na exchangeable). The disadvantage of this method resides in the characteristic of the reagent used: the ammonium acetate solution brings in significant quantity of extract calcium from the limestone fraction
- *Extraction with barium chloride (BaCl<sub>2</sub>):* This method has many variations which contemplate the extraction with barium chloride in aqueous solution or in ditrietanolamina solution with buffer at pH 8.1. In alkaline soils, while also extracting calcium from limestone fraction, it provides a margin smaller than the ammonium acetate method error.
- *Extraction with Silver-Thiourea (AgTU):* This method studied by Chabra (1975) produces results that are found to be unreliable for this instability caused by chemical analysis resulting in precipitation of Ag<sub>2</sub>S which leads to an overestimation of the CEC. This is probably caused by an adsorption excess of a part of AgTU cations, due to a hydrophobic interaction mechanism. Following these initial findings on the method, Dohrmann (2006) proposed a reworking overcoming these problems, adding two steps of washing with deionized water, after an initial saturation AgTU cations.

CEC procedure used for this thesis was conduct in the CREMINER Water Laboratory of the Evora University and the protocol used has been developed from T. Canario. The method proposed was an interpretation of ammonium acetate method:

The samples have been treat with ammonium acetate solution at pH 7 to remove the exchange cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>), which will remain in the filtrate where will be dosed by atomic absorption spectrometry. The residue, after washing with ethanol to remove excess ammonium, has been treat with an KCl solution. Ammonia is determined by steam distillation and acid-base volumetry, corresponding to the value of the cation exchange capacity of the sample. The peculiarity of the method consists in trying to simulate as much as

possible the mechanism of the interaction that occurs between water and sediment, in particular, with certain features used in the step of stirring and filtering.

### **Bridge protocol**

The last step that was conducted after obtaining a complete data set on areas of interest, has been make the determination of natural background values and limit values. The procedure that has been selected to carry out this work is the BRIDGE PROTOCOL - Background criteria for the identification of thresholds groundwater. This provided guidelines for the development of a common strategic action (Common Implementation Strategy-CIS) for estimating NBLs. Main objective of this methodology was to establish a procedure applicable even in situations where the type and amount of data available was not able to allow the use of more sophisticated hydrogeochemical modeling methods (Muller et al. 2006). Threshold values for the groundwater define the extent to which the concentration of a certain substance may exceed the natural background level (NBL) without failing good chemical status. Therefore, the NBL plays a central role in the derivation of threshold value, as it is the starting for the whole process (Karro and Marandi 2008). The NBL derivation process requires a high level knowledge of geochemical transfers and processes. It also requires groundwater monitoring data for the whole country, specific groundwater typologies or for a specific groundwater body.

The composition of groundwater depends on the hydrological and hydrodynamic. Apart from these natural conditions the groundwater quality is influenced by anthropogenic inputs. Some of these inputs such as pesticides, may be used as a measure of human activity on water resources. This delicate system makes it difficult to distinguish between what is real and original composition of underground water and the solution result by the action of pollutants. For the management of the underground resource becomes a fundamental tool determining the natural background values and thresholds values. According to the EU Groundwater Directive Article 3 (GWD 2006/118/EC), EU Member States were obliged to establish groundwater threshold values (TVs) by the end of 2008 and to publish them in the EU Water Framework Directive (WFD) (WFD 2000/60/EC) river basin management plans.

Reproduce a paragraph exposed in the WFD guidance document:

*-according to Annex II Part C GWD Member States need to summarise the way the procedure set out in Part A of Annex II GWD has been followed and, where feasible:*

- *Information on the number of groundwater bodies at risk, the size of the bodies and the pollutants and indicators of pollution contributing to this classification;*
- *The relationship between the groundwater bodies and the associated surface waters and directly dependent terrestrial ecosystems (GWDTE);*
- *The threshold values (TVs) for each parameter and indicator of pollutants contributing to the risk classification and at which level the TVs apply (groundwater body, River Basin District, part of the international River Basin District, territory of the Member State);*
- *Relationship between TVs and background levels for naturally occurring parameters; and*
- *Relationship between TVs and environmental quality objectives and other standards.*

The natural background concentrations are a result of a number of water-rock interaction processes, chemical and biological processes that occur, interaction with bodies of water, residence time, and the paths that accomplish groundwater flows in the subsoil with mixing processes that can occur and the interaction of the water with the natural recharge. For the co-presence of all these situations the determination of natural background values varies according to the context that is considered and can also vary spatially within the same stratigraphic complex (Wendland et al 2003).

Given the spatial variability and the variability due to the large number of factors on which depend the natural background values, European legislation establishes to define a single threshold value within each water body identified. The threshold value is established for each of those chemical compositions which are considered fundamental for the distinction of the value of the given parameter.

The threshold values define how a certain substance exceeds the NBL observed without cause a deterioration of the quality status of water. It represent an Upper Tollerance Limit which is possible to consider as the high probability percentage to to found that values in successive sampling.

So the NBL has a fundamental role in the determination of the thresholds thus representing the starting point for the whole process.

BRIDGE has proposed a methodology of NBL derivation which can be schematized as follows (ISPRA 2009):

- *Determination of the aquifer typology on the basis of a hydrogeochemical typing of European aquifers operated taking into account the lithology, the degree of salt intrusion, hydrodynamic parameters, redox conditions, organic matter content, mineral oxides and sulfides, as well as the geological age .*

- Identification of an approach to use based on the type, the quantity and reliability of available data.

The approach proposed by the protocol used here is a "focused approach" (Muller et al 2006). It is recommended approach derive TVs for underground water bodies. Each branch of this process requires a knowledge of the area in which we act and a good collection and data analysis. The start point is an intensive knowledge of the system in which the protocol have to be used.

There are numerous applications of the methods for the determination of background values (Wendland et al 2005, Wendland et al 2008, Ducci et al 2016, Preziosi et al 2014, Rotiroti et al 2013, Molinari et al 2012).

In the present work it was decided to use the statistical derivations proposed in the basic methodology proposed by the Bridge Protocol, and a proposed amendment by ISPRA in 2009 for Italy.

The study focused on A0 and A1, A2, A3 , the A4 was not taken into account because it has at its disposal only a well and is not statistically valid estimate these parameters on the values attributed to a single well.

The wells have been selecte on the base of available information related to the structural characteristics. In this way the composition is not affected by shuffles between waters belonging to different levels of the aquifer.

The threshold values for groundwater define the extent on which the concentration of a substance may exceed background levels without lessening the chemical status. The background value is not determined for those elements clearly derived from anthropogenic effects.

The parameters that were taken into consideration for the determination of NBL are those same parameters that define the water quality status in the Legislative Decree 30/09 and the table establish in 152/06:

*-Electrical conductivity*: it is given by the content of dissolved mineral salts. Represents an indicator of the saline content and degree of mineralization of water, can therefore be used as an overall indicator of the quality of water characteristics.

Degree of mineralization of waters contextually increases the permanence of the water in contact with the aquifer sediments, it is therefore implied that the infiltrating water have minimum values of conductivity on the contrary instead of the waters that have a lower speed of movement, and are farther from infiltration and recharge areas. By comparison with the

regional values of the Ferrara area reaches higher values associated with presence of salt "ancient water" trapped in pre Quaternary deposits in the Dorsal Ferrarese structure.

- *Chlorides*: these represent one of the main terms which causes the increase of the specific electrical conductivity in respect to which their distribution has strong similarities. This however is not always a discriminant. Chlorides can present substantial differences with the conductivity as it does not represent the degree of mineralization of waters but are connected with other phenomena.

- *Iron*: The aquifer characteristics greatly influence the presence of this element in groundwater. It increases where the aquifer becomes confined and where there is a water evolution. It is strongly influenced by the conditions of pH and redox potential. The dissolution and precipitation of iron minerals that are present in the aquifer matrix most affect the distribution of iron in groundwater. The iron concentrations in water also depend on the solid matrix, which derive from dissolution of ferrous minerals present in the solid matrix of the aquifer.

- *Manganese*: This has a very similar behavior to iron, this is subject to redox excursions that depend from Eh and pH. It is present in high concentrations in the floodplain. As already noted it often accompanies iron, but has a different response to the environment oxidation-reduction.

- *Ammonium ion*: Its distribution in the groundwater of the plain was affected by the evolutionary framework of the same waters clearly indicating its ancient water source under reducing conditions. When nitrogen comes in groundwater in oxidized conditions it occurs mainly as nitric. Natural occurrence of  $\text{NH}_4$  in the groundwater reservoirs is essentially linked to the organic matter cycle and, in particular, to the anoxic decomposition of paleo peats. (Molinari A. et al 2012). The increase can be connected with the use of fertilizers.

- *Boron*: The presence of boron is due to specific site mineralogy or in the presence of thermal waters, marine and paleo waters where this element is abundant. The events linked to human presence of boron may be due to changes in redox conditions due to human activity that can be produced by a boron enrichment dissolved or contaminated flows arising from the use of livestock substances on the surface. These sludges are rich in boron and may enter the groundwater system through free surface bodies from which can enrich deep bodies.

- *Arsenic*: The mechanisms that govern the presence of arsenic in groundwater are governed by the pH of the redox potential and its oxidation state. This element is commonly found in geothermal waters, in mineralized areas, volcanic glass and rhyolitic to intermediate composition. It can be associated with minerals and organic carbon sulfites. The natural



arsenic may also be associated with denitrification processes like clay and metal oxides. Arsenic can also be introduced into the groundwater from anthropogenic sources such as non-ferrous metal mining and smelting, fossil processing and combustion, wood preserving, and pesticide production and application and disposal of municipal and industrial waste incineration (Prosun et al 2002).

Research conducted by the CNR (conducted by the Defense of the Hydrogeological Disasters group) showed that arsenic occurs locally even with values above the national limit of 10  $\mu\text{S} / \text{l}$  for reasons that can not be attributed to anthropogenic pollution. The highest values were found longer confined aquifers of the region, low transmissivity stationed where the waters even for thousands of years, far surface supply.

The arsenic presence has been traced to a depth primary origin, linked to the aquifer substrate materials, high clay content or fossil organic. To verify the origin of the element in the groundwater of the region, ARPA Emilia Romagna has carried out research on the chemical and physical dynamics of the aquifer. Significant changes in the redox potential were also recorded in conjunction with local seismic events. The variations of the redox potential can simultaneously generate variations of arsenic and iron observed in the sampled groundwater, there confirm that the stability of the crystalline structure of iron hydroxides, capable of adsorbing arsenic, is dependent on the redox potential. The in-depth studies that have been conducted on the solid matrix has confirmed the participation of arsenic to the dissolution and precipitation of iron oxides. Furthermore, another result of the studies was to determine the behavior of the opposite arsenic compared to that of manganese.

The methodology starts from a selection of available data, samples useful are selected according to certain criteria and are chosen only those samples that can be considered unaffected by human influence.

The correct pre-selection of samples on which to play the estimate is a key factor for the right fit of the natural background. The pre-selection criteria of the samples on which carry out the study, suggested by the protocol used are :

- Samples with incorrect ion balance are excluded (exceeding 10 %).
- Sample locations with median  $\text{NO}_3^-$  concentration > 10 mg/L are indicative of human effects and should also be excluded;
- Concentration chlorides <1000 mg / l;
- $\text{NH}_4^+$  concentration of <0.5 mg / l.

The methodology estimate natural background on 97.7 percentile. In this work, was decided to use the 95th percentile as suggested by Ispra in 2009. The values obtained were then

compared with those of the Directive in Italian waters. In this way, was compared the values of natural background with the ref and then proceed to the calculation of thresholds

### Statistical analysis and software

The statistical calculations made were performed using the Statistica software 7.0. It was carried out a correlation matrix and factor analysis to obtain a correlation and a variables reduction of the chemical-physical parameters and of major and minor ions, (T, pH, EC, Na, K, Mg, Ca, Cl, SO<sub>4</sub>, HCO<sub>3</sub>, Sr, As, B, Fe, F, Mn) to highlight the correlations between parameters and samples.

To display the trend of the salts dissolved in the water content is helpful to observe the distribution of the electrical conductivity, using Surfer 11 are represented Electrical conductivity maps based on the Kriging method interpolation. Kriging is one of the more flexible and accurate gridding methods; typically the one that is recommended when gridding data. Kriging is effective method because it produces a good map for most data sets. It also can compensate for clustered data by giving less weight to the cluster in the overall prediction. It also can extrapolate grid values beyond the range of the data's Z values.

Each grid node value is based on the known data points neighboring the node. Each data point is weighted by its distance away from the node. This way, points that are further from the node will have less weight in the estimation of the node. If it is considered Z value at grid node A, this equation is used:

$$Z_A = \sum_{i=1}^n W_i Z_i$$

Where  $Z_A$  is the estimated value of grid node A, n is the number of neighboring data values used in the estimation,  $Z_i$  is the value at location i with weight,  $W_i$ . The value of weights will sum to 1 to make sure there is no bias towards clustered data points. The formula can get more complex if things such as drifts and a search radius are applied.

For the calculation of the SI (Saturation Index) of calcite it has been used the software PHREEQC 2.13 (Parkhurst and Appelo 1999) developed specifically for geochemical modeling and speciation calculations in the aqueous phase.

This software was also used to interpret the eventually mixing between water with inverse modeling. This last tool is based on ion association models and is used to determine set of minerals and transfers of gas to explain the differences in composition between waters, by imposing certain limits of uncertainty.

The Inverse Modeling is a block of data that uses calculations based on mass balances, to go up to the final composition of water resulting from the mixing of two or more different waters to quantify the chemical changes that affect the long evolution of the water underground route. The basic approach is to solve a set of linear equations that takes into account the changes of moles for each element by dissolution or precipitation processes (Garrels et al. 1967). Also includes mixing equations, the electron storage (redox equations) and budgets of isotopic piers. Of inequalities are used instead for sizing of uncertainty limits within which you experience the transfers of moles.

Must be considered the assumptions in order to propose the inverse model:

- selected samples as end member must be part of the same stream;
- water must be present in the aquifer;
- end member not need temporal and spatial homogeneity.

The groundwater complex has several sources of uncertainty that contribute to the accuracy of the final calculation of mixing proportions, the most important are:

- end member compositions;
- end member variability;
- chemical reactions could contribute to the system groundwater evolution, the non-conservative behavior of events during the mixing. (Gomez et al. 2008)

The number of mineral phases as well as the size of the uncertainty should be varied to simulate different possible situation. The uncertainty is recommended by 5%, greater uncertainty can produce unrealistic results. The models obtained from output simulations can be varying in number from 2 to +100. Models can be grouped by similarities, a good statistical analysis, which groups the variables, it can be helpful to get a more limited number of models, skimming the inverse modeling results (Gómez et al. 2008).

### **New monitoring system: technology architecture of the system**

Observations extended in space and in time are essential to better understand environmental phenomena, on this assumption in this project I have been studying new possibilities for

optimizing the control actions in the area through the search for new information technologies that contribute to improve the quality of monitoring systems used. The use of intelligent sensors for monitoring physical and chemical parameters of interest has an important impact in facing environmental challenges. Applications of sensors in many fields such as water and industrial process control networks contribute significantly to a more efficient use of resources and thus to a monitoring to take appropriate action in the event of the occurrence of anomalies. Recent developments in information technologies such as the spread of low-cost sensors and dissemination of the concept of Big Data have opened new prospective to innovative scenarios of application of information technologies to the field of environmental monitoring. Technological progress has enabled the creation of smaller and more efficient hardware in terms of energy consumption, known as Wireless Sensor Network (WSN).

The continuous monitoring system that we have created as prototype to create a new possible solution was born from the need to simplify the monitoring operations.

The research has focused on delivering a comprehensive, affordable, easy installation and management through which it will be possible to view and manage the data detected in the monitored area via web browser.

Smart system for the acquisition of data groundwater monitoring consists of a technological interface based substantially on a ARDUINO IDE, an electronic board with an ATmega microcontroller programmed with a standard Arduino language, that is connected to sensors that monitor parameters of interest.

Arduino is an open-source platform based on hardware and software resources flexible and easy to use. It is designed for users with little experience in the world of microcontrollers, in fact, thanks to the rich documentation, active community and numerous libraries it is possible to work with these tools easily. One feature that made Arduino so widespread globally is its ease of use: hardware and software are open source and can also be used by the least computer experts, giving the opportunity to know the technical patterns in order to fully understand the operation. The integrated development environment (IDE) of Arduino is an application in Java that allows you to simply write programs with little knowledge of programming. In fact, it is based on a high-level programming language and thanks to the pull-down menu, you can import all the necessary libraries. The editor also enables you to compile the program and run it on Arduino board connected to the computer.

Everything is made even easier by the low cost and the open-source license that allows you to make public all the physical implementation details. For more advanced users instead Arduino detects a good prototyping platform: it is possible to load the code, make the necessary

connections (often possible via jumpers on a breadboard) to get a quick preview of the final result (Cillo S. master thesis 2013). The Arduino UNO board mounts a microcontroller (MCU - MicroController Unit) Atmel ATmega328P2, and makes accessible all of the micro-pins via the headers on the side. The card is provided with a voltage regulator of 5 Volts that provides adequate power to the MCU, and is connected to one of the headers. There also a second microcontroller (a Atmel ATmega8) with specific functions of serial to USB converter, thanks to which it's possible connect it to the USB port of a PC, and after a special driver has been installed, Arduino is seen as a serial device with which you can communicate via RS-232, the native protocol of each PC COM port.

## Results and discussion

### Hydrogeochemical groundwater characterization

#### -Statistical analysis

Chemical composition and physical-chemical parameters of the deep water are reported in Table 2. Statistically significant differences ( $p < 0,05$ ) by ANOVA analysis were detected for all values except for pH, E.C, Mg,  $\text{NH}_4$ , Fe, F and  $\text{NO}_3$ .

High values of Na, K and Cl are resulted in A1 followed by A3, A2 and A4 except for Ca cation that is resulted high value in A1, A2, A4 and A3. For Anion  $\text{HCO}_3$  high values are resulted in A3 followed by A2, A4 and A1. Concerning the trace element B and major element Fe are resulted high value in A3.

Geochemical signature is conditioned by the presence high concentration of Na that could suggest a deep origin of these waters trapped in deep sediments (Martinelli et al. 1998).

Regarding high concentration of Cl (375 mg/l average) in A1 could be correlated to the excessive pumping of wells and for mixing dynamics (Martinelli et al. 2014). Where, in A2 and A3 the concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  are low (32,14 and 8,71 mg/l in A2; 43,23 and 3,59 mg/l in A3 respectively) due to long paths circulations, and the distance from the recharge area (Molinari et al. 2007). According Dc.Lgs 152/99 the values of  $\text{Cl}^- > 250$  mg/l in comparison with table 2 may be imputed to an area suffering for the return of the salt wedge..

	A1			A2			A3			A4			p-value
	Min	Max	Media	Min	Max	Media	Min	Max	Media	Min	Max	Media	
pH	7.27	8.45	7.74	7.03	8.12	7.62	1.78	8.24	7.56	7.40	8.12	7.79	n.s
E.C.	321.50	4150.00	1603.63	693.50	1171.00	870.35	530.00	1367.50	1044.65	511.50	716.00	682.00	n.s
Na	4.60	698.11	220.27	63.00	96.50	79.97	82.50	224.02	158.81	53.69	67.61	59.34	*
K	0.85	20.40	5.85	1.23	3.90	1.96	1.42	16.88	4.30	1.13	7.17	2.22	**
Mg	10.60	120.00	36.26	29.00	44.96	35.76	22.10	62.34	44.68	29.00	33.54	31.13	n.s
Ca	34.40	406.00	96.65	55.70	156.70	92.66	29.90	103.41	59.09	71.75	82.50	75.16	*
Cl	7.50	1314.00	375.76	13.85	80.65	32.14	10.00	165.00	43.23	7.10	9.00	8.20	***
$\text{SO}_4$	0.00	106.90	30.93	0.50	32.45	8.71	0.50	20.95	3.59	0.50	11.00	2.42	***
$\text{HCO}_3$	2.80	1312.00	401.50	506.50	820.50	622.35	399.50	951.50	774.05	503.50	582.50	551.64	***
$\text{NH}_4$	0.00	36857.00	2790.06	0.00	4766.00	2326.23	0.00	17671.50	1783.36	0.00	2432.50	641.09	n.s
As	0.28	15.50	3.37	0.00	11.50	5.51	0.00	10.00	3.03	0.50	0.80	0.54	*
B	45.00	1191.00	261.04	0.00	517.50	324.03	0.00	1494.50	782.90	324.00	477.00	395.29	***
Fe	14.50	14099.00	1904.96	0.00	3643.00	1709.26	0.00	9718.00	2140.45	316.50	1015.00	722.21	n.s
F	0.00	7513.50	312.20	0.00	524.50	279.50	0.00	775.00	462.95	250.00	426.50	292.00	n.s
Mn	11.43	1232.50	357.21	0.00	226.00	142.21	0.00	345.00	157.20	155.00	210.00	179.79	***
$\text{NO}_3$	0.50	25.00	2.07	0.00	30.00	5.69	0.00	30.00	2.82	0.50	1.50	1.21	n.s

Tab 2 Tab. 2 ANOVA test on deep groundwater (A1, A2, A3, A4). All the data are expressed in mg/l

Chemical composition and physical-chemical parameters of the phreatic water are reported in Table 3. Statistically significant differences ( $p < 0,05$ ) by ANOVA analysis were detected for all values except for pH,  $\text{NO}_3$  and Al.

