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ANALYSIS OF GROUNDWATER POLLUTION IN THE SANT'EUFEMIA PLAIN (CALABRIA – SOUTH ITALY)

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EXTENDED ABSTRACT

Le piane costiere sono spesso affette da fenomeni di intrusione salina connessi al sovrasfruttamento delle falde acquifere che produce una risalita dell'interfaccia acqua dolce/salata (upconing). La salinizzazione delle acque di falda interessa diversi acquiferi costieri nel mondo ed è spesso correlata alla crescita della pressione antropica, che rappresenta l'innesco della rottura dell'equilibrio dell'interfaccia acqua dolce - acqua salata. Le piane costiere fortemente antropizzate, come quella di Sant'Eufemia (Calabria, Italia Meridionale), oltre all'intrusione marina sono soggette ad altri potenziali fattori di inquinamento delle falde, rappresentati da: complessi agricoli e zootecnici, aree industriali e sversamenti antropici all'interno dei corpi idrici superficiali (fiumi, laghi).

La Piana di Sant'Eufemia è ubicata nel settore centrale dell'Arco Calabro, in particolare lungo il margine occidentale della Stretta di Catanzaro. Quest'ultima rappresenta una depressione tettonica orientata Est-Ovest e bordata da allineamenti tettonici NO-SE di importanza regionale a componente trascorrente. Il basamento igneo-metamorfico affiorante lungo i margini della Piana è costituito da Unità filladiche e ofiolitifere a Nord e rocce prevalentemente granitoidi a Sud. Sul basamento poggia una successione sedimentaria costituita alla base da depositi silicoclastici ed evaporitici del Miocene Superiore che passano a depositi Plio-Pleistocenici. Il margine settentrionale è caratterizzato dalla presenza di grandi conoidi alluvionali, che rappresentano il principale corpo acquifero della Piana. La Piana vanta una tradizione agricola profondamente radicata di differenti coltivazioni mediterranee come vite, ulivo e agrumi. Sono inoltre presenti coltivazioni a livello industriale di fragole, mais e avena. L'area è caratterizzata da una grande crescita demografica dovuta alla presenza di infrastrutture come l'unico aeroporto internazionale a livello regionale e un'area industriale altamente sviluppata e come estensione seconda solo a Bagnoli nell'Italia Meridionale.

L'obiettivo del seguente lavoro è investigare i possibili fenomeni di inquinamento antropico dell'acquifero e valutare la potenziale risalita del cuneo salino nella Piana di Sant'Eufemia attraverso un approccio idrogeochimico. A tale scopo sono state campionate e analizzate 42 aliquote di acqua prelevate sia lungo i due principali sistemi fluviali della Piana (Fiumi Bagni e Amato) che da pozzi omogeneamente distribuiti lungo l'area esaminata. Lo studio geochimico ha portato all'individuazione di 4 principali famiglie geochimiche caratterizzanti gli acquiferi superficiali: acque a composizione clorurato sodica, bicarbonato sodica, bicarbonato calcica e solfato calcica. Le basse salinità individuate per le acque a composizione clorurato sodica hanno permesso di escludere fenomeni di intrusione marina, mentre le alte concentrazioni in Ca e SO_4 riscontrate nelle aliquote prelevate lungo il Fiume Bagni permettono di identificare fenomeni di miscelazione fra le acque del Fiume e quelle delle Terme di Caronte. Il sistema termale è ubicato nel settore settentrionale della Piana ed è caratterizzato da elevate portate all'emergenza (circa 100 L/s) e da composizioni prettamente solfato calciche. Queste acque fortemente caratterizzate da elementi come As e F vengono costantemente riversate nell'alveo fluviale posto immediatamente a valle dello stabilimento. La miscelazione fra acque fluviali e termali è responsabile delle elevate concentrazioni di SO_4, F e As riscontrate anche nella falda ubicata nella paleo conoide del Fiume Bagni. Le concentrazioni relative ai principali costituenti maggiori e in tracce disciolti sono state confrontate con i valori limite imposti dalla normativa italiana (D.Lgs. 152/2006) e con le linee guida fornite dall'Organizzazione Mondiale della Sanità (OMS). Il confronto ha messo in luce concentrazioni di As, F, K e NO_3 superiori alle soglie indicate da questi, ascrivibili sia a fattori naturali che all'intensa attività antropica dell'area. La costante crescita della pressione antropica (crescita demografica, espansione industriale, agricoltura intensiva) rendono la Piana estremamente vulnerabile a fenomeni di inquinamento della idrosfera, acque superficiali e sotterranee, biosfera e atmosfera.

ABSTRACT

In order to highlight possible aquifer pollution phenomena and rising of a salt wedge in the Sant'Eufemia Plain (southern Italy), forty-two samples of rivers and groundwater were analyzed. The Sant'Eufemia plain is located in the middle-western Calabria and represents one of the main agricultural and industrial area of the region. Four main geochemical types have been identified (Na-Cl, Na-HCO_3, Ca-HCO_3 and Ca-SO_4 waters). The low salinity of Na-Cl waters allowed to exclude sea water intrusion phenomena. High concentrations of Ca and SO_4 suggest mixing processes among the thermal waters (Caronte Spa), the Bagni River and the groundwater, identifying Bagni River mouth as the most vulnerable area. Furthermore, waters showed concentrations of As, F and NO_3 higher than Italian law and World Health Organization threshold limits. High concentration of K and NO_3 can be ascribed to anthropogenic activities. The presence of widespread anthropogenic activities make the plain an area exposed to pollution problems.

Keywords: *groundwater pollution, Southern Italy, sea water intrusion, geochemical characterization, thermal water*

INTRODUCTION

Many worldwide coastal plains are affected by groundwater salinization (De Montety *et alii*, 2008; Somay & Gemici, 2009; Wang *et alii*, 2013). The source of groundwater salinity can be identified in several phenomena as seawater intrusion, due to excessive groundwater pumping; fossil seawater and wastewater. Since the last decades, the growing anthropogenic activities on the coastal aquifer represents the cause of the rupture of equilibrium interface between seawater and freshwater, as a trigger for seawater intrusion.

Furthermore, the sprawl of the anthropogenic activities, as intensive agricultural and industrial settlements, increases the risk of heavy metals pollution and the presence of nitrate and potassium in groundwater.

This paper deals with groundwater geochemical features of the Sant'Eufemia Plain (SEP) (Calabria, Southern Italy). The work takes place from the Project PON Amicus focused on the analysis of asbestos cement (Cannata *et alii*, 2015a; Lucadamo *et alii*, 2015), marine intrusion (Vespasiano *et alii*, 2015c), waste disposal aboard ship and pollution of selected coastal area of Calabria (Cannata *et alii*, 2015b). SEP spreads across an area of about 120 m^2. In the last century, it had been affected by a strong increase of anthropogenic activities: building of the biggest Calabrian airport; industrial districts and other working activities. As many place in Calabria, Lamezia Terme is characterized by a deep-seated agricultural tradition of various Mediterranean cultivations, like grapes, strawberries , wine and olives, but also wheat, oat, corn and citrus fruits all over the Europe. Beyond the airport, by the way the biggest in Calabria, Lamezia Terme hosts the main goods yard for Calabria and one of the most important railway yards for passengers. Moreover, the industrial field "Papa Benedetto XVI" occupies a surface of about 1.100 ha and is the biggest in the south of Italy, with the exception of Bagnoli. Forty-two samples representative of superficial waters and groundwaters were analysed in order to create a conceptual environmental model for the site and to evaluate the presence of risk factors.

