

HYDROGEOCHEMICAL INVESTIGATIONS FOR AQUIFERS CHARACTERIZATION AND PROPOSAL OF A NEW TRANSMISSION PROTOCOL FOR CHEMICAL-PHYSICAL PARAMETERS

ANTONELLA DI ROMA

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara, Via Saragat 1, 44121 Ferrara

INTRODUCTION

This article 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. 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; Marcaccio *et al.*, 2012).

The rainfall 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). 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) established quality standards and specific thresholds for defining the chemical status of groundwater, as well as settled 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 and provides a constant monitoring system for all bodies of groundwater. In this project, a constant monitoring network with seasonal control of chemical and physical parameters of phreatic waters based in a plain area has been realized. Sampling points were set out in Mirabello (24), Sant'Agostino (6), Cento (11), and Bondeno (7) and the resulting data were compared with those resulting from the WARBO project area, near Copparo (5). These sites were 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. The data resulting from the study of the aquifer A0 (unconfined aquifer, phreatic groundwater) allowed us to determine the natural background values and limits (Bridge Protocol) for A0 and waters stored in the deeper fractures (confined aquifer). The conclusion of the research was the study of existing innovative technology possibilities as well as the 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. 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.

MATERIALS AND METHODS

Sampling area

The research was conducted in wells located in the area around the towns of Bondeno, Cento, Copparo, Mirabello, and Sant'Agostino, Emilia-Romagna Region, NE Italy (Fig. 1). 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 of clay, sandy-clay, and silty-clay. The multilayer aquifer is subdivided into three groups: Group A (in turn subdivided into four layers: A1-A4), Group B, and Group C. (Dugoni *et al.*, 1998; Molinari *et al.*, 2007). The phreatic aquifer of the plain A0 is formed mainly by a thin layer of fine sediments that towards North across the plains. These sediments have been formed by fluvial channel deposits, bank and flood plains in direct contact with surface water, and it is influenced by

human activities. This aquifer has a thickness of about 10 meters and it is developed in the hydrostratigraphic unit A0.

