Hydrogeochemical features of spring waters in the Sheet N. 348 "Antrodoco" area

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Abstract

The Geological Survey of Italy/Land Resources and Soil Protection Dept. of ISPRA is achieving a project which foresees the harmonized realization of different surveys, including hydrogeological activities, as an approach for a possible improvement of the CARG Project (Italian geological mapping), in the test-site of the Antrodoco Sheet territory, located between Lazio and Abruzzo regions (Rieti and L'Aquila province, Central Italy). One of the first targets was the hydrochemical characterization and classification of springs, along with their grouping on the basis of their affiliation to hydrogeochemical facies and the definition of their hydrogeochemical trends, contributing to assess groundwater circulation model in the involved aquifers. In addition, the study allowed us to evidence, by means of different analytical criteria, two aspects of the hydrogeochemical asset of the territory: (i) a regional variability model, which is explicative of the most examined factors; (ii) a residual number of outlier elements after the results of the principal component analysis, due to local (e.g., geological-structural or anthropogenic) factors.

The main obtained results were: (i) all samples may be classified as bicarbonate-calcic waters; (ii) the main outlier values of the chemical parameters of the analyzed waters are probably due to the uplift of deep sulfuric/sulfate waters along local structural-tectonic alignments; (iii) the PCA allowed the distinction of two main ion groups including bicarbonate and Ca, in one hand, and Mg, Na, K, Cl and sulfates, in the other hand; (iv) these two main previous groups of ions resulted to be correlated to lithological typology, explaining about 60% of the variance, and length of the underground paths (16% of variance); (v) it was possible to distinguish two significant bicarbonate-calcic aquifer types, the first one includes all "autochthonous" calcareous and marly formations of the Umbria-Latium-Abruzzi series (excluding the

calcareous-dolomitic rocks) and the other one characterized by "allochthonous" arenaceous-pelitic flysch deposits; (vi) the peculiar hydrogeochemical characteristics of the water affiliated to flysch deposits, as well as their spatial lithological uniformity, may be related to the occurrence of evaporitic and dolomitic deposits in the terrigenous successions of the North and Central Apennine, where they crop out in.

Samples from Antrodoco Sheet area and those from the neighboring areas of Campotosto Lake and Mt. S. Franco show very similar features, according to their affiliation to similar geologic environment facies of the hosting formations, contributing to validate the reconstructed hydrogeological picture of the study area in a regional scenario. In addition, spring waters of the study area also showed similar features respect to other springs of Central Apennines circulating in carbonate geological environment.

Key words: hydrogeochemistry; spring waters; chemical analyses; Antrodoco sheet area; central Italy.

Introduction

The hydrogeological features of the central Apennine area at regional scale are well known (e.g., Giuliano & Sciotti, 1981; Celico, 1983; Boni et al., 1986; Boni et al., 1995). Nevertheless, groundwater hydrochemical information is inadequate to the plenty of both streambed and localized springs fed by Apennine carbonate aquifers, representing the final discharge sites of groundwater flow pathways. During its movement towards springs (or to other aquifers), groundwater from the carbonate massifs is subject to physical-chemical changes, which are due to ion exchange with reservoir rocks and/or mixing with deep fluids, both causing different hydrogeochemical characteristics to groundwater (e.g., Celico et al., 1984; Celico, 1986; Castracani et al., 1995; Petitta, 2009).

In this respect, the present paper deals with the results of hydrogeological and hydrogeochemical activities conducted in the study area of the Antrodoco Sheet territory, located between Lazio and Abruzzo regions (Rieti and L'Aquila province, Central Italy). Contrarily to the previously cited works, the present study has been conducted at a detailed local scale and takes into consideration also minor springs, cropping out in flysch lithologies as well, having subordinate

hydrogeological potentiality, but of main importance for local water supply purposes. Furthermore, the features of the studied spring waters have been compared with those of other springs of Central Apennines circulating in similar geological environment.

The study was conducted by a useful collaboration among ISPRA-Geological Survey of Italy (Applied Geology and Hydrogeology Unit), ISPRA-Environmental Status and Metrology Dept. (Environmental Metrology Unit) and ARTA Abruzzo-L'Aquila Province Dept.

Geological and structural settings

In the Antrodoco sheet four main structural units occur (Figure 1). They are the M.Sibillini, the Gran Sasso-Cittareale, the M.Giano-M.Gabbia and the Acquasanta-Montagna dei Fiori units (e.g.: Bigi et al., 1991). The first two units are separated by the Olevano-Antrodoco-Posta-M.Sibillini overthrust alignment (average trend N10-20° in this area), which is part of the *Ancona-Anzio* regional tectonic alignment as described in the literature. N-S trending reliefs with sharp morphologies and elevations reaching over 2,000 m a.s.l. characterize the M.Sibillini structural unit. Outcropping formations span from Calcare Massiccio (Lower Jurassic p.p.) to
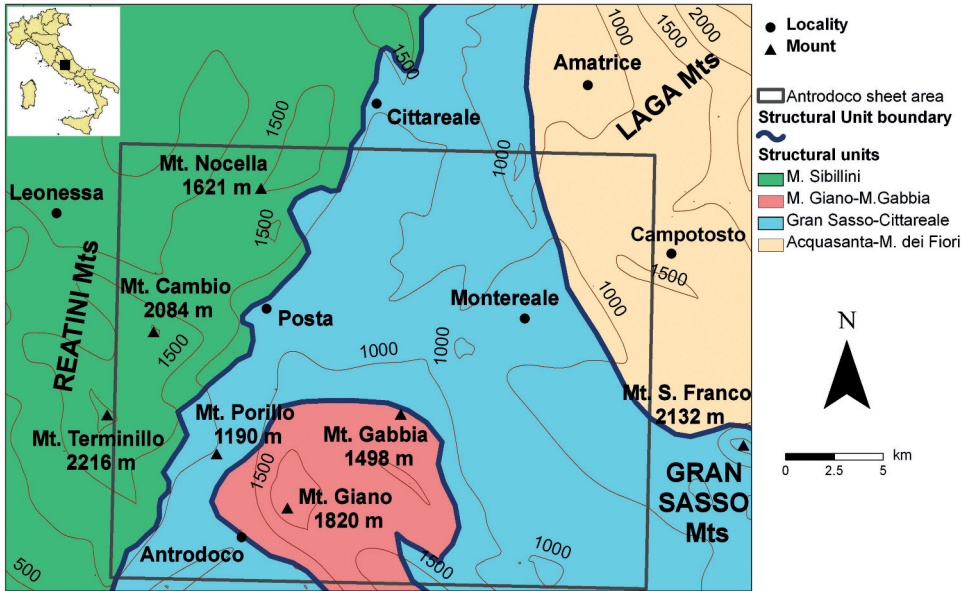
Figure 1. Geographical and structural sketch map at regional scale of the study area, evidenced within the dark-grey rectangle (inset map shows context in Italy).

Marne con Cerrogna (Miocene p.p.) of the Umbro-Marchigiano-Sabina Succession and its marly-arenaceous Neogenic cover, and are characterized by carbonatic platform passing to slope and marine basin environment deposits (e.g.: Bigi et al., 1991; Piana, 1995; Deiana et al., 1995; Pierantoni et al., 2005).

The Gran Sasso-Cittareale domain defines a long relief with Apenninic trend (NW-SE), with elevations reaching about 1,500 m a.s.l., constituting the westernmost sector of the Gran Sasso-M. S.Franco chain; the northern sectors of this area show outcrops of pre-evaporitic terrigenous turbiditic deposits of the Laga Formation (Upper Miocene p.p.) on top of the previously defined succession. A normal fault with a NW-SE trend cropping next to Pizzoli town occurs in the SE part of the unit, along the transition towards the M.Giano-M.Gabbia domain (e.g.: Ghisetti and Vezzani, 1988; Capotorti et al., 1991; Centamore et al., 1991; Piana, 1995).

The M.Giano-M.Gabbia unit also displays an Apenninic structural trend (NW-SE) with maximum elevations of about 1,800 m a.s.l. The outcropping formation deposition environments range from marine carbonatic platform, with a stratigraphical sequence similar to that of the Laziale-Abruzzese Succession (general time interval from Upper Triassic to Paleogene), to slope (formations from Maiolica, Upper Jurassic-Lower Cretaceous, to Marne con Cerrogna, Miocene). The unit is bordered at N and E by the curve shaped overthrust M.Cagno-M.Gabbia and at SW by the normal fault with a NW-SE trend cropping next to the Antrodoco town (e.g.: Capotorti et al., 1991; Centamore et al., 1991; Capotorti et al., 1995a, 1995b; Piana, 1995).

Reliefs with NW-SE trend and elevations reaching 1,600 m a.s.l. characterize the Acquasanta-Montagna dei Fiori structural domain. It crops out without evident tectonic discontinuity toward NE, moving on from the Gran Sasso-Cittareale unit. Terrigenous

Tortonian-Messinian formations (top part of Marne con Cerrogna, Marne ad Orbulina and Laga Formation) crop out in this unit, which represents the evolution towards a foredeep environment of the previously descibed slope-basin succession. The Olevano-Antrodoco-Posta-M.Sibillini tectonic alignment separates this unit from the M.Sibillini domain (e.g.: Ghisetti and Vezzani, 1988; Capotorti et al., 1991; Centamore et al., 1991; Piana, 1995).

Hydrogeological complexes

The terrains outcropping in the study area may be distinguished, on the basis of relative hydraulic permeability and other hydrogeological features (Servizio Geologico Nazionale, 1995), in the following main hydrogeological complexes (from bottom to top; Figure 2):

- Dolomitic complex, it generally shows a low relative permeability degree and includes: a) massive dolostone with evaporitic intercalations (Dolomia Principale; Triassic; thickness about 150 m), representing the basal aquiclude of the regional hydrogeological system; b) calcareous-dolomitic deposits (Middle Jurassic; thickness about 400 m); c) dolomitized limestone horizon developed after dolomitization processes within the Calcare Massiccio and/or Corniola formations. b) and c) usually act as aquiclude of local hydrogeological systems. This complex may show medium relative permeability degree when tectonic and karst secondary processes, leading to formation of local aquifers of variable hydraulic potentiality, occurred in it.

- Calcareous complex (Lower Jurassic-Upper Cretaceous; total thickness 1000-1500 m), high relative permeability degree, it includes (from
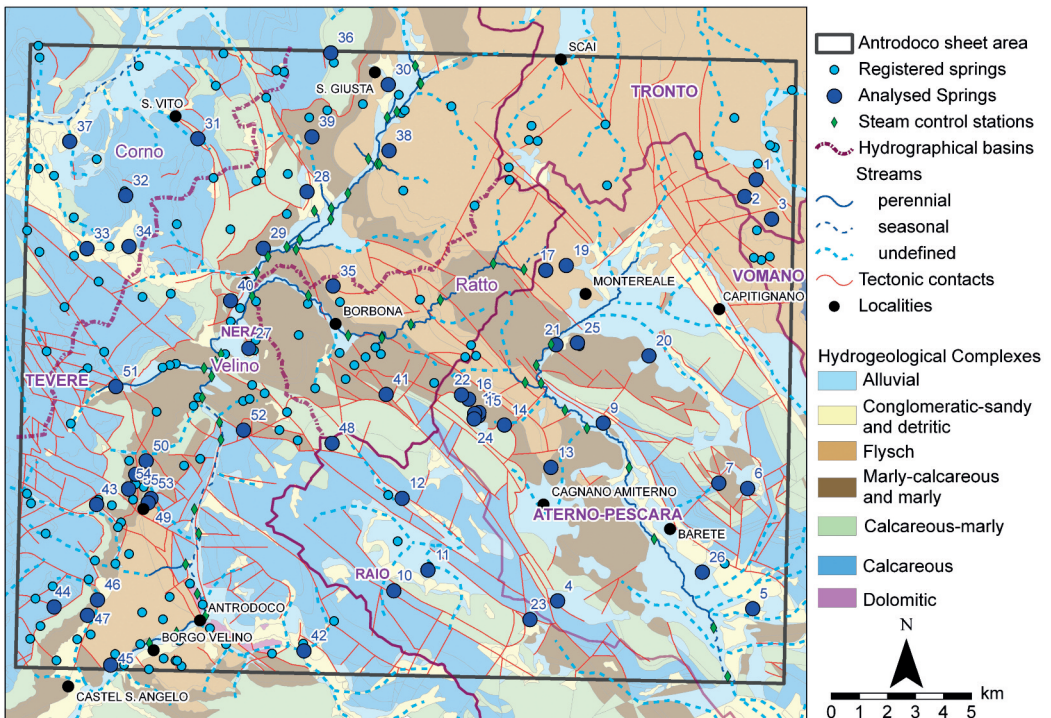

Figure 2. Hydrogeological Sketch Map of the Antrodoco sheet area.

bottom to top): a) calcareous formations with high secondary permeability, due to occurrence of fracturation and karst processes, and hosting a very productive regional basal aquifer at the Calcare Massiccio and lower part of the Corniola stratigraphic levels; b) marl and marly limestone, sometimes cherty, deposits having relatively low permeability and scarce fracturation degree and mainly aquiclude role (upper clayey Corniola, Marne del Monte Serrone, Calcari e Marne a Posidonia, Calcari Diasprigni); c) stratified fine grained limestone having secondary medium-high permeability due to fracturation and subordinately karst processes and hosting suspended aquifers (Maiolica). The presence of the aquiclude (b) may also lead to distinguish a basal (a) and an upper (b) calcareous complex.

