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EFFECT OF AGRICULTURAL PRACTICE ON GROUNDWATER QUALITY IN SOUTH-EASTERN SICILY

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EXTENDED ABSTRACT

Nel settore meridionale della Sicilia è presente una intensa attività agricola che rappresenta la principale risorsa economica dell'area. Per garantire uno sviluppo sostenibile di tale attività è cruciale una corretta gestione delle risorse idriche. Il fabbisogno idrico delle colture è infatti soddisfatto da acque di falde emunte attraverso numerosi pozzi in acquiferi carbonatici.

L'impatto delle attività agricole sulle acque di falda è ben conosciuto in tutto il mondo, nella Sicilia orientale soltanto a partire dall'ultimo decennio si sta studiando il fenomeno. In particolare Ferrara & Pappalardo (2003; 2004) studiando i principali acquiferi della Sicilia orientale ne denunciano l'intenso sfruttamento dovuto ad attività antropiche. Questi descrivono un abbassamento dei livelli di falda che, in qualche caso, ha provocato la scomparsa di sorgenti soprattutto in vicinanza della costa. Il rapporto IPCC International Panel Climate Change (2013), annovera tra le principali cause antropiche della desertificazione l'adozione di pratiche agricole non sostenibili. Nel contesto nazionale italiano, la Sicilia è la regione maggiormente esposta alla Land Degradation ad opera dei sistemi agricoli.

Al fine di valutare la pressione esercitata sull'ambiente dall'attività agricola, sono stati censiti i principali fattori di vulnerabilità degli acquiferi (sistemi fognari, attività zootecniche) presenti nel territorio. Ciò al fine di distinguere le eventuali elevate concentrazioni di nitrati nelle acque prodotte da fonti di inquinamento o da pratiche agricole quali lo spandimento di liquami di origine zootecnica e l'accumulo di fertilizzanti.

È stato inoltre effettuato un monitoraggio al fine di valutare la qualità delle acque in accord con la Direttiva 91/676CE relativa alla protezione delle acque dell'inquinamento provocato dai nitrati provenienti da fonti agricole, che ne impone una soglia di 50 mg/L.

L'area di studio si trova nel settore sud-occidentale ibleo, che consiste in una sequenza carbonatica spessa di età mesozoica - quaternaria interessata da un'intensa tettonica estensionale durante la fase orogenica alpina. Molti autori (Rigo & Cortesini, 1959; Pieri, 1967; Mascle, 1974; Grasso *et alii*, 1979; Carbone *et alii*, 1982) identificano in quest'area faglie normali orientate circa NE-SW che costituiscono il "sistema Scicli" e NNE- SSW denominate "sistema Marina di Ragusa". Questi sistemi di faglie hanno portato alla formazione di graben e horst orientati circa NE-SW come quelli di Santa Croce Camerina, Pozzallo e Marina di Ragusa.

Sono presenti due tipi di acquiferi carbonatici, sia confinati che non confinati, con uno spessore compreso tra la decina e centinaia di metri. La presenza di grotte carsiche e l'intensa fratturazione degli ammassi rocciosi determinano condizioni di elevata permeabilità ($0,1 \div 10^{-2}$ m/s).

Per questo lavoro campioni d'acqua sono stati prelevati da pozzi utilizzati a scopo irriguo che sfruttano gli acquiferi carbonatici, libero ed in pressione, per misurare le variazioni del livello di falda e del chimismo delle acque sotterranee nel periodo 2006-2008. I dati ottenuti evidenziano la pressione esercitata dall'agricoltura sull'ambiente e consentono una prima valutazione della sostenibilità ambientale delle produzioni agricole in particolare di quelle intensive e fortemente impattanti quali la serricoltura in suolo.

Dei campioni prelevati sono stati determinati i principali parametri fisici (pH, EC, TDS) e chimici (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^-, NO_3^{2-}, B^-, and Br^{2-}) ed è stata valutata la tendenza evolutiva nel periodo in esame. Le acque delle falde sono prevalentemente di tipo Ca-Mg-Cl e secondariamente di tipo Na-Cl and Ca-Cl. Soltanto il 20% circa dei campioni conservano il chimismo bicarbonato-alcalino terroso tipico degli acquiferi carbonatici. Il rimanente 80% dei campioni presenta una buona correlazione positiva tra SO_4, Cl, NO_3 e la concentrazione TDS a causa dell'utilizzo di fertilizzanti. Si è si rilevato inoltre, l'aumento della concentrazione di B nelle acque sotterranee conseguente alla pratica di sterilizzazione delle aree coltivate.

L'incidenza negativa sulla qualità delle acque è confermata dal rapporto dell'Agenzia Regionale per l'Ambiente (ARPA, 2013), nella parte riguardante le acque ad uso idropotabile prelevate nell'area in esame nel periodo 2008-2011, nel quale si evidenzia che il 50% delle acque analizzate ha caratteristiche chimiche classificate non buone per la presenza di elementi chimici riconducibili all'uso di pesticidi e fertilizzanti. Il rapporto evidenzia inoltre la presenza nelle acque di sostanze riconducibili ad attività agricola, vietate da oltre dieci anni, in concentrazioni nettamente superiori alla media.

ABSTRACT

Agricultural practice in southeastern Sicily is among the most important activities carried out in the island from the economic point of view. For this reason, groundwater has been exploited in the latest 20 years by all the agricultural companies of the area. Such activity persisted with no management of the resource, thus compromising the water quality. The goal of this paper is to highlight the worsening of the groundwater quality due to the intense agricultural practice. The evolutive trend of chemical indicators testify the efficiency of the productive system and their knowledge can lead the producers to choice of the best available technology non entailing excessive costs (BATNEEC). The carbonate aquifers, because of their permeability, are exposed to pollution, especially in agricultural areas where fertilizers and pesticides are intensively used. The confined and unconfined aquifers exploited in the study area have been monitored in 1996, 2006 and 2008 to outline the groundwater quality. Most of the analyzed samples are enriched of elements deriving from the use of fertilizers. Particularly the nitrate, in both aquifers, overcomes 50 mg/l concentration (the legal limit value of drinking water). To classify the groundwater suitability for irrigation purpose, chemical indices like TDS, Percent Sodium (Na%), Sodium Adsorption Ratio (SAR), Permeability Index (PI) and residual sodium carbonate (RSC) were carried out. Results show a worsening of the groundwater quality in the time interval 1996-2008, which makes the water not suitable for farming activity.

Keywords*: agricultural activity, carbonate aquifers, groundwater quality, nitrate contamination, Southern eastern Sicily*

INTRODUCTION

The impact of agricultural activities on groundwater quality is well known all over the world (OECD, 2001; Re *et alii*, 2017). The fifth Intergovernmental Panel Climate Change (IPCC, 2013) mentions, among the highest anthropogenic causes of desertification, the adoption of unsustainable agricultural practices. In the Italian context, Sicily is the most exposed region to the Land Degradation (Perini *et alii*, 2007) by agricultural systems. This phenomenon is being studied in the southeastern Sicily for a few decades (Ferrara & Pappalardo, 2003; 2004a; 2004b). Ferrara & Pappalardo (2008) noticed the intense exploitation of water resources by human activity that caused a drop of the groundwater levels and, somewhere near the coast, the spring drainage. Guastaldi *et alii* (2014) have shown how the seawater intrusion and the following salinization of aquifers along the coast can be induced by groundwater exploitation exerted by agriculture and industrial plants. Notwithstanding agricultural production is strictly dependent on the quality and availability of water, irrigation and fertilizers can have profound impacts on the hydrology and quality of water resources in agricultural regions (Johnston *et alii*, 1998; Böhlke, 2002). The irrigation water can move contaminants (eg. nitrate) towards the aquifer, thus worsening the quality of groundwater. The high concentration of nitrates in groundwater represents one of the most alarming aspects, with respect to the water pollution, worldwide. The average annual concentration of nitrates must not exceed 50 mg/L (WHO, 2011; D.L. 152/2006), which is both the standard of chemical quality of groundwater and the limit for the human consumption. In particular, it allows identifying and addressing the remediation actions to perform and, then, it allows monitoring their effects in order to verify the proper prosecution of environmental purposes. The study area lies in the southern coast of Sicily (Fig. 1) where the National Institute of Statistics (ISTAT, 2005) recognized 44.8% of the Sicilian farms. Nitrate ingestion with drinking-water by infants can cause low oxygen levels in the blood, a potentially fatal condition (Spalding & Exner, 1993). Moreover, nitrate concentration of 4 mg/l or more in water from community wells in Nebraska has been associated with an increased risk of non-Hodgkin's lymphoma (Ward *et alii*, 1996). The investigation conducted by local public health officials in Indiana implicated nitrate-contaminated drinking-water as the possible cause of several miscarriages (Schubert *et alii*, 1997). ISPRA (2013) highlights that in 2012 over 4.7 millions of tons of fertilizers were marketed. Among these, 55.7% is represented by mineral compost, whose employment increased of about 17.8%, and there is a progressive lowering of the consumption of organic fertilizers (-25.6%).

Farming is the main economic resources of the study area and it represents the main cause of groundwater nitrate pollution as point out Regional map of vulnerable areas to nitrates of agricultural origin (Regione Sicilia, 2005) and the following webGis data processing (Regione Sicilia, 2007-2013). Along the coastal zones, arable land and land with trees in the foothills and greenhouse cultivation are present (Regione Siciliana, 1999). In order to evaluate the effects of agricultural activities on the quality of the water, water samples from irrigation wells were taken in 1996, 2006 and 2008.

The monitoring has been carried out to check the compliance of groundwater quality to the European Directive 91/676EEC "on water pollution protection from nitrate deriving from agriculture activity", that states a threshold limit value (TLV) of 50 mg/l. The purposes of this work were to monitor wells for groundwater quality and to quantify the nitrate in the groundwater. The main physical (pH, EC, TDS) and chemical parameters (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^{2-}, B^{3+}, and Br^-) show the high pressure of agriculture on aquifers and allow a preliminary assessment of the main agricultural practices that affect groundwater as the intensive ground sowing within plastic greenhouses.

GEOLOGY AND HYDROGEOLOGY

The study area is located in the south-western Hyblean foreland (Fig. 1) consisting of a thick, Mesozoic to Quaternary, platform-type carbonatic sequence. It is separated from the thrust zones to the north by the Gela-Catania foredeep and bounded eastwards by the Malta Escarpment, which is one of the main seismogenic sources of eastern Sicily (Manuella *et alii*, 2013; Barbano *et alii*, 2014; Pappalardo *et alii*, 2016). In the study area, an intense extensional tectonics occurred during the Alpine orogenic phase (Ogniben, 1969; Caire, 1970; Tapponier, 1976; Ghisetti & Vezzani, 1980; Tortorici *et alii*, 2006). Many authors (Rigo & Cortesini, 1959; Pieri, 1967; Mascle, 1974; Grasso, 1999; Grasso *et alii*, 2000a; 2000b; Carbone *et alii*, 1982) identify in this area normal faults trending NE-SW constituting the "Scicli system" and NNE-SSW named "Marina di Ragusa system". These fault systems led to the formation of grabens and Horsts oriented NE-SW such as the Santa Croce Camerina and Pozzallo Horsts (Ferrara & Pappalardo, 2004b) and the Marina di Ragusa Graben (Grasso & Reuther, 1988).