GEOLOGICAL SETTING

The Calabrian Arc (CA) represents a fault-bounded continental fragment within the Western Mediterranean orogen, located at the intersection of the E-W-trending Sicilian Maghrebides on the South and NW-SE-trending Southern Apennines on the North. The origin of Calabrian Arc is related to episodic Neogene roll-back of a NW-dipping subduction zone with the associated opening of backarc basins in the western Mediterranean (Malinverno & Ryan, 1986; Gueguen *et alii*, 1998). During Neogene-Quatenary, the backarc extension had been produced by the progressive eastward migration of the CA and an intense thrusting in the Apennine chain (Malinverno & Ryan, 1986; Gueguen *et alii*, 1998). The Arc migration was accommodated by NW and WNW-trending strike-slip fault systems, which are responsible of CA dissection in correspondence of Catanzaro and Siderno Basins and the development of intra-arc basins (Crati and Mesima Basins) (Knott & Turco, 1991; Van Dijk *et alii*, 2000; Tansi *et alii*, 2006). A widespread uplift affected CA, starting from the latest part of early Pleistocene epoch (Westaway, 1993), although currently local subsidence phenomena are observed, e.g. in Sibari Plain and in Crati Valley (Cianflone *et alii*, 2015a, b, c). SEP is located along the western edge of Catanzaro Trough (also called Catanzaro Graben), which represents a tectonic depression confined between the Soverato-Lamezia (southward) and Catanzaro-Amantea (northward) strike-slip fault zones (Van Dijk *et alii*, 2000) (Fig. 1). The trough is characterized by a basin-fill succession made up by upper Miocene terrigenous and evaporitic deposits (Cianflone & Dominici, 2011; Cianflone *et alii*, 2012), overlapped by Plio-Pleistocene sediments deposited in a tectonically confined strait (Longhitano *et alii*, 2014). SEP is characterized by upper Miocene-Quaternary deposits overlying the igneous-metamorphic basement. These deposits are made up by terrigenous, evaporitic and carbonate deposits passing upward to a marine succession of clays, sands, sandstones and conglomerates. The sedimentary fill reaches thicknesses up to about 1500 m as showed by offshore (ViDEPI project) exploration wells. The northern side of SEP is marked by the Feroleto–Santa Eufemia fault, characterized by several discontinuous E-W and ESE-WNW which are considered responsible of the

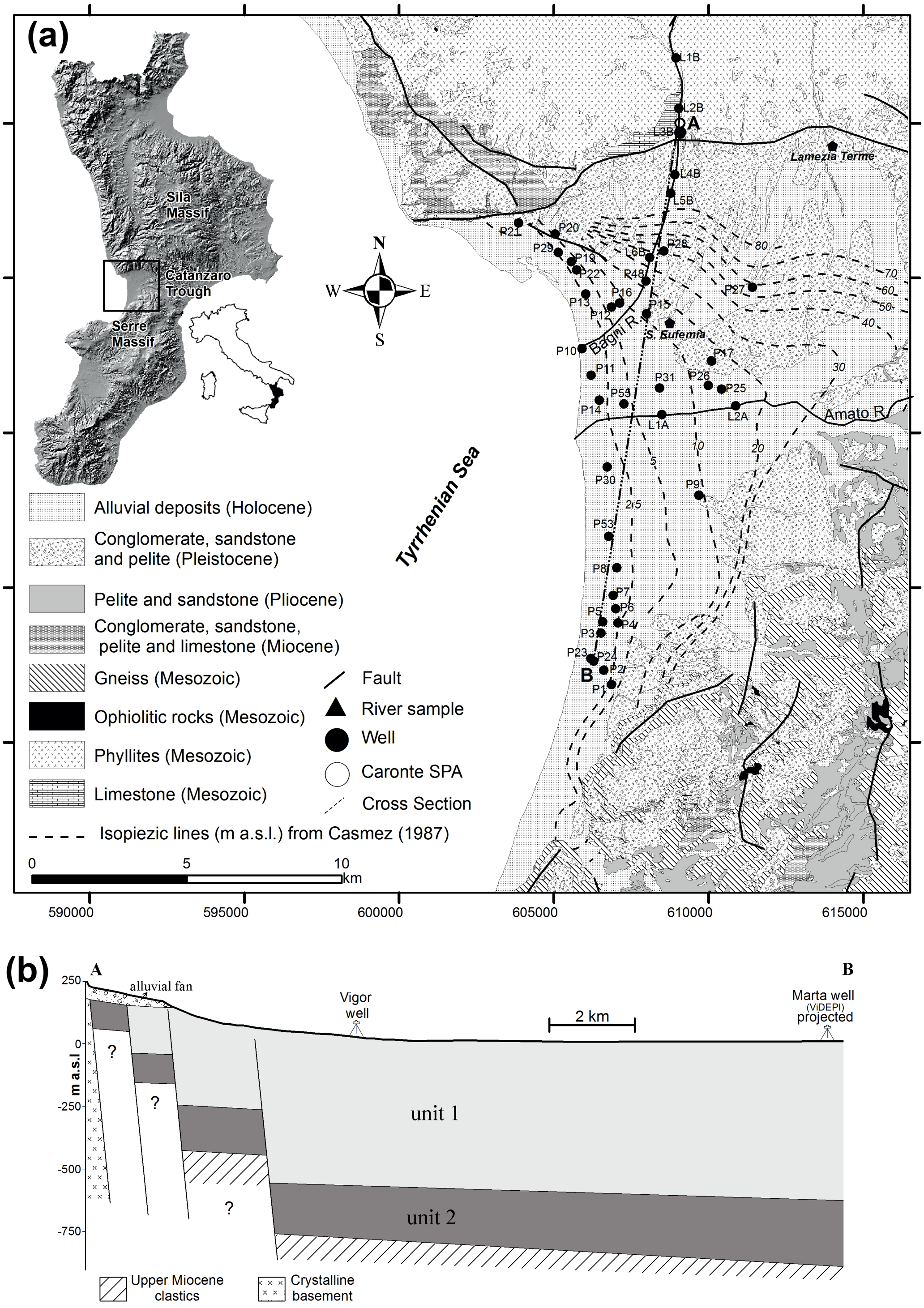

Fig. 1 - a) Simplified geological map of the Sant'Eufemia Plain; the fault traces are reported from Comerci *et alii, 2013. In the map is showed the location of river, groundwater and thermal samples. b) Simplified cross section where are reported the two main hydrostratigraphic units: Unit 1 made by sandy and gravely Quaternary deposits representing a multilayered aquifer and Unit 2 consisting of Pliocene clay which plays the role of aquiclude. Data of VIGOR well are available at http://www.vigor-geotermia.it*

northernmost main shock (Me = 7) of 28th March 1783 (Galli & Bosi, 2004). Along the northern side, the ophiolite-bearing rocks belonging to the Palezoic Bagni Unit (slate and metapelite) and Gimigliano Unit (Bloise *et alii*, 2009; Critelli *et alii*, 2015a; b; Vespasiano *et alii*, 2012b); the Castagna Unit (orthogneiss) and the Mesozoic carbonates complex crop out. The last one has been interpreted as a tectonic window of the Apennines chain (Amodio-Morelli *et alii*, 1976; Tansi et alii, 2007). The northern side is also characterized by large and widespread alluvial fans (Gullà *et alii*, 2005). Close to the Feroleto–Santa Eufemia fault rise the Caronte springs which represent the main thermal system of northern Calabria (Apollaro *et alii*, 2012; Vespasiano *et alii*, 2012a, 2014, 2015b, d, e). The thermae are characterized by Ca-SO_4 waters (Vespasiano, 2015; Vespasiano *et alii*, 2015b); the springs pour highly concentrated waters in the Bagni River, one of the main superficial system of the Valley. The southern side of the plain is highlighted by the northwestern Serre Massifs made up by Hercynian migmatitic paragneisses (upper nappe) and medium to low-grade metamorphic rocks, representative of CA intermediate and lower nappes (Langone *et alii*, 2006 and references therein).