- Calcareous-marly complex (Middle Cretaceous-Middle Eocene; total thickness 250-400 m), intermediate relative permeability, it includes marl, limestone and cherty-marly limestone (Marne a Fucoidi) and cherty-marly limestone (Scaglia Bianca and Scaglia Rossa), hosting local and perched aquifers.

- Marly-calcareous and marly complex (Upper Eocene- Upper Miocene p.p.; total thickness 300-500 m) with scarce relative permeability, it includes marl and marly detritic limestone (Scaglia Cinerea), marly limestone and calcareous marl (Bisciaro), marl, calcareous marl and calcarenite (Marne con Cerrogna, Marne ad Orbulina formations); the highly permeable lithotypes may host small local aquifers, contrarily to the marly formations, which are nearly impermeable.

- Flysch complex (Upper Miocene p.p.; total thickness about 1500 m), scarce relative permeability, it includes pre-evaporitic arenaceous, arenaceous-pelitic and pelitic- arenaceous deposits of the Laga Formation and hosts local and perched aquifers occurring in the highly permeable horizons.

- Conglomeratic-sandy and detritic complex (Upper Pliocene-Pleistocene; total thickness up to some hundred meters), intermediate to scarce relative permeability, it includes polygenic cemented and stratified conglomerate, sand and sandy clay and slope and conoid deposits, sometimes cemented and hosts local aquifers.

- Alluvial complex (Quaternary; total thickness from few metres to about 100 m), scarce relative permeability, it includes alternating argillite, silt, sand and gravel, with peat and hosts aquifers of variable importance.

Materials and methods

Overview on the main research activity results

Research activities consisted in the hydrogeological characterization of water sources (springs, wells), streams and waterways existing in the study area. In particular a detailed screening of the springs (about 250 water points collected) was carried out and about 70 of them constituted a control network. A monitoring activity aimed to the measurement of the water discharge and of some in situ physical-chemical parameters (temperature, pH and electric conductivity) was performed by monthly surveys. Field investigations (distributed during October 2007, January and June 2008 and March 2010) finalized to chemical element and compound analyses of waters from about 50 springs and 2 wells (N.11 and 24 in Table 1) were carried out too. Since so far it was possible to perform only a single analysis for each water point, seasonal variations were not taken into consideration in the present work. The few sulphuric/sulphate springs occurring in the Antrodoco sheet territory, likely related to deep hydrogeological systems, were not sampled for this work, in order to focus the discussion on groundwaters linked to shallow systems.

These data were uploaded in a Geographical Information System (GIS) appositely constituted to perform the graphic and cartographic elaboration showed in this work.

Regarding the physical-chemical parameters

Table 1 - Major and minor element contents and other main features of the analysed spring and well (N.11 and 24) waters (E.C.: specific electrical conductivity; TDS: total dissolved salts; bdl: below detection limit; Fe: total Fe; nd: not detected).

	SampleLabel	Name	Municipality	Litofacies	Elevation m a.s.l.	E.C. μS/cm	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Fe mg/l	HCO_3 mg/l	Cl mg/l	SO_4 mg/l	NO_3 mg/l	SiO_2 mg/l	TDS mg/l
1	ATS14	Spinilli	Campotosto	Flysch	1380	412	75	9.6	4.1	0.8	bdl	226	4.2	10.7	0.5	5.6	330
2	ATS15	Petriano	Capitignano	Flysch	1468	332	63	5.7	3.1	0.8	bdl	235	3.0	7.1	0.9	4.7	318
3	ATS16	Capporone	Campotosto	Flysch	1450	391	63	14.4	4.2	1.3	bdl	215	9.3	15.0	3.4	5	322
4	ATS17	La Foce	Pizzoli	Detritic	820	390	68	12.3	2.8	0.3	bdl	274	4.8	5.4	<0.4	3.2	367
5	ATS24	Fonte	L'Aquila	Calcar.-marly	820	726	101	29.9	9.8	13.5	0.013	418	21.0	16.6	59.5	7.9	609
6	ATS19	I Pozzilli	Pizzoli	Calcar.-marly	1325	392	88	1.0	1.9	0.3	bdl	268	4.6	2.2	1.1	4.1	366
7	ATS20	S.Pupa	Barete	Calcar.-marly	1275	321	74	0.8	1.2	0.1	bdl	219	2.2	1.6	0.8	3.7	298
8	ATS21	Pannacio/Aringo	Montereale	Flysch	1050	458	68	19.7	8.5	1.2	bdl	290	15.3	5.6	2.6	18.6	408
9	ATS03	Ost. del Sambuco	Cagnano Amit.	Marly	792	502	105	1.8	3.1	0.2	0.005	323	7.6	3.6	0.1	31.1	441
10	ATS04	Calabritto	Cagnano Amit.	Calcareous	1145	342	68	1.2	2.3	0.2	0.005	201	3.1	2.3	0.2	13.5	276
11	ATP01	Pozzo Cascina	Cagnano Amit.	Calcareous	1023	335	68	0.8	2.6	0.1	0.005	202	2.1	1.7	4.5	7.5	281
12	ATS23	Casciana	Cagnano Amit.	Calcareous	1010	280	57	0.7	2.2	0.1	0.005	172	2.6	2.3	0.5	30.7	235
13	ATS10	dei Frati	Cagnano Amit.	Flysch	900	426	64	14.0	6.5	0.8	0.005	250	6.2	6.6	3.6	23.5	345
14	ATS07	Fontanelle1	Montereale	Marly	975	518	107	2.5	7.4	2.7	0.005	277	31.1	9.6	12.2	16.4	440
15	ATS08	Mad. delle Grazie	Montereale	Marly	1066	497	99	1.8	2.6	0.2	0.005	293	5.9	9.2	2.5	14.3	405
16	ATS09	Gabbia1	Montereale	Marly	1100	485	101	1.6	1.6	0.2	0.005	293	5.1	4.6	1.4	20.8	404
17	ATS22	Busci	Montereale	Flysch	923	553	82	25.7	8.5	1.3	0.009	356	14.6	15.5	0.7	14	489
18	ATS26	Gabbia2	Montereale	Marly	1090	334	71	1.0	8.0	1.3	0.009	212	17.5	12.7	1.4	2.9	312
19	ATS12	Fra'Clemente	Montereale	Flysch	916	570	79	24.1	8.0	1.3	0.010	342	17.4	12.7	1.4	13	473
20	ATS18	S.Giovanni	Montereale	Marly	858	408	93	1.6	4.7	0.4	0.005	289	3.0	2.7	0.4	8	392
21	ATS01	Molinello	Montereale	Marly	821	378	83	1.4	2.6	0.4	0.009	265	4.7	3.2	1.5	9	359
22	ATS27	F.te Palomba	Montereale	Marly	1191	298	84	2.3	2.3	0.4	12	189	4.4	2.4	0.8	5.1	283
23	ATS11	del Peschio	L'Aquila	Calcareous	1074	371	59	10.0	2.2	0.2	13	218	5.4	2.6	1.3	1.8	296
24	ATP02	Pozzo Cabbia	Montereale	Calcareous	1115	398	83	2.2	2.2	0.4	82	272	3.9	2.6	0.1	5.3	364
25	ATS25	Casale d'Abruzzo	Montereale	Marly	945	440	105	2.0	2.5	0.4	bdl	300	5.7	4.3	0.1	4.2	415
26	ATS02	Toppo	Pizzoli	Dolom. limest.	716	573	72	26.2	6.8	6.3	0.005	311	13.2	13.3	34.5	56	470
27	VMS58	Vecchia V.C.	Posta	Marly	990	347	67	1.2	2.0	1.0	0.002	211	2.9	3.0	1.3	nd	320
28	VMS03	Capo d'acqua	Posta	Calcar.-marly	790	396	61	1.0	1.8	0.4	0.054	204	3.3	2.0	1.7	nd	292
29	VMS05	Acqua Calda	Posta	Marly	730	444	89	1.7	2.4	0.4	0.083	289	3.6	5.0	0.6	nd	327
30	VMS01	S.Giusta	Cittareale	Flysch	807	490	91	2.7	3.4	0.9	0.002	285	4.0	4.0	0.8	nd	399
31	VMS37	Scendelle	Leonessa	Marly-calcar.	1099	474	99	1.8	1.9	0.5	0.005	311	3.4	2.7	bdl	nd	371
32	VMS10	Catarna	Leonessa	Marly-calcar.	1049	519	99	1.7	2.0	0.5	0.002	326	4.5	1.7	0.8	nd	415
33	VMS31	Stefano	Leonessa	Detritic	1033	413	84	1.4	1.6	0.4	0.002	251	2.9	2.6	0.4	nd	346
34	VMS32	Pratali	Leonessa	Detritic	1027	428	83	1.5	1.4	0.2	0.002	281	1.9	1.4	2.8	nd	354
35	VMS19	Sommatine	Borbona	Flysch	780	428	108	20.4	6.8	1.3	0.019	325	6.9	12.8	1.8	nd	470
36	VMS54	Vecchia S.G.	Cittareale	Calcar.-marly	1352	278	94	0.2	1.6	0.6	0.001	246	4.6	1.8	8.4	nd	355

Table 1 (continued) - Major and minor element contents and other main features of the analyzed spring and well (N.11 and 24) waters (E.C.: specific electrical conductivity; TDS: total dissolved salts; bdl: below detection limit; Fe: total Fe; nd: not detected).