Two types of carbonate aquifer occur in the study area, both confined and unconfined, with thickness ranging between tens and hundreds of meters. The confined aquifer is in the northern sector, while this becomes unconfined moving southwards (Pappalardo, 2012). The presence of karst caves and the intense fracturing of the rocks, lead to high permeability conditions ($0.1\div10^{-2}$ m/s) (Ferrara & Pappalardo, 2003). The reconstruction of the water table, performed by taking into account 34 measurements carried out in 1996, shows a preferential direction of the unconfined flow towards the coastline (Fig. 2a). On the other hand, the unconfined water table is more articulated. In fact, the flow direction, assessed through 14 measurement points, is towards areas affected by a prolonged pumping activity (Fig. 2d).

In 2006, 40 different points of the phreatic aquifer and 21 points of the confined show that the groundwater table of the phreatic aquifer (Fig. 2b) decreases from inland (40 m) to the coast (-2 m). The 2008 measurements in 25 points of the unconfined aquifer (Fig. 2c) show a further lowering between the inland area (61.76 m) and the coastal zone (-10.3 m).

Total stationary is the confined aquifer, whose main differences regard only the minimum values that varies from -1.5 m in 2006 (Fig. 2e) to -1.7 m in 2008 (Fig. 2f), while the maximum values remained almost at about 55 m a.s.l.

METHODS AND SAMPLING

The water characterization has been carried out in compliance with the D.L. 152/2006 that transpose the main EU Directives on water protection (WFD-2000/60/EEC) and pollution by nitrates from agricultural sources (Nitrate Directive 91/676/EEC). The water samples have been collected from 84 irrigation wells after at least 4 continuous hours of water pumping from the aquifer and then stored in polyethylene bottles (HDPE).

The measurement points close to the coast, where

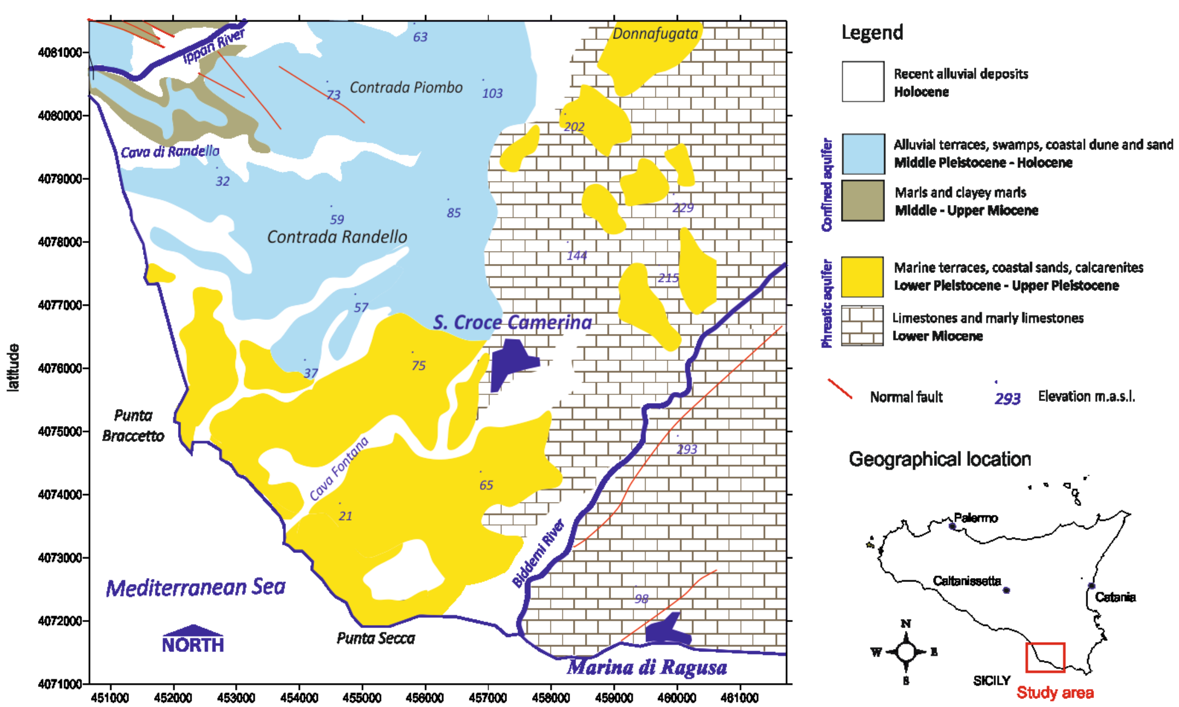

Fig. 1 - Localization of the study area and geological framework

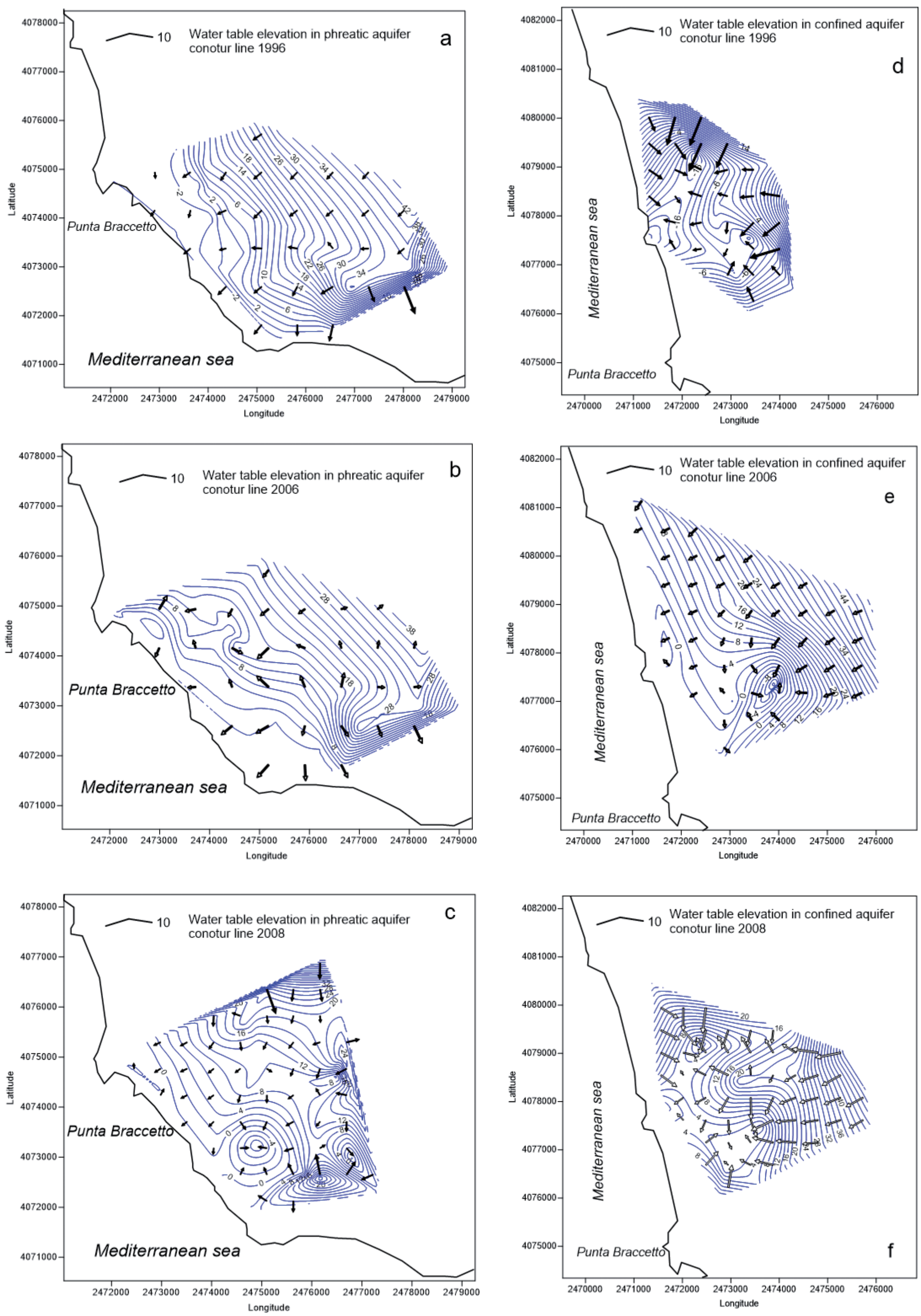

Fig. 2 - Groundwater level and flow direction deduced from 1996 (a: phreatic aquifer; d: confined aquifer), 2006 (b: phreatic aquifer; e: confined aquifer) and 2008 surveys (c: phreatic aquifer; f: confined aquifer)

conductivity exceeds 2600 mS/cm, were excluded from the data set as the samples belong to brackish water deriving from marine ingression. 41 groundwater samples from confined aquifer and 43 samples in the phreatic aquifer were collected from June to October 1996, 2006 and 2008 (Tab. 1 and 2).

Field parameters were analyzed at the laboratories of University of Catania (1996), ARPA Agenzia Regionale per l'Ambiente of Catania (2006) and ENEA Italian National Agency for New Technologies, Energy and Sustainable Economic development (2008).

Samples for cation analyzes were acidified with concentrated nitric acid and subsequently analyzed by Inductively Coupled Plasma emission spectrometry atomics (ICP) while anions were analyzed by ion chromatography. Following data processing Regarding groundwater quality for irrigation indices such as TDS, Sodium Absorption Ratio (SAR), Percent Sodium (Na%), permeability index (PI) and residual sodium carbonate (RCS).

RESULTS

Groundwater chemistry

The water quality and irrigation parameters are summarized in Table 1 for phreatic aquifer and table 2 for confined aquifer.

The pH measured in 2006 ranges between 6.11 and 8.08, agreeing with the absence of CO_3, which is found if the pH is greater or equal to 8.3.

The average EC (ElectricConductivity) valuedecreases between 1996 and 2008 in the unconfined aquifer (from 1548.4 microS/cm to 1001.1 microS/cm), while there is an opposite trend for the confined aquifer, where values increase from 1318.4 microS/cm (1996) to 1849.3 microS/cm (2008) (Table 1 and 2). The same trend is for TDS (Tab. 1).

The average values of the main ions, during the monitoring time interval (1996-2008) (Tables 1 and 2), are affected by an increase due to the use of fertilizers and/or to ions exchange of clay minerals (TDS, Mg, Br, SO_4 e NO_3) (Fig. 3).