	S1			S2			S3			S4			S5			p-value
	Min	Max	Media	Min	Max	Media	Min	Max	Media	Min	Max	Media	Min	Max	Media	
pH	6.61	9.47	7.69	7.28	9.66	8.15	7.89	8.7	8.2	7.91	8.3	8.08	7.57	8.41	7.98	n.s
EC	732	3182	2081	213	3263	1102	200	2274	1289	704	3660	1883	635	1670	1153.67	***
Ca	75.97	337.4	187,95	14,34	374.28	116,71	13.16	316,80	129	58.51	501	165,95	19,39	324	101	**
K	1.29	19.74	14.03	0.41	30.57	9.74	1.18	23.51	8.78	0.59	32.76	12.47	1.79	12.05	4.92	**
Mg	19.79	166.1	64.17	2.54	145,92	40,12	2.22	186,60	69,14	34,30	328	99,66	13,99	92,07	40,76	***
Na	30.91	179,30	100,45	20,14	162	49,04	34,0	148	77,06	40,4	202,43	89,93	120,53	485	176,26	***
Cl	31.26	1680.03	429.65	18.37	569.04	96.75	47.96	326.6	185.25	134.48	403.75	240.22	6.52	499.51	74.83	***
$\text{NO}_3$	0	37.66	5.42	0	55.05	5.59	0	0	0	0	0	0	0	332.27	27.05	n.s
$\text{SO}_4$	30.08	242.07	104.66	50.15	114.57	72.1	60.76	180.74	112.22	70.05	83.54	71.79	50.16	250.8	107.44	***
$\text{HCO}_3$	300	840	596.16	120	958	450	60	765	509	360	920	608	210	900	475	***
$\text{NH}_4$	0	44.26	5.27	0	0.39	0.05	0	0	0	0	0	0	0	0.27	0.11	**
TDS	412	1864	1142	128	1958	664.67	59	1364	781	626	2065	1096.75	381	1002	694.42	***
Sr	480	3350	1680	100	3510	1190	70	1700	1080	1010	2530	1790	600	2760	1390	***
Fe	20	3510	732	10	4506	2057	20	4883	446	20	10330	1197	0	1560	200	***
Al	0	1940	120	0	60	0	0	140	20	0	0	0	0	150	10	n.s
As	0	70	10	0	147	19.48	0	180	27.79	0	28.40	6.32	0	42.72	3.51	*
B	0	682	219,51	0	1280	345,85	0	849,50	338,80	0	1048	321,07	0	1038	421,92	***
Mn	0,02	1876	396	0	3816	305	0	3816	331,99	0,07	1311	323	0	1112	96,28	***

Tab.3 ANOVA test on phreatig groundwater. All the data are expressed in mg/l

Electrical conductivity (EC) and TDS shown high values in S1 and S4 but still below the critical value indicated by Dc.Lgs 152/99. The ground water show a high content of Ca and  $\text{HCO}_3$  characteristic of the area.  $\text{HCO}_3$  dissolved is controlled by the interaction rock and water from the degradation of organic matter (Deng et al. 2009). The distribution of Cl seems to be significantly high in S1 and S4 (429 mg/l and 240 mg/l).

The average values of K is particularly high in samples S1 and S4 (average: 14,5 mg/l and 12,47 mg/l, respectively) which can be set to Cl an indicator of ion exchange, mixing with old water present or may be due to the use of fertilizers on the soil (generally present up to a maximum concentration of 5 mg/l).

High value  $\text{SO}_4^{2-}$  in S3 may be subjected by the influence of the Po river, while high values of  $\text{SO}_4^{2-}$  in S5 are hypothesized mixing of saline water from the aquifer substrate through faults and fractures, with fresh ground water. Mixing between freshwater and saline water are discussed by several authors confirming that the hydrogeological complex of floodplain is subjected a phenomenon of deep water along faults and fractures (Giuliano 1995; Martinelli et al 1998; Sciarra et al. 2013; Conti et al. 2013). This phenomenon is detected by the high

concentrations of Cl and  $\text{SO}_4^{2-}$  that has stated in the table record values of  $\text{Cl} > 200 \text{ mg / l}$  and  $\text{SO}_4^{2-} > 300 \text{ mg / l}$ .

In addition,  $\text{SO}_4^{2-}$  values can derive from the oxidative weathering of sulphide-bearing minerals, such as pyrite, gypsum and anhydrite (Singh et al. 2013; Mastrocicco et al 2014).

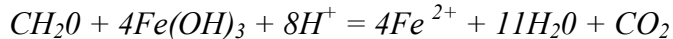
The presence of ancient salts in shallow water studied reflects their origin in the sea ingression/regression that occurred during the Quaternary age, and determines a high salinity of sodium chloride type.

The presence of a reducing environment and organic matter degradation is an absolutely crucial factor in understanding the geochemistry of the waters of this flood plain (Shiller A. et al 2016)

Fe show a high concentration in S2 and S4 in comparison to S1 and S3 due to the interaction with sediments and non oxidizing environment-

In such reducing conditions are those which characterizes the aquifer and in the presence of organic matter, iron oxides dissolve with effects on the high pH of the system and release amount of Fe in aqueous phases.

Using the stoichiometry for iron reduction by organic matter:



Because ferrous ion is strongly active in ion exchange, it is difficult to conclude to what extent the current distribution of ferrous ion is due to past or to on-going iron-reduction activity (Bierg Poul et al. 1995).

B in Table.3 could to be related to the dissolution of clay-silt matrix of the aquifer. The main source of the large concentration of B in the waters is attributable to a natural source due to washout of the aquifer matrix, or due to seawater intrusion. There is an enrichment of B in A3, which in depth aqueous environment it can be absorbed or released by the clay minerals, depending on the conditions of temperature, pH, salinity and mineralogy of the aquifer. (Hem et al. 1989).

As element in groundwater in some areas of the Ferrara province is linked to the existence of reducing groundwater conditions confined in layers of peat-rich loamy soil of organic material. The concentration of arsenic is low and never exceeds the limit value of  $10 \mu\text{g/l}$  (Dc.Lgs 152/99).



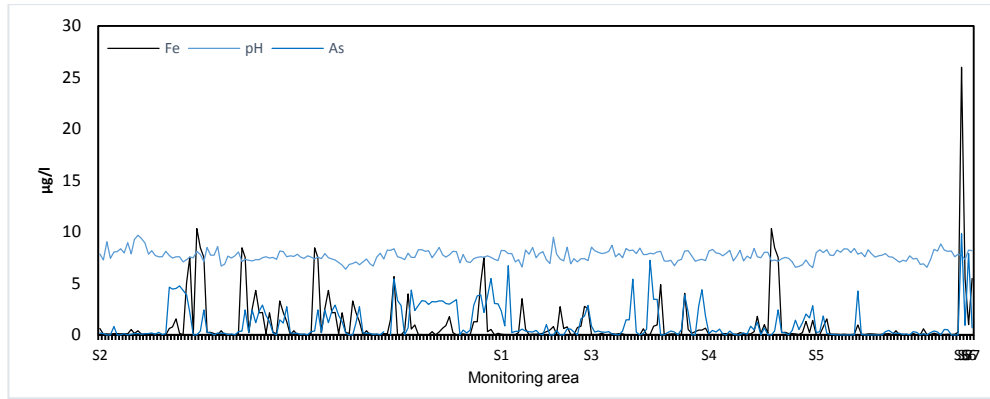


Fig. 20 Graph which relates the pH, As and Fe

Fe and As are inversely related to pH (Fig 20). These effects are due to localized phenomena of dissolution of the organic matter which causes a change in the pH. These conditions supported the mobilization of As and Fe elements which by sediment pass to the waters. The biomass of microbial growth that develops makes available organic carbon gradually making the anoxic conditions. The prokaryotic bacteria which grow in these conditions reduce the arsenic and iron making them soluble in water, with consequent release (Dinelli et al. 2010). To define the difference between the elements composition in statistical terms into the two group (phreatic aquifer and depth aquifer) are plotted the minor elements in Box and Whisher Plot. This help to recognize also the median and the range of maximum values distribution and the outliers for each element considered.

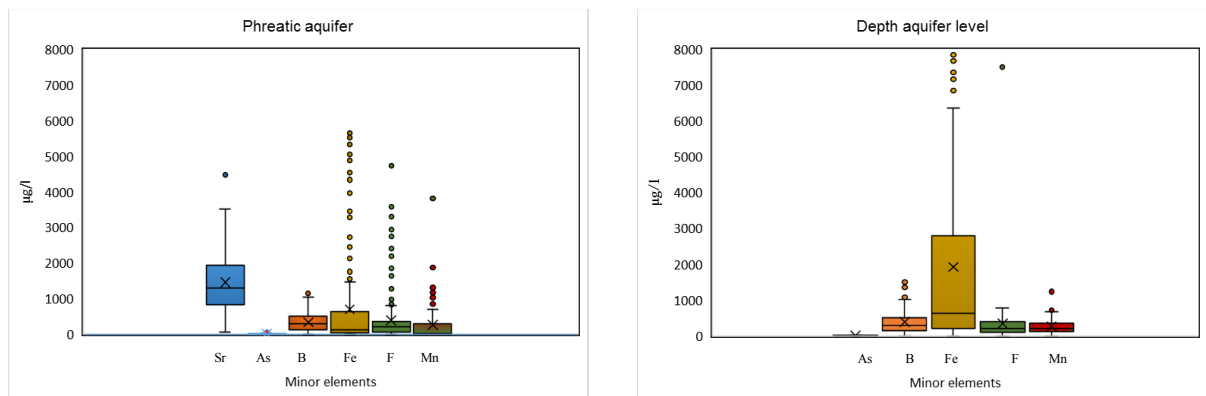


Fig. 21 Box and Whisher plot on minor elements ( $\mu\text{g/l}$ ) in phreatic aquifer and in depth aquifer (A1,A2,A3,A4).

Phreatic aquifers are characterized by high concentration of Sr with an elevated distribution of values. It is not possible to have a comparison with deep aquifer because this element is not registered. For As, F and Mn the concentration is the same, but in phreatic aquifer there are

more outlayers then in depth aquifer probably due to interaction with antropic pollution and with phenomena of dissolution of organic matter. Fe present high number of outlayer in phreatic aquifer and values higher in depth groundwater. The order of values is very different, in phreatic groundwater some outlayers arrive to concentration of depth groundwater, in which the median is around 2000  $\mu\text{g/l}$  and the outlayer have values upper 8000  $\mu\text{g/l}$ . Ferrous have a natural origin in the alluvial plain but the different concentration in the two dinsint groups and the presents of outlayer with very high values in prgeatic levels coulbe due to mixing with different water composition.

In table 4 cation, anions and physical-chemical parameters shown a good correlation (pearson correlation coefficient,  $p\text{-value}<0.05$ ) except for K cation. This suggested a multivariate statistical approach to better address the mutual relationships that affect them.

Since most of these parameters are statistically significant ( $p\text{-value}<0.05$ ) for the geochemical evolution of the water, it is chosen to proceed by keeping them in the factorial analysis next, preparing a matrix also containing the minor and trace elements, not characterized by redundancy. By the correlation matrix containing the chemical and physical parameters, major and minor ions can be drawn clear hydrochemical relationships: a high and positive correlation (underlined values) is observed (Tab.4)

Variables	Temp	pH	E.C.	Na	K	Mg	Ca	Cl	SO4	HCO3	As	B	Fe	F	Mn
Temp	<b>1</b>														
pH	0,28	<b>1</b>													
E.C.	-0,14	-0,51	<b>1</b>												
Na	-0,15	-0,49	<b>0,98</b>	<b>1</b>											
K	0,34	-0,02	0,03	-0,02	<b>1</b>										
Mg	-0,06	-0,52	<b>0,74</b>	<b>0,71</b>	0,49	<b>1</b>									
Ca	-0,04	-0,54	<b>0,87</b>	<b>0,83</b>	0,34	<b>0,77</b>	<b>1</b>								
Cl	-0,16	-0,49	<b>0,98</b>	<b>0,99</b>	-0,05	<b>0,61</b>	<b>0,82</b>	<b>1</b>							
SO4	0,21	0,42	<b>-0,63</b>	<b>-0,65</b>	0,30	-0,46	-0,34	<b>-0,65</b>	<b>1</b>						
HCO3	-0,02	-0,39	<b>0,56</b>	0,50	0,43	<b>0,87</b>	<b>0,62</b>	0,44	-0,36	<b>1</b>					
As	0,17	-0,17	0,00	-0,05	<b>0,58</b>	0,37	0,25	-0,08	0,13	0,48	<b>1</b>				
B	-0,00	-0,46	0,55	0,49	0,49	<b>0,80</b>	<b>0,64</b>	0,45	-0,33	<b>0,85</b>	<b>0,58</b>	<b>1</b>			
Fe	-0,05	-0,32	0,52	<b>0,55</b>	-0,06	0,28	0,48	0,54	-0,31	0,09	0,18	0,26	<b>1</b>		
F	0,30	0,07	0,00	-0,01	0,19	0,06	0,07	-0,01	0,04	0,09	0,19	0,26	0,05	<b>1</b>	
Mn	-0,11	-0,22	0,38	0,37	0,17	0,20	0,47	0,38	0,00	0,06	0,21	0,07	0,51	-0,22	<b>1</b>

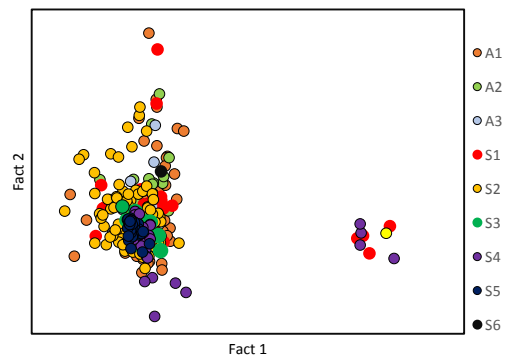
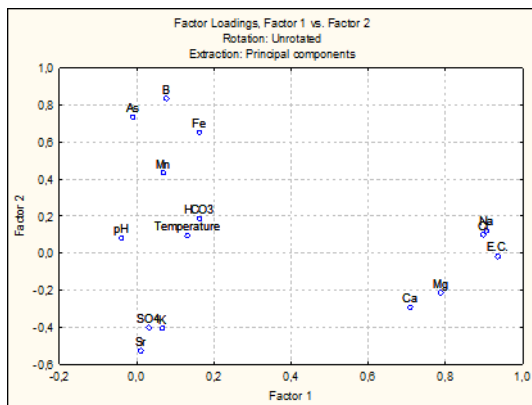
Tab.4 Correlation matrix (Pearson)

The correlation matrix shows that E.C. has a good correlation with  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ , and  $\text{HCO}_3^-$  and a negative correlation with  $\text{SO}_4^-$ .  $\text{Na}^+$  has a good corelation with  $\text{Mg}^+$ ,  $\text{Cl}^-$ , and a negative corelation with  $\text{SO}_4^-$ . Potassium correlates with As,  $\text{Mg}^+$  and  $\text{HCO}_3^-$ , The  $\text{HCO}_3^-$  is correlated

with B and As. The analysis conducted on the main components allowed to distinguish the components that best summarize and explain the total variance of the original variables. In particular, three factors, determined by the method Cattell and Jaspers (1967) (Scree plot) are useful in explaining the total variance.

VARIABLES	F1	F2	F3
<i>Temperature</i>	0,132	0,098	<b>-0,572</b>
<i>pH</i>	-0,040	0,081	0,027
<i>E.C.</i>	<b>0,935</b>	-0,015	-0,067
<i>Na</i>	<b>0,907</b>	0,124	-0,178
<i>K</i>	0,066	-0,406	0,403
<i>Mg</i>	<b>0,788</b>	-0,214	0,275
<i>Ca</i>	<b>0,709</b>	-0,293	0,192
<i>Cl</i>	<b>0,897</b>	0,101	-0,255
<i>SO4</i>	0,031	-0,401	0,324
<i>HCO3</i>	0,162	0,187	<b>0,555</b>
<i>Sr</i>	0,011	0,527	0,281
<i>As</i>	-0,010	<b>0,734</b>	0,215
<i>B</i>	0,076	<b>0,836</b>	0,323
<i>Fe</i>	0,162	<b>0,651</b>	0,088
<i>Mn</i>	0,069	0,433	0,157
<i>Expl.Var</i>	3,712	2,662	1,379
<i>Prp.Totl</i>	0,247	0,177	0,092

Tab.5 Factorial analysis in 3 components that syntetized the samples dipendent from this groups factors.



a

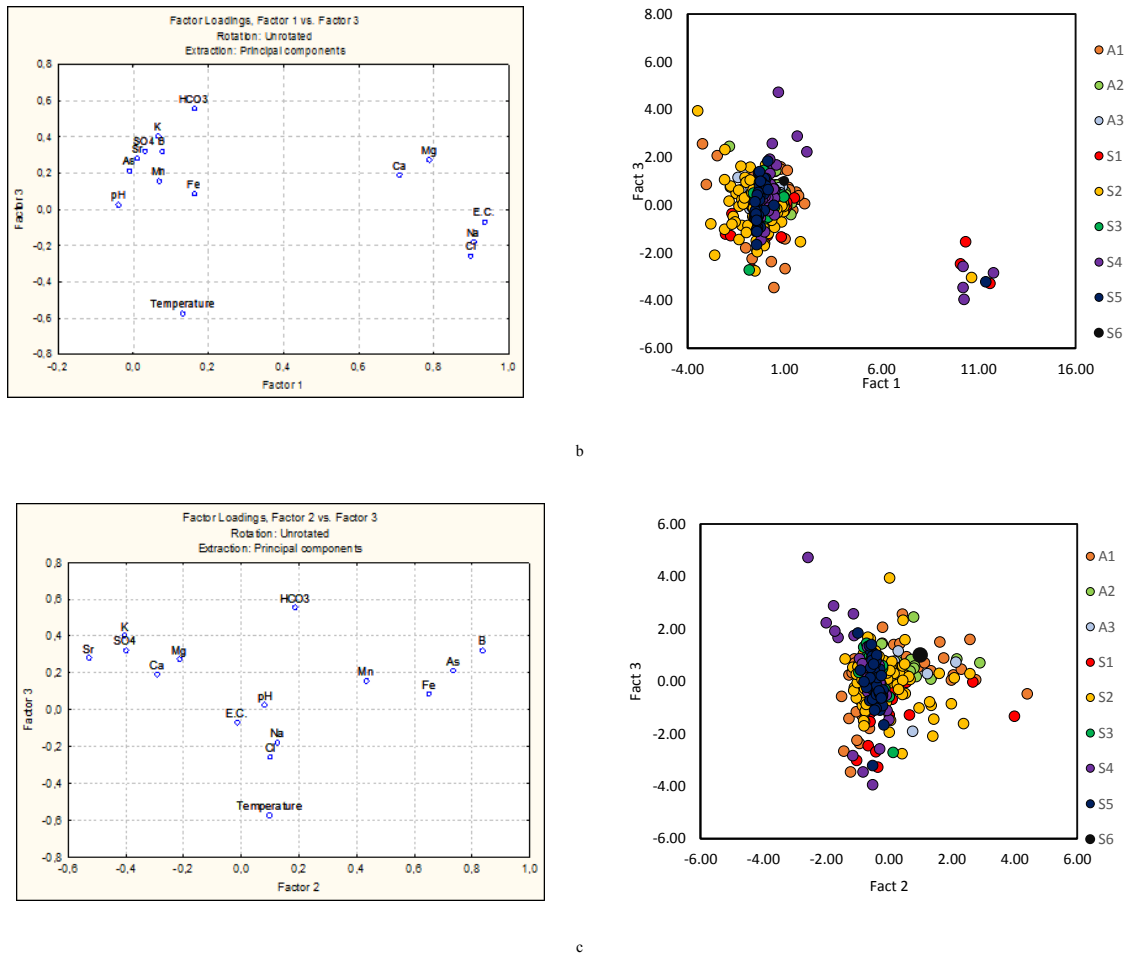


Fig.22 Correlation between the factor. A) factor 1-2 (49,22%), B) factor 1-3, (45,21%), C) factor 2-3 (42,68%).

