

Hydrogeochemical investigations and groundwater provinces of the Friuli Venezia Giulia Plain aquifers, northeastern Italy

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Abstract Water resources are a key factor, particularly for the planning of the sustainable regional development of agriculture, as well as for socio-economic development in general. A hydrochemical investigation was conducted in the Friuli Venezia Giulia aquifer systems to identify groundwater evolution, recharge and extent of pollution. Temperature, pH, electric conductivity, total dissolved solids, alkalinity, total hardness, SAR, Ca^{2+} , Na^+ , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- , HCO_3^- water quality and type, saturation indexes and the environmental stable isotope $\delta^{18}\text{O}$ were determined in 149 sampling stations. The pattern of geochemical and oxygen stable isotope variations suggests that the sub-surface groundwater (from phreatic and shallow confined aquifers) is being recharged by modern precipitations and local river infiltrations. Four hydrogeological provinces have been recognised and mapped in the Friuli Venezia Giulia Plain having similar geochemical signatures. These provinces have different degrees of vulnerability to contamination. The deep confined groundwater samples are significantly less impacted by surface activities; and it appears that these important water resources have very low recharge rates and would, therefore, be severely impacted by overabstraction.

Keywords Hydrochemistry · Groundwater maps · Aquifers · Water management · Italy

Introduction and study area

The assessment of geochemical element distribution and the natural background are of paramount importance in reconciling the exploitation of surface and groundwaters with the protection of the environment, including the well being of both mankind and the local fauna and flora (Darnley et al. 1995; Edmunds et al. 2002). Following this understanding the Italian Government has recognised the need to identify geochemical baselines that clarify hydrodynamics and recharge periods in large Italian sedimentary basins. This has resulted in a re-evaluation of existing geochemical data and the acquisition of new data in order to understand the factors controlling both the hydrochemical concentration levels and the distribution of potentially toxic constituents. In order to fulfil these requirements the Friuli Venezia Giulia Environmental Protection Unit (ARPA FVG) has created a network of water chemistry monitoring sites, and since 1995 more than 1,000 groundwater and surface samples have been analysed for physical and chemical characteristics. The Friuli Venezia Giulia Plain located in northeast Italy hosts well-developed alluvial aquifers composed of Eocene to Quaternary aged thick gravel and sand beds interbedded with clay and silty layers (Stefanini and Cucchi 1976, 1977; Mosetti 1983; Cucchi et al. 1998, 1999, 2000, 2006). The goal of this research is to use major ions and stable isotope data to evaluate water quality and to statistically summarise these data in order to define hydrochemical groundwater provinces. The characteristics of these provinces can then be utilised for water management by other research organisations with similar interests. In addition, this will provide local authorities with a framework, which can be used to understand the degree of pollution in groundwater resources, the recharge areas and may provide useful

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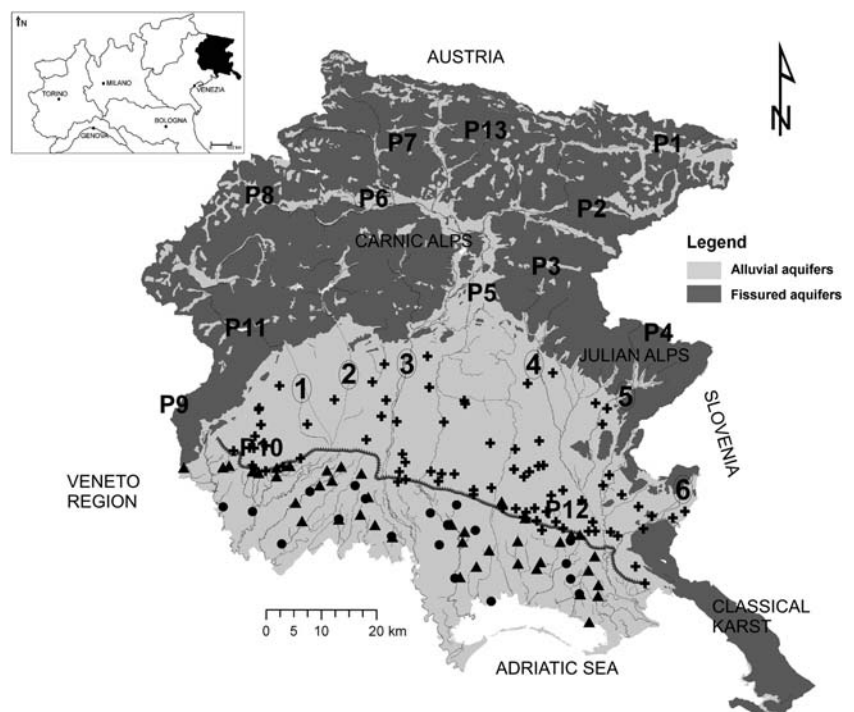
information for better preservation of these important water bodies.