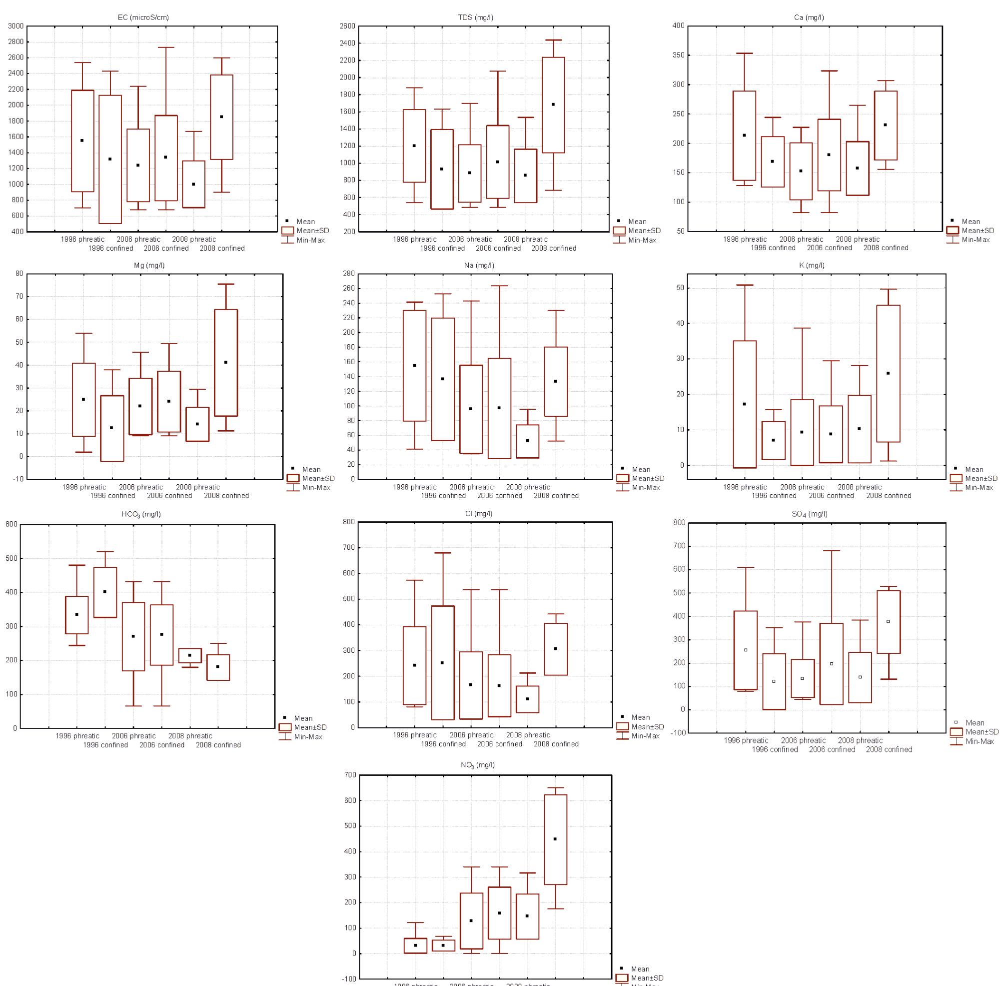

Fig. 3 - Chemistry of the 1996, 2006 and 2008 phreatic and confined groundwater

Phreatic aquifer

	pH	EC (microS/cm)	TDS (mg/l)	Na (mg/l)	K (mg/l)	Mg (mg/l)	Ca (mg/l)	Cl (mg/l)	Br (mg/l)	SO_4 (mg/l)	NO_3 (mg/l)	HCO_3 (mg/l)	SAR	Na%	PI	RSC
	7.5	1552	1174.8	225.3	3.9	21.9	172.1	330.1	0.0	247.8	16.7	352.0	16.5	53.2	10.6	-4.6
1996	6.45	940	760.3	57.5	2.0	16.0	136.9	109.9	0.0	96.1	26.0	316.0	4.8	27.1	9.0	-3.0
	6.51	720	540.0	62.1	3.4	5.3	128.1	95.0	0.0	80.2	11.2	319.7	5.7	31.2	7.7	-1.6
	6.97	1600	1097.1	41.4	2.7	26.3	244.3	173.0	0.0	288.2	25.4	295.9	2.7	13.2	15.5	-9.5
	7.15	1779	1353.0	206.9	4.7	28.7	237.9	228.0	0.0	424.1	60.8	400.2	13.0	43.3	14.5	-7.6
	7.5	703	655.9	156.3	6.6	5.3	130.5	81.2	0.0	159.9	7.4	288.0	14.0	52.3	7.3	-2.2
	6.45	1806	1316.5	241.4	6.6	12.3	153.7	500.2	0.0	104.2	18.0	280.0	19.3	58.3	8.9	-4.1
	6.32	2270	1733.3	200.0	46.9	42.3	294.8	449.9	0.0	352.0	55.2	292.2	13.4	34.2	18.4	-13.4
	6.34	2230	1480.0	229.9	7.4	54.0	264.3	343.9	0.0	280.0	56.4	244.0	13.3	41.4	17.8	-13.6
	6.52	2190	1415.0	46.0	0.0	37.9	306.0	267.0	0.0	343.9	122.2	292.2	2.5	11.8	19.4	-13.6
	7.14	2540	1879.4	216.1	39.1	50.6	353.3	242.1	0.0	610.0	14.3	364.2	12.7	32.8	22.0	-15.8
	7.21	2040	1632.4	197.7	43.0	35.5	329.3	202.1	0.0	599.9	19.2	480.1	12.6	32.7	19.6	-11.4
	6.87	2240	1687.7	234.5	50.8	35.5	231.5	574.0	0.0	223.8	18.0	319.7	17.5	42.5	14.7	-9.2
	6.89	830	1087.0	117.2	27.4	25.5	205.8	132.9	0.0	220.0	6.2	352.0	9.5	31.2	12.8	-6.6
	7.01	931	787.8	206.9	28.9	1.9	141.7	131.2	0.0	96.1	24.2	380.1	19.7	54.5	7.5	-1.0
	7.14	999	813.6	64.4	6.6	12.6	150.5	113.1	0.0	87.9	18.6	359.9	5.6	27.5	9.4	-2.6
	7.15	952	881.9	124.1	11.7	11.2	141.7	120.2	0.0	120.1	21.1	331.9	11.0	43.0	8.4	-2.5
min	**6.3**	**703.0**	**540.0**	**41.4**	**0.0**	**1.9**	**128.1**	**81.2**	**0.0**	**80.2**	**6.2**	**244.0**	**2.5**	**11.8**	**7.3**	**-15.8**
max	**7.5**	**2540.0**	**1879.4**	**241.4**	**50.8**	**54.0**	**353.3**	**574.0**	**0.0**	**610.0**	**122.2**	**480.1**	**19.7**	**58.3**	**22.0**	**-1.0**
average	**6.9**	**1548.4**	**1193.9**	**154.6**	**17.2**	**24.9**	**213.1**	**240.8**	**0.0**	**254.9**	**30.6**	**333.4**	**11.4**	**37.1**	**13.1**	**-7.2**
2006	7.56	1732	1314.0	159.1	38.7	38.0	180.7	278.0	12.4	376.6	182.9	88.5	13.4	38.2	12.3	-10.7
	7.2	857	650.0	48.0	2.3	10.8	139.1	77.4	2.6	103.0	73.3	278.2	4.1	24.0	8.8	-3.3
	6.82	1344	1019.0	188.2	4.4	28.9	178.3	386.0	2.9	147.6	120.4	226.9	13.4	47.1	11.5	-7.5
	6.23	2240	1699.0	243.2	5.1	37.0	223.2	536.2	0.0	149.7	101.1	306.3	15.4	47.8	14.4	-9.1
	6.45	1842	943.2	92.0	3.1	15.6	170.5	209.9	0.0	144.1	36.0	272.1	7.0	32.7	10.3	-5.3
	8.08	785	561.0	49.4	8.1	11.1	92.2	112.9	1.0	55.2	40.3	184.2	5.7	30.7	6.3	-2.5
	6.83	679	486.0	49.0	7.5	10.9	91.4	91.1	0.0	44.4	36.7	233.1	5.6	30.8	6.4	-1.6
	6.78	848	643.0	48.1	3.4	9.5	131.5	80.6	1.5	48.8	95.5	294.1	4.3	25.0	8.4	-2.5
	6.26	759	543.0	35.1	6.4	9.1	131.8	57.7	0.0	49.8	80.3	311.8	3.5	19.3	8.8	-2.2
	6.85	812	581.0	35.1	7.3	9.5	126.3	62.9	2.5	62.9	102.6	252.0	3.6	19.7	8.4	-2.9
	6.21	1092	828.0	115.1	10.5	39.2	94.6	122.4	0.0	138.3	1.0	432.5	10.9	44.4	8.5	-0.8
	7.67	1416	709.0	123.2	12.1	45.7	82.3	134.8	0.1	170.2	9.9	385.0	12.0	46.8	8.3	-1.5
	6.45	1268	962.0	83.3	2.4	23.6	186.4	122.1	0.0	161.4	237.8	269.0	5.9	28.2	11.8	-6.8
	6.97	1037	787.0	53.2	2.0	18.0	172.4	114.7	8.0	192.9	258.0	66.5	4.0	21.7	10.5	-9.0
	6.16	1547	1173.0	104.8	20.0	22.3	227.3	113.4	0.0	148.6	327.3	419.7	7.9	28.0	13.7	-6.3
	6.79	1578	1197.0	101.2	14.6	22.5	212.6	134.9	6.9	159.2	340.1	300.8	7.6	28.8	12.9	-7.5
min	**6.2**	**679.0**	**486.0**	**35.1**	**2.0**	**9.1**	**82.3**	**57.7**	**0.0**	**44.4**	**1.0**	**66.5**	**3.5**	**19.3**	**6.3**	**-10.7**
max	**8.1**	**2240.0**	**1699.0**	**243.2**	**38.7**	**45.7**	**227.3**	**536.2**	**12.4**	**376.6**	**340.1**	**432.5**	**15.4**	**47.8**	**14.4**	**-0.8**
average	**6.8**	**1239.8**	**881.0**	**95.5**	**9.2**	**22.0**	**152.5**	**164.7**	**2.4**	**134.5**	**127.7**	**270.0**	**7.8**	**32.1**	**10.1**	**-5.0**
2008	7.14	810	677.3	34.0	6.4	10.4	134.0	71.0	2.2	83.0	116.3	220.0	3.4	18.4	8.8	-3.9
	7.15	880	938.5	34.9	7.8	11.2	137.1	85.8	224.5	87.4	122.8	226.9	3.5	18.3	9.0	-4.0
	6.11	902	684.0	52.1	2.3	11.3	158.7	74.3	0.0	99.7	69.7	726.6	4.2	23.2	10.3	3.1
	6.85	1470	1324.1	94.0	27.0	28.0	225.0	134.0	21.9	310.0	304.3	180.0	7.6	25.1	13.9	-10.6
	6.75	1670	1534.4	95.4	28.2	29.4	265.1	212.7	23.2	384.2	316.3	180.0	7.2	22.8	16.0	-12.7
	7.01	750	587.4	29.0	2.9	7.8	127.0	60.0	0.9	47.0	82.9	230.0	2.7	17.4	8.5	-3.2
	7.01	940	742.7	52.9	3.9	9.0	131.1	113.4	87.1	144.1	89.9	234.3	4.8	26.9	8.1	-3.4
	7.07	960	891.0	48.0	13.4	13.0	149.0	191.4	4.5	103.0	168.7	200.0	4.8	21.5	9.4	-5.2
	7.9	990	795.3	50.1	13.7	14.5	151.3	86.9	4.8	104.7	170.5	198.9	5.0	21.8	9.5	-5.5
	7.04	750	589.8	39.4	2.2	9.9	123.0	59.0	1.4	45.0	79.9	230.0	3.6	22.6	8.1	-3.2
	7.04	890	618.8	41.8	4.3	11.1	129.3	124.1	2.4	115.3	81.9	234.3	3.9	22.4	8.4	-3.5
min	**6.1**	**750.0**	**587.4**	**29.0**	**2.2**	**7.8**	**123.0**	**59.0**	**0.0**	**45.0**	**69.7**	**180.0**	**2.7**	**17.4**	**8.1**	**-12.7**
max	**7.9**	**1670.0**	**1534.4**	**95.4**	**28.2**	**29.4**	**265.1**	**212.7**	**224.5**	**384.2**	**316.3**	**726.6**	**7.6**	**26.9**	**16.0**	**3.1**
average	**7.0**	**1001.1**	**853.0**	**52.0**	**10.2**	**14.1**	**157.3**	**110.2**	**33.9**	**138.5**	**145.7**	**260.1**	**4.6**	**21.9**	**10.0**	**-4.7**