The analysis conducted on these values of the main components has separated the components that best explain the total variance of the original variables (Tab.5). In particular, three factors (F1) (F2) and (F3), determined by the method Cattell and Jaspers (1967) (Scree plot) are useful in explaining the total variance. Almost all the variables are distributed on F1; that explains the relationship of the samples EC, Ca, Mg, Cl, Na, F2 explains the relationship between As, B and Fe, F3 explains the relationship between HCO<sub>3</sub> and the inverse relationship with the temperature.

From these factors we could summarize 3 group samples:

Group 1: samples dominated by ion exchange processes

Group 2: pH reactions on heavy metals, waters with low pH and high metals concentration;

Group 3: samples affected by inverse correlation between T and HCO<sub>3</sub>.

The pH is inversely correlated with the parameters of the first group. Fig. 22 shown in a two-dimensional plot of the F1 and F2 of non-rotated Cartesian axes, represented the main components that explain the higher percentage of the total variance (49,22%). From the graph

it is possible to identify groups of variables that have a high correlation with the main components derived from statistical analysis (F1 and F2): values close to unity indicate the highest correlation.

They were applied rotational strategies on the Cartesian axes representing the three factors to try to assess the variance increase. The relationship between the F1 and F3 does not produce a variance increase (45.21%) but well represents the correlation between the factors that characterize the ion exchange processes and factors dominated by the ion  $\text{HCO}_3$  (typical of these areas of the floodplain).

Most of the samples have the highest correlation with the F2, which is indicative of the main water-rock interaction processes that take place in the aquifer of the plain as seen from the distribution of the variables, it represents the waters of the plains affected by dissolution of organic matter processes that create favorable conditions for the mobilization of Fe and As.

S1-S4-S2 are subject to processes of water rock interactions and ion exchange, they are in fact represented by pH, Temperature, EC,  $\text{HCO}_3$ , Na, Cl. The inverse correlation of pH with the chemical and physical parameters may be explained because pH interferes with the cation exchange capacity influencing the properties of the soil to retain adsorption cations: to decrease the pH of the exchange capacity It is reduced due to the neutralization of the electro-negative charges on the part of  $\text{H}^+$  ions. It follows that in pH low values of the supplied elements is significantly reduced due to the lower absorbency.

Interesting to note the arrangement of the samples S4 represented by the grouping: Sr,  $\text{SO}_4$ , K. Samples seem to be dominated by As, Fe and contributions of B. B enrichment in an depth aqueous environment it can be absorbed or released by the clay minerals, depending on the conditions of temperature, pH, salinity and mineralogy of the aquifer. (Hem JD et al 1989)

#### *-Hydrodynamics*

Depth analysis of provincial wells showed strong annual variations (wells distribution in Fig.23) These oscillations can be considered the product of the water resources exploitation and Po river idrometric variation in neighboring wells of the river. The observations on the recorded parameters were conducted in a interval time from 1978 to 2014.

The values for each wells monitored have been analize to understand the trend and have been calculate the line equation of every trend, the angular coefficient have been use to construct a map in which is present the trend of depth level in the period considered.

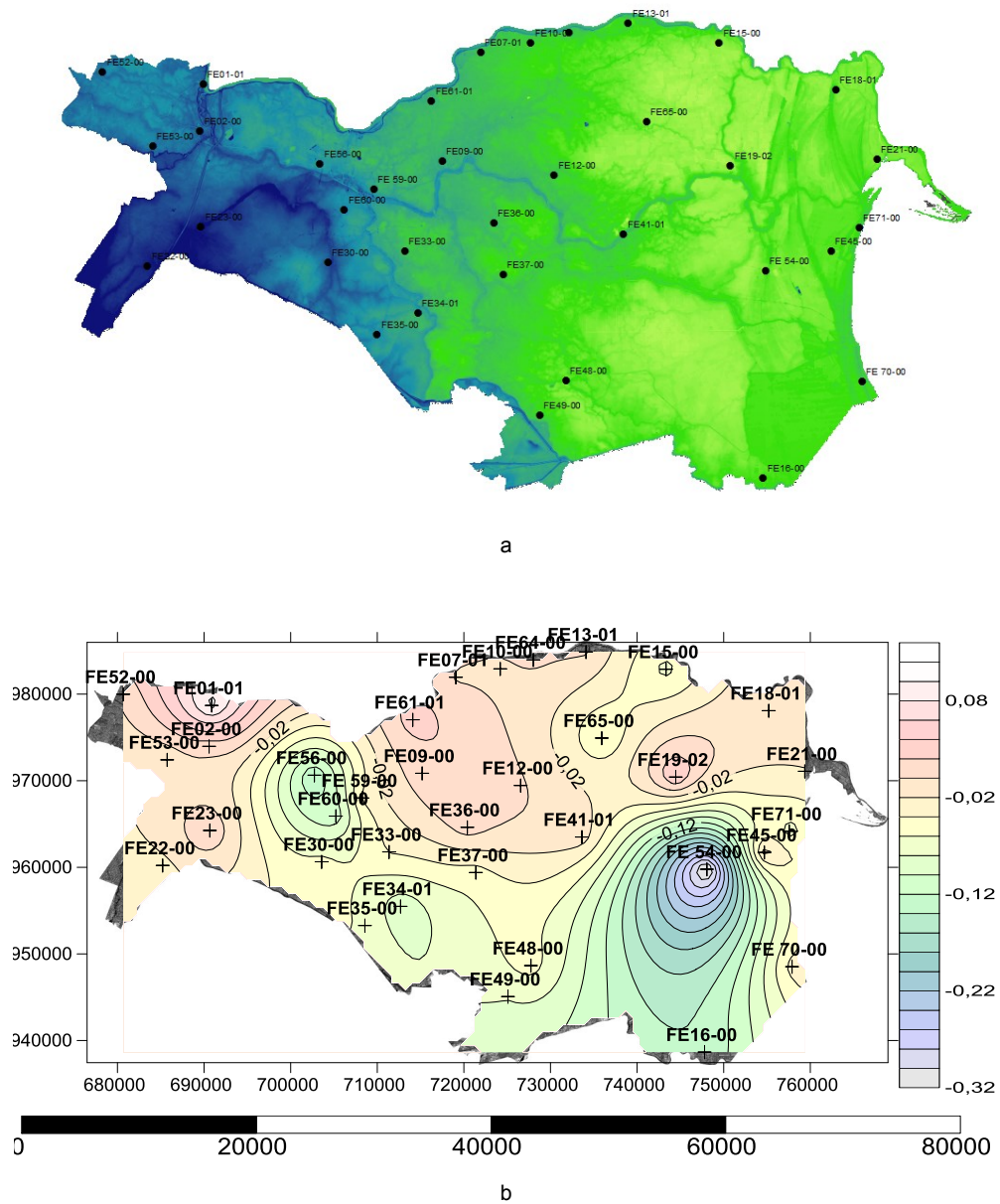
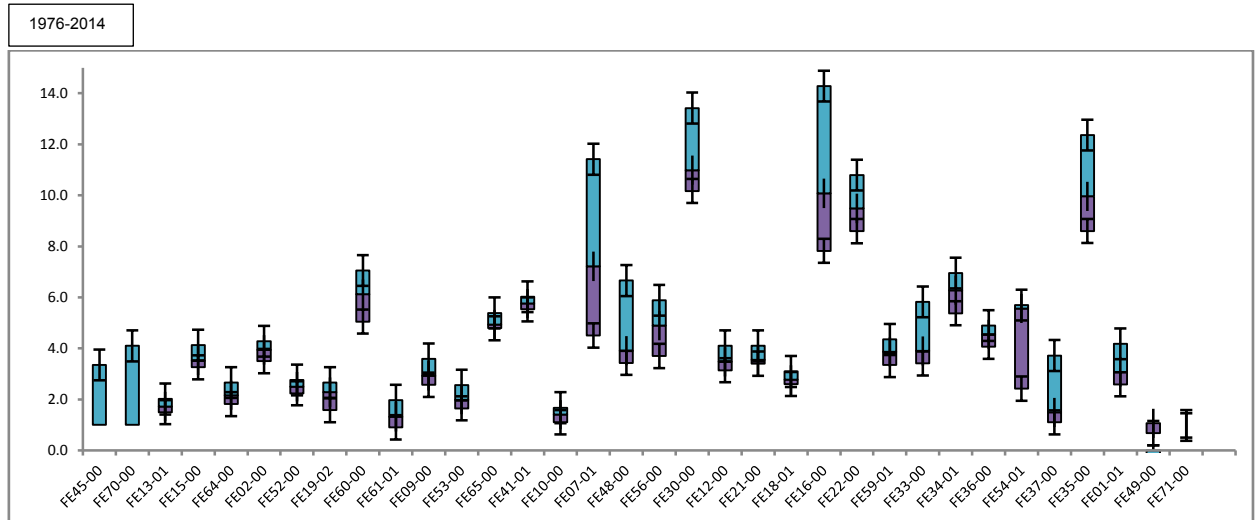
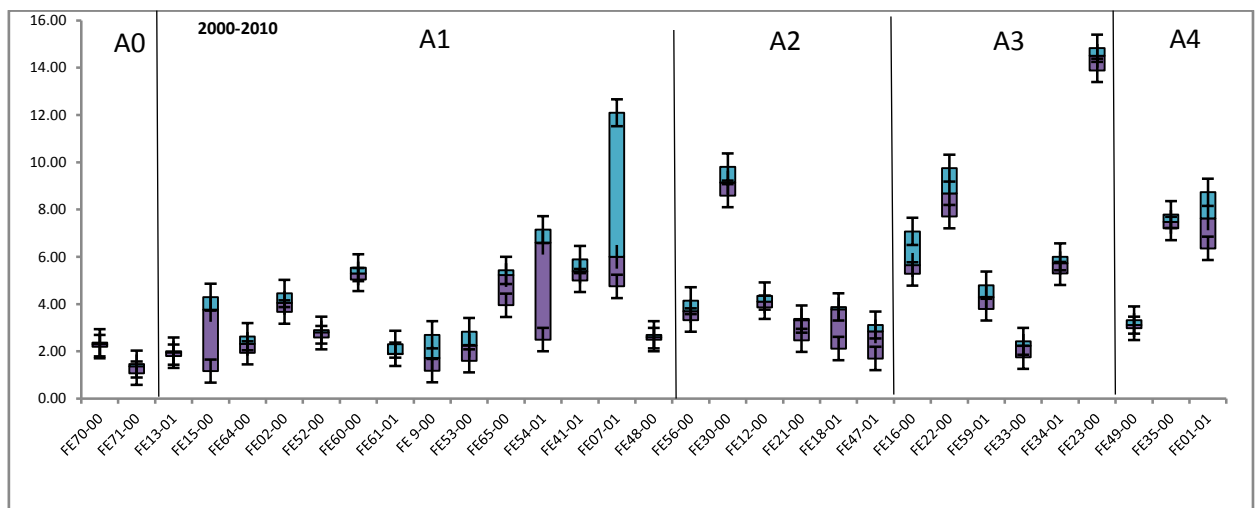


Fig.23a. Distribution of monitoring points of the depth managed by ARPA Emilia Romagna. b distribution of transverse regression lines during the period observed.

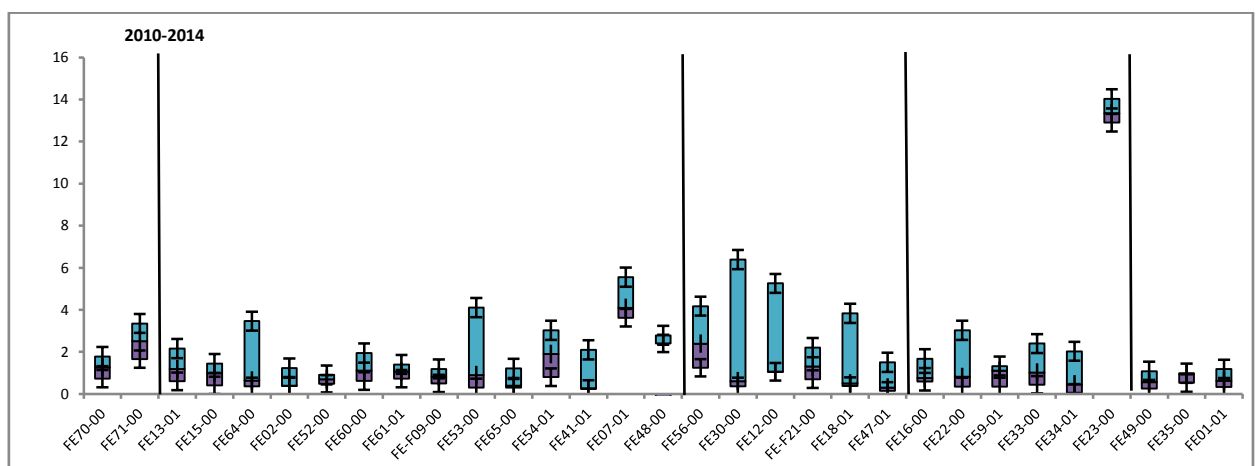
From the analysis of cartography of the depth, referred to the period 1978-2014 it is possible to distinguish two major sectors of the Ferrara plain, according to the depth values: an oriental south and a north-west area. Near the south coast line, the depth values show a decreasing trend as well as in the industrial area located in the city of Ferrara. In other sectors, however the levels of depth do not show large variations in the observed period. Another situation instead is evident if the values are considered as dispersed concentration in box plot. The values have been subdivided according to the different aquifer values and according to different ranges of observation.



a



b



c

Fig.24 a) Box plot of the variation depth parameters. Historical series 1976-2014 (monitoring points of the depth managed by ARPA Emilia Romagna) b) 2000-2010 series; c) 2010-2014 series.

In the box plots are plotted, the maximum and minimum speeds that have been record in individual wells observed in the years from 1976 to 2014 (Fig.24 a). The wells are divided by aquifer complex. FE70, FE45 and FE71 wells located near the coastline does not show a wide variation in the observed parameter, while FE07, FE01, FE15, and FE60 located near the Po River show wide variation and very high values of underlying aquifer.

The trend of depth of the parameter in the time interval: 2000-2010 proposes always a wide variation of 07 well with very dipersal values around the median, also 23, 15 and 54-01, the latter is situated near the coastline. What we see from the comparison chart 24 b and 24 c is that the depth of the wells increased.

#### *-Bex index*

Cation exchange processes who is supposed with FA could be described by a specific Base Cation Exchange Index (BEX index) (Stuyzand 1985), which can be used as an indicator of the tendency to salinization/softening of the aquifers, the index BEX can interpret the trend of the on going processes in the aquifer:

Positive BEX index is resulted in A2-A3 , negative resulted for S1-A1(52-58)-S2-S4. But this is not an intrusion determined by a increase of saltwater intrusion but of an increase of carbonate dissolution introducing different processes.

As can be seen from the arrangement S6 waters represent a landmark settlement that we can use as an end member to calculations that follow.

#### *-CEC: Cation exchange capacity*

The method to determine the capacity exchange has been patented by the laboratory of the University of Evora, Lisbon, Portugal, this method is based on the exchange due to leaching. This appears is much more representative of what happens in the environment.

The CEC analysis was performed on different depth sediments of S1-S2-S4 (Fig.25), the sites were selected on the basis of statistical interpretation results (Group 1, Tab.5).

The results obtained by the application of the CEC analysis show as there is great variability in the exchange capacity in the three sites analyzed.

Soil CEC is normally expressed in one of two numerically equivalent sets of units: meq/100 g (milliequivalents of charge per 100 g of dry soil) or cmolc/kg (centimoles of charge per kilogram of dry soil).



Diagram in Fig. 25 show high variability of CEC in S1, a medium variability in S4 and a low variability in S2. In correspondence of the sediments collected in the site S1 the presence of organic matter and the presence of paleo channel sands produces high values of CEC, which determines a very important contribution of Na from cation exchange with the sediments.

In S4 the exchange capacity increases in the levels in which we find sand beige silty with organic substance spread (references stratigraphic taken from stratigraphy commissioned by Region Emilia Romagna for San Carlo, Ferrara, 01/06/2012). Although less than S1 also in this case there is a large influence of the cation exchange capacity in the resulting composition of the water.

In S2 the CEC has less values of two orders of physical quantity lower than S1. The ion exchange processes are certainly less influential on the composition of the water from the previous site.

Soil organic matter will develop a greater CEC (Ross and Ketterings 2011). Soil's CEC can decrease with time as well, through natural or fertilizer-induced acidification and/or organic matter decomposition.

CEC is directly related to the presence of organic substance and the reactions associated with the presence of organic matter resulting in a production of  $\text{CO}_2$ ,  $\text{NO}_3$ ,  $\text{SO}_4$ ,  $\text{NH}_4$ .

$\text{Na}^+$  is often present in large quantities in soils but the concentration values found in this samples are characterized by variability and high values (min:7,5 - max 55,1 cmol/Kg). The application of this method to the selected samples is helpful to understand the reason for high concentrations of Na found in the waters can be determined by the solubility of the sediments in which these waters are in contact. The solubility of such sediments varies according pH conditions in which they are located, is therefore clear that reducing or oxidizing conditions affect this process.

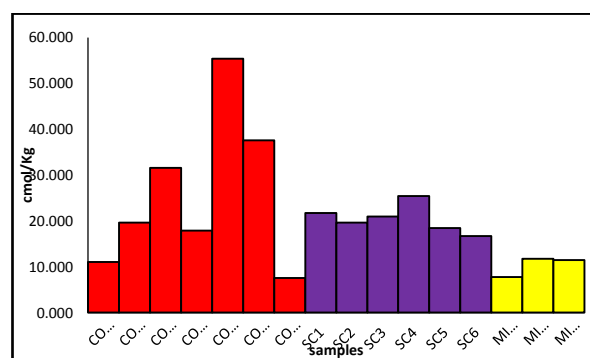


Fig.25 CEC analysis results for the three group samples : S1, S2, S4.

*-Isotope geochemistry*

The shallowness of these wells connects them to the idea of the presence of an unconfined aquifer of which is not known the exact geometry. This aquifer has a lateral continuity across the entire area in which the study was conducted, in which the monitoring was programmed. The main recharge of these wells is meteoric infiltration of precipitation and to a lesser extent also a side feed from the hydrographic network channels. Considering principal meteoric recharge is immediate as the piezometric level varies seasonally and it depends on the amount of rainfall. The isotope ratios of heavy isotopes of water molecules identify the origin of water.