	SampleLabel	Name	Municipality	Litofacies	Elevation m a.s.l.	E.C. µS/cm	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Fe mg/l	HCO$_3$ mg/l	Cl mg/l	SO$_4$ mg/l	NO$_3$ mg/l	SiO$_2$ mg/l	TDS mg/l
37	VMS59	Orlando	Leonessa	Pedog. volc.	890	406	77	1.5	3.6	1.8	0.099	301	3.9	4.1	1.3	nd	390
38	VMS26	Mandra Vecchia	Cittareale	Flysch	825	508	79	22.5	12.1	2.0	0.002	373	10.7	18.7	1.1	nd	500
39	VMS40	La Moglia	Cittareale	Marly	1061	473	125	1.3	3.0	0.5	0.002	301	4.2	6.0	0.9	nd	436
40	VMS27	Fratoldi	Posta	Calcar.-marly	844	391	97	0.3	2.6	0.2	0.002	309	3.5	2.2	0.2	nd	413
41	VBS15	Brignola	Borbona	Marly	1188	369	80	1.3	1.7	0.5	bdl	298	2.8	0.9	0.2	369	385
42	VBS25	Vignola	Antrodoco	Detritic	765	603	116	2.0	13.5	1.4	0.007	372	24.9	4.2	8.0	nd	538
43	VBS09	Presa S.Angelo	Micigliano	Calcar.-marly	960	437	54	4.9	1.9	0.5	0.005	205	3.9	2.9	1.2	nd	271
44	VBS22	Molina	Castel S.Angelo	Calcareous	1175	286	58	0.8	2.3	0.6	0.001	194	4.2	3.6	1.4	nd	261
45	VBS17	del Rio	Castel S.Angelo	Flysch	460	837	153	20.6	4.0	1.3	0.006	563	5.2	32.2	2.7	nd	749
46	VBS23	Malanotte	Castel S.Angelo	Marly	960	318	65	0.8	3.0	0.7	0.002	217	6.3	4.3	0.9	nd	294
47	VBS22a	Capelacqua	Castel S.Angelo	Marly	820	440	93	2.9	3.7	0.6	0.001	318	5.8	4.0	0.8	nd	425
48	VBS14	del Lago	Borbona	Calcar.-marly	1340	323	83	0.4	2.3	0.5	0.001	262	4.3	2.6	0.9	nd	353
49	VBS11	Campetto	Micigliano	Marly	904	308	100	1.7	3.3	0.4	0.002	222	5.0	8.5	0.7	nd	333
50	VBS03	Regnola	Micigliano	Marly	1070	334	73	1.0	2.4	0.2	0.004	262	3.5	5.3	0.3	nd	342
51	VBS60	I Pisciarelli	Posta	Calcar.-marly	950	229	39	3.0	1.3	0.3	0.002	206	2.2	1.9	0.8	nd	253
52	VBS13	Palombara	Borbona	Calcar.-marly	1080	323	109	0.7	2.8	0.2	0.001	317	5.9	2.4	0.3	nd	436
53	VBS20	le Fontanelle2	Borgovelino	Flysch	925	315	202	22.3	4.2	1.2	0.001	619	4.7	43.4	2.2	nd	855
54	VBS08	Faugette	Micigliano	Marly-calcar.	1114	398	91	1.1	3.1	0.3	0.002	293	4.2	5.4	0.2	nd	393
55	VBS04	Cechi Alta	Micigliano	Marly	1117	309	74	1.5	2.4	0.2	0.005	230	4.5	4.5	0.3	nd	312
56	CT03	Campotosto1	Campotosto	Flysch	1330	583	119	12.3	6.8	2.8	10	359	14.5	11.4	20.3	5	535
57	CT04	Campotosto2	Campotosto	Flysch	1330	513	83	21.0	7.5	5.4	7	299	13.4	23.0	16.7	2.6	446
58	CT05	Campotosto3	Campotosto	Flysch	1330	329	51	16.2	3.4	1.2	8	192	4.6	27.4	0.9	5.6	269
59	S01	M.S.Franco 1	L'Aquila	Marly	1471	206	49	1.0	1.3	0.6	6	214	2.2	2.3	1.4	2.1	270
60	S02	M.S.Franco 2	L'Aquila	Marly-calcar.	1475	206	65	2.7	4.0	0.2	5	229	3.6	1.5	0.04	4.4	305
61	S05	M.S.Franco 3	L'Aquila	Marly	1600	215	50	0.6	0.9	0.2	8	238	1.3	1.5	1.4	2.3	292
62	S06	M.S.Franco 4	L'Aquila	Marly-calcar.	1730	240	55	0.6	1.2	0.3	5	228	2.0	2.1	2.0	2.3	289
63	S07	M.S.Franco 5	L'Aquila	Marly	1225	275	62	1.7	2.7	0.4	9	199	5.1	2.7	0.6	2.6	272
64	S08	Valle dell' Acqua	Pizzoli	Calcar.-marly	1315	259	58	0.8	1.6	0.3	7	250	2.0	1.9	0.5	20.9	313
65	S10	Terre di Mocco	Pizzoli	Detritic	1448	416	83	14.1	2.9	0.8	bdl	201	3.4	16.2	0.4	9.5	306
66	S09	Rio del Colle	Pizzoli	Calcar.-marly	1330	270	61	1.2	1.6	0.2	15	189	2.1	2.2	0.5	7	256
67	S12	Renoso	Assergi	Marly	1225	314	76	1.7	1.7	0.3	5	204	3.5	1.7	0.9	13	288
68	S13	Colle Falcone	Assergi	Marly	1150	300	77	2.2	2.0	1.1	20	190	17.4	0.9	1.3	12	291
69	S14	Pratonisco	Pizzoli	Calcar.-marly	1825	185	44	0.6	1.2	0.02	10	114	1.8	1.7	0.4	6.4	162

of the spring waters, they do not evidence significant trends with time. As concerns electrical conductivity, it is possible in any case to group the average value characterising each spring in discrete intervals (Figure 3). Excluding the few sulphuric/sulphate water springs having values >700 µS/cm, it was possible to define two classes with low-intermediate (180-360 µS/cm) or intermediate-high (380-680 µS/cm) ranges of values. In these two classes are mainly included springs occurring within the calcareous to marly and within the flysch deposits, respectively. This preliminary evidence has addressed the grouping criteria here adopted.

It is worthy of note that most of springs show perched and high altitude features and have low discharge values (<10 l/s), while springs occurring at the piedmont and down-valley may reach 10-100 l/s, with the exception of one spring reaching few hundreds l/s.

Furthermore, the ion chemistry information allowed us to target a hydrogeochemical characterization and classification of the springs and their grouping in hydrogeochemical facies, contributing to the definition of hydrogeochemical trends. This topic will be in detail discussed in this paper.

Analytical methods

Sampling and analysis of spring and surface waters were performed by the Environmental Metrology Unit of ISPRA and by ARTA Abruzzo-L'Aquila Province Dept. The analytical procedures not reported in the present section were performed according to Belli et al. (2003).

Spring water sampling was performed at some fountains and at several water supply system collection points. Considering the characteristics of the sampling sites and that in the second situation the samples were taken at the outside of sedimentation tanks, we assumed that in all these cases no suspended solid was present in the waters and so no field filtration was performed in order to determine the concentration of
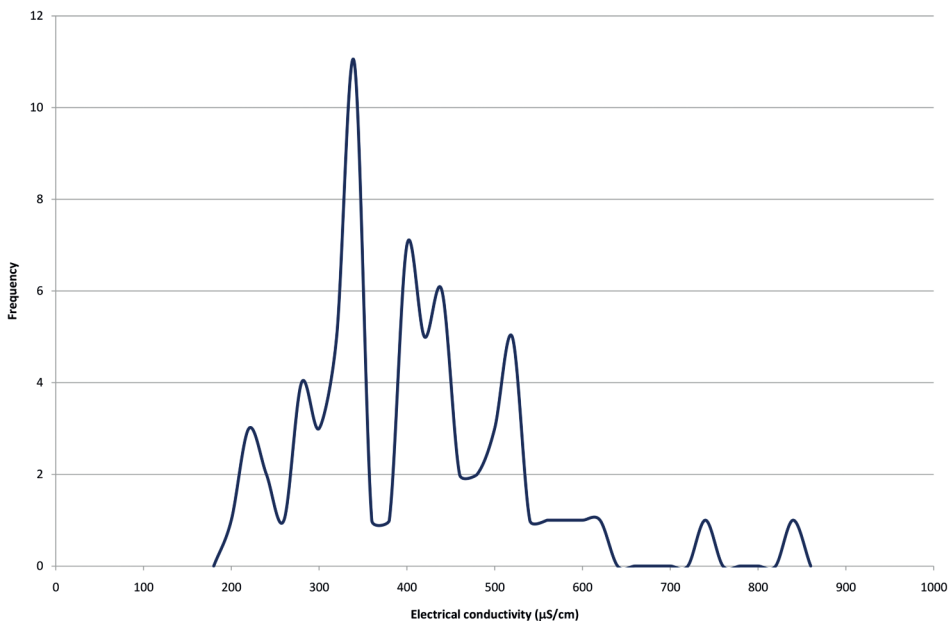

Figure 3. Distribution frequency of electrical conductivity values of the analysed spring waters.

dissolved elements. For only one surface water sample the acid extractable concentration (Belli et al., section 3000, 2003) was performed.

Well water sampling was conducted after well purging by a submerged pump, in order to obtain a representative groundwater sample for chemical analysis by the removal of stagnant water in the well casing and in its immediate nearby. It was estimated that at least two/three well volumes were purged. Sampling was conducted with the same device used for purging.

Physical-chemical parameters

As concerns temperature, pH and electrical conductivity of waters, they were analysed in situ using a multiparametrical portable instrument equipped with a four electrode measurement cell conductivity sensor and with a pH electrode system sensor, both enclosing a separate temperature sensor.

Sampling

At each sampling station four samples were separately taken in PET bottles for the analysis of trace elements, carbonates, anions and cations, respectively. The samples for the analysis of trace elements were acidified with 1% (in volume) of ultrapure nitric acid (67% vol/vol). The samples for the analysis of cations were acidified to pH 3 with ultrapure nitric acid (67% vol/vol). All samples were stored and transported at 4°C of temperature. The analyses were performed in laboratory within 24 hours from sampling. All samples for ionic chromatography, after conditioning at ambient temperature, were however filtered at 0.45 μm (IC Acrodisc) before analysis as safeguard of the chromatographic columns and in order to get the best performance.

Anion and cation measurements

The measurements of dissolved anions (chloride, nitrate, sulfate) and dissolved cations (sodium, potassium, calcium and magnesium) were performed by a double Metrohm IC761

ionic chromatograph equipped respectively with an anionic exchange column and a cationic exchange column in according to Italian official analytical methods APAT-IRSA 4020 and APAT-IRSA 3030 (Belli et al., 2003). The analysis of carbonate and hydrogen-carbonate was performed by a volumetric titration and a sodium carbonate 3.2 mM/sodium-hydrogen-carbonate 1.0 mM solution was used as eluent for the analysis of anionic species. For the analysis of cationic species an HNO_3 2.5 mM solution was used as eluent. After a screening analysis, the instrument calibration was performed with certified reference solution on five level of concentration. For each sample, three independent aliquots were analysed and all analytical procedure was controlled by using quality control solutions and quality control charts. The results were calculated as average of the three independent results and the repeatability standard deviation was used as uncertainty estimation (approximative reference value in mg/l: Cl= 0.05, NO_3= 0.05, SO_4= 0.05, Na= 0.05, K= 0.05, Ca= 0.5, Mg= 0.05).

Carbonate and hydrogen carbonate measurements

The analysis of carbonate and hydrogen-carbonate was performed by a volumetric titration in according to Italian official analytical method APAT - IRSA 2010 (Belli et al., 2003). The titration was performed using an HCl reference solution 0.02 N as titrant and a mixed indicator (Methyl Red - Bromocresol Green) and phenolphthalein indicator for the determination of equivalence point. For each sample, three independent aliquots were analysed and all analytical procedure was controlled by using quality control solutions. The results were calculated as average of the three independent results and the repeatability standard deviation was used as uncertainty estimation (approximative reference value in mg/l: HCO_3= 5, CO_3= not detected).

Trace element measurements

The measurements of the following dissolved elements, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn, has been performed using a quadrupole ICP-MS (inductive coupled plasma mass spectrometer) Agilent 7500ce in according to UNI EN ISO 17294-2. The instrument was equipped with a Babington nebulizer and with an octopole collision cell in order to eliminate or reduce the isobaric and spectral interferences. External calibration and quality control has been applied using reference solutions certified in according to ISO Guide 34 and ISO 17025. For each sample, three independent aliquots were analysed and the results were calculated as average of the three independent results and the repeatability standard deviation was used as uncertainty estimation (approximative reference value in ppb: As= 0.005, Cd= 0.001, Co= 0.005, Cr= 0.05, Cu= 0.05, Fe= 0.1, Mn= 0.05, Ni=0.01, Pb= 0.01, Sn= 0.001, Zn= 0.1).

Results and discussion

The obtained major, minor and trace element contents of spring waters, along with other features of the sampling stations, are listed in Tables 1 and 2.

The spatial distribution of water points through the total territory of the sheet (about 605 km^2) is: i) 1 point each 2-3 km^2 for censed water points (total about 250); ii) 1 point each 9 km^2 for the monitored control points (total about 70); i) 1 point each 11 km^2 for the analysed control points (total 55).