Tab. 1 - Field parameters, concentrations of dissolved elements in groundwater samples for the phreatic aquifer

	Confined aquifer															
	pH	EC (microS/cm)	TDS (mg/l)	Na (mg/l)	K (mg/l)	Mg (mg/l)	Ca (mg/l)	Cl (mg/l)	Br (mg/l)	SO_4 (mg/l)	NO_3 (mg/l)	HCO_3 (mg/l)	SAR	Na%	PI	RSC
	7.1	2290	1392	229.9	2.7	37.9	193.8	302.1	0.0	72.0	34.1	519.8	15.3	49.5	43.0	-4.2
	6.85	2430	1829.1	252.9	15.6	20.4	244.3	680.0	0.0	352.0	67.6	440.0	16.5	47.4	39.3	-6.6
1996	6.97	825	556.7	64.4	3.9	1.5	136.1	114.2	0.0	32.2	17.4	400.2	5.8	31.3	121.4	-0.3
	6.78	825	567	64.4	3.9	1.5	136.1	114.2	0.0	32.2	17.4	400.2	5.8	31.3	121.4	-0.3
	7.25	810	718	103.5	3.8	6.3	150.5	151.0	0.0	118.1	21.7	339.8	8.6	39.2	83.5	-2.4
	7.21	730.3	708	103.5	11.7	6.3	150.5	151.0	0.0	118.1	22.0	339.8	9.2	38.0	83.5	-2.4
min	**6.8**	**730.3**	**556.7**	**64.4**	**2.7**	**1.5**	**136.1**	**114.2**	**0.0**	**32.2**	**17.4**	**339.8**	**5.8**	**31.3**	**39.3**	**-6.6**
max	**7.3**	**2430.0**	**1829.1**	**252.9**	**15.6**	**37.9**	**244.3**	**680.0**	**0.0**	**352.0**	**67.6**	**519.8**	**16.5**	**49.5**	**121.4**	**-0.3**
average	**7.0**	**1318.4**	**961.8**	**136.4**	**7.0**	**12.3**	**168.5**	**252.1**	**0.0**	**120.8**	**30.0**	**406.6**	**10.2**	**39.5**	**82.0**	**-2.7**
	7.2	857	650	48.0	2.3	10.8	139.1	77.4	2.6	103.0	73.3	278.2	4.1	24.0	133.1	-3.3
	6.87	1074	955.6	55.2	3.1	21.9	175.4	164.1	0.0	135.9	27.9	372.1	4.2	21.6	136.5	-4.4
	6.82	1344	1019	188.2	4.4	28.9	178.3	386.0	2.9	147.6	120.4	226.9	13.4	47.1	57.8	-7.5
	6.23	2240	1699	243.2	5.1	37.0	223.2	536.2	0.0	149.7	101.1	306.3	15.4	47.8	58.3	-9.1
	8.08	785	561	49.4	8.1	11.1	92.2	112.9	1.0	55.2	40.3	184.2	5.7	30.7	109.5	-2.5
	6.83	679	486	49.0	7.5	10.9	91.4	91.1	0.0	44.4	36.7	233.1	5.6	30.8	120.3	-1.6
	6.78	848	643	48.1	3.4	9.5	131.5	80.6	1.5	48.8	95.5	294.1	4.3	25.0	135.4	-2.5
	6.26	759	543	35.1	6.4	9.1	131.8	57.7	0.0	49.8	80.3	311.8	3.5	19.3	178.3	-2.2
	6.85	812	581	35.1	7.3	9.5	126.3	62.9	2.5	62.9	102.6	252.0	3.6	19.7	163.3	-2.9
	6.21	1092	828	115.1	10.5	39.2	94.6	122.4	0.0	138.3	1.0	432.5	10.9	44.4	84.1	-0.8
	7.67	1416	709	123.2	12.1	45.7	82.3	134.8	0.1	170.2	9.9	385.0	12.0	46.8	77.7	-1.5
	6.45	1268	962	83.3	2.4	23.6	186.4	122.1	0.0	161.4	237.8	269.0	5.9	28.2	92.2	-6.8
2006	6.97	1037	787	53.2	2.0	18.0	172.4	114.7	8.0	192.9	258.0	66.5	4.0	21.7	78.2	-9.0
	6.3	2530	1919	251.6	5.7	46.3	323.4	350.3	0.0	680.9	159.9	269.7	13.4	40.1	62.1	-15.5
	7.28	2733	2073	263.8	5.2	49.4	262.6	386.1	11.7	632.0	188.8	108.6	15.2	45.4	51.8	-15.4
	7.24	1470	1343.7	55.8	15.3	28.5	234.0	140.0	16.0	360.0	304.2	190.0	4.4	16.7	109.7	-10.9
	7.26	1489	1348.4	57.7	16.0	29.4	235.5	140.0	16.0	360.2	303.8	189.7	4.5	17.0	107.4	-11.0
	6.88	1723	1307	103.3	29.1	40.3	238.7	179.8	17.3	399.0	208.3	238.5	7.9	25.1	82.2	-11.3
	6.35	1680	1274	99.4	29.5	37.7	250.1	166.5	0.0	368.5	182.7	336.8	7.6	23.9	92.9	-10.0
	6.55	983	746	49.8	1.6	10.9	176.3	72.2	0.0	71.0	154.5	367.3	3.8	20.9	145.9	-3.7
	7.24	992	752	52.0	1.6	11.4	160.8	72.1	5.2	77.0	170.5	304.4	4.1	23.0	130.7	-4.0
	7.34	1222	927	80.0	3.4	15.5	172.8	135.9	2.8	106.3	236.9	226.3	6.1	29.4	88.3	-6.2
	6.51	1149	872	73.5	2.5	13.0	182.0	120.1	0.0	90.8	199.5	307.5	5.4	27.1	103.3	-5.1
	6.16	1547	1173	104.8	20.0	22.3	227.3	113.4	0.0	148.6	327.3	419.7	7.9	28.0	93.7	-6.3
	6.79	1578	1197	101.2	14.6	22.5	212.6	134.9	6.9	159.2	340.1	300.8	7.6	28.8	85.9	-7.5
min	**6.2**	**679.0**	**486.0**	**35.1**	**1.6**	**9.1**	**82.3**	**57.7**	**0.0**	**44.4**	**1.0**	**66.5**	**3.5**	**16.7**	**51.8**	**-15.5**
max	**8.1**	**2733.0**	**2073.0**	**263.8**	**29.5**	**49.4**	**323.4**	**536.2**	**17.3**	**680.9**	**340.1**	**432.5**	**15.4**	**47.8**	**178.3**	**-0.8**
average	**6.8**	**1332.3**	**1014.2**	**96.8**	**8.8**	**24.1**	**180.0**	**163.0**	**3.8**	**196.5**	**158.5**	**274.8**	**7.2**	**29.3**	**103.1**	**-6.4**
	6.11	902	684	52.1	2.3	11.3	158.7	71.0	0.0	99.7	69.7	726.6	4.2	23.2	184.1	3.1
	6.93	1300	1094	129.0	1.3	14.7	156.0	227.0	9.4	131.0	175.8	250.0	10.0	42.9	68.1	-4.9
	6.93	1350	1099.2	130.6	1.2	15.0	159.9	226.9	9.6	131.1	175.5	249.5	10.0	42.6	67.8	-5.1
	6.79	2200	2101	141.0	19.4	59.6	294.0	372.0	33.1	419.0	593.3	170.0	8.5	27.4	69.8	-16.7
	6.81	2540	2221.6	193.1	20.3	60.5	307.0	425.4	32.8	432.3	593.4	170.2	11.1	33.2	63.2	-17.5
2008	7.1	1700	1621	108.0	45.0	35.0	215.0	228.0	16.4	411.0	403.1	160.0	9.7	26.8	71.1	-11.0
	7.1	1750	1600	108.0	45.0	35.0	215.0	228.0	16.4	411.0	403.1	160.0	9.7	26.8	71.1	-11.0
	7.12	1850	1660.7	111.5	49.7	35.2	220.4	231.2	18.4	415.4	412.4	166.6	10.1	26.7	71.0	-11.1
	7.12	1850	1660.7	111.5	49.7	35.2	220.4	231.2	18.4	415.4	412.4	166.6	10.1	26.7	71.0	-11.1
	7.14	2300	2287.7	150.0	23.3	74.4	292.0	442.0	39.8	466.0	650.2	150.0	9.1	27.8	67.7	-18.2
	7.18	2600	2437.2	229.9	27.0	75.5	295.4	442.1	39.2	528.3	650.5	149.5	13.3	36.6	59.6	-18.5
min	**6.1**	**902.0**	**684.0**	**52.1**	**1.2**	**11.3**	**156.0**	**71.0**	**0.0**	**99.7**	**69.7**	**149.5**	**4.2**	**23.2**	**59.6**	**-18.5**
max	**7.2**	**2600.0**	**2437.2**	**229.9**	**49.7**	**75.5**	**307.0**	**442.1**	**39.8**	**528.3**	**650.5**	**726.6**	**13.3**	**42.9**	**184.1**	**3.1**
average	**6.9**	**1849.3**	**1678.8**	**133.2**	**25.8**	**41.0**	**230.4**	**284.1**	**21.2**	**350.9**	**412.7**	**229.0**	**9.6**	**31.0**	**78.6**	**-11.1**

Tab. 2 - Field parameters, concentrations of dissolved elements in groundwater samples for the confined aquifer

European regulations (152/2006 and 91/676ECC) limit to 250 mg/l the maximum amount of sulfates in the water. With respect to the study area, measurements point exceeding this limit were 36% in 1996, 17.5% in 2006 and 47.6% in 2008.