MATERIALS & METHODS

Forty-two water samples (2 from Amato River, 6 from Bagni River and 34 wells) were collected between June and July 2015 (Fig. 1). Depth is known for 11 wells and it varies from 2m to 80m, with an average of 22 m and a standard deviation of 31m. The methodology for water sampling and analysis was already described by Apollaro *et alii* (2007a, 2013a, 2013b and 2015) and Vespasiano *et alii* (2014 and 2015a) and it is reported below. Some groundwater parameters, such as temperature (T °C), pH, Eh, electrical conductivity (EC), and alkalinity were measured in the field by means of portable instruments (HI 9828). Measured Eh values were corrected for temperature and reported to hydrogen electrode using the ZoBell's solution as reference (Nordstrom, 1977). Total alkalinity was determined by acidimetric titration with HCl 0.01 N using methylorange as indicator. A specially designed microdosimeter was used to minimize the amounts of reactants and facilitate the analysis under field conditions. Waters were filtered in situ through 0.45 μm pore size polycarbonate membrane filters, although this method has some limitations because some colloidal particles may pass through the filters (e.g., Kennedy & Zellweger, 1974; Laxen & Chandler, 1982). Samples for determination of

Sample	X	Y	Ph	Eh *mV*	EC *μS/cm*	T *°C*	Salinity *p.s.u.*	TDS *ppm*	DO *%*	DO *ppm*	Ca *ppm*	Mg *ppm*	K *ppm*	Na *ppm*	Sr *ppm*	NH_4 *ppm*	Cl *ppm*	SO_4 *ppm*	HCO_3 *ppm*	F^- *ppm*	NO_3 *ppm*	NO_2 *ppm*	Br *ppm*	PO_4 *ppm*
Thresholds groundwater Italian Law D.Lgs.			-	-	-	-	-	-	-	-	-	-	-	-	-	***0.5***	***250***	***250***	-	***1.5***	***50***	***0.5***	-	-
(WHO) guideline value			-	-	-	-	-	-	-	-	-	-	-	-	-	-	***250***	***500***	-	***1.5***	***50***	***3***	-	-
L1A	608492	4305587	8.39	42.9	527	23.77	0.25	369	98	8.48	60.81	10.90	2.74	25.22	0.65	0.21	27.02	42.05	205.93	1.29	7.31	1.97	1.37	0.85
L1B	608949	4317108	8.25	63.6	493	14.66	0.24	345	78	7.73	72.03	11.40	0.99	8.97	0.36	0.10	11.29	82.91	181.53	0.23	0.71	n.d.	0.56	n.d.
L2A	610878	4305866	8.38	44	514	22.08	0.25	360	95.2	8.45	59.09	11.31	2.87	24.49	0.43	n.d.	25.30	42.68	218.14	0.19	6.11	0.78	4.99	0.74
L2B	609040	4315487	8.24	32.6	544	14.82	0.27	381	89.1	8.89	81.08	11.90	1.15	10.09	0.45	n.d.	11.48	81.54	210.51	0.11	0.47	n.d.	1.54	n.d.
L3B	609043	4314693	7.11	-271.4	2557	36.77	1.29	1790	18	1.19	299.57	98.72	9.16	121.23	4.05	1.78	108.42	1177.93	215.08	2.61	9.20	n.d.	n.d.	8.61
L4B	608910	4313344	8.15	46.3	2151	25.7	1.1	1505	89.7	7.26	252.20	84.22	8.16	101.51	3.21	0.84	89.36	1036.22	155.59	n.d.	n.d.	9.49	n.d.	10.02
L5B	608771	4312737	8.26	57	2094	22.79	1.07	1462	81.5	6.58	254.53	84.58	12.24	102.57	4.33	1.29	86.57	1025.49	149.49	4.73	1.15	n.d.	6.87	n.d.
L6B	608099	4310666	8.64	55.2	2087	20.24	1.07	1460	78.7	7.08	250.46	86.11	7.80	102.78	3.29	1.20	91.98	1065.14	157.12	9.14	n.d.	n.d.	n.d.	5.45
P01	606614	4297326	6.74	85	509	19.9	n.d.	n.d.	n.d.	n.d.	34.18	17.25	29.11	28.84	0.48	n.d.	61.48	64.82	62.54	0.51	55.38	n.d.	0.31	n.d.
P02	606867	4296861	6.7	160.3	465	18.2	n.d.	n.d.	n.d.	n.d.	30.95	16.18	24.02	33.02	n.d.	n.d.	60.77	35.69	99.15	0.47	35.85	n.d.	n.d.	n.d.
P03	606525	4298526	6.88	103	493	19.7	n.d.	n.d.	n.d.	n.d.	42.40	15.63	13.65	27.47	n.d.	n.d.	47.40	43.99	138.81	0.63	20.54	n.d.	0.30	n.d.
P04	607074	4298857	7.01	5	480	18.7	n.d.	n.d.	n.d.	n.d.	41.58	15.63	38.31	25.56	n.d.	0.30	69.03	57.98	118.98	0.70	5.76	n.d.	n.d.	n.d.
P05	606576	4298894	7.1	125	504	18.7	n.d.	n.d.	n.d.	n.d.	50.29	16.83	7.92	24.07	n.d.	0.09	35.30	57.15	122.03	0.48	49.54	n.d.	n.d.	n.d.
P06	606998	4299310	7.08	120	560	18.2	n.d.	n.d.	n.d.	n.d.	42.42	19.30	3.77	31.01	0.55	n.d.	41.45	67.51	114.41	0.36	29.03	n.d.	n.d.	n.d.
P07	606918	4299741	7.06	115	612	19.4	n.d.	n.d.	n.d.	n.d.	47.54	19.28	34.22	27.93	n.d.	n.d.	56.34	62.29	144.92	0.37	36.41	n.d.	n.d.	n.d.
P08	607034	4300635	7.05	120	702	20.6	n.d.	n.d.	n.d.	n.d.	79.18	25.41	4.25	29.94	n.d.	n.d.	34.19	56.72	291.36	0.63	9.99	n.d.	n.d.	n.d.
P09	609691	4302976	7.18	-34.3	862	18.1	n.d.	n.d.	n.d.	n.d.	108.32	14.96	2.21	35.02	n.d.	1.91	47.55	0.39	434.75	1.30	n.d.	n.d.	n.d.	n.d.