	Year	Season	TEMPERATURE		$\delta^{18}O$		$\delta^2H$	
			MIN	MAX	MIN	MAX	MIN	MAX
S1	2014	summer	14,1	20,3	-8,1	-6,7	-52,6	-44,1
		autumn	15,6	19,1	-9,1	-7,7	-56,2	-52,0
		winter	11,2	13,3	-9,1	-6,5	-63,2	-49,0
	2015	summer	18,0	23,9	-7,7	-6,6	-53,4	-47,5
		autumn	16,4	16,8	-8,9	-8,1	-61,6	-56,7
	S2	2014	summer	14,8	18,6	-8,8	-7,2	-59,0
autumn			13,0	18,5	-10,7	-6,0	-71,3	-43,4
winter			8,3	12,3	-8,8	-7,0	-59,2	-46,5
2015		summer	15,8	20,0	-7,8	-7,0	-51,8	-46,5
		autumn	14,6	18,4	-9,1	-6,3	-59,2	-47,1
S3		2014	summer	16,7	22,6	-6,9	-6,7	-49,8
	autumn		12,3	14,7	-8,1	-6,4	-50,7	-45,8
	winter		9,0	13,1	-8,3	-7,8	-53,6	-50,0
	2015	summer	16,8	19,3	-7,2	-6,5	-48,8	-43,7
		autumn	15,8	17,3	-8,3	-6,5	-53,6	-43,7
	S4	2014	summer	14,7	22,8	-8,5	-7,4	-53,8
autumn			14,5	15,9	-10,4	-8,1	-70,4	-51,5
winter			9,0	12,9	-8,5	-7,2	-55,8	-50,4
2015		summer	15,9	17,6	-8,5	-7,5	-55,9	-46,9
		autumn	16,3	19,6	-8,3	-7,1	-56,8	-47,9
S5		2014	summer	19,2	20,3	-8,1	-7,6	-55,4
	autumn		14,4	16,3	-8,6	-7,6	-59,0	-51,9
	winter		10,2	18,3	-8,4	-7,3	-55,0	-47,4
	2015	summer	15,1	18,5	-7,7	-7,6	-46,9	-45,4
		autumn	15,1	16,1	-8,4	-7,3	-55,0	-47,4

Tab. 6 Geochemical composition of phreatic groundwater

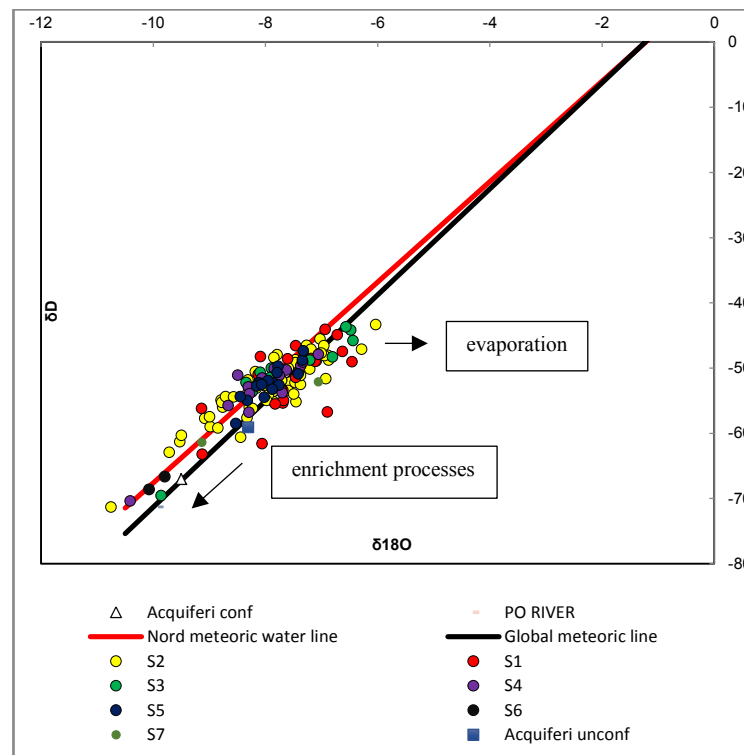


Fig.26 Sampling Isotopic composition. plotted in the graph also: Meteoric precipitation sampled in the project area, isotopic of unconfined and confined aquifer according Rapti Caputo and Martinelli 2008 and meteoric line for north italy and Gblar meteoric water line.

Seasonal temperatures and heavy ground water isotopes are shown in Table. 6. All data results indicate an enrichment in heavy isotopes in autumn and winter of both years. S1, S2 and S3 have revealed the lowest values of heavy isotopes. S2 and S4 have had a clearer enrichment in autumn 2014 compared to S3 and S5. Copparo has revealed an increase in the ratio of heavy isotopes in 2015 compared to the other groups of samples.

The composition of water wells is in the range:  $^{16}\text{O}/^{18}\text{O} = -10,75; -6,03$  (Fig.26). This suggest a meteoric recharge and it's clear also by the isotopic diagram of  $\delta^{18}\text{O}/\delta\text{D}$  in which the samples flow the North Meteoric Water Line NMWL, (Longinelli and Selmo 2003), the Global Meteoric Water Line GMWL (Craig 1976). In the diagram are plotted also some compare values as found in literature like the isotopic composition of confined and unconfined aquifer defined by Martinelli and Rapti-Caputo (2007). Most of phreatic water fall near the unconfined composition. The groundwater isotopic composition is strongly influenced by the short and intense meteoric events.

High  $\delta^2\text{H}$  values which move the samples to the left of NMWL and register a  $\delta^2\text{H}$  enrichment compared to  $\delta^{18}\text{O}$ , could be due to the effects of the presence of methanogenic bacteria or

reactions due to the presence of hydrocarbons (Horita et al. 2005; Gargini et al. 2011). Moreover,  $\delta^2\text{H}$  isotope could be derived or heavily contaminated by hydrocarbons and  $\text{Cl}^-$ .

Some of deuterium enrichment cases may be also explained as exchanges of water hydrogen with the  $\text{H}_2\text{S}$  hydrocarbons hydrogen (Gargini et al. 2011; Filippini et al., 2015; Negrel et al., 2017). D-excess that characterizes the waters, has an average of 11.6 ‰ and it is included in a range from 4 to 19 ‰ similar to the component measured in 2014 (Martinelli et al., 2014).

The decrease of rainfalls associated with a change in its distribution throughout the months of the year, the temperature fluctuations of seasonal nature of a continental climate, with high summer temperatures and low winter temperatures, and its variation in the last two years, have caused changes in hydrogeochemical and isotopic composition of ground water.

Temperature influences the evapotranspiration, which is an important variable for water balancing, and it can be studied in order to understand the changes in evaporation power in different periods.

The isotopic signature is mainly determined by local precipitations, however the climate change is causing an alteration in the slope of reference lines (NMWL, GMWL). This can be due to the decrease of precipitation percentage and to the simultaneous increase of temperatures. D-excess significantly increases during autumn and winter seasons, due to interactions of different masses of steam, to the evapotranspiration effects and to the local humidity (Laskar et al. 2014). The shift of samples that move to the right of the reference lines indicate a depletion of the both considered isotopes and this process could be read as a result of the action of evaporation.

The amount of rainfall and rising temperatures, creating variations in isotopic ratios, play a key role which determines two main changes that are the evaporation and the enrichment processes. The evaporation creates a new ratio which shifts isotopic values to the right of the GMWL. The combined effects of precipitation anomalies and increased temperatures of waters in recent years have induced an evaporation addition in vapour masses that causes a loss of light isotopes (Simpson et al. 1992; Mazor 2004; Mawgoud et al. 2016; Jianwiev et al. 2016).

Over the years marked by meteoric deficit and/or increase in temperature, the samples are even more enriched in heavy isotopes. In the past two years the synchrony of the effects previously described has caused an inclination of the ground water line in the flood plain of the selected areas in the province of Ferrara .

For this research, the equation of the calculated line is represented by:

$$\delta^2\text{H} = 5,27\delta^{18}\text{O} - 10,9$$

These values are lower in oxygen, hydrogen isotopes and d-excess.

D-excess values, show an equally marked seasonality that tends to increase when precipitation preferentially occurs during winter months (Rozanski et al. 1993). The study of d-excess, shows that the vapor masses mainly deriving from the hinterland, from the front of the Apennines. The range of this values is wide and between 3 and 22,21. The low values of d excess highlighted the presence of evaporation phenomena (Lacelle et al. 2011; Martinelli et al. 2014).

It is thus deducible that the variation in the distribution of rainfall has led to a different response to the isotope ratio by producing a change in the inclination of the line and a shift of values in the rainy seasons, determined by the variation of vapor masses.

In order to evaluate the change in isotopic composition due to the climate change some samples from Friuli wells were added .

In Figure 27 It is possible observe that the differences between the isotopic composition could be attribuite to a rapid charge for the friulan area respect the composition of meteoric precipitation while the delta area responds less quickly to the change.

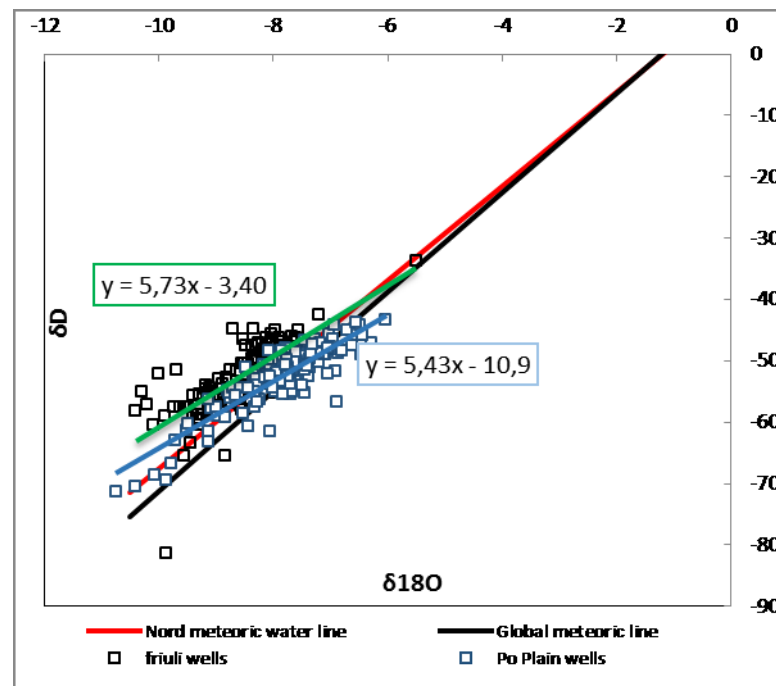


Fig.27 Isotopic diagram in which are represented the tendency line of two group of wells samples: in black Friuli wells and in violet Po plain wells.

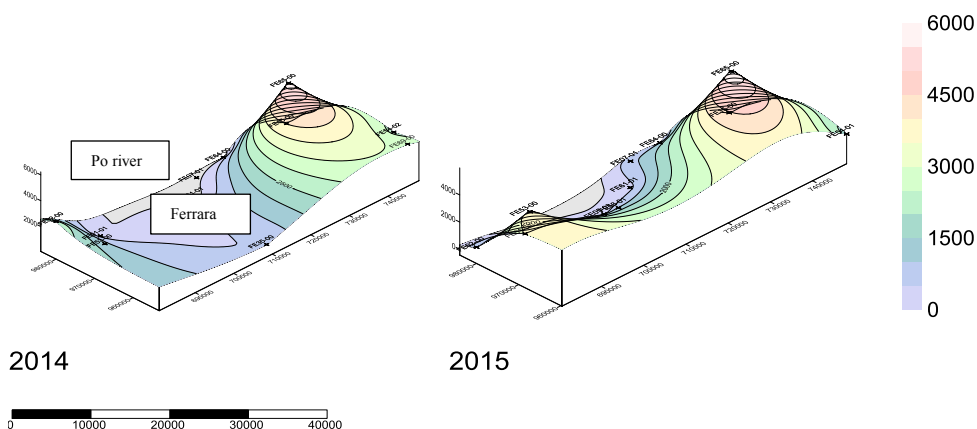
### *-Geochemical characterization*

An important feature of the Ferrara aquifers is the presence of saline or connate water, due to the presence of sandy sediments which pass after a saturated fluvial deltaic sediments of fresh water (Giambastiani et al. 2013). The fresh water passes to saline water and the passage is seen an increase of NaCl in water composition.

According to the publications of ground Water Reserves of Emilia Romagna Region (1998) the limit that marks the interface between fresh water and salt water is placed into an electrical conductivity corresponding to 1000  $\mu\text{S}/\text{cm}$ . Representatives in the aquifer maps A1 wells is very high values of up to 6000  $\mu\text{S}/\text{cm}$  (Fig.28). The interface changes can be depending on the weather conditions, the change of the coastline or anthropogenic effect.

The anthropic action causes sudden changes in the interface displacement fresch/saline water leading to an intrusion into the highest levels of brine. In the case of the distribution of the electrical conductivity of the A1 level checked on the observed wells, (maps presented only years 2010-2015 and in the 2003 year in which there was a deficit in rainfall) the interface displacement appears to have been produced by an active intrusion due to a high pumping of water at industrial areas (FE 52-00). The high 2014 EC values would derive from an anomaly in temperature which has determined the increase of evaporation and salt in waters (Fig.13).

The increase in this aquifer water level pumping means in consequence of the recall water from areas of recharge. The charging of the A1 is the bed of the river Po and emerging areas in the Adriatic Sea (Molinari 2007). High values E.C are also found in FE 58-00 E 65-00 (Jolanda di Savoia) following an intrusion axis, this axis was already identified in 2002 as the preferred line in which there is upwelling of saline water due to the presence of the industrial center.



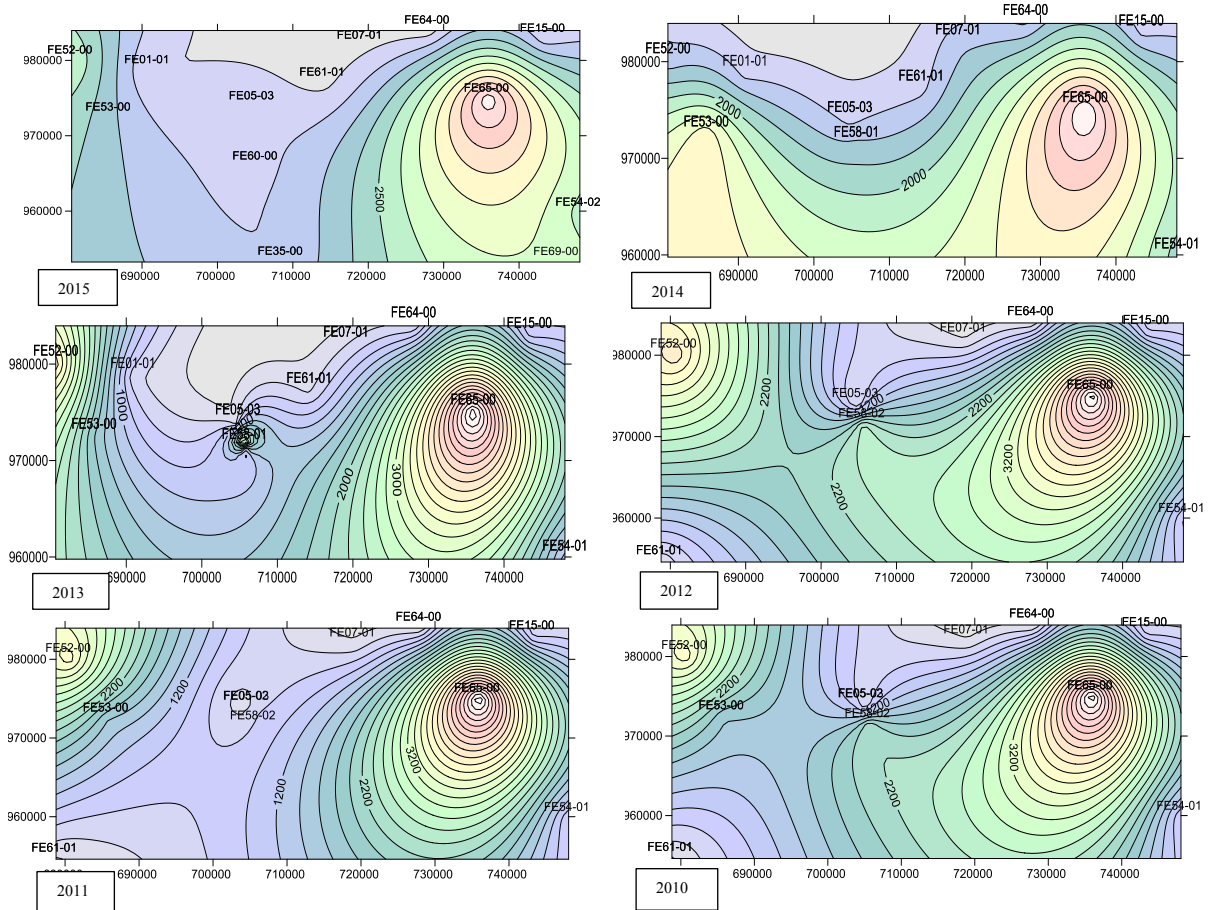


Fig.28 E.C. in aquifer A1 in different years: 2015, 2014, 2013, 2012, 2011, 2010.

The year 2003 is one of the most particular from the climatic point of view with anomalies in precipitation and in temperature, in this case is possible see the decrease of the electrical conductivity with an input come from the river. The river action have contribute to a freschening of the aquifer (Fig.29)

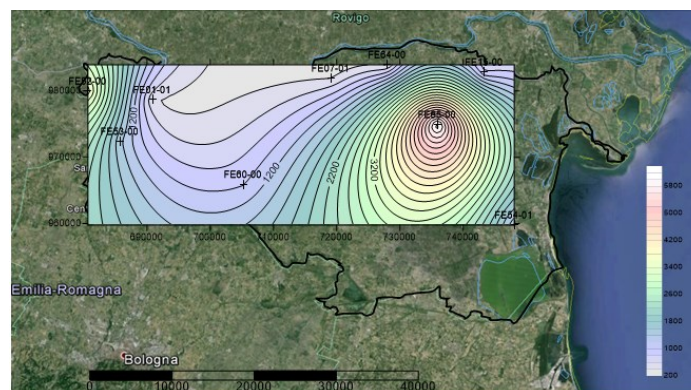


Fig.29 E.C. in aquifer A1 in 2003.

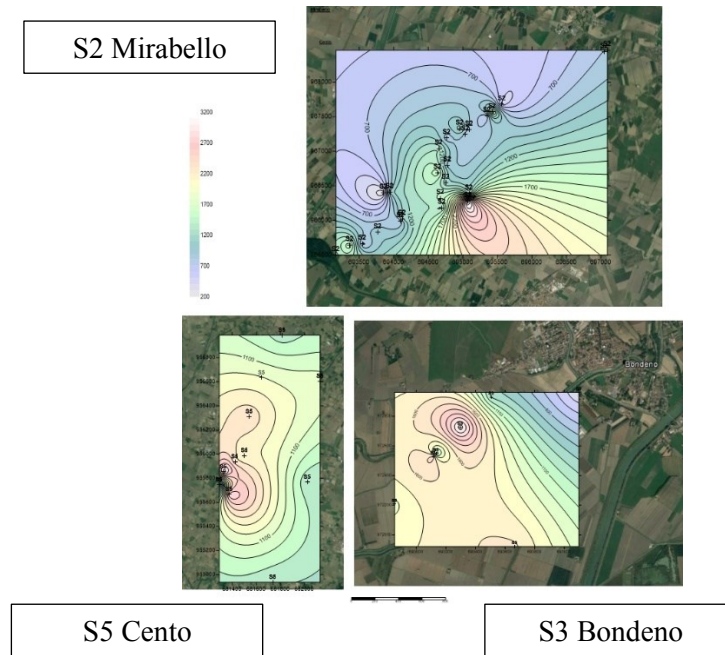


Fig.30 Kriging interpolation on the sampling sites. In the maps are Represented the electrical conductivity.

By comparing the performance of the parameter with a table showing abnormalities in regional precipitation (Fig.28), we can see that between the years 2011 and 2012 depicted abnormal periods. In these same years, the electrical conductivity increases, in this sense can be defined as the rainfall affects conductivity. The EC distribution in A1 have been represent also for 2003, a particular year in which there has been anomalies in temperature and precipitation. From the picture is visible as the conductivity values decrease and that there is a freschening of the water who come from the Po river direction.