The sulfates enrichment of both aquifers is probably due to the mobilization of SO4 ions exerted by water irrigation, which solubilizes the chemicals used in agriculture. Chlorides in both aquifers show values falling in the categories fresh (0.85-4.23 meq/l), fresh-brackish (4.23-8.46 meq/l) e brackish (8.46-28.21meq/l), according to Stuyfzand (1989). The increase in chlorides instead, could be either of organic origin (animal manure and/or sewage), or due to the release of chlorine caused by the degradation of the plastics used to cover greenhouses and to contain agricultural products, that often are abandoned on land after use.

Noteworthy is the average increase of bromides concentration from 2.4 mg/l (2006) to 33.9 mg/l (2008) observed in the water of the unconfined superficial aquifer and from 3.8 mg/l (2006) to 21.2 mg/l (2009), probably due to the use of pesticide and to the disinfection of greenhouses before starting a new sowing (Tab. 1).

The Piper trilinear diagram shows that groundwater samples are Ca-HCO_3 type, mixed Ca-Mg-Cl type and Ca-Cl type for phreatic aquifer (Fig. 4a); the confined aquifer shows the same type of water, but in 2008 the water points Ca-Cl type are more numerous (Fig. 4b).

The water enrichment of alkalis, particularly in the superficial aquifer, could be caused by the abovementioned ion exchange processes between the minerals of clay and marl of the stratigraphic succession.

Diagrams Cl/TDS, SO_4/TDS, NO_3/TDS (Fig. 5) of the different monitoring surveys have linear and positive trends with good correlations. Diagrams NO_3/Cl, NO_3/SO_4 and NO_3/K, show positive and linear trends, with R2 values not satisfactory for 2006. Contrariwise, good correlations are for 1996 and 2008, except for NO_3/K, where a scattering is outlined because of the influence of fertilizers, pesticides and ionic exchange (Fig. 5).Agricultural sources of nitrate contamination have also been associated with the increased Cl in groundwater (Hill, 1982; Pionke & Urban, 1985; Pawar & Shaikh 1995; Koh *et alii*, 2007). KNO_3, $(NH_4)_2SO_4$ and KCl are in fact the main fertilizers which may contaminate the aquifer, although the use of the latter is limited because it is harmful for vegetables that do not bear the Cl ions.

Groundwater quality

The World Health Organization (WHO, 1989) states that the amount of nitrates in groundwater may arise because of excessive use of fertilizers, leaching of wastewater or other organic wastes. The European Directive 91/676EEC defines the nitrate vulnerable zones deriving by leaching from agricultural sources the ones having a NO_3>50 mg/l concentration.

Figure 6a and b Diagrams report the nitrates concentration increasing since 1996 up to 2008 s for the unconfined and confined aquifers respectively,

These values can be related to the farming activities and agree with data of the Assessorato Agricoltura e Foreste della Regione Siciliana (2009) carried out according the Nitrates Directive (91/676/EEC) (Regione Siciliana, 1999).

Quality of the irrigation water

The main representative parameters of the water quality for irrigation use, such as TDS, Percent Sodium (Na%), Sodium

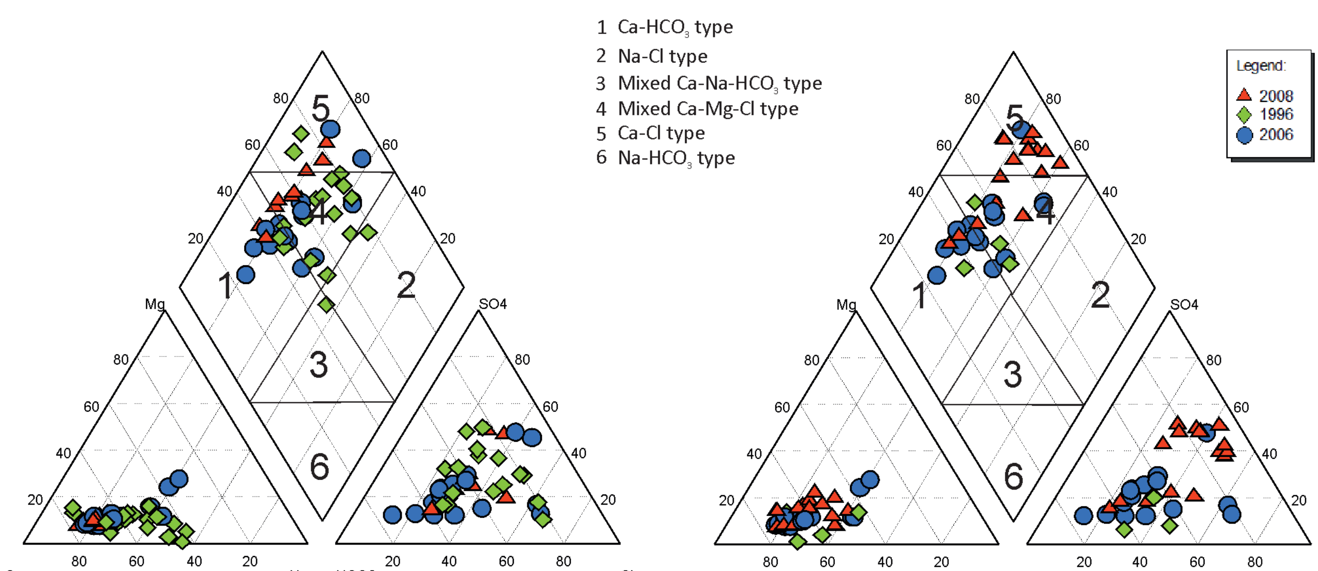

Fig. 4 - Piper diagram of the phreatic (a) and confined (b) aquifers (1996, 2006 and 2008)

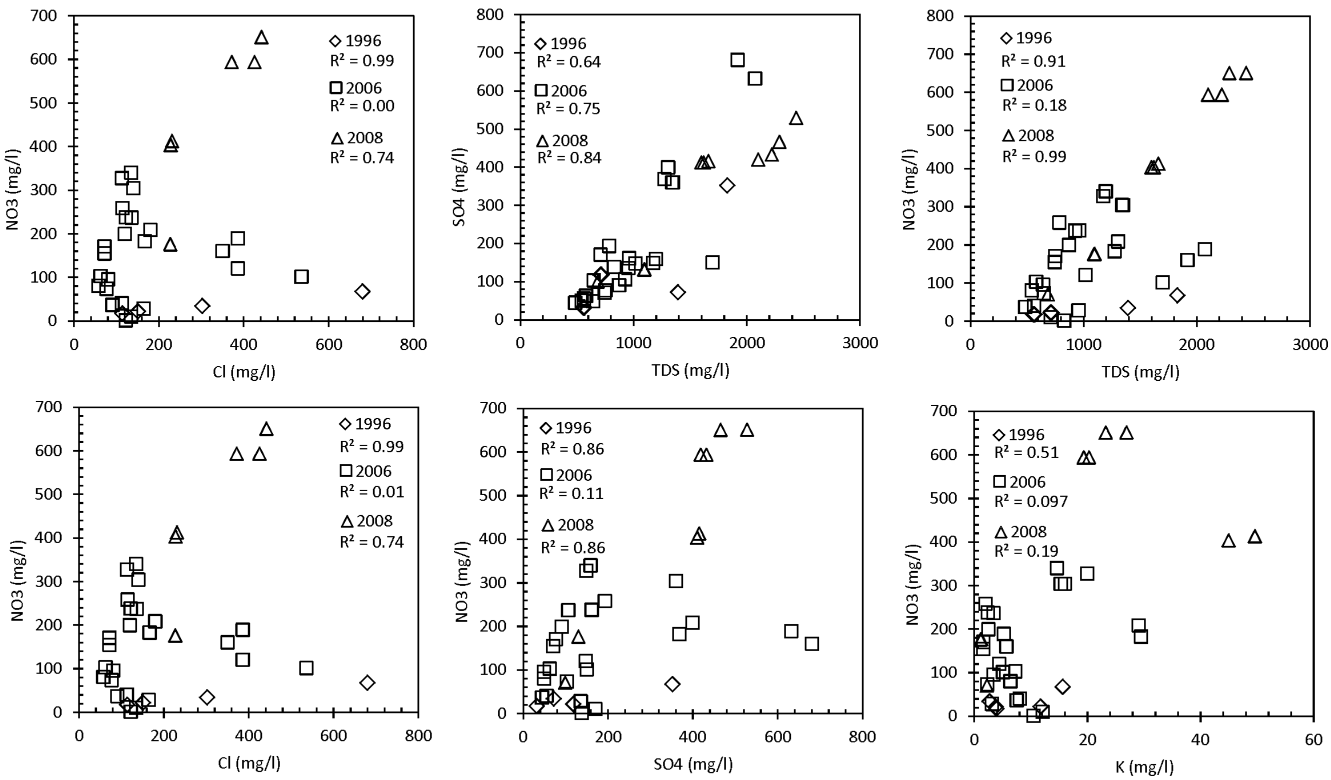

Fig. 5 - Bivariate diagrams; rhombus (1996), squares (2006) and triangles (2008)

Adsorption Ratio (SAR), Permeability Index (PI) and residual sodium carbonate (RSC) have been calculated and are summarized in Tables 1 and 2. TDS constrains the use of groundwater for irrigation purposes, which are classified also on the basis of their salinity according to the Ministerial Law of 23 March 2000. Most of values are index of high (500-1500 mg/l) and very high (1500-3200 mg/l) salinity. Only less than 10% of values are index of low (< 165 mg/l) and medium salinity (165-500 mg/l) (Fig. 7). When salinity is high, water cannot be used in poor-drained terrains and plants must tolerate salinity.

Another parameter useful to determine the suitability of groundwater to farming use is the evaluation the sodium percentage (Na%) according the following equation (Wilcox, 1948).

All the ions are expressed in meq/l.