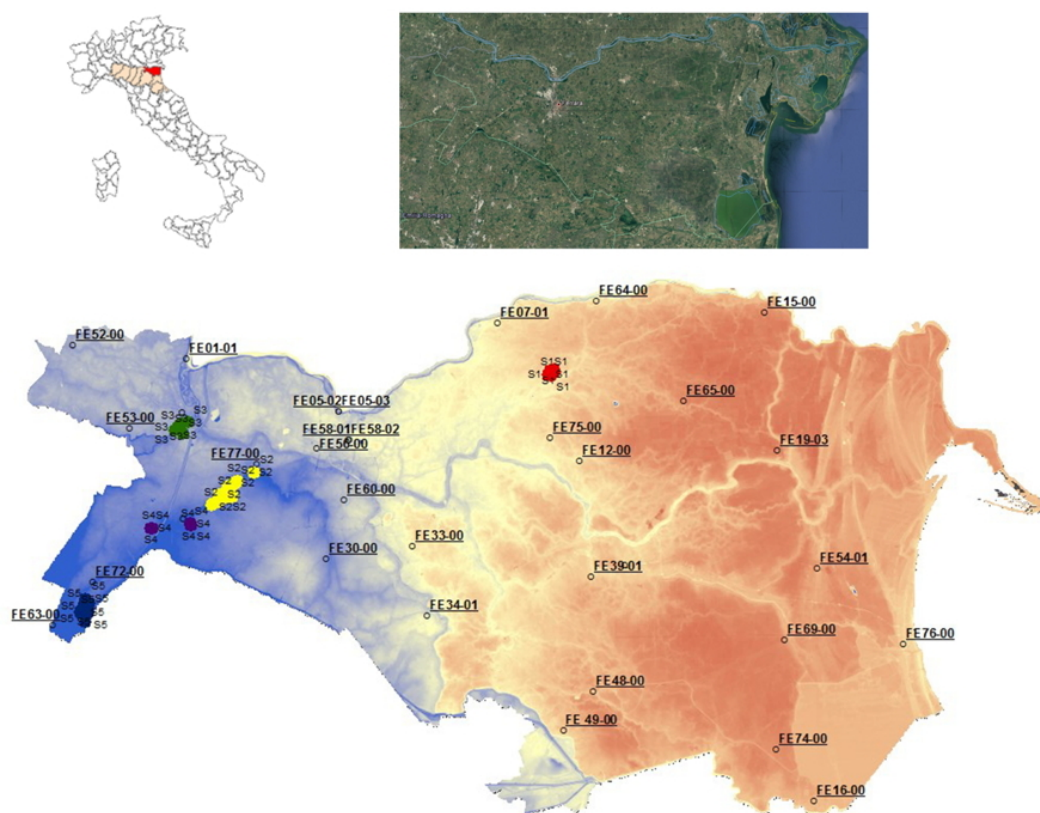


Fig. 1 - DTM (Digital Terrain Model) of the Ferrara's Province with the collected data points. The black dots are part of the data collected from ARPA Ferrara; the red dots are the sampling points at Copparo (S1); the yellow dots are the wells sampled at Mirabello (S2); the green dots are the sampling points in Bondeno (S3); the purple dots are the wells sampled at Sant'Agostino (S4); the blue dots are the wells sampled at Cento (S5).

Sampling treatments

Three aliquots of water were collected for each sample point; the waters were stored in polyethylene bottles and filtered with a 0.45 micron filter samples. For the measurement of minor and trace elements the samples were acidified with diluted HNO_3 (1:10).

The temperature, pH, Electrical Conductivity and TDS were measured *in situ* using a multiparametric probe (Hanna instrument, HI 9828). The HCO_3^- was measured *in situ* with the Alkalinity Test Kit (Hanna instrument, HI3811).

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. Ion chromatography 883 Basic IC plus was used at the Department of Earth Sciences of Technical University of Darmstadt (Germany) to obtain anions concentrations of Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} (mg/L). The samples were prepared by dilutions calculated on the basis of the electrical conductivity of the samples.

Finally, heavy isotopes of water samples were analysed at the Department of Earth Sciences of the Darmstadt University by means of the instrument Picarro L2140.

Quality of data for each water sample was verified and all the samples having an estimated error rate above 10% were rejected. The statistical calculations were performed using the Statistica software 7.0. Data elaboration was made with GW_Chart (Version 1.29.0.0 U.S. Geological Survey, Reston).

RESULTS AND DISCUSSION

The chemical characteristics of the aquifers were investigated through 343 chemical tests conducted on

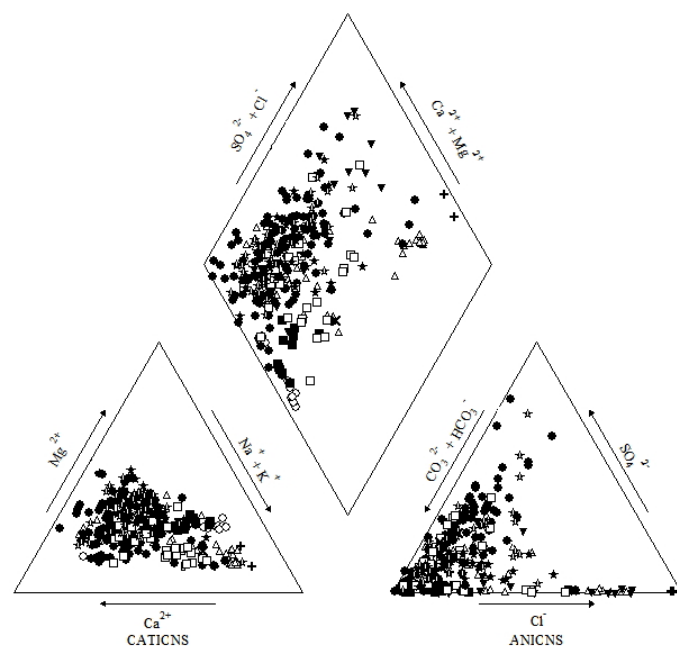


Fig. 2 - Piper plot of all analysed samples: A1 (open triangle), A2 (open circle), A3 (square; from ARPA database), S1 (inverted triangle), S2 (circle), S3 (open square), S4 (star), S5 (open star), S6 (cross), S7 (X; new monitoring data).

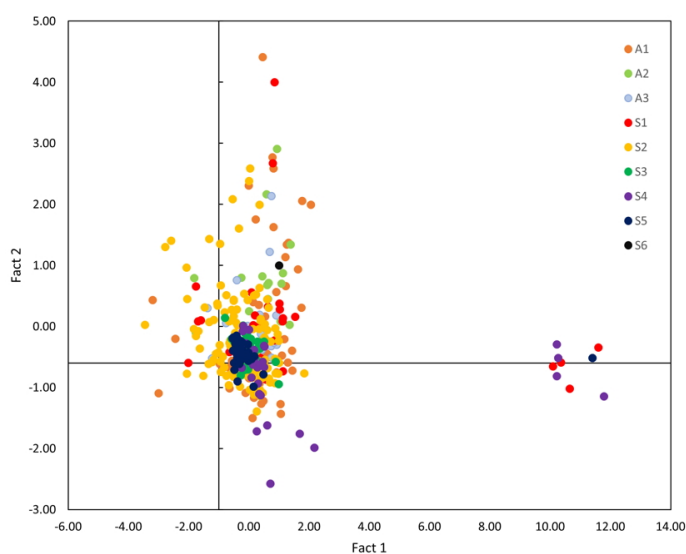


Fig. 3 - Factorial analysis, correlation between the factor. A) factor 1-2 (49.22%).