In the Ferrara province all aquifers are confined, the only one who suffers from meteoric charging is the A0, in some cases, at the sandy limit represented by paleochannel, A0 and A1 are mixed, this mixing causes a mixing tank aquifer. Map of E.C.distribution in phreatic water (Fig. 30) the line between S2 and S5 show the direction of increased conductivity. In S3 which is located in the western sector of the province instead is possible see how the salinity input is derived from the river Po and from the province of Modena.

Piper plots help to distinguish graphically between different hydrochemical species based on the water types.



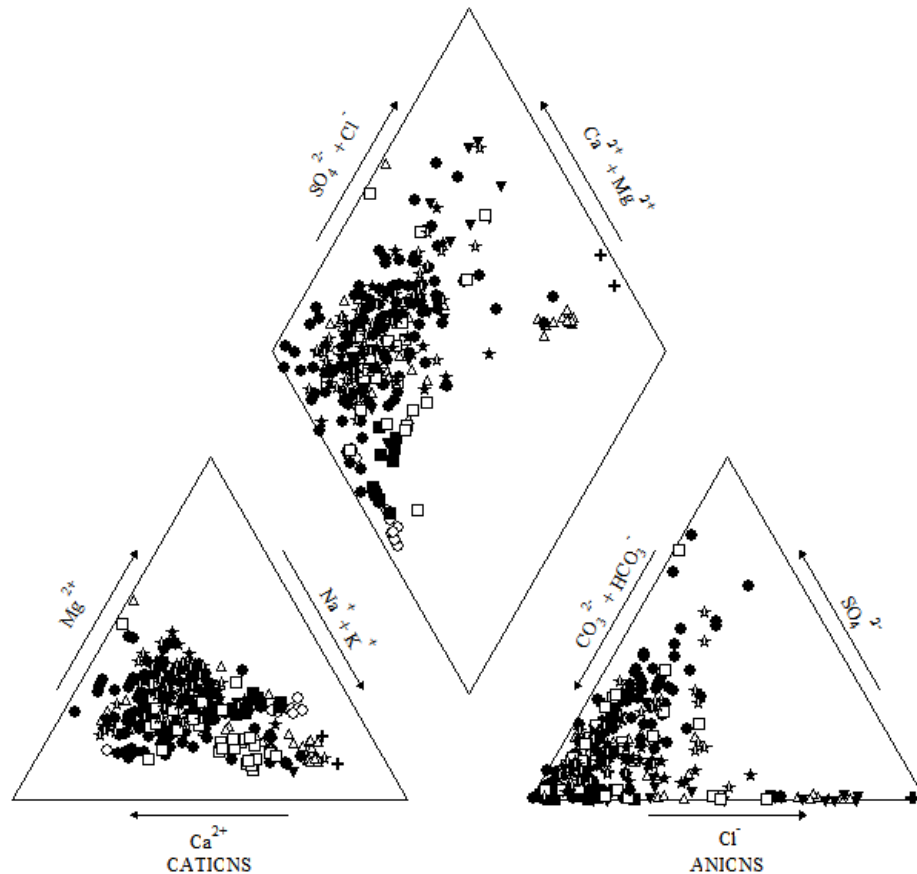


Fig. 31 Piper plot of all analysed samples: A1(open triangle),A2 (open circle),A3( square)ARPA dates, S1(inverted triangle),S2(circle),S3(open square),S4(star),S5( open star),S6(cross),S7(X) new monitoring data.

Piper diagram can distinguish the different facies and split the samples into different groups (Fig.31):

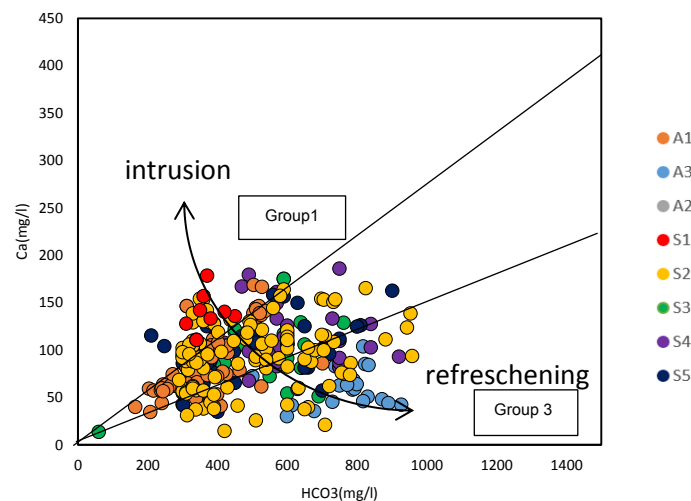
- The majority of samples (S2-S3-S4-S5-S7) falls within the facies Ca-HCO<sub>3</sub> these are continental fresh water with low salt content;
- a limited group of waters of the sectors S2 S3 have a geochemical behavior characterized by an increase of sulfate which makes these waters to facies Ca-SO<sub>4</sub>, typical of gypsum groundwaters and high drainage;
- Samples belonging A2 and A3 have composition presenting a Na-HCO<sub>3</sub> composition typical of deep waters and aquifers affected by ion exchange.
- Samples belonging to A1 and S6 have been represent by a facies Na-Cl with high salinity content and electrical conductivity.

High levels of HCO<sub>3</sub> may be due to carbonate dissolutions or an increase due to the product of the reduction reactions in presence of organic matter. The presence of carrier gas creates conditions that facilitate the upwelling. This catalyst, which was set in correspondence of

faults, it interacts with water and conveys toward the surface at preferential via always consist of faults.

The literature values for depths to 20 m in the areas between Ferrara and Modena have a median of 6 ppm/v CH<sub>4</sub> (Sciarra et al 2013)

The HCO<sub>3</sub> contributions enrich the water after the precipitation of calcite and determine the onset of phenomena of ion exchange. Waters that most emphatically a Na-HCO<sub>3</sub> signature are the A2-A3 waters showing precisely a typical depth behavior. Ferrara anticline presence affects the Na-HCO<sub>3</sub> behavior even of surface water from the piper diagram can see how many sample points following the freshening line generated from the input Na-HCO<sub>3</sub>. Some samples A1 and S6 have a NaCl composition. The isotopic composition of the Na-Cl waters has a clear meteoric signature (Fig.31) and no inflows of present day seawater seems necessary to justify such a composition although mixing between meteoric phenomena originated groundwaters and brines hosted in Pliocenic or pre- Pliocenic. The high concentration of Na may be due to layers deposited in Pleistocene. Rise of old water could be the source of the natural presence of Na in the waters of the flood plain. The Na excesses are then explained by means of ion exchange processes.



Fug.32 Ratio HCl3 VS Ca expressed in mg/l. Diagram adapted from Capaccioni et al 2005.

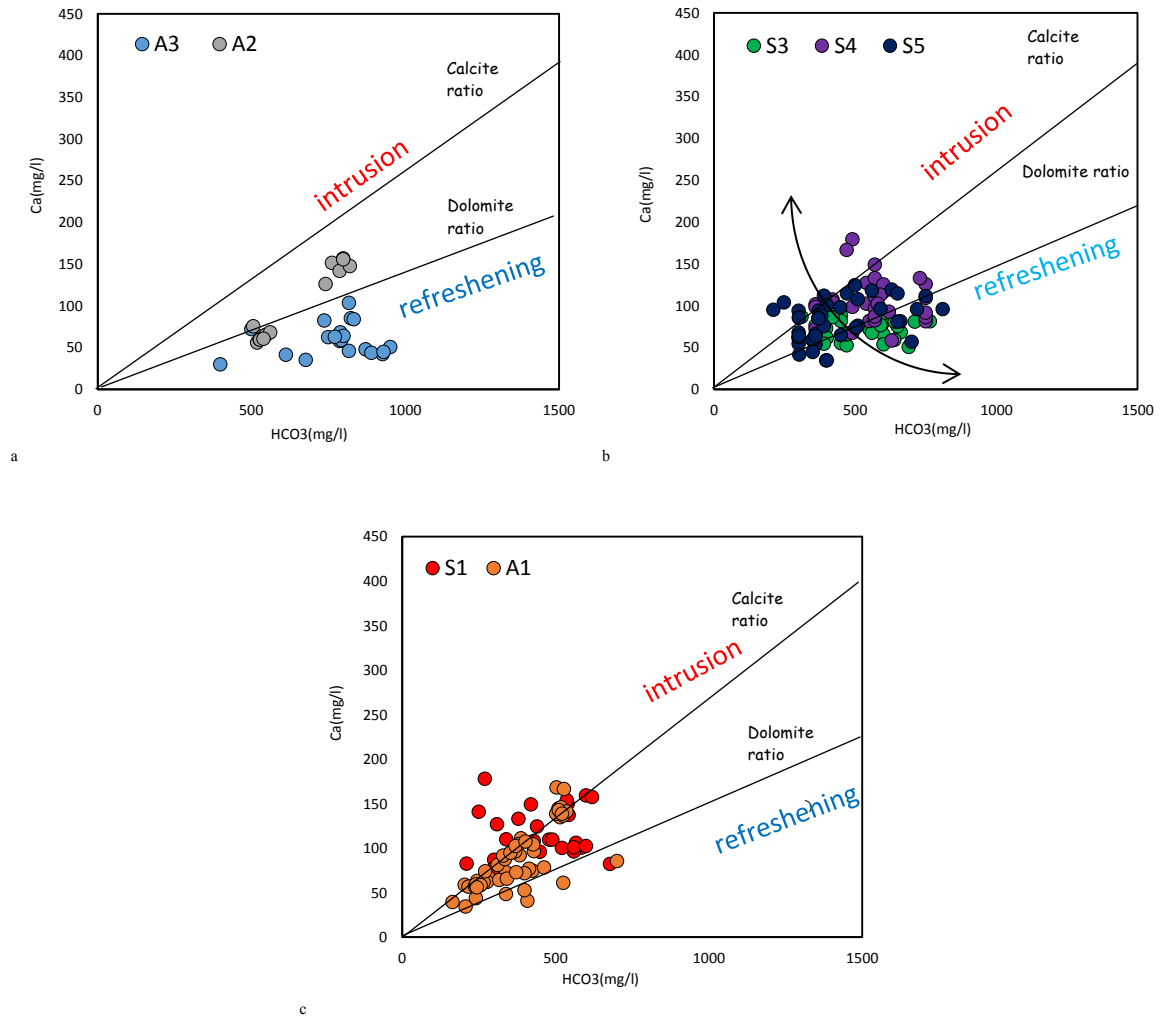
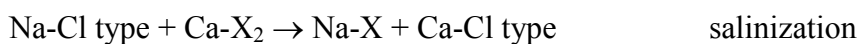
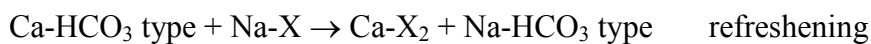


Fig. 33 a HCO<sub>3</sub>/Ca diagram show different field attributable to intrusion and refreshening effect and the correspondence with the FA subdivision groups : a HCO<sub>3</sub>/Ca in A3,A2; b HCO<sub>3</sub>/Ca in S3,S4,S5; c:HCO<sub>3</sub>/Ca in S1,A1. Elements composition expressed in mg/l.

The two equation on which are based the reaction indicate the two process explained in the graph are:



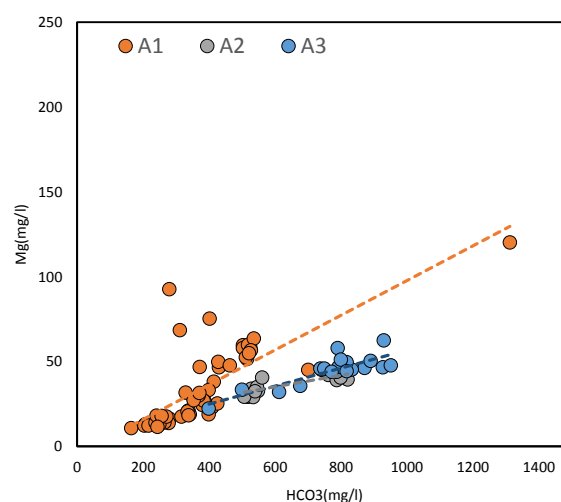
Depletion of Na<sup>+</sup> together with the enrichments of Ca<sup>2+</sup> plus Mg<sup>2+</sup> shifts the composition towards the Ca–Cl water type, changing the water compositions.

It seems like both of intrusion processes and freschening take place (Fig.32). The group indicated in the area related to the intrusion is represented by Group 1 in the FA (Tab.5) that have been indicate as dominated by ion exchange, the area in which indicates the refreshening instead is occupied by the samples in the group 3 where they occur dissolution processes of bicarbonates.

Some selected groups show the same behavior. The deeper waters of the aquifers A2, A3 (Fig 33a) are represented by clear refreshing conditions. They were formed in the interglacial periods and are therefore characterized by a more fresh composition.

The surface groups S3, S4, S5 (Fig.33b) show a behavior attributable to both processes, while the waters A1, S1 (Fig.33c) show a very similar behavior probably due to the communication between the two levels in correspondence of permeable sands of paleochannel. The salt intrusion processes may be due to different factors such as temperature changes and rainfall amount that causes an increase in evapotranspiration (Fig 26), a higher concentration of anions in the groundwater and a rising deep plume. The high levels of  $\text{HCO}_3$  may be due to carbonate dissolutions or an increase due to the product of the reduction reactions in presence of organic matter. May be a correlation between the  $\text{HCO}_3$  variable values in the areas observed and the presence of  $\text{CH}_4$ . The microbial  $\text{CH}_4$  oxidation can lead to an increase in  $\text{HCO}_3$  in superficial waters (St Thomas et al 2016).

The different aquifer complex are signed from different marker composition that could be seen in the proposed diagram in which are shown the  $\text{HCO}_3/\text{Mg}$  (mg/l). A positive correlation between this elements is present in the deep aquifer A1,A2,A3 (Fig. 34 a), in S3, S4, S5 there isn't correlation (Fig. 34 b) while S1 and A1 seem to have a good relationship (Fig. 34 c). This elements ( $\text{HCO}_3$  and Mg) are more important to explain the deep groundwater composition. The deep waters are characterized by a marked presence of  $\text{HCO}_3$  and low Mg, the surface water are characterized from a magnesium marker.



a

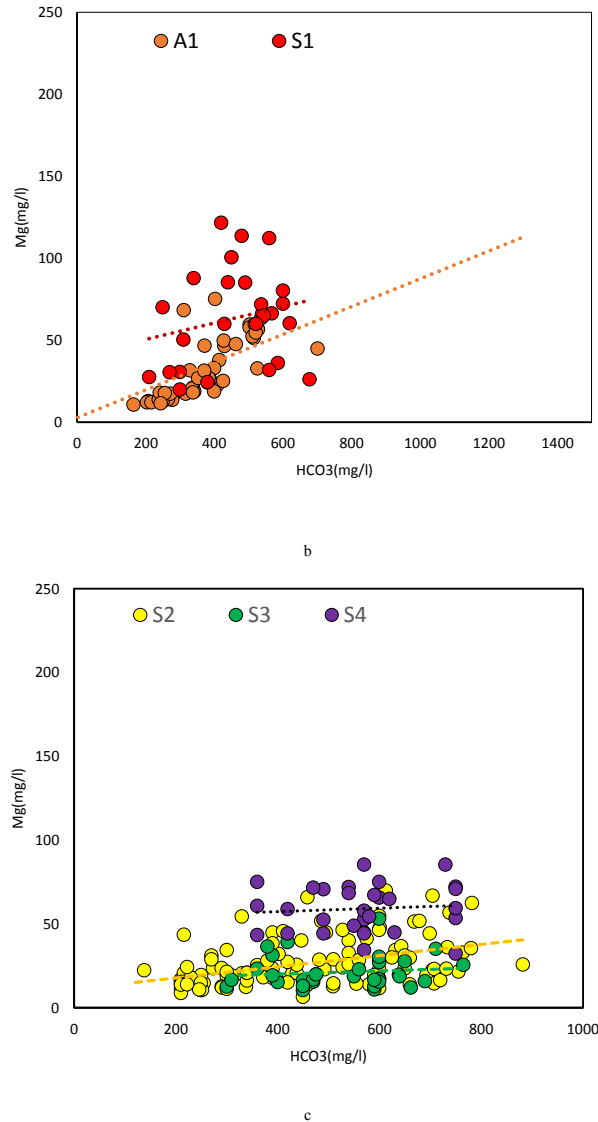


Fig.34 HCO<sub>3</sub><sup>-</sup>/Mg (mg/l) a: A1, A2, A3 grouping of groundwater and trends of developments in the relationship between the items shown. b: A1, S1, c: S2, S3, S4.

Mg<sup>2+</sup> comes from the dissolution of carbonates and magnesium chloride. It is a very important element in the system under consideration and will be more evident in terms of Mg/Ca ratio which allows to see the possible water-rock interaction and assessment of saturation indexes. Mg/Ca ratio can be used as an hydrogeochemical markers sensitive to modification of the processes of water-rock interaction as well as the saturation index and the pH. It could be used as origin recharge marker. The dispersion of the values is probably due to a prolonged interaction with sediments or injections of elements with different origins.

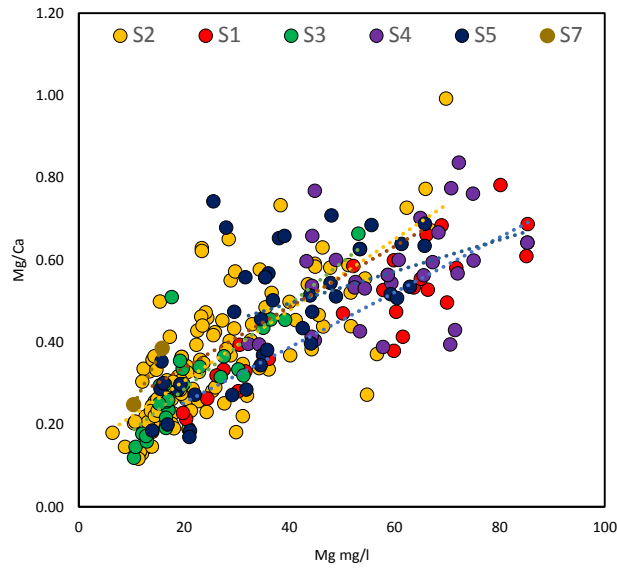


Fig. 35 Correlation  $Mg^{2+} / (Ca^{2+} + Mg^{2+})$  on phreatic samples. Values expressed in mg/l.

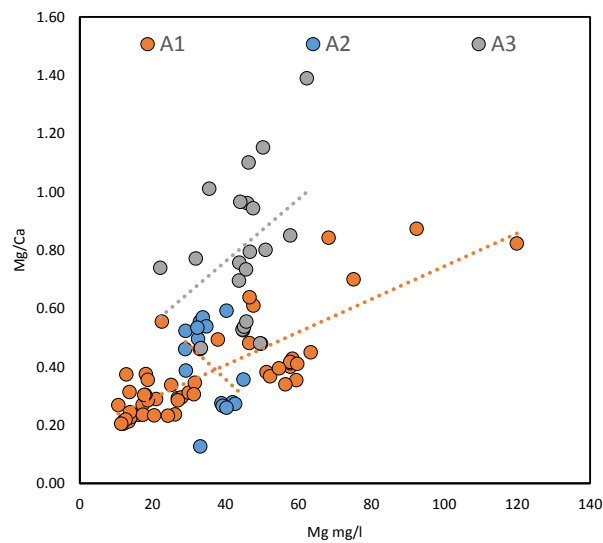


Fig. 36 Correlation  $Mg^{2+} / (Ca^{2+} + Mg^{2+})$  on deep samples. Values expressed in mg/l.

The biggest changes in geochemical composition can be attributed to changes in sediment patterns that occurred as a result of the sea level changes (Amorosi et al. 2002). These changes may explain the difference in composition between the shallow and deep waters. It is possible not how the  $Mg^{2+}/Ca^{2+}$  ratio is highly dependent on Mg showing a positive correlation with  $R^2 > 0.5$  for S1 ( $r^2:0,799$ ) - S2 ( $r^2:0,5608$ ) - S3 ( $r^2:0,723$ ) - A1 ( $r^2:0,640$ ) while lower  $R^2$  for A2 ( $r^2:0,175$ ) - A3 ( $r^2:0,151$ ) - S4 ( $r^2:0,185$ ) - S5 ( $r^2:0,464$ ). The phreatic water and A1 are signed by a good correlation between this ratio for the recharge apport (Fig. 35, Fig 36) while the prolonged interaction with sediments of the deep water create a dispersion of this ratio (Fig.