The sodium excess induced by its fixing, in place of calcium and magnesium, within clay minerals constituting the agricultural

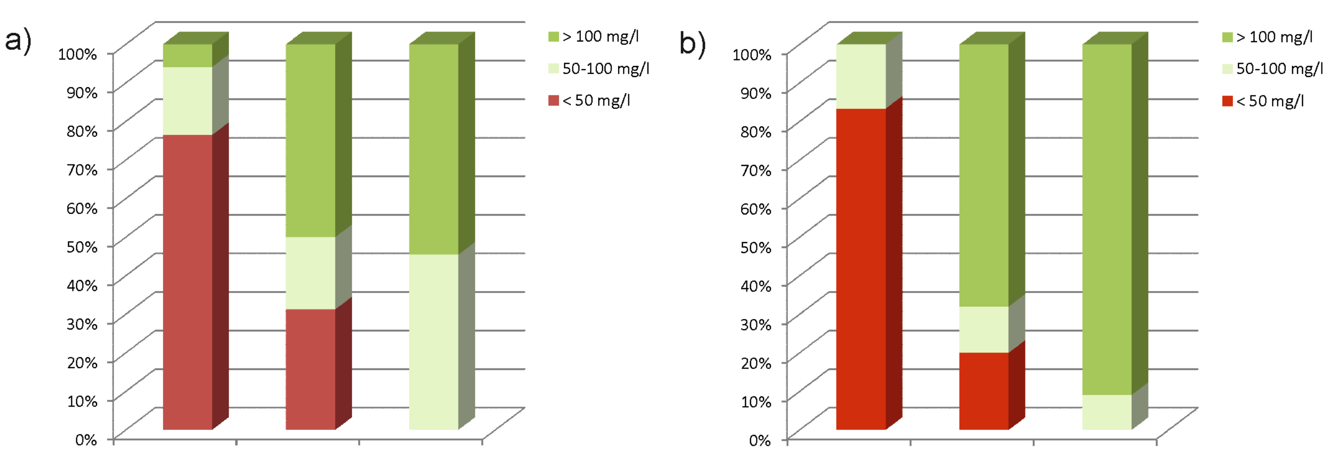

Fig. 6 - Groundwater nitrate concentration measured in 1996, 2006 and 2008. a) phreatic aquifer; b) confined aquifer

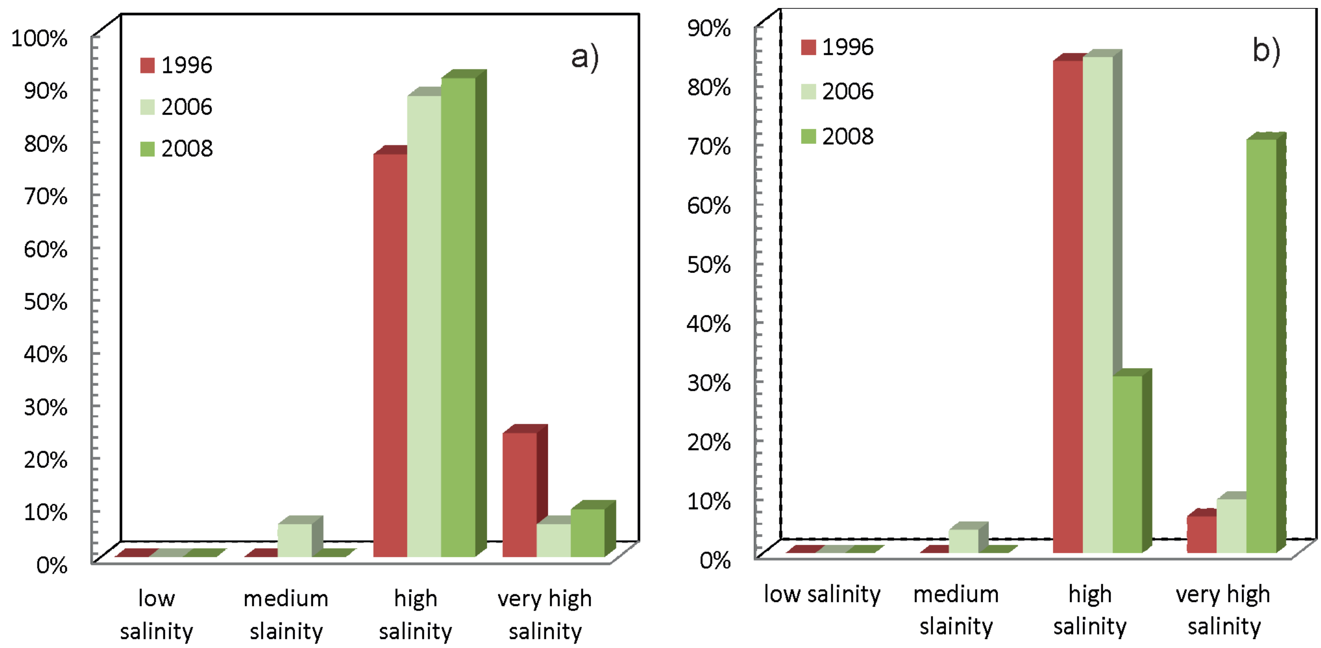

Fig. 7 - Average values of TDS, a) phreatic aquifer and b) confined aquifer

soil, damages the soil structure and causes its waterproofing.

The Na% index represents the ratio between exchangeable sodium. In both aquifers, most of the water falls within the excellent and good quality classes. Moreover, in the confined aquifer, the permissible class shows a decrease of cases in 1996 and an increase in 2008 (Fig. 8).

The water classification according Wilcox ranges from good to unsuitable for agricultural use both in the confined and unconfined aquifer (Table 1 and 2 and Fig. 9).In detail the water of the confined aquifer shows a relevant increasing of the doubtful class and at the same time a drastic reduction of the water classified good.

The results agree with the method proposed by US Salinity Laboratory Staff (1954) that relate the salinity of water (through the conductivity values) with the SAR index (Richards, 1954; Ayers & Westcot, 1994; Shaki & Adeloye, 2006).

The method regards the unfavorable effects of sodium abundance and excessive salinity on water for agriculture use. The high mineralization in fact, prevents the water absorption of the plants from soil through the osmosis process.

Groundwater of both aquifers falls in the low and medium classes of the SAR index, according to the D.M. 23/2000 (Fig. 10), with an increase in 2008. In these two classes water is

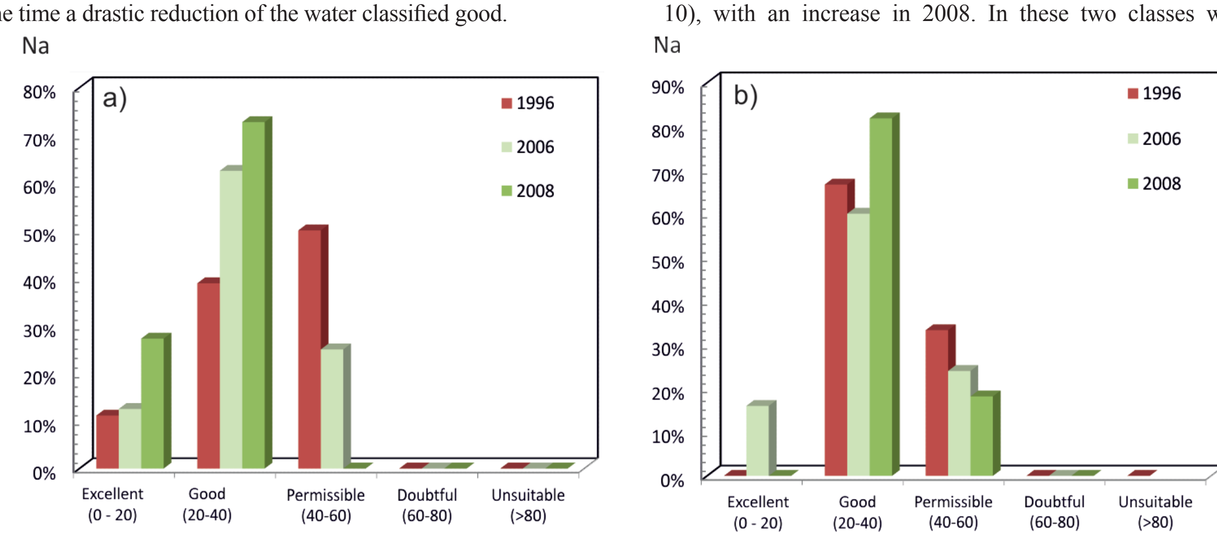

Fig. 8 - Average values Na%, a) phreatic aquifer and b) confined aquifer

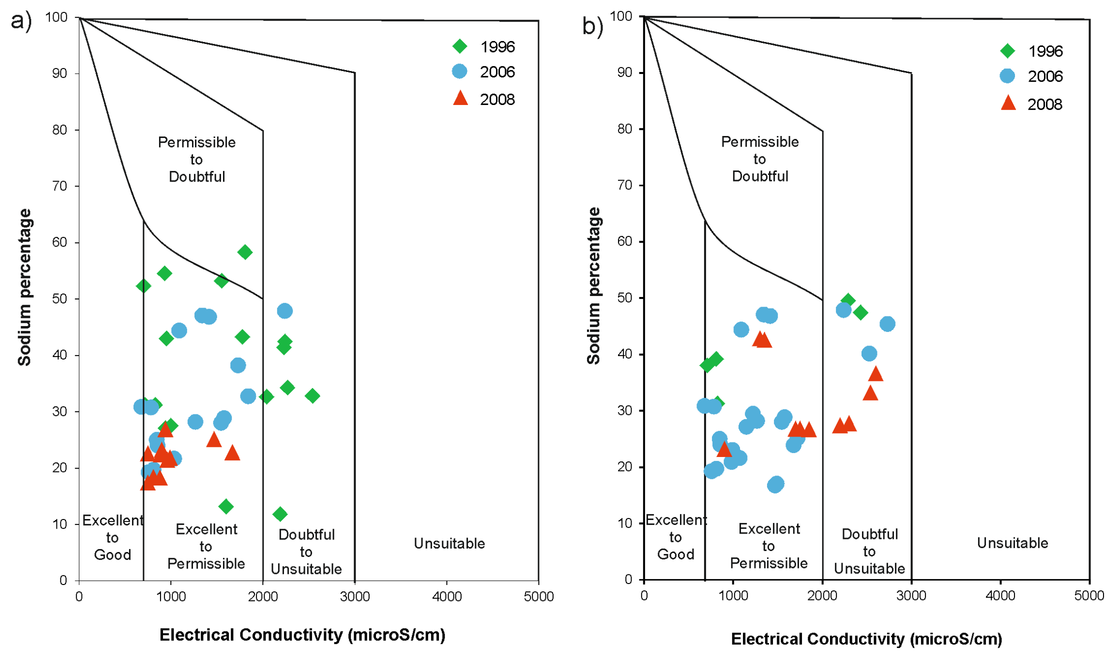

Fig. 9 - Suitability of groundwater for irrigation based on sodium percent (Wilcox diagram)

suitable with no danger and, in case of fine grained terrains poor-drained, there is a danger of an enrichment in sodium.

Figure 11 shows the correlation between SAR and EC, highlighting that the confined aquifer a great percentage of water falling within the S3 High. This underlines that salinity rather than sodium concentration, deeply affects groundwater for irrigation use.