P10	605916	4307717	7.41	178.2	1087	16	n.d.	n.d.	n.d.	n.d.	131.25	34.41	32.53	50.79	n.d.	n.d.	74.30	179.24	382.88	0.37	1.41	n.d.	n.d.	n.d.
P11	606205	4306857	7.37	186.5	731	17.1	n.d.	n.d.	n.d.	n.d.	85.59	23.44	39.37	33.28	1.24	0.64	59.18	80.70	298.98	0.54	n.d.	n.d.	n.d.	n.d.
P12	607131	4309193	6.9	213	889	16.8	n.d.	n.d.	n.d.	n.d.	123.04	26.28	2.76	29.61	1.68	n.d.	27.47	231.70	236.44	0.61	6.92	n.d.	n.d.	n.d.
P13	606030	4309485	7.06	130.2	1129	21.2	n.d.	n.d.	n.d.	n.d.	155.48	37.22	5.33	37.55	n.d.	n.d.	39.49	249.39	347.80	0.55	17.67	n.d.	n.d.	n.d.
P14	606473	4306050	7.33	160.8	891	17.6	n.d.	n.d.	n.d.	n.d.	123.71	21.38	22.01	37.99	2.24	n.d.	58.48	82.67	381.36	0.45	1.94	n.d.	n.d.	n.d.
P15	607996	4308842	6.55	163.4	960	20	n.d.	n.d.	n.d.	n.d.	108.56	33.31	45.36	43.70	n.d.	n.d.	69.31	205.26	256.27	0.51	22.84	n.d.	n.d.	n.d.
P16	606864	4309059	6.9	135.1	1075	20.01	n.d.	n.d.	n.d.	n.d.	151.51	34.54	2.65	36.70	2.50	n.d.	34.50	264.60	312.71	0.56	11.21	n.d.	n.d.	n.d.
P17	610098	4307314	8.13	-113	575	22.1	n.d.	n.d.	n.d.	n.d.	32.50	18.20	31.26	52.86	0.78	1.20	44.39	101.76	170.85	0.62	n.d.	n.d.	n.d.	n.d.
P18	610093	4307329	6.6	95.3	481	20.4	n.d.	n.d.	n.d.	n.d.	31.40	13.78	3.10	38.31	n.d.	n.d.	34.93	72.13	97.63	0.36	21.25	n.d.	n.d.	n.d.
P19	605568	4310528	7,12	-29,5	1096	18,1	n.d.	n.d.	n.d.	n.d.	133.18	39.67	6.13	37.70	1.04	0.67	39.10	307.78	294.41	0.65	n.d.	n.d.	n.d.	n.d.
P20	605043	4311418	7,63	132,6	679	17,8	n.d.	n.d.	n.d.	n.d.	59.11	23.95	4.23	39.26	1.63	n.d.	37.60	91.90	228.81	0.71	7.60	n.d.	n.d.	n.d.
P21	603866	4311783	6,93	150,1	821	19,1	n.d.	n.d.	n.d.	n.d.	98.39	13.98	5.26	49.75	n.d.	n.d.	40.82	158.50	216.61	0.56	24.63	n.d.	n.d.	n.d.
P22	605741	4310264	7,41	143	1200	18,3	n.d.	n.d.	n.d.	n.d.	156.91	40.96	4.67	39.66	0.95	n.d.	40.50	346.78	332.54	0.69	3.03	n.d.	n.d.	n.d.
P24	606199	4297704	8.38	230	667	15.8	n.d.	n.d.	n.d.	n.d.	34.52	20.38	39.49	41.92	n.d.	n.d.	70.83	75.71	146.44	0.28	1.59	n.d.	n.d.	n.d.
P24	606289	4297618	7.17	203	561	16.8	n.d.	n.d.	n.d.	n.d.	35.58	19.92	47.47	39.85	n.d.	n.d.	87.18	85.45	134.24	0.35	4.72	n.d.	0.35	n.d.
P25	610419	4306414	8,17	127,2	597	18,8	n.d.	n.d.	n.d.	n.d.	77.19	13.13	37.06	39.03	1.02	n.d.	41.24	19.23	320.34	0.39	3.70	n.d.	n.d.	n.d.
P26	609988	4306526	7,09	-10	918	19,9	n.d.	n.d.	n.d.	n.d.	120.18	22.29	5.08	36.35	n.d.	0.71	51.35	39.58	448.47	0.43	2.05	n.d.	n.d.	n.d.
P27	611420	4309701	5,08	180,5	472	20,5	n.d.	n.d.	n.d.	n.d.	19.43	20.33	13.50	36.24	n.d.	n.d.	45.66	56.29	97.63	0.23	26.01	n.d.	n.d.	n.d.
P28	608557	4310871	9,12	109,5	388	21,3	n.d.	n.d.	n.d.	n.d.	23.13	12.25	15.86	37.89	n.d.	2.16	19.83	6.40	190.68	0.36	1.34	n.d.	n.d.	n.d.
P29	605148	4310828	7.36	274,4	760	18,4	n.d.	n.d.	n.d.	n.d.	85.73	24.35	5.67	32.48	1.38	n.d.	35.97	74.25	331.02	0.48	7.86	n.d.	n.d.	n.d.
P30	606727	4303893	7.82	141	548	21,4	n.d.	n.d.	n.d.	n.d.	64.58	13.91	5.17	23.80	0.61	0.87	24.74	12.62	279.15	0.33	0.19	n.d.	n.d.	n.d.
P31	608416	4306447	7,10	-101,4	968	22,3	n.d.	n.d.	n.d.	n.d.	101.41	29.53	6.19	44.45	n.d.	4.03	53.23	30.44	478.98	0.49	1.32	n.d.	n.d.	n.d.
P48	607981	4309903	7.2	136.8	133	18.3	n.d.	n.d.	n.d.	n.d.	14.25	2.13	28.85	4.60	n.d.	n.d.	31.24	11.27	15.25	0.12	17.35	n.d.	n.d.	n.d.
P53	606776	4301649	7.62	17.5	735	20.1	n.d.	n.d.	n.d.	n.d.	70.02	25.44	15.19	33.14	n.d.	n.d.	44.15	41.92	343.22	0.68	n.d.	n.d.	n.d.	n.d.
P55	607266	4305932	7.31	150.2	704	16.9	n.d.	n.d.	n.d.	n.d.	53.37	15.55	34.24	59.72	n.d.	n.d.	88.91	47.76	244.07	0.49	4.08	n.d.	n.d.	n.d.
CARONTE 1	609136	4314715	6.61	-230.7	2750	37.55	1.39	1925	22.1	1.42	329.42	107.05	10.81	137.88	9.60	2.16	120.22	1417.44	262.37	3.16	n.d.	n.d.	n.d.	n.d.
CARONTE 2	609078	4314787	6.83	-168.5	2736	38.36	1.38	1915	27.7	1.76	329.28	106.54	9.88	137.25	9.42	1.64	119.38	1434.53	244.07	2.84	n.d.	n.d.	n.d.	n.d.
S.ELIA	609091	4314651	7.22	32.6	1134	21.91	0.56	794	59.1	5.01	129.65	44.30	3.64	42.39	3.70	n.d.	39.81	415.94	213.56	1.35	n.d.	n.d.	n.d.	n.d.
CARONTE R.	609050	4314722	6.62	-136.3	2540	35.97	1.28	1778	15.7	1.04	304.17	99.11	9.83	125.53	8.91	1.87	108.14	1314.67	247.12	2.86	n.d.	n.d.	n.d.	n.d.