The approximate spring distribution through the single most representative hydrogeological complexes is as follows: Calcareous complex (25%); Calcareous-marly complex (35%); Marly-calcareous and marly complex (15%); Flysch complex (25%). It is evident that most of the springs are distributed in the Calcareous-marly and Calcareous complexes, the most productive ones from the hydrogeological point of view, but a considerable number of them are also in the Flysch and Marly-calcareous and marly complexes, having as a matter of fact an essential role for groundwater supply purposes at the local scale. This means that we have assumed to have a sufficiently representative distribution of control points for a general reconstruction of the hydrogeochemical picture of the sheet area, representing the aim of the present work.

Finally, some samples from the neighbouring areas of Campotosto Lake and Mt. S. Franco were also analysed and their characteristic values were compared with those of samples collected within the Antrodoco Sheet area.

Hydrogeochemical characterization and classification of springs

The hydrogeological complex classification and the lithological features of the rocks where the spring waters crop out have been taken into account in the present section to delineate the hydrogeochemical features of the groundwater in the study area. As a consequence, the following classification in lithological categories has been adopted: arenaceous-pelitic deposits of the Laga Formation in flysch environment; calcareous deposits of carbonatic platform environment; marly-calcareous deposits of marine slope/margin environment; calcareous-marly and marly deposits of marine pelagic environment; dolomitized limestone and pedogenized volcanic rocks, each represented by a single sample. Finally, since the detritic (and alluvial) covers have a subordinate hydrogeological role, the samples cropping out within these deposits have been affiliated to the lithological category of the respective local substrate, as already defined by the former groups. The samples from the neighbouring areas of Campotosto Lake and Mt. S.Franco have also been considered and included in all the figures here reported.

The obtained chemical data have been

Table 2 – Trace element contents of a selection of the analyzed spring waters.

Sample	Label	Name	Litofacies	Elevation m a.s.l.	Cu µg/l	Mn µg/l	Cr µg/l	Co µg/l	Ni µg/l	Zn µg/l	As µg/l	Cd µg/l	Sn µg/l	Pb µg/l
27	VMS58	Vecchia V.C.	Marly	990	0.5	bdl	0.3	0.1	0.6	bdl	0.1	bdl	bdl	bdl
28	VMS03	Capo d'acqua	Calcareous-marly	790	0.5	21	0.2	0.2	0.1	bdl	0.1	bdl	bdl	0.1
29	VMS05	Acqua Calda	Marly	730	0.8	7	0.2	0.2	2.8	0.9	0.1	bdl	bdl	0.02
30	VMS01	S.Giusta	Flysch	807	0.3	bdl	0.3	0.1	0.2	0.3	0.1	bdl	bdl	bdl
31	VMS37	Scendelle	Marly-calcareous	1099	0.2	bdl	0.04	0.1	0.1	bdl	bdl	bdl	bdl	0.4
32	VMS10	Catarna	Marly-calcareous	1049	0.3	bdl	0.1	0.1	0.1	0.6	bdl	bdl	bdl	bdl
33	VMS31	Stefano	Detritic	1033	0.2	bdl	0.3	0.1	0.1	bdl	bdl	bdl	bdl	bdl
34	VMS32	Pratali	Detritic	1027	0.2	bdl	0.4	0.1	0.1	bdl	0.01	bdl	bdl	bdl
35	VMS19	Sommatine	Flysch	780	0.3	4	0.9	0.04	0.1	0.4	0.3	0.01	0.003	0.05
36	VMS54	Vecchia S.G.	Calcareous-marly	1352	0.2	bdl	0.2	0.03	0.1	0.7	0.1	0.004	bdl	bdl
37	VMS59	Orlando	Pedog. volcanics	890	0.7	6	0.4	0.1	0.4	0.7	0.3	0.02	0.01	0.6
38	VMS26	Mandra Vecchia	Flysch	825	0.1	bdl	1	0.03	0.1	0.1	0.3	0.01	bdl	bdl
39	VMS40	La Moglia	Marly	1061	0.5	bdl	0.1	0.04	1.1	2.6	0.1	0.01	0.004	0.02
40	VMS27	Fratoldi	Calcareous-marly	844	0.2	0.4	0.3	0.04	0.3	0.4	0.1	0.01	0.001	0.01
42	VBS25	Vignola	Detritic	765	0.1	0.3	0.8	0.1	0.2	1	0.2	0.02	0.0004	bdl
43	VBS31	Presa S.Angelo	Calcareous-marly	960	0.2	0.1	0.2	0.04	0.2	0.8	0.2	0.01	0.002	bdl
44	VBS22	Molina	Calcareous	1175	0.2	bdl	0.2	0.04	0.1	0.3	0.1	0.01	0.01	bdl
45	VBS17	del Rio	Flysch	460	3.6	0.1	0.5	0.1	1.2	0.8	1.0	0.01	0.004	bdl
46	VBS23	Malanotte	Marly	960	1.5	bdl	0.2	0.1	0.2	2.5	0.1	0.01	0.04	bdl
47	VBS22a	Capelacqua	Marly	820	0.1	bdl	0.2	0.1	0.5	1.2	0.1	0.01	0.004	bdl
48	VBS14	del Lago	Calcareous-marly	1340	0.2	bdl	0.3	0.03	0.1	0.4	0.1	0.01	bdl	bdl
49	VBS11	Campetto	Marly	904	0.6	bdl	0.3	0.03	0.1	0.6	0.1	0.01	0.01	bdl
50	VBS03	Regnola	Marly	1070	0.3	0.02	0.2	0.03	0.4	0.03	0.7	0.01	bdl	0.01
51	VBS60	I Pisciarelli	Calcareous-marly	950	0.4	0.1	0.2	0.02	0.2	0.8	0.1	0.01	0.002	0.3
52	VBS13	Palombara	Calcareous-marly	1080	0.4	bdl	0.2	0.05	0.3	1.3	0.1	0.01	0.001	0.01
53	VBS10	le Fontanelle	Flysch	925	0.2	bdl	0.5	0.03	0.4	0.4	0.6	0.01	0.001	0.01
54	VBS08	Faugette	Marly-calcareous	1114	1	bdl	0.2	0.03	1.7	1.3	0.1	0.02	0.01	0.02
55	VBS04	Cechi Alta	Marly	1117	1	bdl	0.2	0.03	0.1	0.8	0.1	0.01	0.04	0.04

(bdl: below detection limit; Mn: total Mn; Cr: total Cr).

represented in a Piper (1944) diagram in order to classify the spring waters on the basis of the major ion contents. All the analysed samples fall indistinctly in the field of the bicarbonate-calcic waters (Figure 4). But, at a more detailed scale, it is possible to distinguish the field of the spring waters that have interacted with flysch deposits from most of those associated to calcareous and calcareous-marly deposits, on the basis of the higher SO_4+Cl and lower HCO_3+CO_3, among anions, and higher Mg, as well as slight higher Na+K, and lower Ca, among cations, in the Piper diagram. This agrees with the distribution fields of terrigenous and carbonatic groundwaters from other locations of the Abruzzo region (e.g., Desiderio et al., 2006). In addition, also considering the ionic formulas of the analysed spring waters (sensu Castany, 1968; i.e., the relative abundance of main cations and anions), it is evident, in agreement with the hydrogeological evidences, a signature inherited from calcareous(-dolomitic) hosting lithologies.
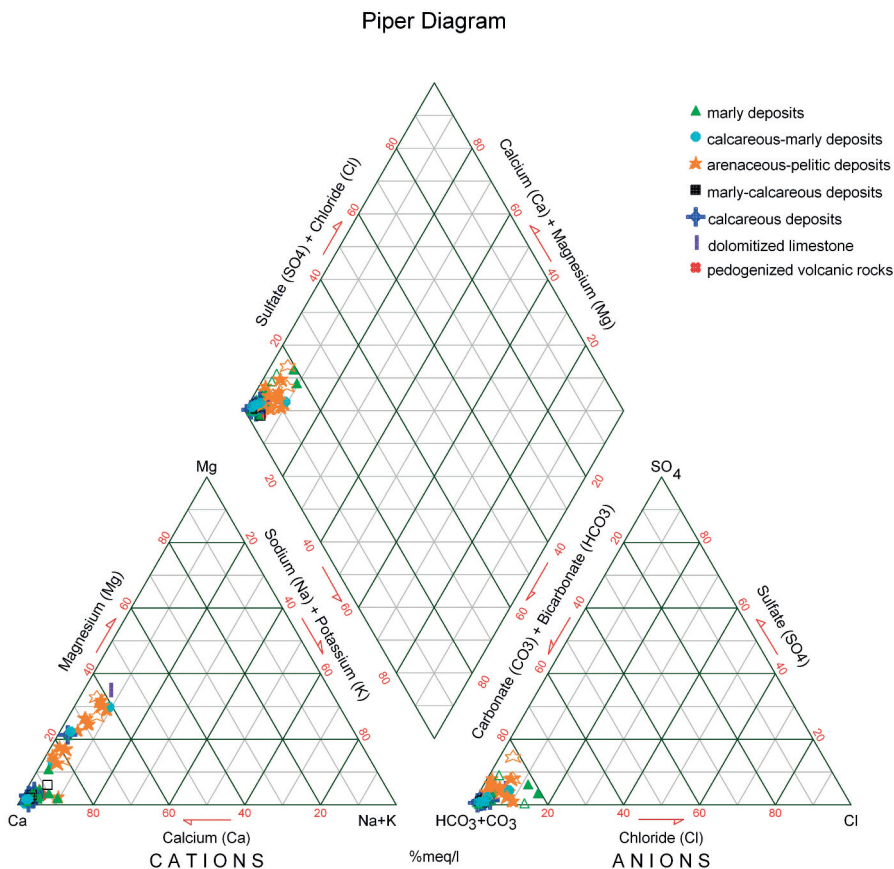
Figure 4. Piper diagram of the analysed spring water samples affiliated to: full orange star: arenaceous-pelitic deposits in flysch environment; full blue cross: calcareous deposits of carbonate platform environment; full black square: marly-calcareous deposits of marine slope margin environment; full light-blue circle: calcareous-marly deposits of marine pelagic environment; full green triangle: marly deposits of marine pelagic environment; full violet vertical stick: dolomitized limestone; full red square: pedogenized volcanic rocks. Open symbols refer to samples from the neighboring areas of Campotosto Lake and Mt. S. Franco.

Furthermore, it is possible to note a peculiar tendency to a relative enrichment in SO_4 and Cl for samples that underwent hydraulic interaction also with flysch deposit formations (see explanation after-written).

Some further aspects may be shown more in detail by a Chebotarev (1955) diagram (Figure 5), in which, within the waters affiliated to carbonate formations, it is evident that springs associated to calcareous deposits of marine carbonate platform environment have a relatively different position respect to those related to marly-calcareous deposits of marine slope margin, and both of them are spread within the field of springs occurring in marly marine pelagic deposits. These features may be due to the fact that samples from calcareous platform environment (representing the purest limestone of the local series) assume the nearest position toward the calcium-carbonate corners of the two previous diagrams, while the marine slope margin samples (since they have been interested by contamination of terrigenous materials in various amount) show a tendency toward the flysch sample field.

The earlier defined general features of bicarbonate waters of the analysed samples may also be established in the TDS (total dissolved solids)-SO_4 plot (e.g., Celico, 1986; Figure 6) and, in addition, the characteristics of waters circulating in limestone-rich formations may be confirmed in the Ca-SO_4 plot (e.g., Celico, 1986; not reported here).