Based on the permeability index (PI), a water suitability classification for irrigation water was developed by Doneen (1964). The PI was calculated by the following equation:

$$PI = [Na + (HCO_3)^{0.5}] \times 100/[Na + Ca + Mg]$$

All the ions are expressed in meq/l.

A classification based on PI was proposed by World Health Organization (WHO, 1989) for assessing suitability of groundwater for irrigation purpose. The soil permeability is affected by the long-term use of irrigated water and the influencing constituents are the total dissolved solids, sodium bicarbonate and the soil type. Accordingly, the PI is classified under class I (>75%), class II (25-75%) and class III (<25%) orders. Class I and class II wateris categorized as good for irrigation with 75% or more of maximum permeability. Class III water is unsuitable with 25% of maximum permeability. In the present study, the PI

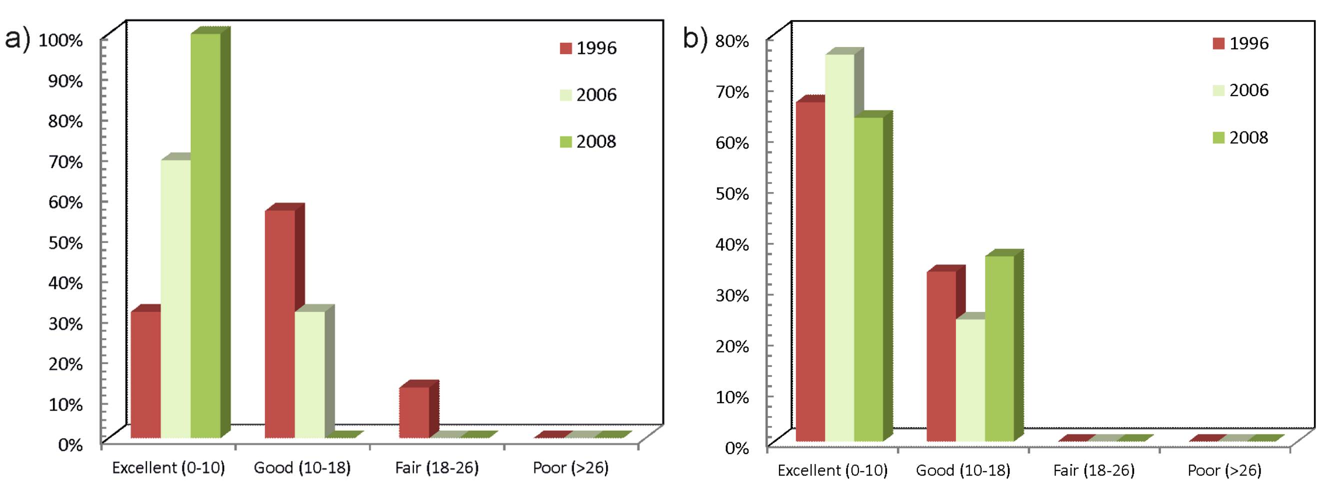

Fig. 10 - SAR% values (Richard, 1954); a) phreatic aquifer and b) confined acquifer

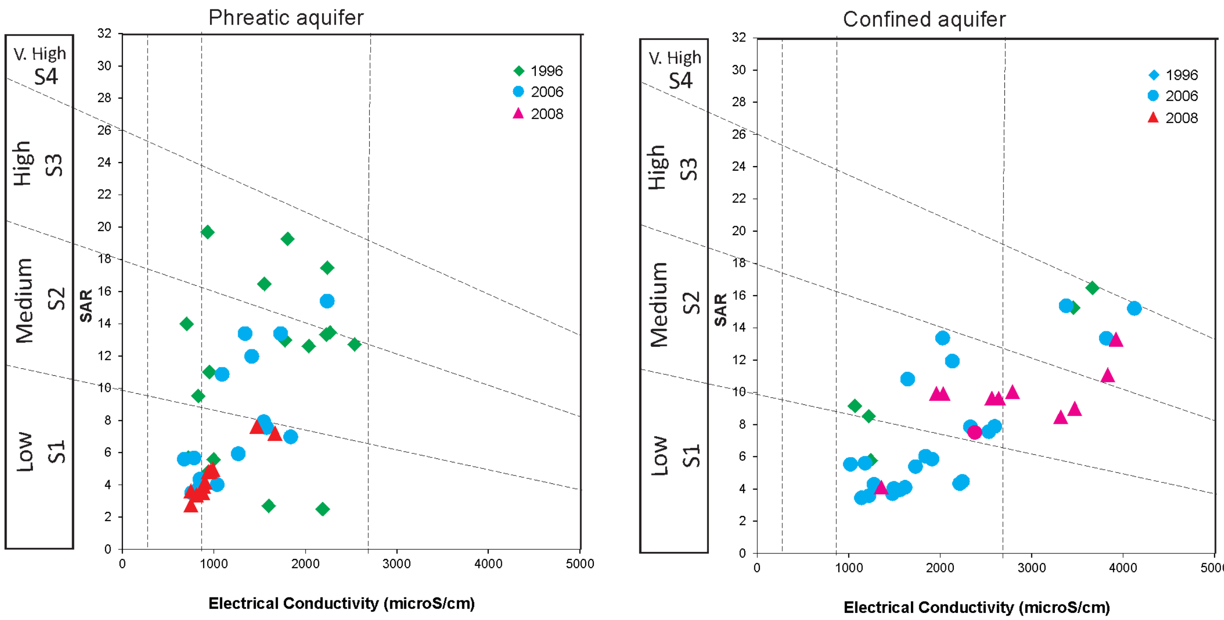

Fig. 11 - US salinity diagram for classification of irrigation water

values for phreatic aquifer, falls under class III (Table 1 and 2) and hence the water is considered unsuitable for irrigation. On the other hand, in the confined aquifer, values fall in the II and I classes, index of good and excellent irrigation water respectively.

A further index of water quality for irrigation purposes is the residual sodium carbonate (RSC), assessed through the following equation (Eaton, 1950):

$$RSC = (CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+})$$

Units are expressed in milliequivalent per liter.

Negative RSC results characterize both aquifers in all the measurement periods (Tables 1 and 2); this implies a surplus of Ca and Mg cations that the HCO_3^-; in this case such cations will be linked mainly with sulphates and chlorides.

Hydrogeochemical index draw the scenario of a cultivated area suffering the effects of the water management missing; this crucial activity have to be accomplished and harmonized by administrative authority, it can't be leaved to the farmer' s choise. To the scope main causes of pollution detection is crucial to efficiently plan the water management for agriculture purpose.

DISCUSSION AND CONCLUSIONS

The research deals with the negative effects on carbonate aquifer exerted by farming; this subject is particularly relevant in south-eastern Sicily where an intensive agriculture, constituting the main economic activity, is well developed. Clear identification of salinization and pollution sources is fundamental for the implementation of locally oriented remedies and long- term management strategies (Re & Sacchi, 2017). The dissemination of the research among administrators and stakeholders will bridge the gap between science and society favoring the adoption of technical solutions useful to the sustainable development of the area oriented.

Groundwater measurements acquired in 1996, 2006 and 2008; a total of 99 measure were carried out in the phreatic aquifer and 52 in the confined groundwater in order to reconstruct the piezometric surface and the water flow direction. The measures show that in the unconfined aquifer the minimum piezometric level was reached in 2008 (-10 m asl), with a lowering of about 4 meters in 12 years. The confined aquifer has a minimum level of -15 m asl, measured in 1996. With respect to maximum levels of confined aquifer, no relevant differences were observed between 1996 and 2008, while in the unconfined part a lowering of about 20 m was recorded (Fig. 2).

Most of groundwater samples are classifiable as mixed Ca-Mg_Cl type, demonstrating an evolution from Ca-HCO_3 type to Ca-Cl type. They show average values decreasing between 1996 (254.9 mg/l and 240.8 mg/l respectively) and 2008 (138.5 mg/l; 110.2 mg/l) in the unconfined aquifer. On the other hand, in the confined aquifer an increase of average values of sulphates and chlorides is recorded, from 120.8 and 252.1 mg/l (1996) to 350.9 and 284.1 mg/l (2008) respectively.

Because of the urbanized area missing the sulphate increasing is mainly caused by fertilizers, while chlorides result by human activities like the cattle breeding; noteworthy is the bad practice to discard plastics films used to cover greenhouses and the abandon on land of the used bins containing fertilizer and pesticides remains. Neglegible is the pollution of anthropogenic organic matter issued by farms. These pollution sources are leached by rainfall and enrich over time the groundwater concentration of chlorides because of their solubility. All the ionic species measured in 2008 in the confined aquifer show the increase of the concentration. Nitrates almost doubled their mean concentration from 30.6 mg/l (1996) to 145.7 (2008) for the unconfined aquifer; while for the confined aquifer the increase is more evident (from 30 mg/l measured in 1996 to 412.7 mg/l measured in 2008), overcoming the limits for human use (91/676/EEC).

The positive correlation between sulphates, nitrates and chlorides (Fig. 8), confirms the negative effect of farming on groundwater resources, analogous effects have been reported in cultivated areas by Re *et alii* (2017). Particularly sulphates and nitrates can be ascribed to the use of fertilizers leached from soil.

Moreover, the salinity affects the water quality; in fact, the increase of some ions (e.g. NO_3, Cl and SO_4) during the monitoring affects also TDS values, which are from high to very high and EC, which showed an average increase of about 500 microS/cm in the confined aquifer between 1996 and 2008.

The index parameters of sustainability of groundwater for agricultural purposes (Na%, SAR, PI and RSC) show worst conditions for the confined aquifer in the time interval between 1996 and 2008. In particular, in 2008 an increase of Na% was recorded in the permissible category; SAR show values falling in the S3C4 class only for 2008, while PI values fall in class III (unsuitable) for the unconfined aquifer. RSC is characterized by negative values, thus recording an increment of calcium and magnesium ions, which link to the more abundant sulphates and chlorides of 2008.

In such context is crucial the accurate planning of land fertilization that for typical products of the area like tomato, melon and vegetables should be made close to the assimilation period of the crops dividing in time the quantities of fertilizers. A correct planning should take account also of the local peak of rainfall distribution (January and April) to prevent the leaching of the nitrogen present in fertilizers, in the dormancy period of the plants.

REFERENCES

Ayers R.S. & Westcot D.W. (1994) - *Water quality for agriculture, irrigation and drainage paper.* http://www.fao.org/DOCREP/003/T0234E/T0234E00.htm

Barbano M.S., Pappalardo G., Pirrotta C. & Mineo S. (2014) - *Landslide triggers along volcanic rock slopes in eastern Sicily (Italy).* Nat Hazards, **73**: 1587-1607. Doi: 10.1007/s11069-014-1160-1.

Böhlke J.K. (2002) - *Groundwater recharge and agricultural contamination.* Hydrogeology J, **10**: 153-179.

Carbone S., Grasso M. & Lentini F. (1982) - *Considerazioni sull'evoluzione geodinamica della Sicilia sud-orientale dal Cretaceo al Quaternario.* Mem. Soc. Geol. It., **24**: 367-386.