Tab. 1 - *Location, chemical-physical parameters and concentrations of major and minor chemical components in the groundwater, rivers and thermal waters from the study area.* HCO_3 *represents alkalinity in mg* HCO_3*/L. In the table are reported the limit values do not be exceeded in the natural waters (according to the law D.Lgs. 152/2006 and the World Health Organization (WHO) drinking water guidelines)* cations and trace elements were collected in polyethylene bottles, after filtration and acidification by addition of supra-pure acid (1% HNO_3), whereas samples for the analyses of anions were stored without additional treatments. Major dissolved anions and cations were determined by HPLC (DIONEX ICS 1100). Trace elements were analyzed by a quadrupole inductively coupled plasma-mass spectrometer (ICP-MS, Perkin Elmer/SCIEX, Elan DRCe) with collision reaction cell capable of reducing or avoiding the formation of polyatomic spectral interferences. Data quality for major components was evaluated by charge balance. Deviation between the sum of concentrations of cations and the sum of concentrations of anions, both in equivalent units, was always less than ±5 %. Precision and accuracy for minor and trace elements was checked against the NIST1643e standard reference solution. Deviations from the certified concentrations resulted to be lower than 5%. All the chemical data were performed at DiBEST laboratory of the University of Calabria. Geochemical data are interpreted following consolidated procedures, which comprises: (i) the classification of waters and the inspection of chloride plots, (ii) the interpretation of distribution maps and (iii) the comparison of the main constituents with the limit values do not be exceeded in the natural waters, according to the law D.Lgs. 152/2006 and the World Health Organization (WHO) drinking water guidelines. For a complete analysis, the composition of wells and rivers were compared to the composition of the Caronte Spa (Vespasiano *et alii*, 2015c).

RESULTS AND DISCUSSION

Field data and compositional features of water samples, in terms of major and trace elements, are listed in Table 1 and Table 2. Physical-chemical parameters of the 34 wells have highlighted the following characteristics: (i) the system is characterized by cold waters with temperatures close to the atmospheric value. The highest values could be affected by heating caused by solar radiation. (ii) pH is mainly circum-neutral, only three samples have slightly acid pH (5.08 - 6.60) and four samples basic pH (pH > 8), up to a maximum of 9.12. (iii) Eh values are variable, although the majority of samples (25) have Eh > 100 mV, 7 samples show Eh value between -100 and +100 mV, and only 2 samples Eh < -100 mV. This variability is evidently due to the presence of both aquifers isolated from the atmosphere, with reducing conditions, and aquifers in contact with the atmosphere, where oxidizing conditions are present. (iv) Finally, also electric conductivity (EC) shows several variabilities, probably due to the different water-rock interaction. Bagni River's water sampled upstream of Caronte Spa showed physical-chemical values comparable to samples of Amato River. The samples L3B, L4B, L5B and L6B (downstream of Caronte Spa) are instead influenced by the interaction with the deep system that is constantly poured in the riverbed (see Tab. 1).

Water chemistry is initially studied by means of: (i) triangular plots involving major cations and anions (Fig. 2), both prepared starting from the concentrations in equivalent units, as this approach is more suitable than that involving concentrations in weight units (e.g., Zaporozec, 1972) and (ii) the correlation graph of SO_4 vs. $HCO_3 + Cl$, in which iso-salinity lines are drawn for reference (Fig. 3). These plots show the presence of four families of water (Fig. 2) in SEP: (i) Na-Cl waters (4 wells); (ii) Na-HCO_3 waters (7 wells); (iii) Ca-HCO_3 waters (18 wells, 2 samples from Amato River and 2 from Bagni River) and (iv) Ca-SO_4 waters (5 wells and 4 samples from Bagni River). Caronte Spa, localized in the northern sector of the Plain, shows also Ca-SO_4 composition. As reported above, thermal water composition have used to evaluate the presence of mixing processes between shallow and deep aquifers. Fig. 2 highlights that Ca^{2+} and Na^+ are the main constituents of the aqueous solutions. K^+ is subordinated to the Na^+ (except for P48 well). Moreover the waters show relatively high concentrations of K^+ (from 2.2 mg/L to 47.5 mg/L, with an average of 18.1 mg/L, median of 13.6 mg/L and standard deviation of 15 mg/L), probably due to the use of K-rich fertilizers in agricultural practices. Even if these diagrams are not very suitable for the detection of possible mixing processes, it is possible to identify a mixing line between waters from the Bagni River sampled upstream of the thermal area with those of Caronte Spa and a few wells (P12, P15, P16, P19 and P22) characterized by Ca-SO_4 composition. Triangular diagrams show the ratios between the variables losing information about the absolute concentration, i.e. the mass of the chemical constituents of interest refers to one kilogram of solvent. To retrieve this kind of

Sample	Li	Be	B	Al	V	Cr	Mn	Co	Ni	Cu	Zn	Sr	Se	Rb	Mo	U	Pb	As	Cd	Ba	Ag	Ti	Sn	Sb
	ppb	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*	*ppb*
Thresholds groundwater Italian Law D.Lgs. 152/2006	-	***4***	***1000***	***200***	-	***50***	***50***	***50***	***20***	***1000***	***3000***	-	***10***	-	-	-	***10***	***10***	***5***	-	***10***	-	-	***5***
(WHO) guideline value	-	-	-	***200***	-	***50***	***400***	-	***70***	***2000***	***4000***	-	***40***	-	-	-	***10***	***10***	***3***	-	-	-	-	***20***
L1A	2.36	0.03	40.46	18.72	1.26	0.71	17.90	0.20	3.78	7.90	8.20	480.51	0.51	2.19	1.01	0.74	1.00	1.89	0.35	32.02	0.01	52.41	0.10	0.50
L1B	1.02	0.00	8.95	4.37	0.10	0.28	2.81	0.16	2.28	0.96	0.24	281.80	0.15	0.55	0.52	0.31	0.04	0.55	0.03	6.79	0.00	64.87	0.03	0.40
L2A	2.34	0.01	38.42	13.56	2.31	0.58	35.18	0.20	1.93	1.36	0.45	478.64	0.56	1.18	1.62	0.72	0.08	2.33	0.07	27.45	0.01	51.50	0.01	1.45
L2B	0.56	0.01	9.43	4.53	0.00	0.10	19.25	0.21	3.19	2.26	3.34	288.43	0.42	0.67	0.59	0.37	0.36	0.67	0.07	8.25	0.00	72.44	0.11	0.44
L3B	88.15	0.04	453.05	3.45	0.00	0.02	19.49	0.51	7.10	1.34	0.77	4050.97	1.45	11.70	0.08	0.11	0.09	21.24	0.04	17.47	0.03	270.60	0.04	0.07
L4B	75.43	0.01	389.25	9.44	0.80	0.39	14.51	0.51	7.07	2.35	3.06	3440.16	1.39	10.56	0.66	0.27	0.23	45.90	0.07	22.24	0.03	242.59	0.07	0.71
L5B	91.10	0.01	461.71	7.17	1.06	0.53	56.22	0.80	8.78	3.23	2.33	4178.84	1.78	13.16	1.15	0.42	0.13	58.56	0.17	26.70	0.04	333.41	0.22	0.56
L6B	88.41	0.00	459.42	12.23	2.44	0.70	2.28	0.61	7.88	2.75	1.11	4054.66	1.70	12.79	1.56	0.35	0.04	48.29	0.12	28.39	0.02	313.65	0.04	0.36