In order to obtain further information on the affiliation of the spring waters to a specific hydrogeochemical facies, the D'Amore et al. (1983) chemical parameters were applied. In the diagram of Figure 7 a general similitude with other spring waters of Central Italy districts (D'Amore et al., 1983; Castracani et al., 1995) which have interacted with reservoir rocks mainly constituted of sediments deposited in calcareous facies, is shown. This is in agreement with the suggestions here previously proposed,

following other hydrogeochemical criteria, and with the hydrogeological evidences. The few exceptions to this general trend are probably due to differences, both in positive and negative, in the values of the chemical parameter D in the horizontal axis in Figure 7, as calculated for samples that interacted with flysch and dolomitic deposits, tending toward the arenaceous and/or evaporitic typical values, likely reflecting terrigenous and/or dolomitic/sulphatic hydrogeochemical facies imprinting. The Schoeller (1958) diagram (Figure 8) confirms the whole similar composition, and then hydrogeochemical facies provenance, for most of the analysed spring waters. In fact, the relative similar characteristic ratios among the considered ions are graphically expressed by the sub-parallel pattern of most of the segments constituting the distinguishing lines of each typology of spring. In addition, the plot of Figure 8 highlights the relatively high variability of ion concentration values of Schoeller's parameters arising after the comparison among each spring group. In this respect, it is possible to support that, with respect to the corresponding values of the other distinguished groups, samples associated to aquifers related to flysch and dolomitic lithologies are enriched in Mg, Na+K, Cl and SO_4, likely due to mineralogical and geochemical composition of these rocks. On the whole, that may be likely explained by the evidence that flysch deposits occurring in the study area are arenaceous±pelitic deposits (e.g. Laga Formation) associated to evaporitic sedimentation during Messinian age and dolomitic deposits have Triassic evaporitic origin or are due to dolomitization processes on calcareous and calcareous-marly rocks; then, both flysch and dolomitic deposits may contain Mg-, Na+K-, Cl- and SO_4-bearing pelitic (e.g., chlorite and clay minerals) and evaporitic (e.g., gypsum and halite) minerals, that may have been leached by groundwaters leading their enrichment in these species. The pattern
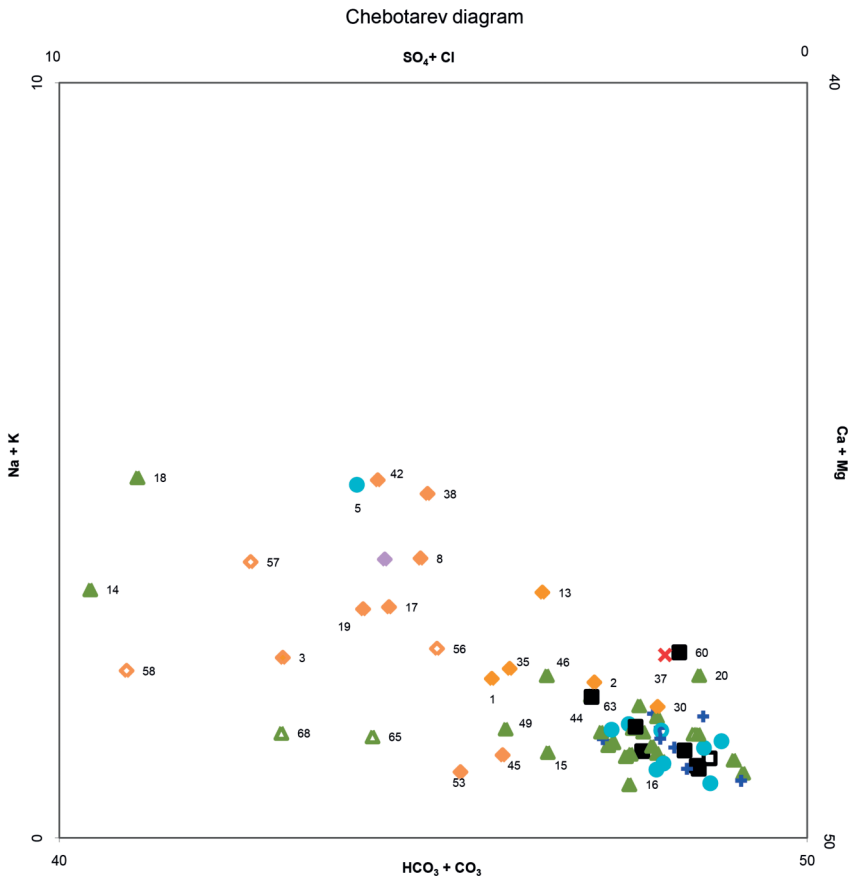
Figure 5. Chebotarev diagram of the analysed spring waters affiliated to: full orange rhomboid: arenaceous-pelitic deposits in flysch environment; blue cross: calcareous deposits of carbonate platform environment; full black square: marly-calcareous deposits of marine slope margin environment; full light-blue circle: calcareous-marly deposits of marine pelagic environment; full green triangle: marly deposits of marine pelagic environment; full violet rhomboid: dolomitized limestone; red slanting cross: pedogenized volcanic rocks. Open symbols refer to samples from the neighboring areas of Campotosto Lake and Mt. S. Franco. Sample numbers refer to Table 1.

displayed by waters which interacted with calcareous-marly deposits shows the clearest correspondence with the line representing the mean values of the considered parameters of the whole waters.

The K-Mg-Na ternary diagram (Boni et al., 1995; not reported here) has been also taken into consideration to exclude, in agreement with the geological evidences and with the element contents of other spring waters of many localities of Latium region, a contribution of water circulating in volcanic rocks and to point out the major interaction with carbonatic rocks (relatively high Mg and Na contents respect to K). It is worth noting that, also in this kind of diagram, the samples associated to the flysch hydrogeochemical facies are mainly disposed towards the Mg corner respect to that of Na.
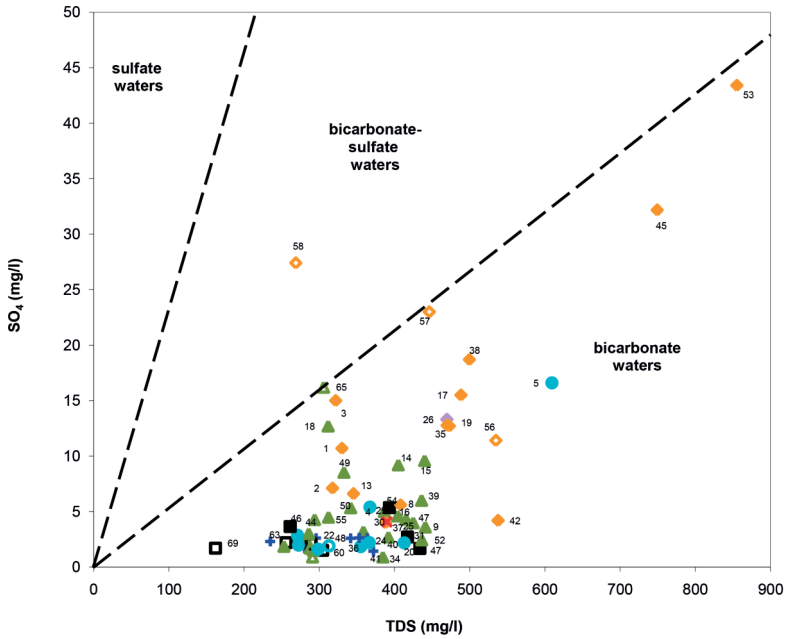
Figure 6. TDS-SO$_4$ diagram of the analysed spring waters affiliated to: full orange rhomboid: arenaceous-pelitic deposits in flysch environment; blue cross: calcareous deposits of carbonate platform environment; full black square: marly-calcareous deposits of marine slope margin environment; full light-blue circle: calcareous-marly deposits of marine pelagic environment; full green triangle: marly deposits of marine pelagic environment; full violet rhomboid: dolomitized limestone; red slanting cross: pedogenized volcanic rocks. Open symbols refer to samples from the neighboring areas of Campotosto Lake and Mt. S. Franco. Dashed lines represent the boundary between fields characterizing bicarbonate, bicarbonate-sulfate and sulfate waters. Sample numbers refer to Table 1.

The mutual relationships among the analysed elements were also discussed by the elaboration of binary concentration diagrams. Taking into account the whole set of data, it is evident a relatively good positive correlation (R^2 is about 0.70) between Ca and HCO$_3$ values (Figure 9), in agreement with the general bicarbonate-calcic features of the spring waters. Furthermore, it is remarkable that, considering the same correlation separately for water samples affiliated to flysch and to carbonate and marly formations, the calculated R^2 resulted 0.83 and 0.52, respectively. The higher R^2 value shown by waters that interacted with flysch deposits respect to those that interacted with calcareous

and marly terrains may explain the different features shown by each subgroup within the former group of waters.

Other ion pairs have also enough good positive correlation (Na-Cl, R^2 is about 0.63; Mg-SO$_4$, R^2 about 0.57) maybe since these pairs represent coupled dissolved species (from NaCl and MgSO$_4$, respectively). On the other hand, further ion pairs are loosely correlated (e.g., Mg-Na, R^2 is about 0.43; HCO$_3$-SO$_4$, R^2 about 0.41; K-Cl, R^2 about 0.31; Mg-HCO$_3$, R^2 about 0.28; Mg-Cl, R^2 about 0.19; K-SO$_4$, R^2 about 0.15). In any case, in all the elaborated plots of reported pairs, as previously noted regarding the Piper (Figure 4) and Chebotarev (Figure 5) diagrams, it has
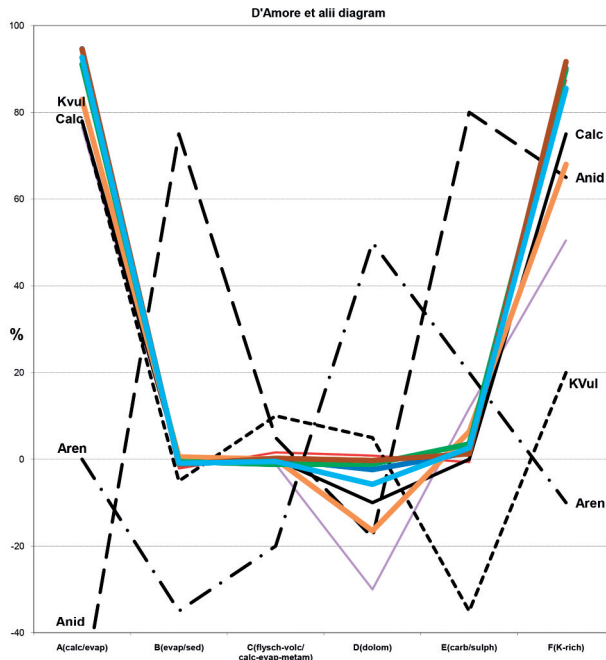
Figure 7. D'Amore et al. (1983) diagram of the mean values of the analysed spring waters grouped according to their affiliation to the following lithological deposit classification: orange line: arenaceous-pelitic deposits in flysch environment; blue line: calcareous deposits of carbonate platform environment; brown line: marly-calcareous deposits of marine slope margin environment; light-blue line: calcareous-marly deposits of marine pelagic environment; green line: marly deposits of marine pelagic environment; violet line: dolomitized limestone; red line: pedogenized volcanic rocks. Reference lines (in black) for waters from Central Italy districts affiliated to: Calc= calcareous rocks; Aren= arenaceous rocks.; KVul= K-volcanic rocks.; Anid= anidritic rocks.

been evidenced a distinct position for spring waters associated to flysch hydrogeochemical facies respect to other spring water groups, in particular to those related to carbonate platform formations. In particular, K, Na, Mg, SO_4 and Cl are the ions showing higher concentrations in waters that interacted with flysch formations within the study area and around it, in agreement with what previously stated about the arenaceous±pelitic and evaporitic features of flysch terrains.