water samples of the above mentioned area (253 phreatic water samples and 90 obtained from the regional database representing waters collected from 2003 to 2015). Most of the waters belong to the Ca-HCO₃ facies, whereas only few are of NaCl, CaCl and NaHCO₃ facies (Fig. 2).

The application of Factorial Analysis to the chemical tests allowed identifying three different groups of water: *i*) Group 1: includes water samples affected by ion exchange processes; *ii*) Group 2: includes waters with low pH and enriched in heavy metals; *iii*) Group 3: includes samples with high concentration of HCO₃ (Fig. 3). Isotopic analysis has permitted to identify climate change effect on phreatic groundwater. This change was observed for the heavy isotopes presence (²H, ¹⁸O). The composition of water wells is in the range: ¹⁶O/¹⁸O = -10.75 to -6.03 (Fig. 4) suggesting a meteoric recharge; moreover it also resulted by the isotopic diagram of δ¹⁸O/ δ²H in which the samples follows the North Meteoric Water Line NMWL (Longinelli & Selmo 2003) and the Global Meteoric Water Line GMWL (Craig 1976). In the diagram are plotted also some comparative values as found in literature, such as the isotopic composition of confined and unconfined aquifer (Dugoni *et al.*, 1998). Most of phreatic water falls near the unconfined composition. The groundwater isotopic composition is strongly influenced by the short and intense meteoric events.

High δ²H values, which move the samples to the left of NMWL and register a δ²H enrichment compared to δ¹⁸O, could be due to the presence of methanogenic bacteria or reactions due to the presence of hydrocarbons (Fig. 4). The decrease of

rainfalls associated with a change in its distribution throughout the months of the year as well as the seasonal temperature fluctuations associated to the continental climate (with high-T in summer and low-T in winter) and its variation in the last two years have caused changes in hydrogeochemical and isotopic composition of ground water. 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).

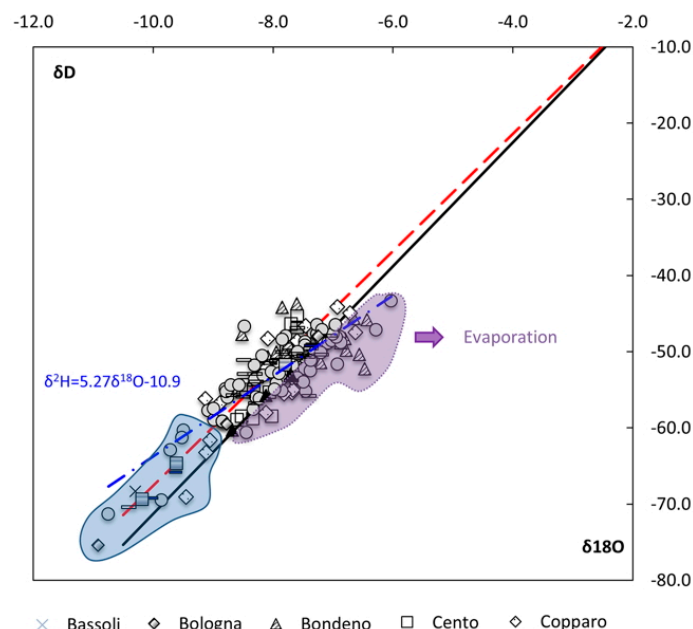


Fig. 4 - Sampling Isotopic composition of meteoric precipitation sampled in the project area, unconfined and confined aquifer according to Rapti-Caputo & Martinelli (2009), Meteoric Water Line for North Italy (NMWL), and Global Meteoric Water Line (GMWL).

Depletion of Na^+ together with the enrichments of Ca^{2+} plus Mg^{2+} shifts the composition towards the Ca-Cl water type, changing the water compositions. It is presumable that both intrusion processes and freshening take place (Fig. 5a, b).

Alteration of the geochemical composition can be attributed to changes in sediment's mineralogy and petrography: deep waters are characterized by a marked presence of HCO_3^- and low Mg^{2+} , whereas phreatic waters are characterized by an Mg^{2+} marker (Fig. 5c, d) due to the leaching of smectite/chlorite-bearing sediments. Moreover, they are also characterized by a high cation exchange capacity for Ca, Na and Mg.