The Friuli Venezia Giulia Plain is located in the eastern part of the Padain Plain, the largest agricultural and industrial area of northeastern Italy (Fig. 1). The studied area is bounded by the Julian and Carnic Alps to the north, the Adriatic Sea to the south and the Classical Karst of Trieste and surrounding areas form the eastern boundary (Fig. 1). The Friuli Venezia Giulia Plain groundwater systems are located in sediments that are underlain by an Eocene to Oligocene succession deposited above a 7 km thick Mesozoic carbonate platform (Cati et al. 1987; Carulli 2006). The Friuli Venezia Giulia Plain is divided into two units, the Upper Friulian and the Lower Friulian, which are separated by the resurgence belt (Fig. 1). The Upper Friulian Plain includes calcareous and dolomitic gravels with a well-developed phreatic (P) aquifer, with an aquifer transmissivity of approximately 10^{-2} to 10^{-4} m²/s in a southerly direction (Mosetti 1983; Carniel 1999). This aquifer has an average thickness of 60–80 m, reaching depths of 200 m close to the border between the plain and the Alps and surfacing in the resurgence belt. The resurgence belt (Fig. 2) is positioned in the zone of slope change (between mean slope of 5‰ for the Upper Friulian Plain and 3‰ in the Lower Friulian Plain) that is related to the last glacial maximum (LGM) deposition of gravels from glacial rivers (Fontana, 2006). The Lower Friulian Plain is characterised by alternating gravels and sand interbedded by clay and silty layers (Fig. 2) that become thicker in a

southerly direction. This area has abundance in surface waters compared to the Upper Friulian Plain (Fig. 1). In the Lower Friulian Plain the groundwater is confined to a multilayer aquifer (Fig. 2). This aquifer system is hydrogeologically divided at approximately 100–120 m depth, into shallow (SC) and deep confined (DC) groundwaters by a 10–15 m thick impermeable layer of silty material dating back to the Late Pleistocene (Fontana 2006). This low permeability layer has an approximate hydraulic conductivity of 10^{-7} m/s (Mosetti 1983) and is almost a continuous layer from Friuli Venezia Giulia to Lombardy (Pilla 1998; Pilli 2005). Thermal aquifers with water temperatures reaching 60° have been found at depths of 550–600 m (Fig. 2) during drilling explorations and are presently partly used by local industries (Stefanini and Cucchi 1976, 1977; Mosetti 1983; Cucchi et al. 1999). These deep geothermal aquifers have not been sampled in this study.

The main surface drainage is the Tagliamento River, which extends across the entire length of the Friuli Venezia Giulia Plain. The headwaters are situated in the Carnic Alps and the river flows first in an eastward direction before crossing the plain to outflow in the south (Fig. 1). Numerous artificial channels carry waters from the Tagliamento River. The average discharge of the Tagliamento River, 40 km inland from the Adriatic Sea, is 90–100 m³/s (Fontana and Bondesan 2006), with a maximum discharge of 3,000–4,500 m³/s (Foramitti 1990). Other perennial rivers in the region (Fig. 1) are the Isonzo

Fig. 1 Location of the study area (dotted line Resurgence belt, P Pluviometer, crosses phreatic well samples, triangles shallow confined well samples and circles deep confined well samples; 1 Cellina River, 2 Livenza River, 3 Tagliamento River, 4 Torre River, 5 Natisone River and 6 Isonzo River)