Tab. 2 - Concentrations of trace elements in the rivers samples. In the table are reported the limit values do not be exceeded in the natural waters (according to the law D.Lgs. 152/2006 and the World Health Organization (WHO) drinking water guidelines)

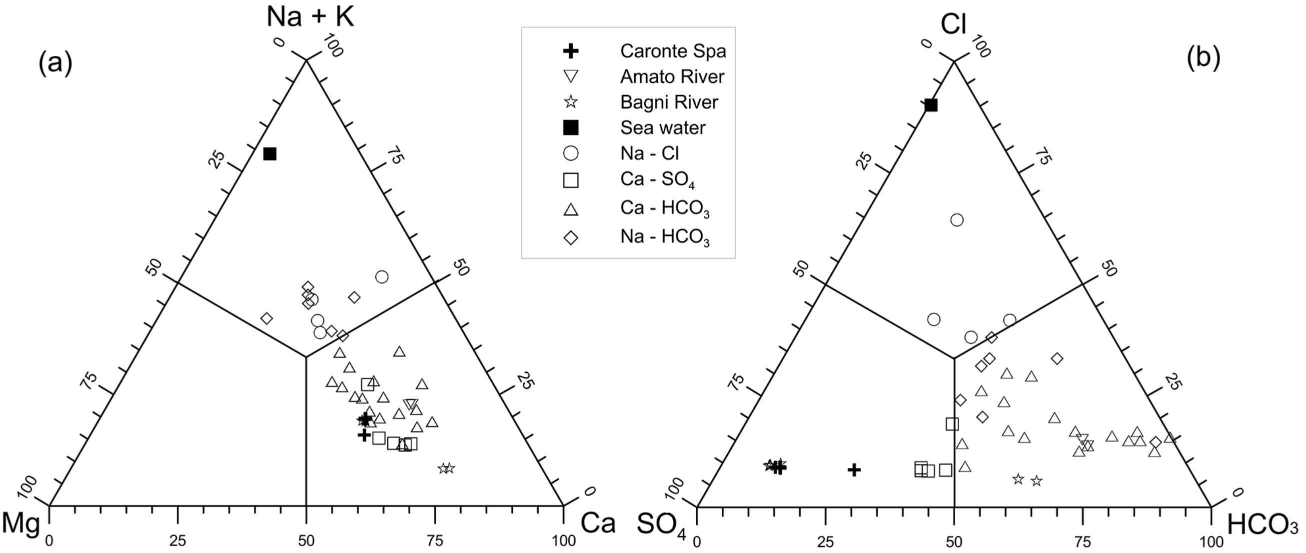

Fig. 2 - Triangular plots of major cations and major anions, both prepared from concentrations in equivalent units, for the water samples from the Sant'Eufemia Plain

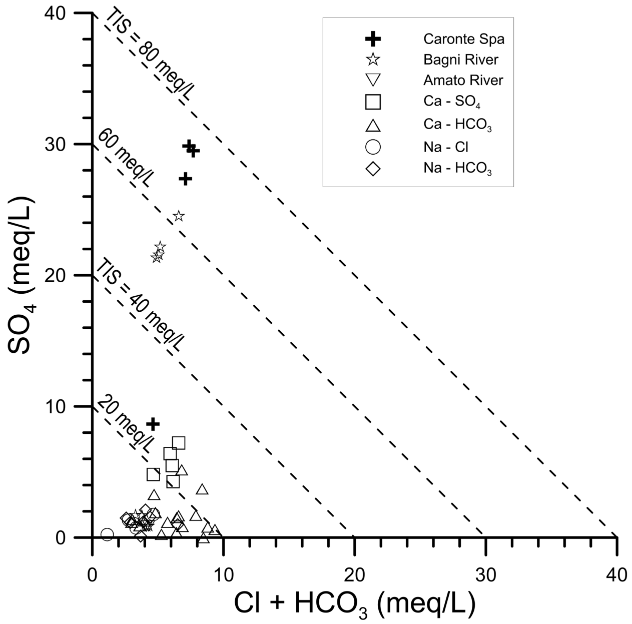

Fig. 3 - Correlation diagram of SO_4 vs. HCO_3 + Cl showing the water samples from the Sant'Eufemia Plain. Isosalinity lines are drawn for reference

information is convenient to refer to the correlation diagram SO_4 vs HCO_3 + Cl (Fig. 3). The diagram shows that Na-Cl waters have the lowest salinity values, followed by Na-HCO_3 waters and Ca-HCO_3 ones. The trend observed in the diagram is easily explained by a natural evolution of a Na-Cl meteoric end-member that, through water-rock interaction, acquires initially a Na-HCO_3 composition and then come to terms more evolved as Ca-HCO_3. Thermal waters composition is reported on the diagram for comparison and, as expected, are the terms with the highest salinity (up to 60 meq/L). Ca-SO_4 wells show concentration comparable or slightly higher than the Ca-HCO_3 waters. Furthermore, the samples are shifted up almost to show a mixing line between the samples from Bagni River, Ca-SO_4 wells and thermal waters. This could indicate possible exchanges between these three systems.

Chloride plots (Fig. 4) are useful for a better appraisal of mixing and other processes possibly occurring during the evolution of the system of interest, such as calcite precipitation. Each diagram is characterized by the presence of the hypothetical dilution line created starting from sea water composition (Nordstrom *et alii*, 1979). Cl vs. Na plot (Fig. 4a) shows as most of the samples (Na-Cl, Na-HCO_3 and Ca-HCO_3 waters) fall in proximity, or slightly above, the sea water dilution line, therefore Na concentration is due only to rainwater composition that undergone negligible water-rock interaction. In particular, Na-Cl waters fall on the seawater dilution line that, in addition to their low salinity, allows us to consider them as immature waters. For these reasons, we suggest that no sea water intrusion occurs in SEP. Some samples with Na-HCO_3, Ca-HCO_3 and Ca-SO_4 composition fall slightly above the dilution line suggesting minor water rock interaction with Na-enriched phases, like Albite. Furthermore, for the Ca-SO_4 sample a mixing with the Caronte Spa waters and the Bagni River is not excluded. All samples show a slightly enrichment in Mg (diagram not reported in the text) probably derived by water-rock interaction with dolomite or Mg-enriched minerals as biotite and olivine wich are abundant in the Castagna and Gimigliano Units (Apollaro *et alii*, 2007b; Guagliardi *et alii*, 2013a, b). Also in Cl vs. SO_4 plot (Fig. 4b), all the samples fall above the dilution line. SO_4 probably derives by dissolution of minerals as pyrite that undergoes dissolution, especially during their interaction with water enriched in O_2 and oxidizing them, thus encouraging the development of sulfuric acid (e.g. eq. 1):

$$2FeS_2 + 7.5O_2 + 4H_2O \leftrightarrow Fe_2O_3 + 8H^+ + 4SO_4^{2-} \qquad (1)$$

The samples P12, P15, P16, P19 and P22 and the waters of Bagni River, taken downstream of Spa, show SO_4^{2-} and Ca^{2+} concentrations higher than the other samples, suggesting that the content of sulphates is provided by the thermal system. In the diagram, is clear a mixing line that could confirm this hypothesis.