Caire A. (1970) - *Sicily in its Mediterranean setting.* In: Geology and history of Sicily. P.E.S.L. Tripoli: 145-170.

Doneen L.D. (1964) - *Notes on water quality in agriculture.* Department of Water, Science and Engineering.University of California, Davis, CA.

Eaton F.M. (1950) - *Significance of carbonates in irrigation waters.* Soil. Sci. **69**: 123-133.

Ferrara V. & Pappalardo G. (2003) - *Salinization of coastal aquifers in the southwestern hyblean plateau (SE Sicily, Italy).* In: López Geta J.A., De la Orden J.A., De Dios Gómez J., Ramos G., Mejías M., Luis Rodriguez. Proc. Intern. Congr. Coastal aquifers intrusion technology: Mediterrarean countries (TIAC 2003). vol. I: 103-111, Madrid.

Ferrara V. & Pappalardo G. (2004a) - Intensive exploitation effects on the alluvial aquifer of the Catania plain (Eastern Sicily, Italy). Geofisica Internacional, **43**: 671-681.

Ferrara V. & Pappalardo G. (2004b) - Sea water intrusion in the coastal aquifers of south-eastern Sicily (Italy). 18th Salt Water Intrusion Meeting, 31 May -3 June 2004, Cartagena, Spain. 729-743.

Ferrara V. & Pappalardo G. (2008) - *The hydrogeological map of the Etna volcanic massif as useful tool for groundwater resources management.* Italian Journal of Engineering Geology and Environment, 1 (08). Doi: 10.4408/IJEGE.2008-01.S-06

Ghisetti F. & Vezzani L. (1980) - *The structural features of the Iblean Plateau and of the Mount Judica area (south-eastern Sicily): a microtectonic contribution to the deformational history of the Calabria Arc.* Bollettino della Società Geologica Italiana, **99** (01-02): 57-102.

Grasso M. (1999) - *Carta geologica del settore centro-meridionale dell'Altopiano Ibleo (Ragusa, Sicilia sud-orientale).* Scala 1:50000. SELCA, Firenze

Grasso M., Pedley H.M., Maniscalco R. & Ruggieri R. (2000a) - *Geological context and explanatory notes of the Carta Geologica del settore centro meridionale dell'Altopiano Ibleo.* Mem. Sco. Geol.It., **55**: 45-52.

Grasso M., Philps B., Reuther C.D., Garofalo P., Stamilla R., Anfuso G., Donzella G. & Cultrone G. (2000b) - *Pliocene-Pleistocene tectonics on western margin of the Hyblean Plateau and the Vittoria Plain (SE Sicily).* Mem. Soc. Geol. It., **55**: 35-44.

Grasso M. & Reuther C.D. (1988) - *The western margin of the Hyblean Plateau: a neotectonic transform system on the SE Sicilian foreland.* Ann. Tecton. **2** (2): 107-120.

Guastaldi E., Carloni A., Pappalardo G. & Nevini J. (2014) - *Geostatistical methods for lithological aquifer characterization and groundwater flow modeling of the Catania Plain Quaternary aquifer (Italy).* Journal of Water Resoruce and Protection, 272-296. http://dx.doi.org/10.4236/jwarp.2014.64032

Hill A.R. (1982) - *Nitrate distribution in the groundwater of the Alliston region of Ontario, Canada.* Ground Water, **20**: 696-701.

IPCC (2013) - *Climate change 2013: impacts, adaptation, and vulnerability. Part A: global and sectoral aspects.* Contribution of Working Group II to the

Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Field C.B., Barros V.R., Dokken D.J., Mach K.J., Mastrandrea M.D., Bilir T.E., Chatterjee M., Ebi K.L., Estrada Y.O., Genova R.C., Girma B., Kissel E.S., Levy A.N., MacCracken S., Mastrandrea P.R. & L.L. White L.L. (Eds.). Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1132 pp.

ISPRA (2013) - *Annuario dei dati ambientali* - Edizione 2013. ISBN: 978-88-448-0662-0.

ISTAT (2005) - *V censimento nazionale dell'agricoltura.* Database on line: sezione 5 - Consistenza degli allevamenti.

Johnston C.T., Cook P.G., Frape S.K., Plummer L.N., Busenberg E. & Blackport R.J. (1998) - *Ground water age andnitrate distribution within a glacial aquifer beneath a thick unsaturated zone*. Groundwater, **36**: 171-180.

Koh D.-C. & Ko K.-S., Kim Y., Lee S.-G. & Chang H.-W. (2007) - *Effect of agricultural land use on the chemistry of groundwater from basaltic aquifers, Jeju Island, South Korea*. Hydrogeology Journal, **15**: 727-743.

Manuella F.C., Brancato A., Carbone S. & Gresta S. (2013) - *A crustal-upper mantle model for southeastern Sicily (Italy) from the integration of petrologic and geophysical data.* Journal of Geodynamics, **66**: 92-102.

Mascle G. (1974) - *Le système de failles de Comiso, bordure nord-occidentale du haut-plateau ibléen (Sicile)*. Soc. Géol. France, **16** (5): 134-136.

Ogniben L. (1969) - *Schema introduttivo alla geologia dei confine calabro-lucano.* Memorie della Società Geologica Italiana, **8**: 435-763

OECD (2001) - *Organization for Economic Co-Operation and Development environmental outlook to 2020*. Paris.

Pappalardo G. (2012) - *Effects of climate change and anthropic activities on groundwater resources in the south-eastern Sicily.* Rendiconti Online Societa Geologica Italiana **21** (part 2): 877-878.

Pappalardo G., Imposa S., Mineo S. & Grassi S. (2016) - *Evaluation of the stability of a rock cliff by means of geophysicaland geomechanical surveys in a cultural heritage site (south-eastern Sicily)*. Ital. J. Geosci., **135** (2): 308-323.

Pawar N.J. & Shaikh I.J. (1995) - *Nitrate pollution of groundwaters from shallow basaltic aquifers, Deccan Trap Hydrologic Province, India.* Environ Geol **25**: 197-204.

Perini L., Salvati L., Sorrenti S., Zitti M. & Ceccarelli T. (2007) - *Valutazione della vulnerabilità ai processi di degrado delle terre e alla desertificazione del territorio italiano*. Italian Journal of Agrometeorology (1) 2007 - supplemento AIAM 2007 - 10° Convegno nazionale di Agrometeorologia: Quaderno degli Abstract, 34-35.

Pieri M. (1967) - *Caratteristiche sedimentologiche del limite cretacico-terziario nella zona di Monterosso Almo (MontiIblei, Sicilia sud-orientale)*. Riv. It. Pal. Strat., **73**: 1259-1294.

Pionke H.B. & Urban J.B. (1985) - *Effect of agricultural land use on groundwater quality in a small Pennsylvania watershed*. Ground Water, **23**: 68-80.

Re V. & Sacchi E. (2017) - *Tackling the salinity-pollution nexus in coastal aquifers from arid regions using nitrate and boron isotopes.* Environmental Science and Pollution Research, **15**: 13149-13153. Doi: 10.1007/s11356-017-9025-2.

Re V., Sacchi E., Kammoun S., Tringali C., Trabelsi R., Zouari K. & Daniele S. (2017) - *Integrated socio-hydrogeological approach to tackle nitrate contamination in groundwater resources. The case of Grombalia Basin (Tunisia).* Science of the Total Environment, **593-594**: 664-676. Doi: /10.1016/j.scitotenv.2017.03.151.

Regione Siciliana (1999) - *Linee Guida Piano territoriale Paesistico Regionale.* 615 pp. http://pti.regione.sicilia.it

Regione Siciliana (2005) - *Carta regionale delle zone vulnerabili da nitrati di origine agricola.* Assessorato Agricoltura e Foreste Dipartimento Regionale Interventi Strutturali Assessorato Territorio ed Ambiente Dipartimento Regionale Territorio ed Ambiente.

Regione Siciliana (2007-2013) - Assessorato Agricoltura e Foreste Dipartimento Regionale Interventi Strutturali Assessorato Territorio ed Ambiente Dipartimento Regionale Territorio ed Ambiente. http://151.99.146.37/SIAS/APD/Viewer/viewer_misura214.aspx?id=misura214&n=t

Regione Siciliana (2009) - *Monitoraggio della Direttiva nitrati in agricoltura.* Assessorato Agricoltura e Foreste, Dipartimento Interventi Infrastrutturali, Area II – Studi e Programmazione. Palermo 56 pp. http://www.artasicilia.eu/old_site/web/servizio_7_dra/site/3acque/Pianificazione/Nitrati/Allegati/Relazione_nitrati_art_10_Allegato_D.pdf.

Richards L.A. (1954) - *Diagnosis and improvement of saline and alkali soils.* Agricultural handbook 60. USDA and IBH Pub. Coy Ltd., New Delhi, 98-99.

Rigo M. & Cortesini A. (1959) - *Contributo alla conoscenza strutturale della Sicilia sud-orientale*.Boll. Serv. Geol.It., **81**: 349-369.

Schubert C., Knobeloch L., Anderson H., Warzecha C. & Kanarek M. (1997) - *Nitrate-contaminated drinking-water followback study.* Submitted to the WI Department of Natural Resources and the WI Groundwater COordinating Council. Department of Preventive Medicine, University of Wisconsin-Madison and the WI Department of Health and Family Services. 17 pp.

Spalding R.F. & Exner M.E. (1993) - *Occurrence of nitrate in groundwater.* Rev. J. Environ. Qual., **22**: 392-402.

Stuyfzand P.T. (1989) - *A new hydrochemical classification of water types with examples of application*. AHS, **184**: 89-98.

Shaki A. & Adeloye A. (2006) - *Evaluation of quantity and quality of irrigation water at Gadowa irrigation project in Murzuq Basin, southwest Libya.* Agric Water Manag, **84**: 193-201.

Tortorici G., De Guidi G. & Sturiale G. (2006) - *Evoluzione tettonica quaternaria del margine settentrionale del Plateau Ibleo (Sicilia sud-orientale).* Boll. Soc. Geol. It., **125**: 21-37, 13 figs.

US Salinity Laboratory (1954) - *Diagnosis and improvement of saline and alkali soils.* Department of Agriculture, U.S. Handbook 60,Washington D.C.

Ward M.H., Mark S.D., Cantor K.P., Weisenburger D.D., Correa-Villaseñor A. & Zahm S.H. (1996) - *Drinking water nitrate and the risk of non-Hodgkin's lymphoma.* Epidemiology, **7**: 465-471.

WHO (1989) - *Health guidelines for the use of wastewater in agriculture and aquaculture recommendations.* World Health Organization, 778 pp., Geneva.

WHO (2011) - *Guidelines for drinking-water quality*. 4th ed.. World Health Organization, 541 pp., Malta.

Wilcox L.V. (1948) - *Classification and use of irrigation waters.* U.S. Department of Agriculture, Washington DC, 962 pp.

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