Among the observed ongoing water reactions, 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 due to density decrease related to the presence of CH_4 in solution. The methane may derive from deep sources and, locally, from organic matter which is a key factor in water/soil cations exchange.

A new monitoring transmission protocol has been created using the microcontroller ARDUINO to help monitoring groundwater. The system is connected to a GSM, which sends data directly to a database stored in the free Google Cloud Platform facility which make possible to read the real-time recorded data.

The Arduino "handles" sensors are programmed to acquire the competence parameters at a specific rate and can be managed through the programming of the electronic board. To process data stored on the database there are a number of tools including the possibility to export data (CSV format) acquired in a specific time interval.

The HCO_3^- variations can be due to the precipitation of calcite as well as by ion exchange reactions. The waters that most emphatically have a Na- HCO_3 signature are the A2-A3 waters showing a behaviour typically associated to depth waters. The presence of the Ferrara's anticline affects the Na- HCO_3 behaviour even on surface water as evidenced by the piper diagram. Some samples A1 and S6 have a NaCl composition. The isotopic composition of the Na-Cl waters has a clear meteoric signature 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 layers.

The high concentration of Na may be due to layers deposited in Pleistocene. The Rise of old water could be the source for the natural presence of Na in the waters of the flood plain. The Na excesses may be explained by means of ion exchange processes.

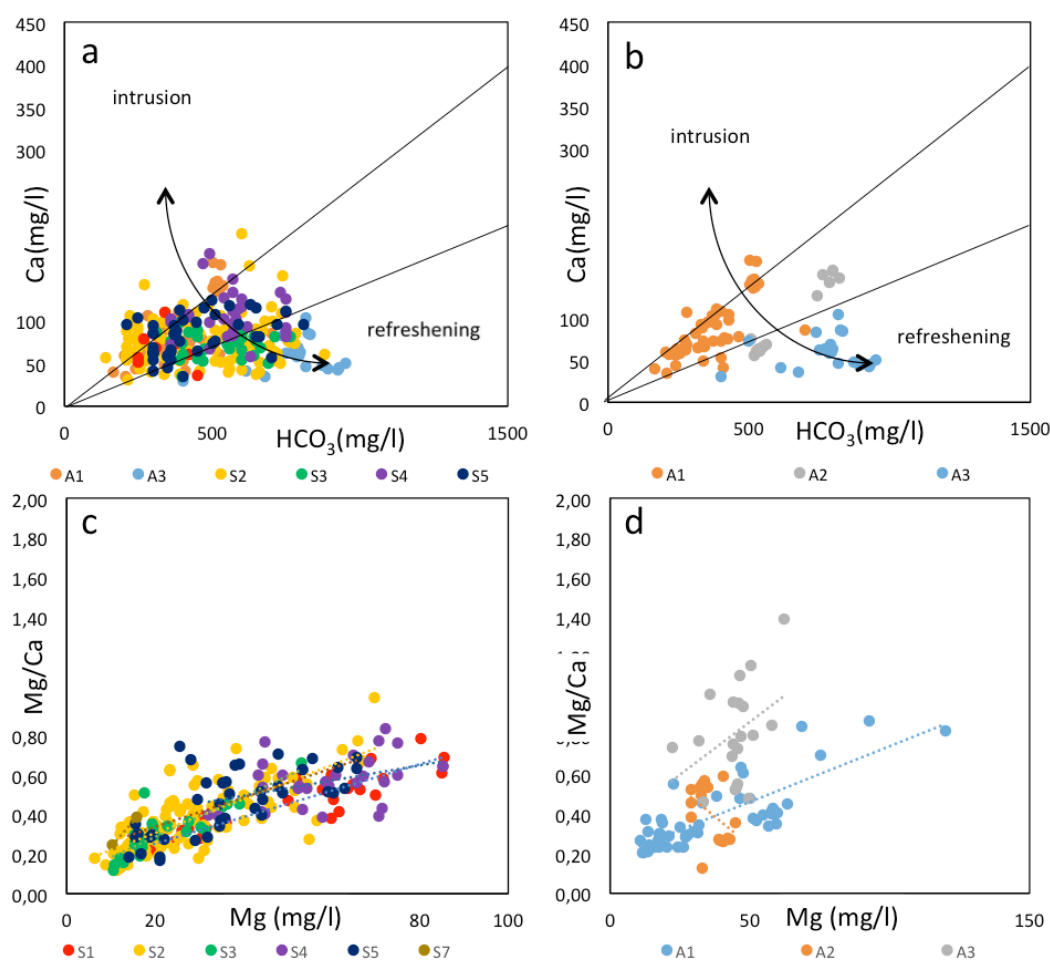


Fig. 5 - a) HCO₃-Ca diagram (adapted from Capaccioni *et al.*, 2005); b) HCO₃-Ca diagram for A1, A2, A3; c) Mg²⁺ vs. (Mg²⁺/Ca²⁺) diagram for phreatic samples. d) Mg²⁺ vs. (Mg²⁺/Ca²⁺) diagram for deep samples.