The characteristic chemical ionic ratios (sensu Celico, 1986; rMg/rCa, rK/rNa, rCa/rNa, rSO_4/rCl) of the analysed samples show that the spring waters of the study area have similar features respect to other springs of Central Apennines circulating in carbonatic geological environment (rMg/rCa<0.4, rK/rNa<0.29, rCa/rNa>10 and rSO_4/rCl<2.6; Celico et al., 1984; Castracani et al., 1995). It is well known that the Mg/Ca ratio in groundwater has clear geochemical implications, i.e. it reflects the composition of the calcareous rocks in the reservoir and the dolomite *vs.* calcite saturation processes (e.g., Langmuir, 1971; Zotl, 1974; Hem, 1985; Zojer and Stichler, 1988). In this respect, among spring waters we supposed were affiliated to arenaceous-pelitic deposits in flysch environment, it is noteworthy that, plotting the rMg/rCa ratios *vs.* TDS values (Figure 10), spring
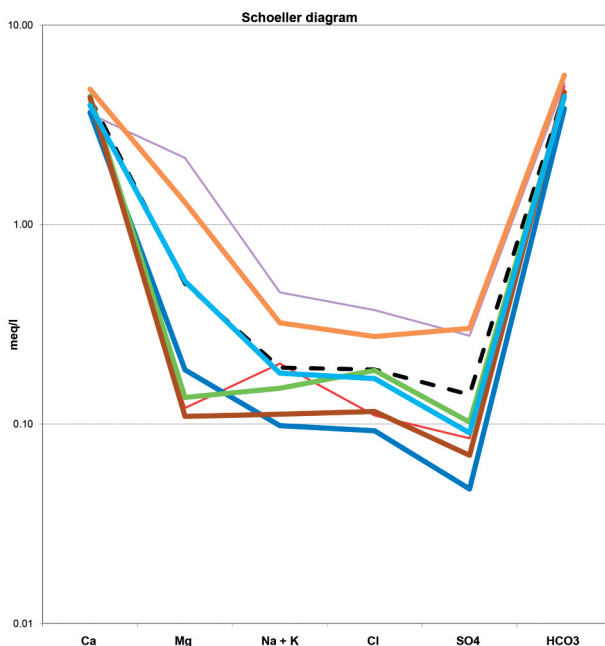
Figure 8. Shoeller diagram of the mean values of the analysed spring waters grouped according to the proposed lithological classification. Colour key legend as in Fig.7.The black line has been traced by the general mean of the obtained values.

waters falling in the field of waters circulating in marly-arenaceous-molassic aquifers correspond to those actually showing evidence of occurrence within the Flysch hydrogeological complex and having the highest rMg/rCa ratios (samples N.8: ATS21, Pannacio/Aringo; N.17: ATS22, Busci; N.19: ATS12, Fra' Clemente; N.38: VMS26, Mandra Vecchia), while the others suggest different degree of contamination and interaction with calcareous aquifers. Assuming that the first four sample mean position represents the end-member composition of waters related to marly-arenaceous-molassic aquifers within flysch deposits and the mean position of the general field of waters associated to calcareous aquifers within platform, basin and margin carbonate deposits corresponds to the opposite end-member, it is possible to estimate, just considering the average values of these two end-members, the

approximate relative flysch-calcareous groundwater mixing percentage of the other samples (samples N.3 "ATS16, Capporone" and N.13 "ATS10, dei Frati": $flysch_{65}$-$calcareous_{35}$; N.35 "VMS19, Sommatine": $flysch_{60}$-$calcareous_{40}$; N.45 "VBS17, del Rio" and N.53 "VBS20, le Fontanelle2": $flysch_{55}$-$calcareous_{45}$; N.1 "ATS14, Spinilli": $flysch_{30}$-$calcareous_{70}$; N.2 "ATS15, Petriano": $flysch_{15}$-$calcareous_{85}$; N.30 "VMS01, S. Giusta" and N.42 "VBS25, Vignola": $flysch_{05}$-$calcareous_{95}$). The rMg/rCa ratios have been selected to discriminate water interaction with flysch deposits since by other ionic ratios (e.g., rK/rNa, rCa/rNa, rSO_4/rCl) this process was less clearly evident. Furthermore, the high rMg/rCa ratio of sample 26 (Figure 10), representative of groundwaters which reacted with dolomitized host-rocks, is likely due to the expected higher degree of saturation of these
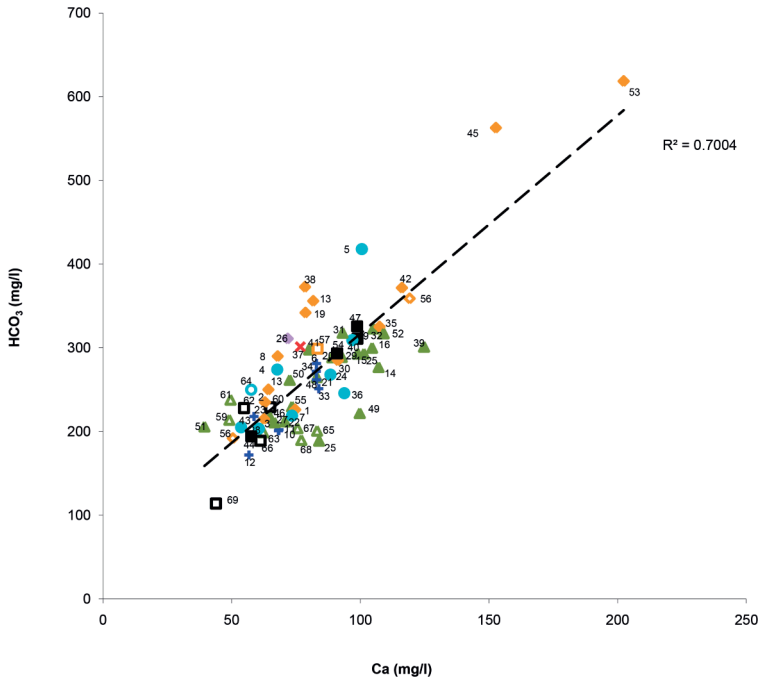
Figure 9. Ca-HCO$_3$ diagram of the analysed spring waters affiliated to: full orange rhomboid: arenaceous-pelitic deposits in flysch environment; blue cross: calcareous deposits of carbonate platform environment; full black square: marly-calcareous deposits of marine slope margin environment; full light-blue circle: calcareous-marly deposits of marine pelagic environment; full green triangle: marly deposits of marine pelagic environment; full violet rhomboid: dolomitized limestone; red slanting cross: pedogenized volcanic rocks. Open symbols refer to samples from the neighboring areas of Campotosto Lake and Mt. S. Franco. Sample numbers refer to Table 1. The regression line and the relative R^2 value are displayed.

groundwaters with respect to dolomite than with respect to calcite, with obvious Mg enrichment.

As concerns trace element contents of metals, analysed only in a selection of spring waters, their values are in general very low (Tab. 2), probably indicating neither relationships among their occurrence in spring waters and the specific features of the groundwater host rocks which springs are affiliated to, nor significant derivation and enrichment of the analysed species by other external sources and/or geochemical processes. In this view, as expected, no clear mutual correlations among metal chemical species and/or parameters have been noted.

Regarding SiO$_2$ composition, the chemical contents within the cluster of detected samples are similar to those of waters that have interacted with calcareous-siliceous-marly formations of the Central Apennines (Celico et al., 1979, Celico et al., 1984; Castracani et al., 1995).

Since some of the analysed waters are used for water supply purposes, it is noteworthy to evidence that their trace element contents are all inside the threshold values defined by the Italian normatives (e.g.: D.Lgs.31/2001, on drinking water, and D.Lgs.152/2006, on protection from pollution, and further integrations and modifications).

Despite the ion chemical data of waters have been collected in different field surveys (October
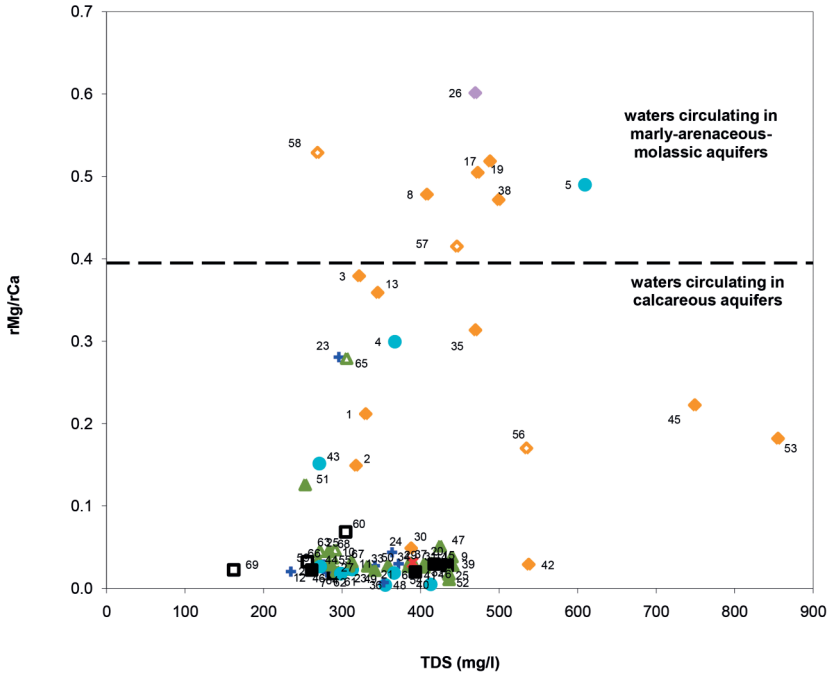
Figure 10. TDS-rMg/rCa diagram of the analysed spring waters affiliated to: full orange rhomboid: arenaceous-pelitic deposits in flysch environment; blue cross: calcareous deposits of carbonate platform environment; full black square: marly-calcareous deposits of marine slope margin environment; full light-blue circle: calcareous-marly deposits of marine pelagic environment; full green triangle: marly deposits of marine pelagic environment; full violet rhomboid: dolomitized limestone; red slanting cross: pedogenized volcanic rocks. Open symbols refer to samples from the neighboring areas of Campotosto Lake and Mt. S. Franco. Fields for waters circulating in calcareous and in arenaceous-molassic aquifers (after Castracani et al., 1993) are marked by a dashed line. Sample numbers refer to Table 1.

2007, January and June 2008 and March 2010), maps and cross-sections of the spatial distribution of the analytical values were constructed. Since no significant spatial trend distributions along cross-section traced both transversally and longitudinally to the main structures were evidenced and, regarding the distribution maps, it was only possible to note sectors with similar value ranges roughly corresponding to the areal distribution of the previously identified hydrogeological complexes, these maps will not be here shown.

Samples from the neighbouring areas of Campotosto Lake and of Mt. S. Franco and those from the Antrodoco Sheet territory show very analogous features, according to their affiliation to similar general geological environment facies (and/or hydrogeological complex type) of the hosting formations; then, independently from the territorial provenance of the samples, the former hydrogeological considerations about the study area may be assessed for a broader regional scenario.

Finally, some anomalous samples (e.g., N.53: VBS20, le Fontanelle2; N.42: VBS25, Vignola; N.45: VBS17, del Rio; N.5: ATS24, Fonte) have been recognised within the previous plots, as they display relative high contents of some of the

main analysed elements (e.g., Ca, K, Na, Cl, HCO_3, SO_4) and thus reflecting high TDS and electric condictivity values. This is likely due to contamination of the bicarbonate-calcic waters, representing the typical local hydrogeochemical facies, with waters of different origin (sulphate, deep seated circulation, etc.).

Analysis of the relationships among physical-chemical variables

Methodology applied for outlier data verification. A preliminary stage of the data evaluation has dealt with the significant deviations from the mean values of some of the analyzed elements (univariate outliers). To this purpose, the results of four different analytical methods were compared.

Figure 11 shows the distribution features of the main significant variables considered in this paper, evidenced by the box-plot graphical method (Tukey, 1977). Another method is based on the following relation:

$$Z = (X - X_m) / S$$

where X_m and S represent the mean and the standard deviation, respectively, X a single sample value and Z the number of standard deviations associated to that value. The sample value having a Z higher than the critical threshold of 3 is considered as an outlier (Norman, 1998) (Table 3).

Alternatively, the *huge rule* empirical formula (De Muth, 1999) may be applied:

$$M = (X - X_m) / S$$

where, instead of the Z parameter, the M parameter is obtained using the mean and standard deviation calculation without taking into account the X value of the sample under examination. The critical threshold M value of 4 is applied in this method for the evidencing of potential outlier samples.

All the three formerly exposed criteria produce their best results if a gaussian data distribution occurs.

An evaluation method not depending from the knowledge or hypothesis on the distribution features is based on the "Chebyshev inequality" (Papoulis, 1991). This criterion evaluates the affiliation probability of a specific element to a reference population.

The inequality is expressed by the relation:

$$P < k^{-2}$$

where k is the number of standard deviations existing between the sample value and the arithmetical mean and P is the probability that the value is included within that range. The criteria is appropriate if k>1. The same Table 3 displays the P values < 20% of the analyzed parameters. Below this value the evidenced outlier elements are the same obtained by the Z and M parameters.