On the correlation diagram Cl vs. K (Fig. 4c), all the samples fall above the dilution line. In this case, it is difficult to explain the enrichment only by water-rock interaction with K-minerals. Definitely more plausible is pollution linked to excessive use of K-fertilizers. Finally, the plot Cl vs. Ca (Fig. 4d) still shows Ca^{2+} enrichment for all samples, probably due to dissolution of calcite that is ubiquitous in the study area.

Distribution maps of some of the most significant elements found in the wells and rivers were obtained using suitable

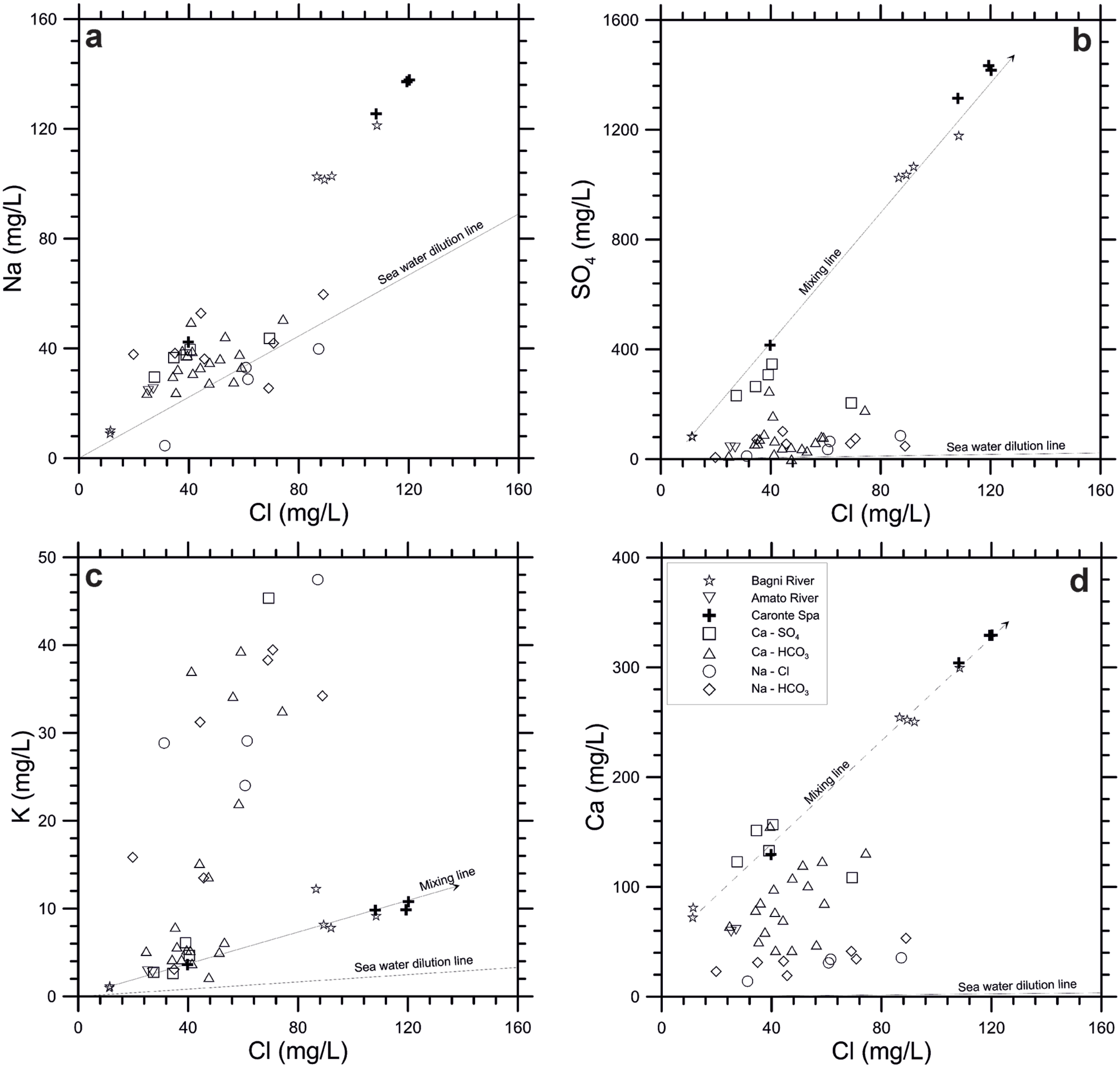

Fig. 4 - *Correlation diagram of (a) Na vs. Cl, (b) SO_4 vs. Cl, (c) K vs. Cl and (d) Ca vs. Cl for the samples from the Sant'Eufemia Plain*