36). The deep aquifers reflect a different interglacial period, the surface water on the other hand, being in contact with smectite clays (Bianchini et al., 2002) receive the magnesium through the leaching of smectite sediments and then characterized in reason of their crystalline structure, since the three-layer clays T-O-T - by a high cation exchange capacity (for Ca, Na and Mg)

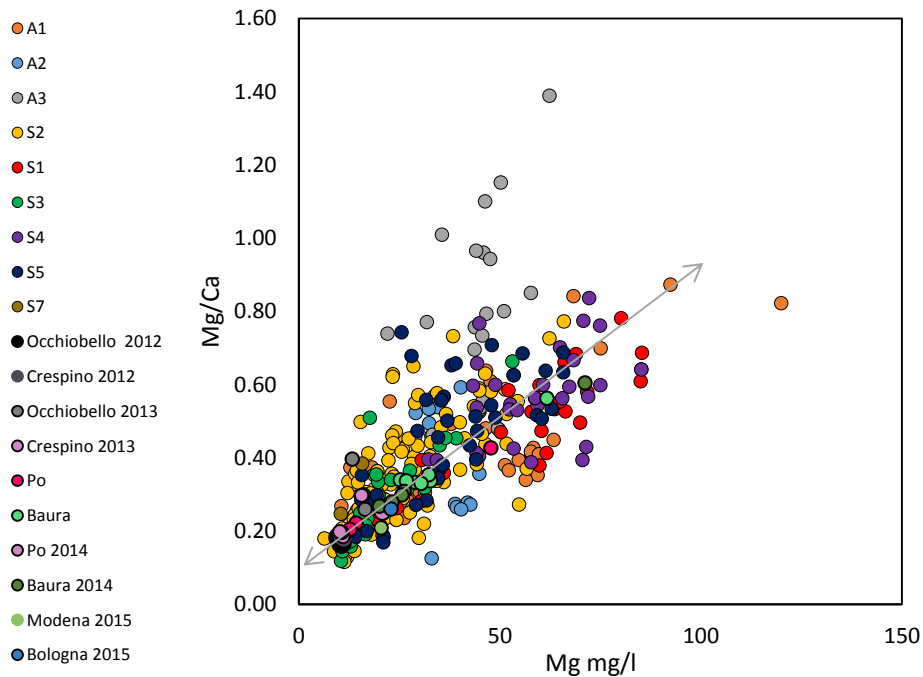


Fig.37 ratio Mg / (Mg / Ca) of all samples analyzed in this project together with ratios of these elements obtained from the analysis ARPAE for provicinia of Ferrara, Bologna, Modena for the years 2014-2015. Report of the Po waters taken from the doctoral thesis of doctors Chiara MARCHINA 2015.

Comparing the results obtained in Figure 35 and Figure 36 with superficial concentration of Ca and Mg of Bologna and Modena (data take from the arpa network) is evident how the phreatic water (S1, S2, S3, S4, S5, S7) follow the same behavior of the superficial water (Fig.37).

Data from superficial water have been taken from 2014 and 2015 grouped according to the basin of origin, the same yers of the phreatic weater sampling.

Phreatic water located near rivers are recharged from them and from rainwater. Deep water instead (A2-A3) show a complitly different trend which could be explain as a complitly

different recharge source. Deep water infact are characterized by  $\text{HCO}_3^-$  signature (Fig. 34 a) from deeper contributions.

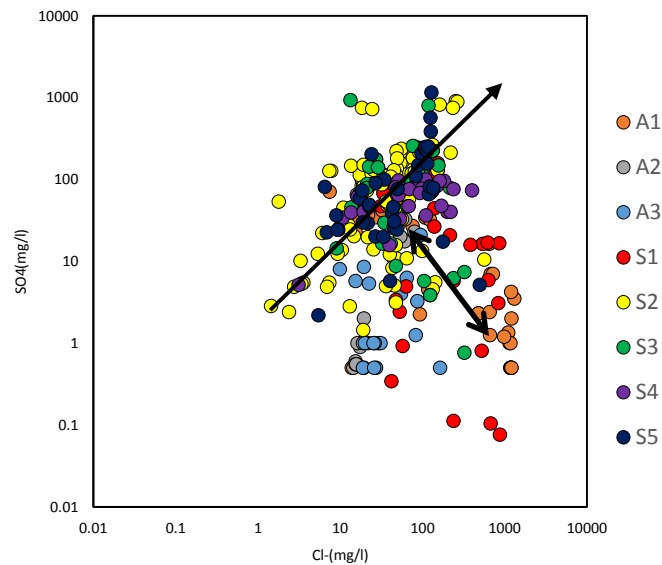


Fig. 38  $\text{Cl}/\text{SO}_4$  Values are expressed in mg/l with a log scale

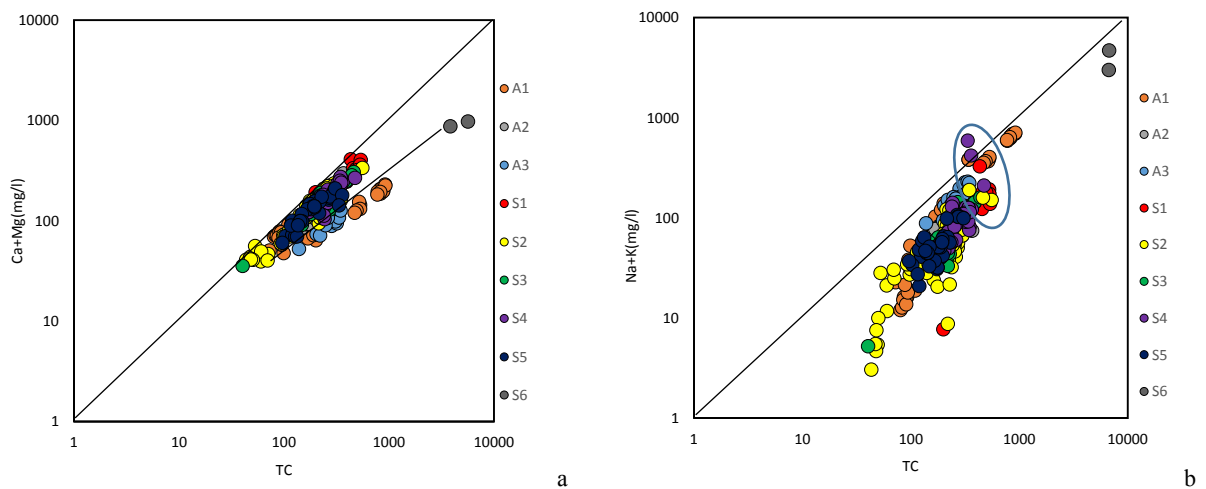


Fig. 39 a)  $\text{TC (SUM CATIONS)}/\text{Ca} + \text{Mg}$ , b.  $\text{TC (SUM CATIONS)}/\text{Na} + \text{K}$ .

The  $\text{SO}_4^{2-}$  ion does not show a good correlation with  $\text{Cl}^-$ , this could be due to oxidation-reduction phenomena in the deepest levels characterised by a strongly reducing environment (A1-A2-A3). A clear division is observed in  $\text{Cl}/\text{SO}_4$  diagram (Fig.38) where are completely dissociate S2-S3-S4-S5 and A1,A2,A3,S1 groups that have high Cl values and very low values of  $\text{SO}_4^{2-}$ . Water collected in phreatic water present sometimes very high values of  $\text{SO}_4$  (up to



300 mg/l). In S3 this  $\text{SO}_4^{2-}$  values can be determined by the action of the river Po on A0.  $\text{SO}_4^{2-}$  content does not seem sufficient to produce a large variation of the hydrogeochemical facies which are representative of aqueous compositions Ca- $\text{HCO}_3$ .

TC indicate the sum of cations (Ca, Mg, Na, K) and plotting this against the sum Ca + Mg (Fig.39 a) the groundwater are all on the line of equiconcentration  $(\text{Ca} + \text{Mg})/\text{TC} = 1$ , instead the deep water are more affected than different contributions. The deepest waters are enriched in Na and K which are representative cations of the salt waters, in the diagram in fact the waters most affected by these anions are localized on a different line that linked to S6 (Methane and deep water)

Diagram TC/ (Na + K) in Fig.39 b relates the total concentration of cations compared to the two characteristic ions of salt waters. In this case S6 stands almost on the equiconcentration line as well as S1-S2-S4 (points that we saw as part of group 1).

#### *-Mix model*

Assuming perfectly conservative behaviour of chloride and considering two end members, Na-Cl depth water S6 and Ca- $\text{HCO}_3$  freshwater, the theoretical composition of mixed water samples was reported. The mixing has been realized through the simulation of a hypothetical mixing of two compositions of water has resulted in a curve line of mixing with respect to which it's possible to compare all the samples.

S6 and S7 samples were chosen to simulate the existing mixing curve between end member, as elements who represent deep water (S6) and samples who represent superficial water (S7).

Using PHREEQC the pattern mix, the chemical compositions of these waters have been used to simulate their composition in different percentages (25,50,75) for reconstructing of the simulated intermediate compositions. The graph proposed a hypothetical mixing line between surface and ground water. S1-S4 follow the mixing curve, this could be explained as a possible composition that is affected by the mixing of different waters (Fig.40). In S1 is also evident a geochemical behavior similar to A1 as also exposed in the previous graphs (Fig. 31, Fig.33c and Fig 38), which can be justified by a variation of the thickness and texture of the hydraulic barrier between A0 and A1 in the areas in correspondence of paleo channel in which the two bodies are in communication. In the inter riverbed areas instead the thickening of aquitard composed of clay prevents the connection.

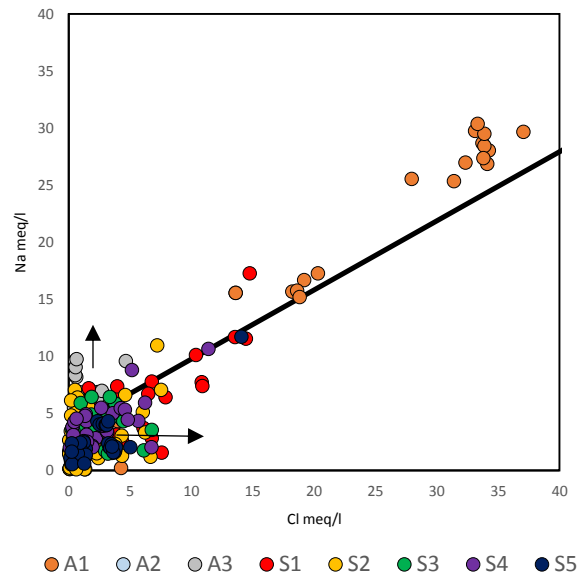


Fig. 40 Mix model with the curve minxing rapresentation

A2 and A3 are enriched in Na as was visible also in Piper diagram (Fig.31). Phreatic groundwater S5 and some samples of S3 are more enriched in Cl and don't follow the curve mixing.

The chlorides are widely distributed in nature, generally in the form of sodium salts (NaCl) and potassium (KCl). Ancient seawater traces may remain trapped for considerable geological time, with fine-grained sediments, such as gypsum and sandstone. Consequently, the water flowing out of these formations can be enriched by chlorides (Bianucci et al. 1985). High solubility Chloride ions and the small ionic radius are not absorbed by the materials with which the aqueous phase is in contact, for which they can be considered a conservative tracer. Chloride ions, usually associated with Na, in Emilia Romagna Region are present in the groundwater of the province of Ferrara and Modena (Martinelli et al. 1998). The model proposed is not enough to explain all the different compositions, which take place in groundwater in all the situations, because there are much different process which condition different characteristic. Mixing can be considered the prime irreversible process that conditioned the chemical evolution of the groundwater in the plain of Ferrara. The successive changed are due to subsequent water-rock interaction process.

*-Inverse modeling*

To simulate hypothetical process that can occur between the waters described and which may justify the occurrence of different mixing events were chosen as solution to insert in the model simulation:

- Sol 1. Fe 54-01; sample of A1 Ca-HCO<sub>3</sub> compositions related to the F2,
- Sol 2. S6 deep origin but the waters were sampled at the surface as a result of a bubbling phenomenon, with T: 20,79 ° C; prheatic water samples collected in the same period show 3-3.5 ° C of difference with respect to them. The temperatures are in agreement with the vertical gradient of the area that is uguale to 3 ° C / 100m.
- Sol 3. S3 (B7) sample in the FA is related to F2
- Sol 4. S5(C1) sample in the FA is related to the F 3
- Sol 5. FE 30-00 sample belonging to the A2 level in the composition Na-HCO<sub>3</sub>
- Sol 6. S7 Sampled surface water at the same event which affected the methanifer well.
- Sol7: S1 Sample in FA related to F1 (Ca, Mg dominated)

Observing the saturation indices (Tab.7) the solutions are under-saturated for all groups containing Si and SO<sub>4</sub>, saturated or equilibrium conditions for calcite, dolomite and aragonite. Halite and gypsum have always values of undersaturation, suggesting that the concentration of the soluble components (Na, Cl, Ca, SO<sub>4</sub>) does not depend on mineral equilibria.

<i>PHASE</i>		<i>Sol1</i>	<i>Sol2</i>	<i>Sol3</i>	<i>Sol4</i>	<i>Sol5</i>	<i>Sol6</i>	<i>Sol7</i>
<i>Anhydrite</i>	CaSO4	-0,06	-2,19	0,3	-2,95	-1,53	0,58	0,15
<i>Aragonite</i>	CaCO3	2,83	0,45	3,28	-0,72	2,77	2,85	2,54
<i>Calcite</i>	CaCO3	2,98	0,6	3,44	-0,57	2,92	3	2,69
<i>CO2</i>	CO2	-0,68	-1,5	-0,89	-0,21	0,17	-0,32	0
<i>Dolomite</i>	CaMg(CO3)2	5,92	1,11	6,58	-1,34	4,91	5,31	4,96
<i>Gypsum</i>	CaSO4:2H2O	0,32	-1,84	0,73	-1,57	-1,12	0,94	0,54
<i>H2(g)</i>	H2	-23,4	-22,04	-23,83	-20,04	-22,03	-22,74	-22,03
<i>H2O</i>	H2O	-1,7	-1,64	-1,85	-1,69	-1,8	-1,69	-1,75
<i>Halite</i>	NaCl	-4,42	-3,53	-5,08	-7,27	-4,87	-4,42	-3,95
<i>O2</i>	O2	-39,05	-40,92	-40,08	-45,62	-43,07	-40,15	-42,35
<i>SiO2</i>	SiO2		-30,66		-30,53			-29,87
<i>Sylvite</i>	KCl	-4,27	-5,06	-4,61	-6,64	-6,03	-4,34	-3,29

Tab 7. Saturation index for the chosen solution

	Model 1 S6-A1		Model 2 S6-S3		Model 3 S6-S7		Model 4 S6-S1	
O2		5,58E+01		3,50E-01		-1,11E+02	5,56E+01	-1,11E+02
Halite	3,25E-02	3,25E-02	1,79E-02		3,40E-02	3,40E-02	1,49E-01	1,49E-01
CaX2			-9,27E+00	-1,18E-01	-9,24E+00	-4,45E-02	3,67E-02	4,25E-03
Calcite	-1,86E+01			-1,81E+01		-5,54E+01		-5,56E+01
Dolomite	1,14E-01	1,14E-01	-9,15E+00		-9,16E+00	3,50E-02	9,90E-02	6,66E-02
Gypsum	1,86E+01	-3,30E-02	1,85E+01	1,84E+01	1,86E+01	5,56E+01	4,26E-02	5,57E+01
CH4	1,85E+01	2,78E+01	1,85E+01	1,85E+01	1,85E+01		2,78E+01	
CO2	1,58E-01	-2,77E+01	1,75E-01		1,86E-01	5,57E+01	2,76E+01	5,58E+01
KX	2,82E-02	2,82E-02	2,30E-02	2,27E-02	2,50E-02	2,50E-02	6,90E-02	6,90E-02
NaX	6,35E-02	6,35E-02	2,20E-02	2,58E-02	6,40E-02	6,40E-02	-7,75E-02	-7,75E-02
MgX2	-4,59E-02	-4,59E-02	9,25E+00	9,36E-02	9,20E+00		-3,24E-02	
H2S	-1,85E+01	7,50E-02	-1,83E+01	-1,85E+01	-1,85E+01	-5,55E+01		-5,56E+01

Tab.8 Chosen model for the inverse modeling taken from selected results.

Two models considered equally valid for each analyzed hydrochemical step were chosen (Güler, 2004)

*(reagents + Addition in solution phase → Products + loss from the solution phase)*

### Model 1

*Halite + CH<sub>4</sub> + K by ion exchange -> Na (ion exchange with Ca) and gaseous CH<sub>4</sub>*

The waters start from Ca-HCO<sub>3</sub> composition, then the solution is enriched in Na and K derived from mixing. This mixing explain the reactions can result between A1 Ca-HCO<sub>3</sub> and S6 NaCl waters. A mixing between these two compositions belonging to the same level A1 would lead to a chemical waters composition from Ca (Mg) -HCO<sub>3</sub> in Na Cl type. Is seen that in the transition between carbonate composition waters and sodium-chlorinated water, there is a dissolution of the halite which correspond to a Na ions contribution.

By PHREEQC was drawn a hypothetical mixing between the two samples (10%, 20%, 30% ... 90%) and the representation of the results it was presented to compare the estimated temperature for each hypothetical mixing of the two aqueous solutions (Fig.41, Fig.42). CH<sub>4</sub> could determine the transmission of elements from depths to surface through preferential ways (Annunziatellis A. et al 2008; Ciotoli G. et al 2007; Baubron et al 2002). In figure 42 are esented all the samples, on the simulated composition are localized also: S4, A1(52,58) S1, S3.

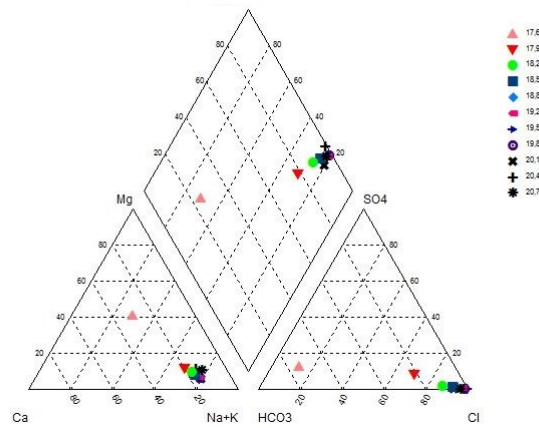


Fig. 41 Piper diagram with the A1 and the S6 samples, simulated mixing between the two compositions.

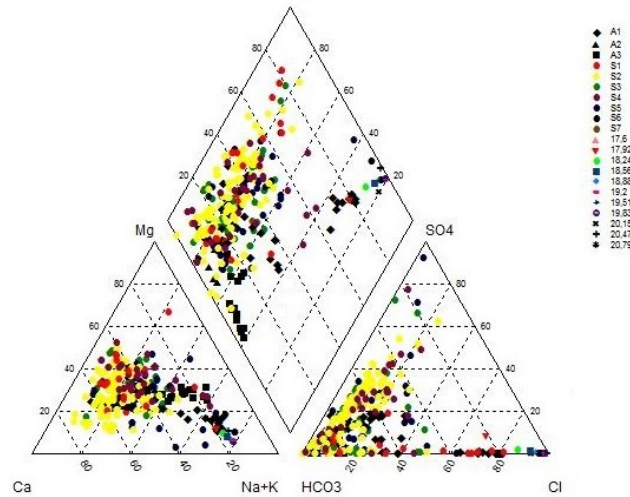
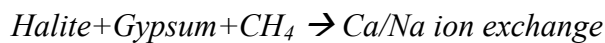


Fig.42 All the samples were presented in Piper with the simulated mixing compositions. The results of synthetically produced from processing the program samples were plotted as a function of temperature.