The next sections will deal with the results of the whole of the three former tests, which have permitted the selection of the most significant elements to be submitted to a detailed verification for explaining the existence of the evidenced potential univariate outliers.
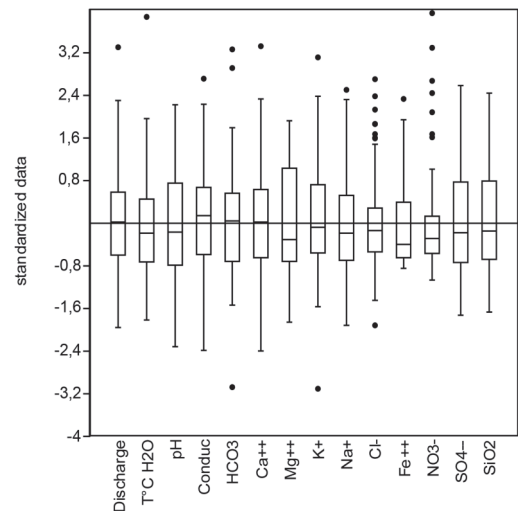

Figure 11. Box-plot of variables of the main analyzed parameters. Conduc= electrical conductivity.

Principal Component Analysis (PCA). The PCA is a multivariate statistical analysis technique, included in the factorial analyses class, aimed to individuate, starting from a huge number of variables, the components (called factors in the factorial analysis) which may explain the similitude among the variables themselves. Subsets of the considered variable set are related to each of the defined factor. In this study, for instance, the relationships among groups of physical-chemical variables and lithology of the groundwater reservoir have been tested.

A detailed description of some essential elements about the factorial analysis techniques are reported in Barbaranelli (2006).

The variables initially considered in this study are reported in Table 4, except for nitrates. Since the present work deals with the characterization

Table 3. Results of the correlation analyses carried out with three of the different criteria used for the individuation of univariate outliers (Temp.= temperature; E.C.= electrical conductivity).

	Sample	Temp	pH	E.C.	HCO_3^-	Ca^{++}	Mg^{++}	K^+	Na^+	Cl^-	Fe^{++}	NO_3^-	SO_4^{--}	SiO_2
Z-values method	n.05						11.61	6.75				6.50		
	n.26											3.61		4.34
	n.14								4.24					
	n.23	3.86												
	n.24										7.47			
	n.38								3.20					
	n.42								3.73	3.18				
	n.45			3.73	3.68								3.25	
	n.53				4.37	4.71							4.69	
Huge–rule method	n.05						11.60					10.27		
	n.26										17.58	8.72		6.10
	n.14								4.83					
	n.23	4.49												
	n.24													
	n.38								3.99					
	n.42								4.11	4.14				
	n.45			4.52	5.63	4.12							4.49	
	n.53				5.39	5.39							5.56	
Chebyshev inequ. meth.	n.05							2.19				2.37		
	n.26											7.67		5.32
	n.14								5.56					
	n.23	6.71												
	n.24										1.79			
	n.38								9.76					
	n.42								7.18	9.87				
	n.45			7.20	7.40	13.07							9.47	
	n.53				5.23	4.51							4.55	

of natural waters, nitrates will not be here discussed in detail, as they are of great importance for water contamination issues. Furthermore, SiO_2 concentration of waters was not considered in this preliminary stage of the study, since this information lacks for the springs of the Velino River Basin.

The distribution pattern of the values of some parameters has led to the necessity of conducting a logarithmic transformation recoding, as well as a standardization, on them.

In a preliminary stage of the analysis the whole of the available data has been considered. After that, a second PCA stage has been performed excluding all the univariate outliers already evidenced. Then, the individuation of multivariate outliers has been carried out by the Mahalanobis (1936) distance calculation criterion. Only one sample (N.53, Fontanelle2) may be considered as an outlier following this

criterion. The multivariate normality of the data has been confirmed by the calculation of the multivariate kurtosis index of Mardia (1974).

The values of probability of the correlation coefficients have been evaluated for each variable in a table showing the inverse image correlation matrix (not reported in this paper) and values very higher than 0.7, except for water temperature, pH and Fe concentrations were obtained. Consequently, the three previous variables were excluded and the PCA has been performed.

The rotated principal component elaboration using the "Varimax" (Barbaranelli, 2006) method has been adopted (Table 5 reports the relative total explained variance).

The number of the extracted components has been defined on the basis of the eigenvalues related to an explained variance higher than 10%. The first two not rotated factors of Table 5

Table 4. Correlation matrix of some of the main analyzed parameters (Temp.= temperature; E.C.= electrical conductivity).

	Altitude a.s.l.	Disch.	Temp. H_2O	pH	E.C.	HCO_3^-	Ca^{++}	Mg^{++}	K^+	Na^+	Cl^-	Fe^{++}	NO_3^{--}	SO_4^{--}
Altitude	1													
Discharge	-0.20	1												
Temp.	-0.31	-0.01	1											
pH	-0.18	0.37	-0.08	1										
E.C.	-0.69	0.04	0.26	-0.18	1									
HCO_3^-	-0.56	-0.12	0.34	-0.22	0.82	1								
Ca^{++}	-0.48	-0.20	0.20	-0.11	0.71	0.75	1							
Mg^{++}	-0.37	0.05	0.22	-0.17	0.50	0.47	0.08	1						
K^+	-0.31	0.19	0.15	-0.08	0.43	0.27	0.08	0.59	1					
Na^+	-0.40	-0.07	0.16	-0.10	0.51	0.45	0.26	0.59	0.54	1				
Cl^-	-0.27	-0.05	0.11	-0.12	0.43	0.24	0.27	0.33	0.55	0.74	1			
Fe^{++}	0.37	-0.11	0.07	-0.25	-0.41	-0.37	-0.29	-0.12	-0.13	-0.25	-0.01	1		
NO_3^{--}	-0.19	0.24	0.15	-0.03	0.29	0.14	0.05	0.38	0.88	0.33	0.43	-0.09	1	
SO_4^{--}	-0.39	0.02	0.05	-0.14	0.65	0.63	0.38	0.76	0.48	0.56	0.37	-0.27	0.24	1

satisfy this condition. Furthermore, their cumulative explained variance is 75.3% and, thus, satisfies an additional criterion, adopted for the definition of the number of principal components, which regards the minimum acceptable value of the cumulative explained variance (70%). A further confirmation is given by the eigenvalues of the other components, reported in Table 6, which may be excluded since their values are < 1 (Kaiser rule; Barbaranelli, 2006).

The obtained rotated component matrix (Tab. 6), that expresses the impact coefficient of the two extracted components, evidences the link between these latter and the groups of variables. It is noteworthy that component 1 is related to alkaline metals, sulfates and chloride variables, while calcium and bicarbonates are linked to component 2. Electrical conductivity displays significant values with respect to both the two components. The situation is graphically evidenced in the two component plot of Figure 12.

The physical interpretation of the two factors is apparent from the principal component saturation plot of the same Figure 12, where two main groups of variables related to physical-chemical features of waters from different aquifer typology are evidenced and, since they both fall within the positive value field, they are anti-correlated. The "A" group includes bicarbonate-calcic waters and electrical conductivity, while the "B" one consists of water with higher concentration of Mg, Cl, sulfates and alkaline metals. The electrical conductivity position may also be considered to be in-between the two previous groups. The elevation a.s.l. of the springs is generally linked to component 2 axes and is then anti-correlated with the bicarbonate-calcic water group and uncorrelated with the other variables (Figure 12). It is noteworthy to recall that this depicted principal component model includes outliers and, as previously introduced, excludes pH and Fe.

Along with the PCA, the group analysis (or hierarchical cluster analysis) of the physical-chemical variables has also been conducted. The obtained results (Figure 13) are in agreement with the PCA inferences, confirm the distinction into the two previous groups of variables and evidence the high Euclidean distances among the

Table 5. Total Variance Explained for some of the main analyzed parameters.

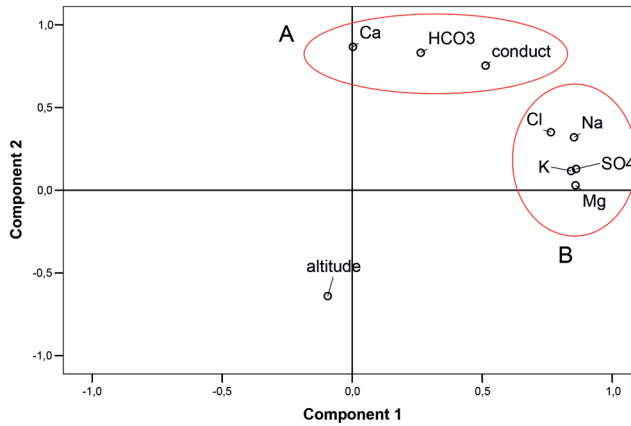| Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.4	59.5	59.5	5.4	59.5	59.5	3.9	43.4	43.4
2	1.4	15.8	75.3	1.4	15.8	75.3	2.9	31.9	75.3
3	0.6	7.2	82.5						
4	0.5	5.2	87.7						
5	0.4	4.0	91.7						
6	0.3	3.3	95.0						
7	0.2	2.4	97.4						
8	0.2	1.7	99.1						
9	0.1	0.9	100.0						

Figure 12. Factor score plot of components 1 and 2 in rotated space of the main analyzed parameters. A and B groups have been evidenced. conduct= electrical conductivity.

positions of both Fe and nitrates respect to the other factors.

Component 1 interpretation. The score values of the two principal components, calculated for each observation, have allowed the elaboration

Table 6. Rotated component matrix of some of the main analyzed parameters. The variables associated to each of the two principal components are evidenced in yellow. The elevation values are anti-correlated with the three variables of the component 2.

Rotated Component Matrix

	Component	
	1	2
altitude a.s.l.	-0.28	-0.75
electr. conductivity	0.57	0.62
HCO_3^{--}	0.30	0.88
Ca^{++}	0.10	0.92
Mg^{++}	0.82	0.17
K^+	0.84	0.22
Na^+	0.87	0.26
Cl^-	0.82	0.22
SO_4^{--}	0.77	0.32

of the dispersion plot of Figure 14, where the observation points (i.e. the analyzed samples) are distributed in the factorial plane. The distribution of the points is in agreement with that already shown in the model of Figure 12 regarding the physical-chemical variables, since the principal components are the same in both plots. The distribution pattern of the points, following a lithological criterion, shows the strong relation between the lithological typology and the component 1. It must be clarified that the proposed lithological classification is referred to the terrains cropping out in the surroundings of the water points. Then, this is really a general classification, since the hydraulic paths of groundwater may actually be very complex and the geochemical features of the reservoir rocks may differ with depth. This interesting issue may be comprehensively taken into consideration in a next paper, when all other local hydrogeological features will be examined in detail.

The factorial plot sketched in Figure 15 has been elaborated excluding the identified outlier samples (as better defined in the next section). The main remarks on this plot are as follows: i) samples associated to calcareous and marly
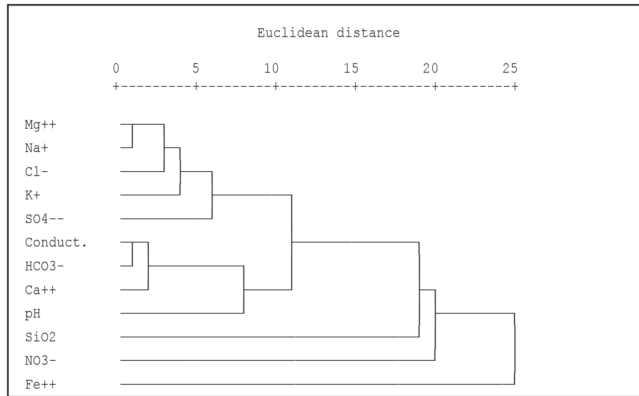
Figure 13. Cluster Analysis Tree Diagram for the main variables. Cunduct.= electrical conductivity.

deposits and having more clear bicarbonate-calcic features are within the A group domain; ii) the other samples, related to the arenaceous-pelitic flysch formation, are concentrated in the B group domain; iii) the only water point connected to a dolomitic aquifer is within the B group; iv) samples referred to detritic (and alluvial) covers and to altered (pedogenized) volcanic rocks are not evidently associated to any group, since no specific distribution has been recognized.