CONCLUSION

Geochemical studies, conducted over the past twenty years in Emilia Romagna, have revealed the presence of ancient water trapped in the Pleistocene sediments which return to the surface through deep structures. The ascent of the salt water is favoured 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.

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

Data has been collected from the monitoring of a system of private wells, realized during the research (2014-2015), and from data of the regional database related to five sub-levels aquifer (from 2003 to 2015).

Starting with a descriptive statistical interpretation of the data, I studied the correlations among elements. This analysis allowed 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 groups of samples were identified: *i*) Group 1 is conditioned by the phenomena of ion exchange; *ii*) Group 2 includes pH effects on heavy metals; *iii*) Group 3s includes high HCO₃ waters.

The $^{16}\text{O}/^{18}\text{O}$ composition of water sampled from wells is in the range of -10.75 to -6.03, suggesting a meteoric recharging as evidenced by the isotopic diagram $\delta^{18}\text{O}/\delta^2\text{H}$ in which samples seem to follow the NMWL.

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 by the increase of summer temperatures and the decrease of precipitations.

The complex geological evolution has significantly conditioned the groundwater resources in the subsoil of Ferrara area. The presence of the Ferrara anticline affects the Na-HCO_3 behaviour of surface water. The slight depletion of HCO_3^- recorded for Ca-Cl waters is probably the result of calcite precipitation, whereas Na-HCO_3 water type increase can be related to the dissolution of calcite and by the removal of Ca^{2+} by cation-exchange reactions.

In order to propose a new low-cost method, and to guarantee a good quality for the measurement of specific parameters, a multimatrix prototype has been realized, with the aim of constant measurement of selected parameters. A specific database collects and stores all decoded data. The system works with an ARDUINO microcontroller which is connected to the online database for real-time data acquisition. This prototype will be implemented with additional enhancements to improve the present monitoring system.

REFERENCES

- Dugoni, G., Molinari, F., Boldrini, G., Severi, P., Caputo, D., Martinelli, G. (1998): Le risorse idriche sotterranee della provincia di Ferrara. Capitolo 6.1. Quadro Conoscitivo - Capitolo 6 Piano di Tutela delle Acque della Provincia di Ferrara. 121-154.
- Capaccioni, B., Didero, M., Paletta, C., Didero, L. (2005): Saline intrusion and refreshing in a multilayer coastal aquifer in the Catania Plain (Sicily, Southern Italy): Dynamics of degradation processes according to the hydrochemical characteristics of groundwaters. *J. Hydrol.*, **307**, 1-16.
- Longinelli, A. & Selmo, E. (2003). Isotopic composition of precipitation in Italy: a first overall map. *J. Hydrol.*, **270**, 75-88.
- Marcaccio, M., Molinari, A., Guadagnini, L., Guadagnini, A., Palumbo, A., Pellegrino, I. (2012): Valori di fondo naturale e valori soglia di specie chimiche potenzialmente contaminanti per l'individuazione dello stato chimico delle acque sotterranee dell'Emilia-Romagna. 2012/11 Ecomondo, meeting 2012, 977-982, Maggioli Editore.
- Martinelli, G., Minissale, A., Verrucchi, C. (1998). Geochemistry of heavily exploited aquifers in the Emilia-Romagna region (Po Valley, northern Italy). *Environ. Geol.*, **36**, 195-206.
- Melo-Gonçalves, P., Roche, A., Santos, J.A. (2016): Robust inferences on climate change patterns of precipitation extremes in the Iberian Peninsula. *Phys. Chem. Earth*, **94**, 114-126.
- Molinari, F.C., Boldrini, G., Severi, P., Dugoni, G., Rapti-Caputo, D., Martinelli, G., (2007). Risorse idriche sotterranee della Provincia di Ferrara. Parte Prima, Ferrara, 1-60.
- Rapti-Caputo, D. & Martinelli, G. (2009): Geochemical and isotopic composition of the groundwater resources of the Po River delta (Northern Italy): implications for the environmental impact. *Hydrogeol. J.*, **17**, 467-480 (DOI 10.1007/s10040-008-0370-6).