### Model 2



The gases dissolved in the waters facilitate the dissolution of carbonates, sulphate and NaCl. The solution loses Ca, but is enriched by Na, K, Mg entering for ion exchange processes. The Gypsum leads to an increase of the SO<sub>4</sub> which leads to the behavior noticed in Figure 38. This contribution comes from the recharge action of the Po river on A0.

### Model 3

*Halite + Gypsum + gaseous CO<sub>2</sub> -> Na / Ca ion exchange*

Contributions of deep CO<sub>2</sub> and CH<sub>4</sub> promote the dissolution of Mg and SO<sub>4</sub>. The evolution of these waters is also characterized by the calcite dissolution. This model shows the chemical reactions that reflect the mix of the line Figure 40. The presence of CH<sub>4</sub> and CO<sub>2</sub> creates deepwater carrier catalysts on the surface. When at a certain depth is the saturation of the water reached, there is a separation of a free gas phase. The water separated gas accumulates in "traps" geological (Chiodini et al., 1995) generating in the subsoil pockets of gas which, in turn, on the surface feeding the gaseous emissions. The mixing of these two compositions produces water with high Na and Mg, the first arising from halite dissolution present in evaporite layers. The second derived from deep level and deep groundwaters, these two effects sign the composition of the water resulting from these processes

### Model 4

*Halite + Gypsum CH<sub>4</sub>+ CO<sub>2</sub>gas -> Na / Ca ion exchange*

The reactions that represent this model are very similar to the previous one. Waters are gypsum and dolomite supersaturated, Ca enters into solution by ion exchange with Na and precipitation of minerals. K enter into the solution by ion exchange processes (Fig.43).

The S6 and S1 areas would be characterized by the presence of high concentrations of CO<sub>2</sub> and CH<sub>4</sub> originate by the decadiment of organic matter (peats). Reaction involve organic matter leads the oxid reaction of Fe, Mn and SO<sub>4</sub> and the CH<sub>4</sub> formation. This gas work as carriers that take depth ion into superficial solution. Deep CH<sub>4</sub> typically rises towards the surface along faults and fractures so influence the carbonate dissolution.

In this last model is important to note the K values that is more present that in other models. This high concentration (high values in S1 and S4 are evident in Tab 3) could be due to illite dissolution, K is freed in solution.

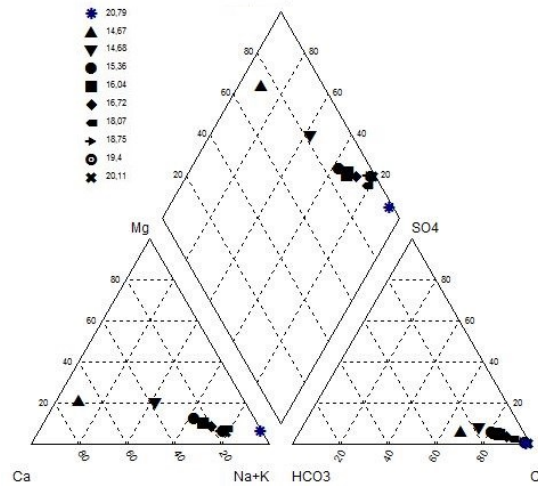


Fig.43 Simulated mix between different solutions: S6-S1

The modeling work on the interactions of the mixing processes between the solutions 2-4, 2-5 have not produced successful reaction. The chemistry of these waters from deep aquifers and ascents bubbling gases, may suggest the presence of relict waters. The hyper-saline waters could result from relict waters trapped in the sediment rather than saline intrusion. Salted sequences could be trapped during the geological eras, particularly during the last glacial age (Amorosi et al., 2003). In this way, the ancient saline waters formed during interglacial events. Marine deposits phases can be formed in fine sediments and may have layers formed salts into the sedimentary basement (Giambastiani B.M.S. et al., 2013) may be formed.

#### Bridge protocol

To define upper tolerance limitis of the values considered in Table of D.Lgs 152/06 have been used the Bridge protocol. After a previously pre selection of samples based on the criteria expressed from the method, BRIDGE methodology suggests deriving TVs for the following two cases (scenarios), which were in our study area as well:

- **Case 1:**  $\frac{NBL}{reference\ value} < 1$ , then  $TV = \frac{(NBL + reference\ value)}{2}$
- **Case 2:**  $\frac{NBL}{reference\ value} > 1$ , then  $TV = NBL$

substance	UNIT	REF	NBL	TV1	TV2
EC	( $\mu$ S/cm)	2500	2565,4		2565,4
Chloride	(mg/L)	250	390,9		390,9
Sulphate	(mg/L)	250	230,5	240,25	
Nitrate	(mg/L)	50	44,9	44,87	
Manganese	( $\mu$ g/L)	200	130,0		130,0
Iron	( $\mu$ g/L)	50	750,0		750,0
Arsenic	( $\mu$ g/L)	10	5,5	7,73	
Boron	( $\mu$ g/L)	1000	964,5	982,25	

Tab.9 Bridge protocol calculation for the A0 level. Temporal series data: 2014-2015

substance	UNIT	REF	NBL	TV1	TV2
EC	( $\mu$ S/cm)	2500	3891,5	3195,75	
Ammonium	(mg/L)	0,5	1,9		1,86
Chloride	(mg/L)	250	111,6	180,8	
Sulphate	(mg/L)	250	85,0	167,51	
Nitrate	(mg/L)	50	3,2	26,58	
Iron	( $\mu$ g/L)	200	7729,9		7729,9
Manganese	( $\mu$ g/L)	50	691,7		691,7
Boron	( $\mu$ g/L)	1000	558,6	779,3	

Tab. 10 Bridge protocol calculation for the A1 level. Temporal series data: 2002-2015

substance	UNIT	REF	NBL	TV1	TV2
EC	( $\mu$ S/cm)	2500	1166,1	1833,1	
Ammonium	(mg/L)	0,5	5,1		5,07
Chloride	(mg/L)	250	66,7	158,3	
Sulphate	(mg/L)	250	40,6	145,3	
Nitrate	(mg/L)	50	1,0	25,5	
Iron	( $\mu$ g/L)	200	3387,6		3387,6
Manganese	( $\mu$ g/L)	50	225,6		225,6
Boron	( $\mu$ g/L)	1000	488,6	744,3	

Tab.11. Bridge protocol calculation for the A2 level. Temporal series data: 2002-2015

substance	UNIT	REF	NBL	TV1	TV2
EC	( $\mu$ S/cm)	2500	1285,6	1892,8	
Ammonium	(mg/L)	0,5	10,4		10,41
Chloride	(mg/L)	250	99,1	174,56	
Sulphate	(mg/L)	250	9,1	129,56	
Nitrate	(mg/L)	50	1,0	25,5	
Iron	( $\mu$ g/L)	200	724,2		724,18
Manganese	( $\mu$ g/L)	50	6,4		
Boron	( $\mu$ g/L)	1000	1365,3		1365,3

Tab 12 Bridge protocol calculation for the A3 level. Temporal series data: 2002-2015



For the investigated bodies were calculated for each chemical value of 95 percentile that was compared with the threshold values set by legislation (REF- D. Lgs. 30/09).

The calculated values when they exceed more than 5% of the limit values are a critical for the definition of good chemical status of the groundwater body.

The different aquifers levels were considered separately since the presence of unpermeable levels makes them independent and separate from the point of view of the movement of the pollutants.

The values obtained for the A0 level (Tab.9) exceed all REF values estimated by D. Lgs.30 / 09. As shown in the table results note chlorides and sulfates are quite high values, even a few meters deep due to the contamination of surface water and deep water. The recorded values of arsenic in the aquifer A0 are not high, they are sporadic cases that exceed the limit values. Nitrates instead show lower values equal the REF.

Fe element presence is not the result of a local contamination of pollution or attributable to anthropogenic effects. High values ( $750\mu\text{S}/\text{cm}$ ) are derived from the interaction between water and sediment (Dugoni G. et al 2007).

A1 level (Tab.10) present very high values of electrical conductivity in excess of about 14% of the REF value. Geochemical processing explain the presence of a chemical composition NaCl and E.C. very high in A1 (Fig 31, Fig 42 and overexploitation). These wells are located in the south shaft of the Po and the surrounding areas to the city of Ferrara. The  $\text{NH}_4$  values, Fe and Mn though higher than REF they still values compatible with the hydrogeological and hydrochemical knowledge related to the water bodies considered.  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are below the REF.

The level A2 (Tab.11) has product values  $>$  REF only for those elements that can be explained as derivatives of natural origin, then products from the interaction between water and sediment.

The same behavior is seen in A3 (Tab.12).

Regards the statistical approach must always take into account the fact that they can be a help in the understanding of the concentration values identified, but that in these studies must necessarily be associated hydrogeochemistry which serve to better understand the complex dynamics of the associated processes.

## Continuously monitoring

Thank to the cooperation with the Region has been possible to install continuously monitoring stations with SEBA probes. These continuously sensors measure temperature parameters, electrical conductivity and piezometric level.

2 probes were installed in January 2016. These wells were selected on the basis of statistical results (in the FA are the group 1), the isotopic results (are more depleted in heavy isotopes), based on the geochemical results (representing those samples are placed in the area of intrusion):

- Mirabello (S2)
- Sant'Agostino (S4)

Localion of the probes are represented in Figure 44, the acquisition frequency was set to 1 h.



Fig. 44 Localization of the continuously probe

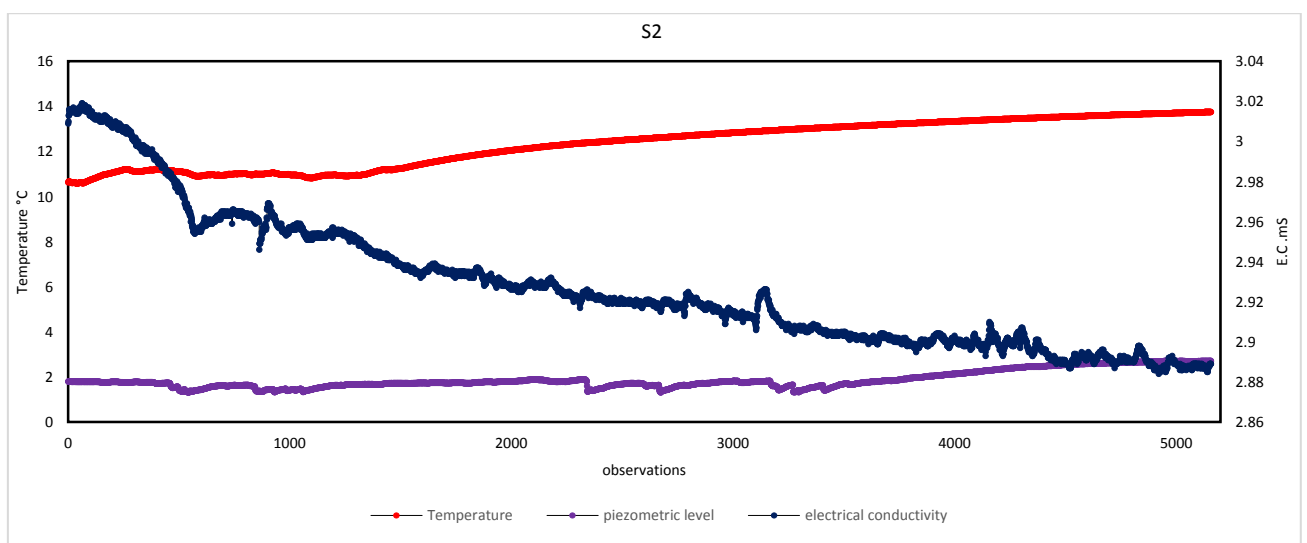


Fig.45 results of the continuously monitoring in the S2 station

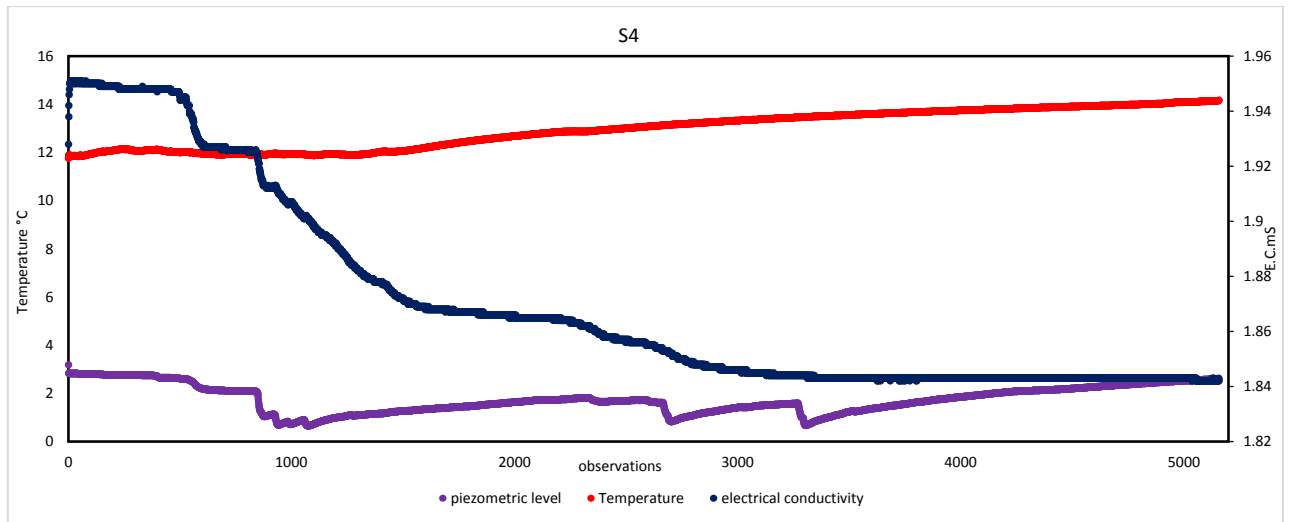


Fig.46 results of the continuously monitoring in the S4 station

The first graph (Fig.45) represents the trend of the three parameters observed in the station S2. Here we see a slight increase of the temperature due to the seasonal factor, a conductivity variation of the fluctuations that do not show remarkable abnormalities but which are constantly present in the time interval. Piezometric level varies from a minimum to a maximum of 1,30 m the 2,71 m on 26/08/2016.

In S4 (Fig.46) observe the same trends of the parameters observed in S2. The electrical conductivity has a maximum of 1.96 and a minimum of 1.84 mS and a decreasing trend, always in function of the relation with temperature. The values are high to be phreatic ground water used for irrigation. The level shows no obvious abnormalities in function of meteor contribution but correlated and to activation of the dewatering of the Consortium of Bonifica. In fact in the locality Sant'Agostino is located a dewatering irrigation system operated by the consortium while in the previous S2 site the answer is less evident and slowed by the distance from it.

In both cases (Fig. 45-Fig.46) is noted an inverse correlation between the temperature and the electrical conductivity. The influence of temperature on conductivity is due to the variation of the degree of molecular dissociation and the same temperature dependence of the dielectric constant  $\epsilon$  and  $\eta$  the viscosity. The temperature modification change the number of ions mobilized in aqueous solution.

The electrical conductivity in S2, however, shows jumps, this changes are not seen in evolution of the same parameter in S4, maybe this is due to a response of the water to the

influences of a plume come from the depths which are found at the bank where it is localized monitoring well S2.

A continuous monitoring of this type produces a large amount of data and supports a better understanding of the hydrological system. This large amount of data must be managed with a complex mathematical approach that guarantees a processing through algorithms and predictive models.

To improve the management of these resources would be useful and effective to control the parametric trend directly, to obtain an intensive knowledge of system in order to have more information for resources management and to be alert immediately by occurrence of possible anomaly.

On the market there are several solutions that allow the continuous monitoring using multiparameter probes for the measurement of chemical and physical parameters of water (pH, redox, oxygen, conductivity, etc.) with connection via GPRS, radio, satellite that allows you to manage data and control very easily even remotely, via common Internet browser, without the aid of specific software. This systems, however, are very expensive and they can't be used to cover many territories to structure a network of efficient monitoring. As a possible solution to solve this problem has been experiment a low cost system for data acquisition and transmission systems in real time, trying to take advantage of the latest technology offerings in the market.

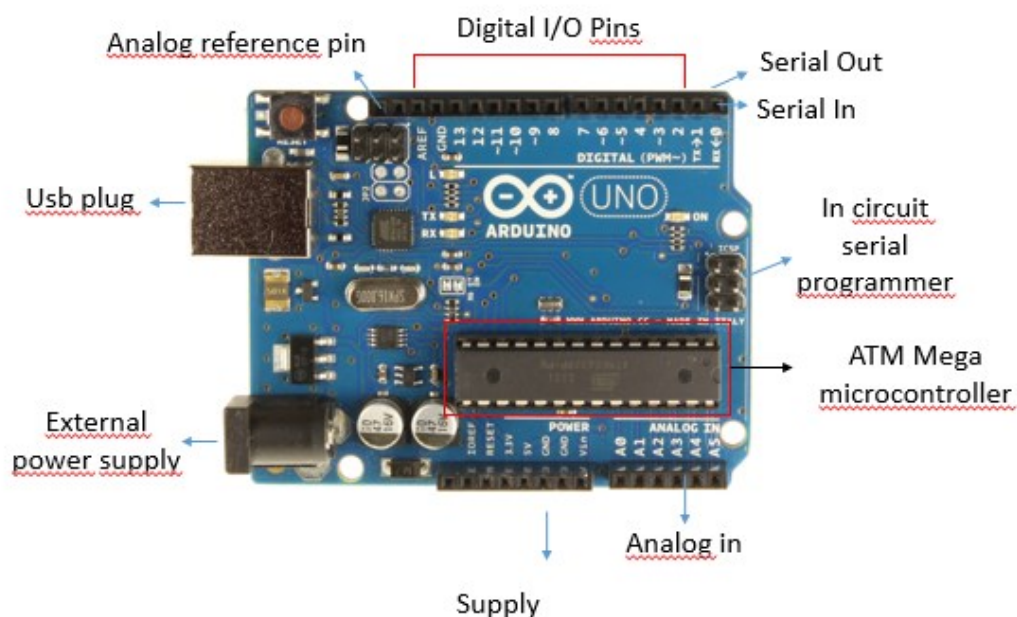


Fig. 47 Scheme of components in Arduino UNO

The prototype is based on a technical schedule, Arduino UNO, composed by ATmega controller 328P-PU: this is the heart of the card, 8-bit microcontroller in 28-pin PDIP format with 32 kB of Flash memory, 2Kb of RAM, twenty digital I / O pins of which six used as analog inputs integrated ADC and six usable as a PWM (Pulse Width Modulation).

Power supply: 5V DC, to be withdrawn externally from a personal computer connected to the USB port, or by a power supply connected to a barrel jack; in this second case the internal current is internally stabilized by the card using an integrated 5V regulator.

USB Interface: the connection to the PC is via USB port; on the card is mounted a microcontroller (ATmega8su2 or ATmega 16su2, according to the Arduino UNO model) with specific functions of serial to USB converter.

The I / O connectors are used to connect the board with the outside world, the ANALOG IN includes all pins connected to the inputs of the analog digital converter of the micro, these pins can be still used as a digital I / O. On the opposite side are the connectors of the digital I / O which also include those used for serial communication and those used for PWM outputs in addition to a power GND, the AREF outlet and also the repetition of signals for communication with the I2C protocol.

The flash memory programming of Arduino is via USB port. First the Arduino IDE compiles the program (also known as the sketch) in a format that can be directly executed by the ATmega processor, then the Arduino bootloader receives the sketch and saves it to the internal flash memory. Serial communication is not used only for the sketch upload from PC to Arduino UNO but if necessary can be used by Arduino IDE to load data intercepted by a serial monitor and shown it on video. It is possible to read the status of a digital I / O pin or the associated value of an analog pin.

Serial communication does not take place directly between the USB port and the micro-ATmega328P PU but is necessary the presence of a circuit able to convert between USB and serial signal and vice versa, such a circuit is represented by ATmega8U2 which contains its own bootloader and a pre-programmed firmware that allows the micro to perform this task. The microcontroller has D+ and D- lines for USB data upstream to the USB port, while on the other end it exposes serial transmit, receive and reset (TX-RX-DTR) lines. Sensor Selection to create the prototype for the transmission protocol has been based on market on line opportunities and on best selection of quality / price. The system structured as in Figure 48 has been programmed to acquire data from the sensors.