Verification and interpretation of the outlier samples. Outlier samples respect to the lithological component 1 have been defined in this study not only on the basis of their isolated or far position within the field of the plot, but also for their incompatible and/or unexpected position respect to the main field occupied by most of water samples related to the same lithological group. For instance, the springs named Fontanelle1 (N.14, ATS07) and Gabbia2 (N.18, ATS26), in the municipality of Montereale (L'Aquila province) are not affiliated to flysch deposits and are settled within the B group in Figure 14; they are about 1 km far one another, crop out within the marly formation of the Marne con Cerrogna and are located along a

tectonic contact with the Laziale-Abruzzese carbonate platform units. The water sample N.14 has displayed high Cl and nitrate concentrations, while sample N.18 has showed not immediately explicable high sulfate amounts. It is noteworthy that the anomalous situation evidenced by sample N.18 on the factorial plane has no confirmation in the high Chebyshev P value (49%) of its sulfate concentration.

Then, some situations may not be recognized as univariate outlier respect to the whole dataset analysis but they may be defined as outliers taking into account some subsets on the basis of selected factors, like the lithological one.

The relatively high Na and Cl concentrations of the Vignola spring water (N.42, VBS25) in the Antrodoco municipality and the high electrical conductivity values and K and nitrates amounts of the Fonte spring (N.5, ATS24) in the L'Aquila municipality, are likely due to local anthropic factors.

It is apparent (Figure 14) that the water samples from Fontanelle2 (N.53, VBS20) and del Rio (N.45, VBS17) springs, located near the Borgo Velino village within arenaceous sediments of Miocene age and near the overthrust alignment putting into contact the Umbro-Marchean terrains with more recent
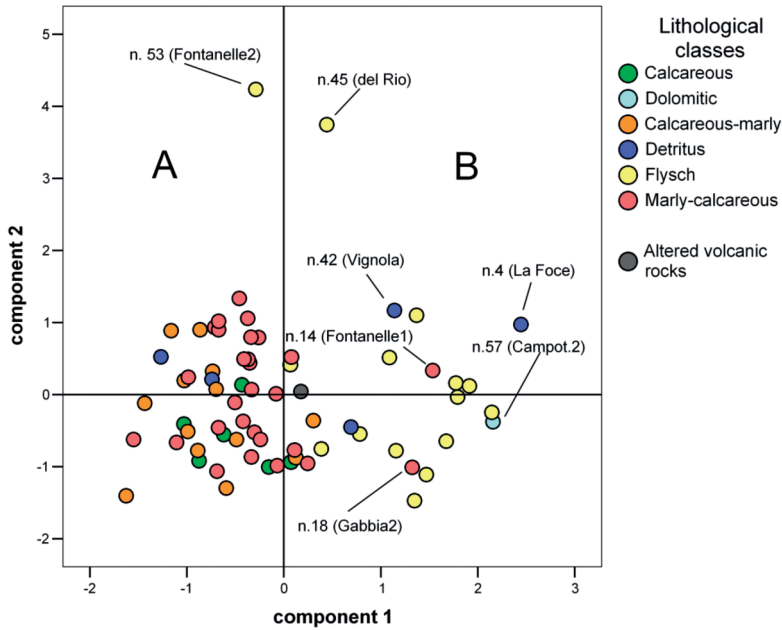
Figure 14. Factor score plot of components 1 and 2. Label indicate some outlier samples.

units, are far from the general field which all other samples fall in. This is probably due to their high TDS and sulfates concentrations, likely related to the presence of sulfuric/sulfate waters in the village surroundings (e.g., some springs next to the Borgo Velino railway station, Antrodoco thermal baths), probably linked to the uplift of deep sulfuric/sulfate waters along local structural-tectonic alignments (e.g., Boni et al., 1986, Desiderio et al., 2006).

Component 2 interpretation. Table 5 shows an explained variance by component 2 of about 16% of the total considering both initial eigenvalues and extraction sums of square loadings methods.

As regards the altitude factor, contrarily to the lithological component, a clear distribution pattern of the observation points has not been obtained on the basis of the same scoring

criterion of the principal component model. Nevertheless, excluding the intermediate elevation class scores and including only the higher and lower elevation classes (>1,300 and <900 m a.s.l., respectively), two distinct groups along the vertical axes (component 2) are evident (Figure 16).

Furthermore, along component 2 axes (Figure 12) is also apparent the anti-correlation of Ca^+, HCO_3^- and electrical conductivity factors of group A respect to the elevation, while the analyzed ions of the B group are not significantly correlated. Is then evident that component 2 is clearly associated to elevation.

A further analysis stage has been carried out, excluding outlier values as previously already defined. Then, it has been obtained, in the factor score plot, a significantly improved two-component model with respect to the previous one. Both the results of the test of adequateness
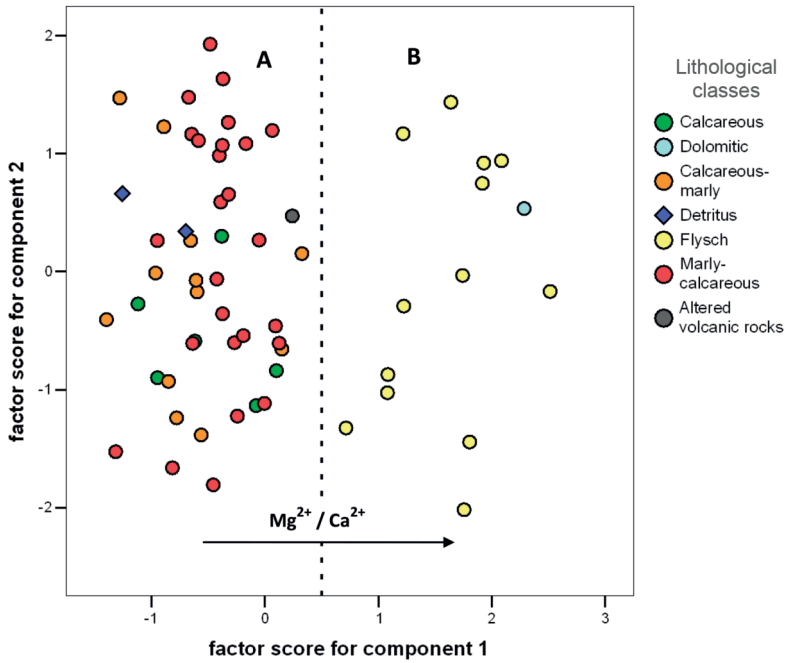
Figure 15. Factor score plot of components 1 and 2, elaborated excluding the observations regarding outlier samples. The A and B groups are distinguished along the component 1 axes on the basis of the lithological classification reported in legend.

of the correlation matrix and the distribution consistency of each of the evidenced groups have been enhanced (Figure 15). In particular, is noteworthy the only presence of springs related to the flysch lithological class in the B group, exception made for the Toppo spring (Pizzoli municipality; N.26, ATS02), associated to the dolomitic complex, having high Mg and sulfate concentrations.

Conclusions

The present work represents an approach for a possible improvement of the CARG Project (Italian geological mapping) by the realization of multidisciplinary surveys, including hydrogeological activities, in the test-site of the Antrodoco Sheet territory, located between Lazio and Abruzzo regions (Rieti and L'Aquila province, Central Italy). Research activities about water sources (springs, wells) existing in the Antrodoco Sheet territory have been carried out in order to characterise the hydrogeological asset of the study area. In particular a detailed screening of the water springs was carried out and a control network has been constituted; some control points were in addition selected to perform chemical analyses of spring water. The obtained information allowed us to target a hydrogeochemical characterization and classification of the springs and their grouping in homogeneous datasets, representing a contribution to the definition of evolutional trends and the assessing of a groundwater circulation model of the involved aquifers.
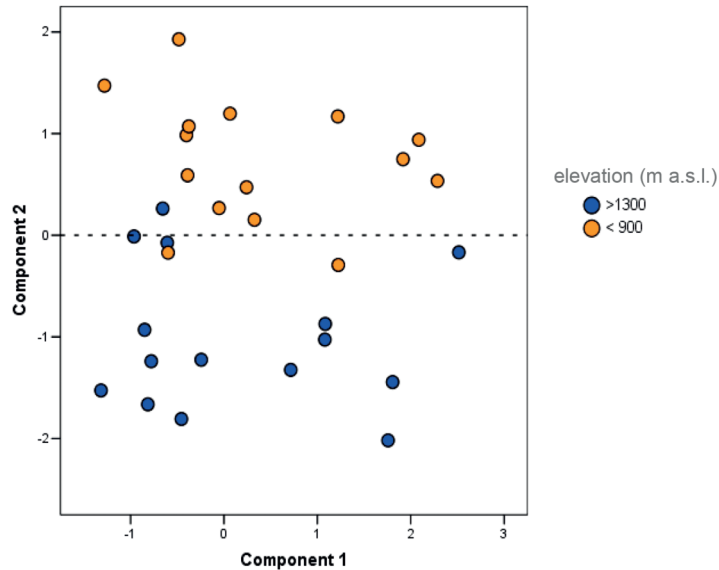
The main remarks obtained after the

Figure 16. Factor score plot of components 1 and 2. Two distinct groups are evident respect to component 2 on the basis of the elevation a.s.l. of the cropping out location of the waters.

discussion of the analytical results are here listed:

- all samples may be classified as bicarbonate-calcic waters. But, at a more detailed scale, it is apparent the possibility to distinguish the spring waters that have interacted with flysch deposits from those associated to calcareous and calcareous-marly deposits, due to relatively higher concentrations of some minor elements (e.g. Mg, Na, K, SO_4 and Cl) of the former waters;

- the main outlier values of the chemical parameters of analyzed waters have been identified and discussed. In particular, the waters of two springs (N.53, VMS20, le Fontanelle 2; N.45, VMS17, del Rio) have displayed high TDS and sulfates concentrations, probably due to uplift of deep sulfuric/sulfate waters along local structural-tectonic alignments;

- the PCA allowed the distinction of two main groups of ions: i) bicarbonate and Ca, ii) Mg, Na, K, Cl and sulfates. Furthermore, dissolved silica is not correlated to the other elements/compounds and no significant results have been obtained regarding Fe and pH;

- two principal components, which the two main previous groups of ions are associated to, have been respectively interpreted as correlated to lithological typology, explaining about 60% of the variance, and length of the underground paths (i.e., the permanence time of groundwater; 16% of variance); 13% of all the examined variables are still not adequately described by the adopted model due to anthropic (4 samples), litho-structural (2 samples) and still unknown (3 samples) factors;

- since lithology has been recognized as the most important factor for explanation of the physical-chemical parameter variability of groundwater in the study territory, it has been possible to distinguish two significant bicarbonate-calcic aquifer types linked to specific reservoir lithologies: i) the first one is

related to all "autochthonous" calcareous and marly formations of the Umbria-Latium-Abruzzi series (A Group; excluding calcareous-dolomitic rocks) showing subordinate Mg component; ii) the other one is associated to "allochthonous" arenaceous-pelitic flysch deposits (B Group) having relatively higher alkali and Mg concentrations. It is also noteworthy that group (hierarchical cluster) analysis is in agreement with these results. Furthermore, bicarbonate and Ca ions, unlike the other analyzed elements/compounds, show a sharp anti-correlation with water sampling station elevation a.s.l.;

- water samples collected in the study area from aquifers affiliated to flysch deposits have different and homogeneous features with respect to those that have interacted with calcareous to marly formations. These latter samples, despite they interacted with different typology of sedimentary formations (calcareous, calcareous-marly, marly-calcareous, marly), do not display any inherited specific hydrogeochemical features;

- the peculiar hydrogeochemical characteristics of the water affiliated to flysch deposits, as well as their spatial lithological uniformity, may be related to the occurrence of evaporitic and dolomitic deposits in the terrigenous successions of the North and Central Apennine, where they crop out in;

- samples from the neighbouring areas of Campotosto Lake and Mt. S. Franco and those from the Antrodoco Sheet area show very similar features, according to their affiliation to similar geological environment facies of the hosting formations, contributing to validate the reconstructed hydrogeological picture of the study area in a broader regional scenario. In addition, the spring waters of the study area have also shown similar features respect to other springs of Central Apennines circulating in carbonate geological environment.

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