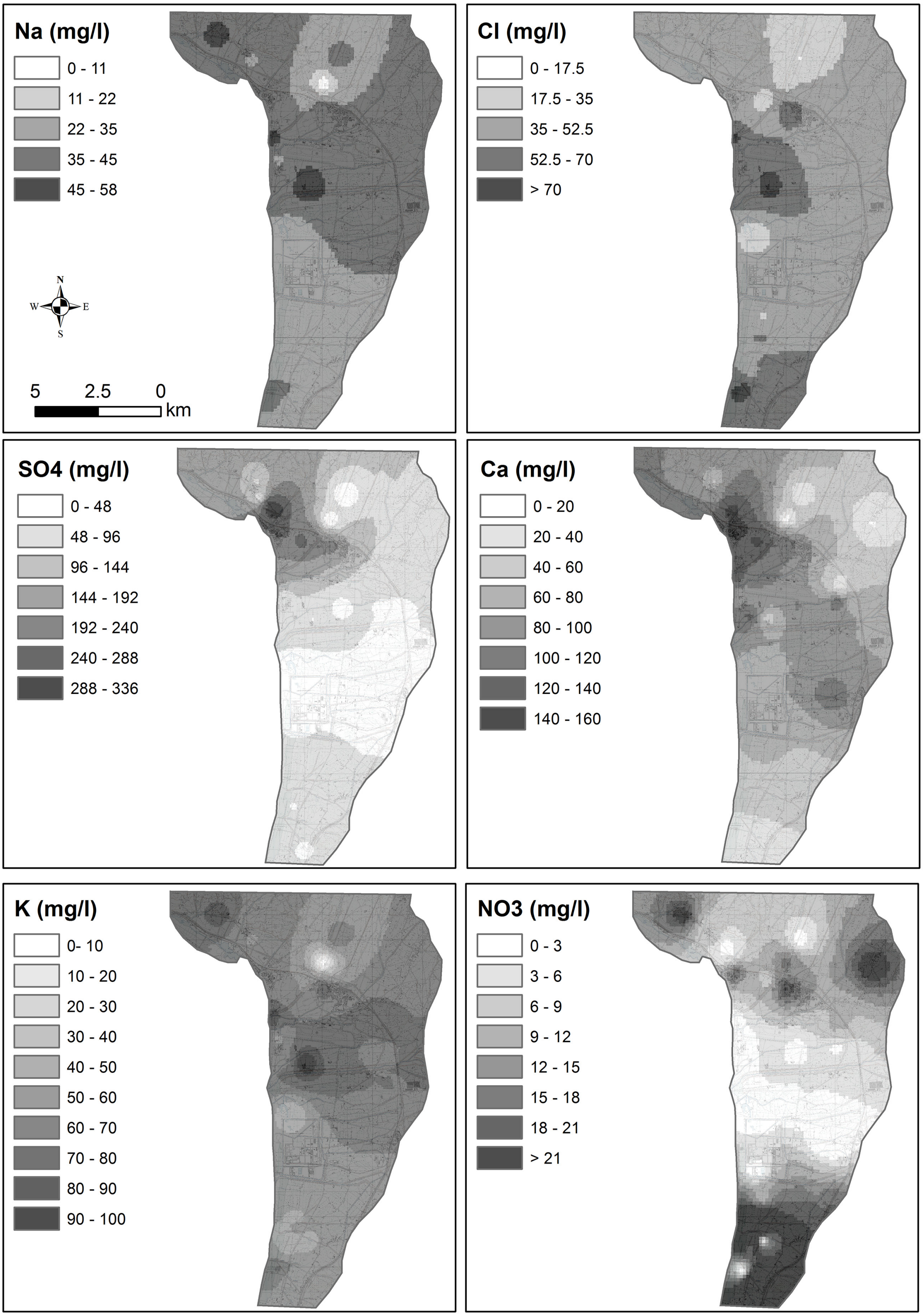

Fig. 5 - Distribution maps of Na, Cl, SO_4, Ca, K and NO_3 in the groundwater

semivariogram models to describe the spatial dependence of the elements and ordinary kriging as interpolation method. Distribution maps of Na and Cl (Fig. 5) pointed out that the areas with the highest concentration falls in the central portion of the Plain and only for Cl in the southern sector. In particular, Cl reaches maximum concentrations of about 88 ppm while Na of about 59 ppm confirming the absence of sea water intrusion in the investigated area. The distribution maps of SO_4 and Ca show high concentrations along the mouth of the Bagni River. SO_4 reaches concentrations that exceed 346 ppm while Ca 156 ppm. Other maps show high concentrations of K and NO_3 (> 50 ppm) in the northern and southern sectors of the area.

Values of a few major and trace elements of fluvial water and wells had been compared with the Italian law limit values of D.Lgs 152/2006, which establishes the lowest threshold of concentration for groundwater, and the drinking water guidelines provided by World Health Organization (WHO) (Tab. 2). The water of Bagni River (downstream of Caronte Spa) shows an As content higher than the lowest threshold provided for by Italian law and WHO (10 ppb and 20 ppb respectively). In addition, F content is higher than the Italian law and WHO threshold (1500 ppb) for few samples of Bagni River (L3B, L5B, L6B). As highlighted before in the text, NO_3 exceed both the limit values (50 ppm).

CONCLUSIONS

This work focused on geochemical characterization of SEP groundwater, in order to highlight possible aquifer pollution phenomena and rising of a salt wedge. Results obtained from analysis carried out on water of Amato and Bagni Rivers, and 34 wells drilled from SEP revealed the presence of four main geochemical types: Na-Cl waters; Na-HCO_3 waters; Ca-HCO_3 waters and Ca-SO_4 waters (see above). SO_4 vs. HCO_3+Cl correlation diagram shows that Na-Cl waters display the lowest salinity values, followed by the remaining water groups (Na-HCO_3 < $CaHCO_3$ < Ca-SO_4). Binary diagrams of major elements K, Ca, Na, SO_4 vs. Cl provided information on the interaction processes among rivers and groundwater. Both Bagni and Amato Rivers waters exhibit high concentration of Ca and Mg as a result of interaction with dolomite outcropping in a tectonic window located westward from Lamezia Terme (see Fig. 1), or else with Mg-rich minerals like biotite and olivine, that are very abundant within Castagna and Gimigliano Units. The low concentrations of Cr and Ni excluded the interaction with the ophiolitic rocks of Gimigliano Unit. Among Bagni River water, four samples (sited downline of Caronte Spa) exhibited high content of Ca and SO_4 and also values of salinity close to those of thermal waters from Caronte Spa, located at the northern side of the plain. High concentrations of Ca and SO_4 confirm the hypothesis of possible exchanges between the water of Bagni River (upstream already mixed with the thermal waters of Caronte) and Ca-SO_4 wells (Fig. 6). In particular, an increment for both elements was recorded at the mouth of Bagni River, where the presence of highly permeable lithologies (alluvial fan) can promotes the exchange between the river and the shallow aquifer. A few wells which lie on the mixing line linking the waters of Bagni River and Caronte Spa show high concentrations in SO_4 too (see distribution maps and Fig. 6). It suggests a continuous exchange between the two feeding systems, which causes an increment in the concentration of such elements like As, in the shallow aquifers. In details, As probably originates from interaction between thermal waters and sulfides from phylladic Unit. The examined wells displayed also high concentrations of K e NO_3. Distribution maps of both elements pointed out high values in the northern, coastal and southern sector of the SEP. High concentrations of K e NO_3 are probably connected to farming activities. As, F and NO_3 content in the analyzed waters are higher than both Italian law and WHO limits.

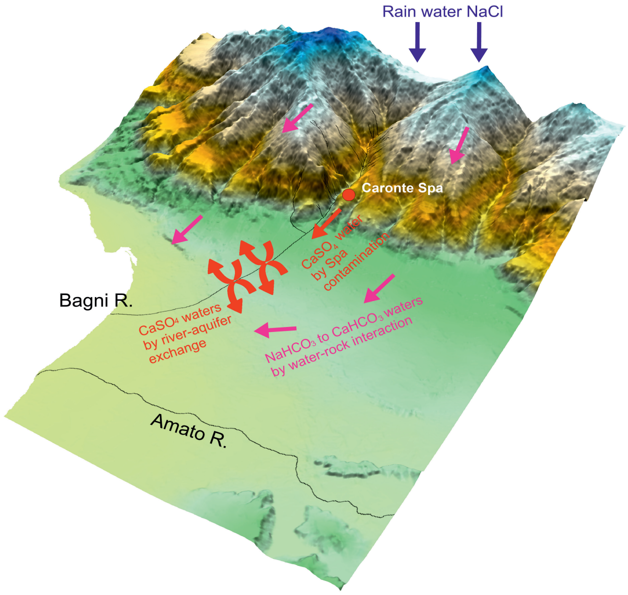

Fig. 6 - Schematic map showing the locations where the interaction among rain water, thermal waters and groundwater takes place

On the whole, geochemical analysis of water from SEP allowed us to exclude a contamination of a rising salt marine wedge, as expected by low salinity and immaturity of Na-Cl waters. Furthermore, we are able to identify the most vulnerable area along the bed of Bagni River, where the continuous exchange with the shallow aquifer causes the increase of such elements as As ascribable to the deep thermal feeding system. Finally, the high concentration of K and NO_3 suggests a substantial anthropogenic use of soil in the studied area.

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