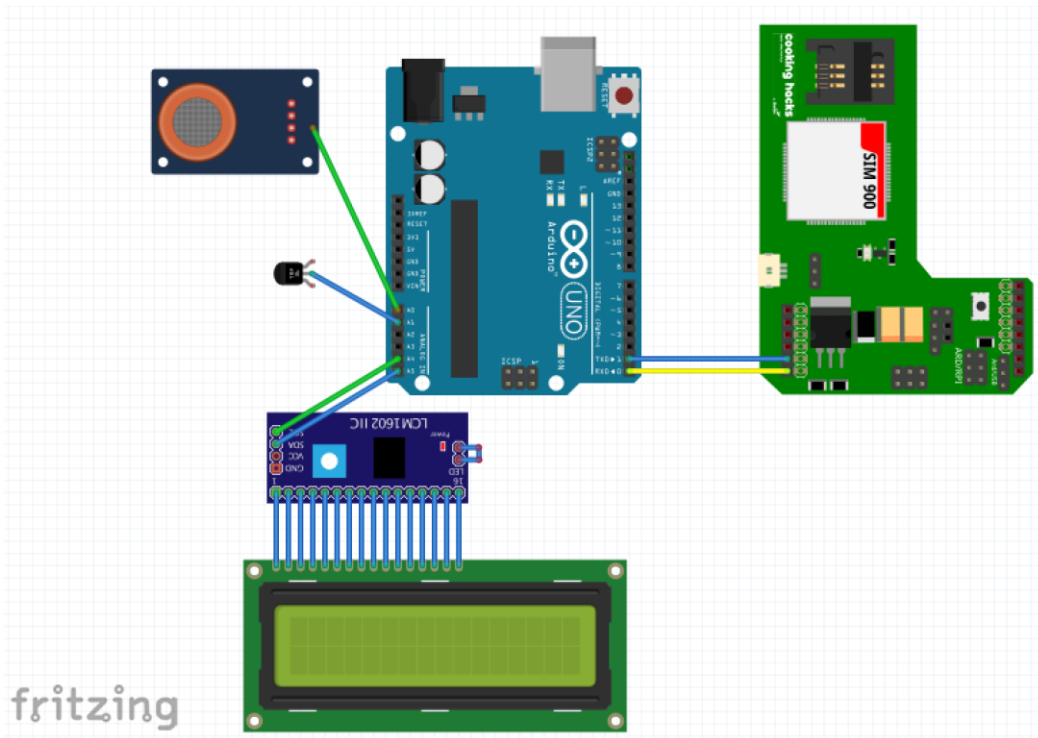


Fig.48 Schematic of the connections between Arduino, MQ5 sensor (top left), temperature sensor (left), display (bottom) and GSM module (right). 5V and GND connections omitted for simplicity. The schematic was created using the open source software Fritzing

In ARDUINO was added a SIM card and a GSM antenna to allow a 2G data connection with the local internet network and to send sensor values in real time. Data is stored in a database specifically developed for this project using the google cloud database.

A  $16 \times 2$  LCD screen (16 columns and 2 lines) has been interfaced with the Arduino to facilitate the immediate reading of real-time data values.

The Arduino "handles" sensors that are programmed to acquire the competence parameters at a rate that is set and managed through the programming of the electronic board. The microcontroller convert the electrical signal in an analogical signal which is send to datastore. The structured system (Fig.49) is connected to a microsim and a GSM antenna, relying on the local internet network, it is able to send captured data in real time. The data is collected in a database hosted on the free Google Cloud Platform and visualized in a web application in which data are plotted on a time trend. To process data stored on the database there are a number of tools including also export data (CSV format) by which you can download the data acquired in a specific interval of time.

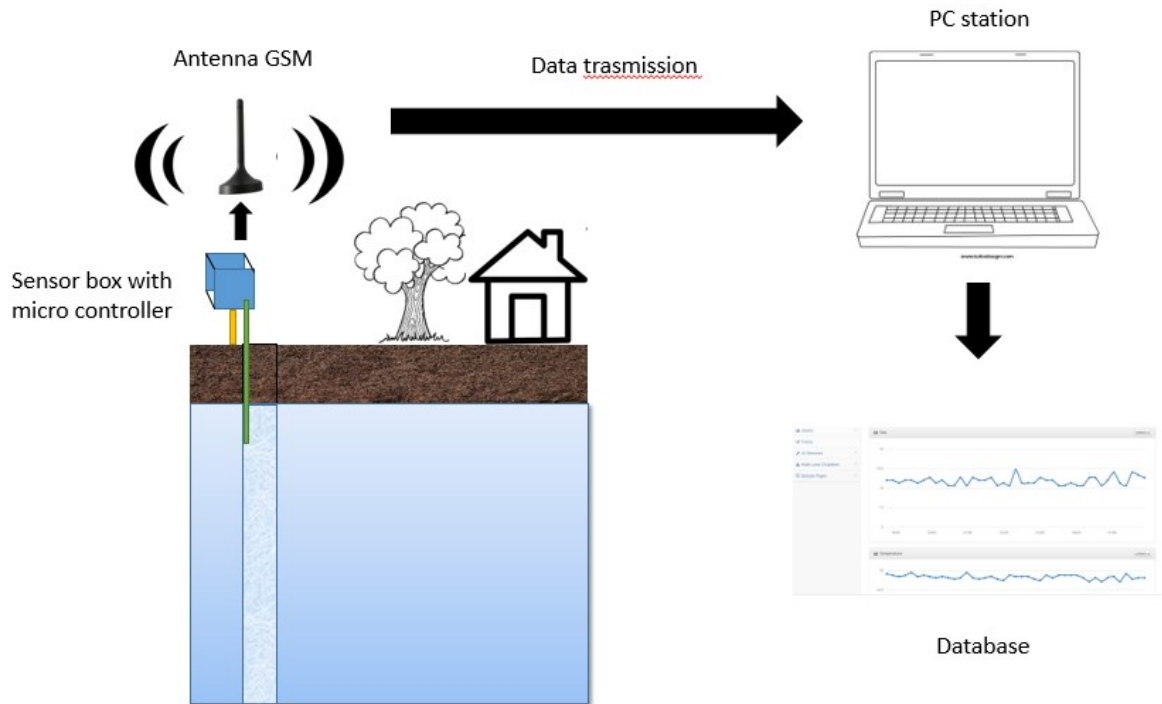


Fig. 49 Simplified diagram of the system implemented. The sensor box is installed at a sufficient height above the ground and placed in a sealed housing to protect it from precipitation and atmospheric phenomena. The gas and air temperature sensors are located inside the sensor box, sensors for water monitoring are lowered into the well through the cable connectors so as to be immersed into the aqueous matrix. The data from the sensors are sent via GSM antenna leaning to the local Internet network to a database. Among the tools of this database is the ability to view real-time each new acquisition, and you can download the data in CSV format.

The first immediate advantage of this system is to quickly receive data on a pc without going on site and any malfunction is signaled by the non arrival of data in the cloud (Fig.50). The resource represented by the use of this system for monitoring the environment not only makes it interesting as regards the economic savings in comparison to the lowest currently provided by companies operating in the industry, but especially for the possibility of inserting those values that have been identified through the bridge protocol which are an environmental control factor. The eventuality of an abnormal is notified immediately as each data is instantly sent to the cloud.

After the design phase, of all the system tests were carried out to determine the validity of the developed architecture, in particular the performance of the sensors. This phase has produced good results for some of the acquired sensors but required improvement and extension of more sensor type.

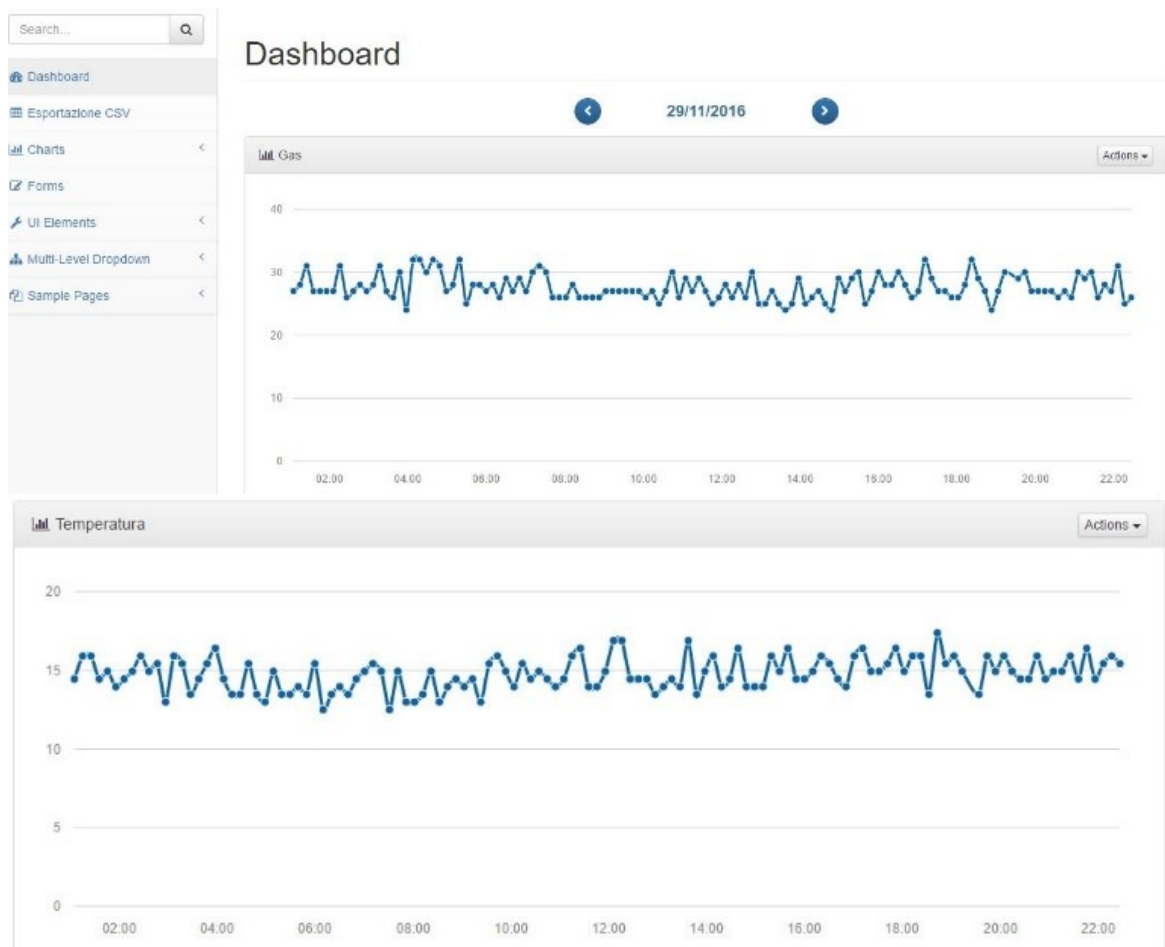


Fig.50 Database Interface google cloud

The use of these intelligent multi matrix monitoring systems low cost, easy installation and management will enable the acquisition of continuous data and real time display of variations in the parameters monitored constituting an instrument of fundamental Importance in the environmental management.



## Conclusions

Over the last decades, the increasing massive abuse of water resources for industrial and agricultural purposes has put the spotlight on how to find a way for keeping the groundwater's quality under control.

The complexity of this situation in addition to the E.U. legislative provisions on this specific field, have brought the scientific community to start taking action and to start studying and managing water resources, in order to be aware of their real state and to take care of the related issues, such as salinization and human pollution. To this qualitative pollution dynamic are added problems of quantitative depletion due to overexploitation and changes in rainfall patterns, testified from ingression of the salt wedge in the river Po (in 2003 for ingression reached in Pontelagoscuro station with critical issues for water in the water supply recharge of Ro Ferrarese).

Geochemical studies, conducted over the past twenty years in Emilia Romagna, have revealed the presence of ancient water trapped in Pleistocene sediments which return to the surface through deep structures. The ascent of the salt water is favored by the presence of dissolved gas in solution that by decreasing the density of the water body allow to overcome the density barriers constituted by the fresh / salt water interfaces that characterize some water bodies.

In this work, the hydrogeochemical phenomenology's knowledge has been used as a basis to build a new system of monitoring groundwater's chemical and physical parameters in selected areas, in accordance with geochemical studies and model interpretation.

The hydrogeochemical approach developed in this study, has had the goal of defining the kind of water reactions occurring in the selected fields.

Data has been collected from a system of private wells monitoring realized during my PhD years (2014-2015) and from data of the regional database which pinpoint five aquifer sub levels (A0-A1-A2-A3-A4 from 2003 to 2015).

Starting with a descriptive statistical interpretation of the data, I studied the correlations among elements. This analysis has allowed me to identify the representative elements and the groups of samples that could be affected by the same phenomena.

Through the use of the Factorial Analysis, three samples groups were identified:

- Group 1: this group of samples is conditioned by the phenomena of ion exchange;
- Group 2: this group of samples includes pH effects on heavy metals;
- Group 3: this group of samples includes high  $\text{HCO}_3$  characteristics.

S1-S4-S2 sampling areas are subject to processes of rock water interaction and ion exchange. They are reflected in pH, temperature, EC,  $\text{HCO}_3^-$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  variations. The inverse correlation of pH with the chemical and physical parameters that affect the ion exchange processes may be explained with pH interference with the cation exchange capacity, which influences the properties of the soil to retain cations adsorption.

The water samples collected during the study of ground water are characterized by a meteoric recharge underlined by the isotopic signature matching the northern meteoric water line.

The  $^{16}\text{O}/^{18}\text{O}$  composition of water taken from wells is in the range of: -10.75 to -6.03, this suggests a meteoric recharging that is evident in the isotopic diagram  $\delta^{18}\text{O}/\delta^2\text{H}$  in which samples seem to follow the northern meteoric water line.

Some points in S1-S2-S4 aquifers are more depleted than the major group of central wells samples. This may be caused by the alteration of the water composition due to climate changes. Changes of temperature and precipitation in recent years have determined an alteration in the isotopic composition of ground water. Autumn precipitations are richer in heavy isotopes and this is could be explained as the consequence of the increasing summer temperatures and the decrease of precipitations.

The complex geological evolution has conditioned the groundwater resources in the subsoil of Ferrara area a great deal. Ferrara anticline presence affects the Na- $\text{HCO}_3$  behavior of surface water as well. The slight depletion of  $\text{HCO}_3^-$  recorded for Ca-Cl waters is probably the result of calcite precipitation, while Na- $\text{HCO}_3$  water type increase can be related to the dissolution of Calcite to  $\text{Ca}^{2+}$  removal by cation-exchange phenomena.

Although meteoric phenomena originated Pliocene sediment's groundwater and salted water, the isotopic composition of the Na-Cl water has a clear meteoric signature and no inflows of the present day's sea water seem to justify such a composition.

Reduction conditions of the water in the deepest levels produces a lack of  $\text{SO}_4^{2+}$ , while water collected in the S2 S3-S4-S5 aquifers presents values of  $\text{SO}_4$  (up to 90 mg/l). This  $\text{SO}_4$  and S3 intake can be due to Po River's influence on A0, or from  $\text{CH}_4$  induced reaction caused by the increasing dissolution processes.

The samples showing Na growth are those of Group 1, which suggest that the source of Na ions is attributable not only to the dissolution of NaCl, but also to salted water, returning from the sediments in which they were trapped, to higher levels to "disturb" surface water.

The graph mix of S6 and S7 the deep waters and superficial water has drawn an hypothetical curve mixing the two components in different proportions. Along this curve, S1-S4 are exactly aligned with the mix line. S1 and A1 show a similar behavior, which can be justified

by a variation of the thickness and texture of the hydraulic barrier between A0 and A1 in communication in the river beds' areas.

The different mentioned groups can be explained on the basis of the various ongoing reactions. The geochemical diagram has been a useful means for interpreting the marker with which it is possible to identify a clear distinction by different aquifer levels. From this result it is possible to see how the deeper aquifers are characterized by  $\text{HCO}_3^-$  while phreatic water by  $\text{Mg}^+$ .

Statistical analysis and hydrogeochemical model results are the starting point for an inverse geochemical modeling with PHREEQC 3.3 software. The numerical model has been useful in order to reconstruct the chemical processes that determine a certain underworld evolution and quantify the mixing processes within the aquifer.

The dissolution/precipitation and ion exchange reactions show an exchange movement with aquifer sediments; for example, the changed composition, which leads to a good blending where more circuits are in contact.

The most interesting models explain the relationship between Ca-HCO<sub>3</sub> and Na-Cl that is seen in the transition from carbonate composition waters to sodium-chloride water, being there a halite dissolution which contributes with Na to the solution. Na enrichment can also be explained by the presence of CH<sub>4</sub> which facilitates the upwelling of trapped salted water. The blending line between these two compositional types presented in a Piper diagram shows how A1 (52,58) and S4 are disposed along the mix.

Model 2 explains the reactions which lead to an enrichment of  $\text{SO}_4^{2+}$  of the top level water, that is due to an enrichment of sulfates derived by the gases rising from the deep fractures. The third model shows the chemical reactions that reflect the mix curve. The presence of CH<sub>4</sub> and CO<sub>2</sub> is responsible for the deep water carrier catalysts on the surface. The mixing of these two compositions produces water with high Na and Mg, the first come from ionic exchange, the second derives from the dissolution sediment. This model explains the presence of  $\text{Ca}^{2+} + \text{Mg}^+$ , waters that are seen in the upper part of the Piper diagram. The last model shows the presence of high concentrations of CH<sub>4</sub>, it can be supposed that deep CH<sub>4</sub> typically rises towards the surface along faults and enables the carbonates dissolution.

As mentioned above, the presence of organic matter affects the ion exchange capacity and dissolution process. The ionic exchange capacity is reflected in the results of the CEC analysis. Na in S1 and S4 samples of the sediments appear to be very high, this could be explained by long-time residence. These waters, characterized by the presence of dissolved gases, are characterized by increased levels of dissolved NaCl, bringing an Na increase in the sediment.

In a methodological approach, that aims to identify areas with specific hydrogeochemical characteristics, it plays an essential role to build up a knowledge of the context on which the study is conducted. Useful results for this knowledge and therefore for the management of water resources is derived from the application of the Bridge Protocol, which shows an exceeding REF value of chlorides levels in A0, and minor elements show high values. High iron values are derived from the interaction between water and sediment. A1 has very high values of electrical conductivity with a surplus of about 14% of the REF, due to the exploitation of water resources in Ferrara's industrial field and due to the Po River's waters intakes in the northern part of the province.

Constant monitoring of S2 and S4 areas, showed that the response to deep water stress due to rising hazes is very different depending on the observed context. S2, which is near the embankment of a buried river, is affected by conductivity variations that are not observed in S4's nearby.

In order to propose a new low-cost method, and in order to guarantee the good quality of the measurement of specific parameters, a Multimatrix Work Prototype has been realized, with the aim of constant measurement of the selected parameters and their decoding and storing in a database made for this purpose. The system works with an ARDUINO microcontroller which controls the sensors connected to it and sends the data to an online database where real-time data are registered. This prototype will be implemented with additional enhancements such as:

- Additional sensors for data acquisition;
- A power-providing system, with energy-saving technology and an external photovoltaic panel.
- The addition of a forecasting tool based on the application of specific management algorithms, for the design and development of models relating to the observed phenomena, which will provide an important basis for making decisions which will represent the future basis for response plans.

The use of these instruments for environmental monitoring is an innovative solution for improving environmental issues management and to collecting the necessary amount of data that will allow the researchers to precisely understand (or even to predict) any possible risks.

This prototype is therefore considered the basis for improving an instrumental and innovative methodological approach, besides, its low costs can allow us to make new and subsequent experiments and become more competitive. The improvement in the time of the proposed transmission protocol of this work, will allow a greater knowledge of water resources from the chemical-physical point of view and a type of parameters monitoring which enables us to

establish the existence of any correlation between the fluctuation of the hydrogeochemical parameters and paroxysmal events.

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