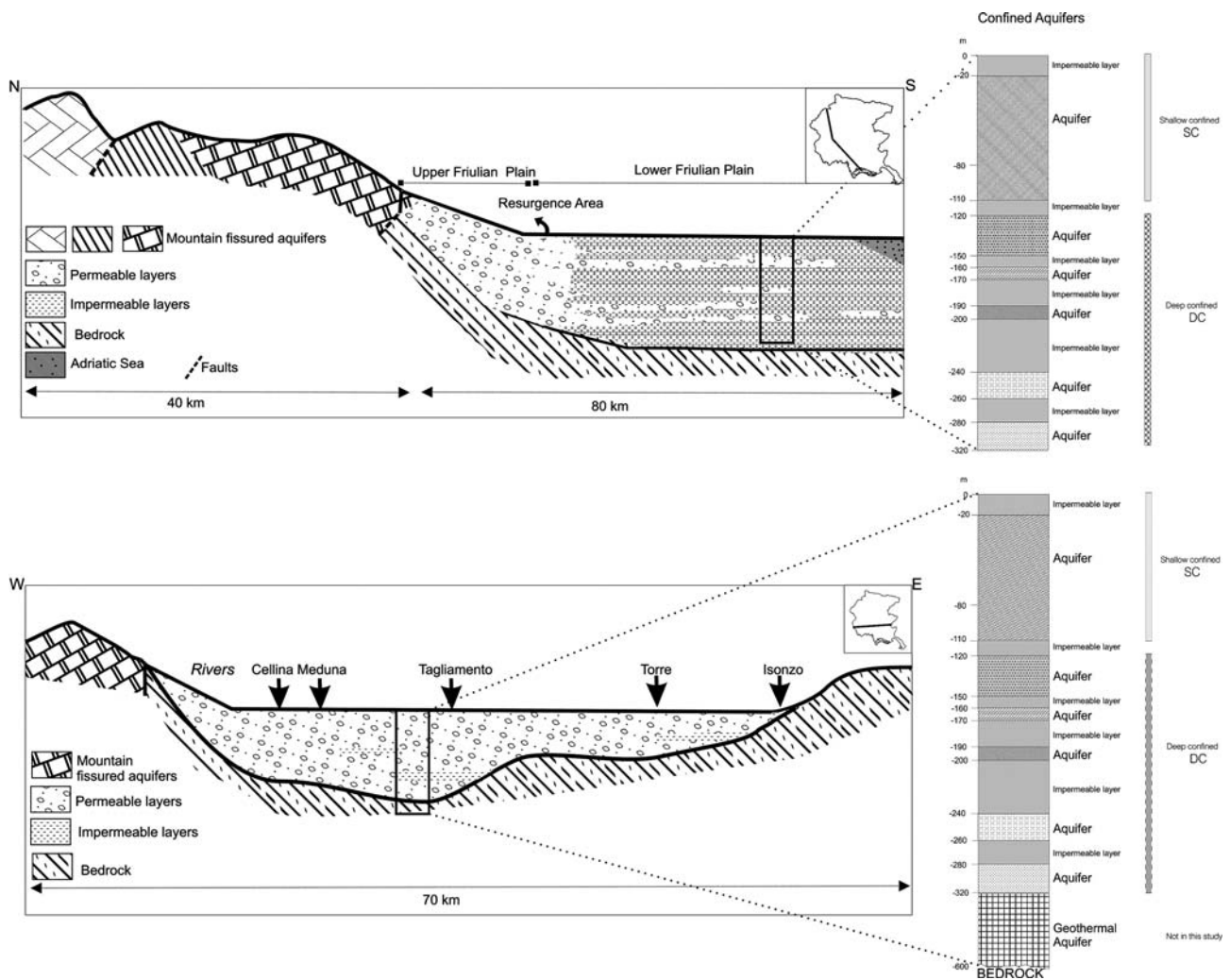


Fig. 2 North–south and east–west simplified cross sections of the study area

(average discharge of 67 m³/s), the Torre/Natisone (average discharge of 17 and 7 m³/s), and Cellina/Meduna rivers (average discharge of 16 and 11 m³/s (Mosetti 1983).

Materials and methods

One hundred and forty-nine wells were selected from the physical-chemical characteristics database of ARPA FVG, all of which have chemical analyses available dating from 1995 to date. Sample location, type, electric conductivity (EC), pH, total dissolved solids (TDS), temperature (T), alkalinity (Alk), total hardness (TH), sodium adsorption ratio (SAR), major ions and stable isotope ($\delta^{18}\text{O}$) are presented in Table 1. The water temperature, electrical conductivity (EC) and pH of each sample were measured in situ by ARPA FVG with a conductivity meter standardised to 20°C and a pH electrode previously calibrated with standard buffers. The water samples were chemically

analysed by ARPA FVG by atomic absorption spectrometry (Ca^{2+} , Na^+ , K^+ , Mg^{2+} , accuracy 5–10%) and ion chromatography (Cl^- , SO_4^{2-} , NO_3^- , HCO_3^- , accuracy 5–10%). All reported values (Table 1) have an ionic balance within 10%. TDS, Alk, TH and SAR were calculated using Aquachem version 4.0 whereas the saturation indices (Table 1) were calculated with PHREEQC (Parkhurst et al. 1980).

A subgroup of 128 of the 149 wells was selected in 2005–2006 for stable isotope ($\delta^{18}\text{O}$) analyses of water, as they cover the Friuli Venezia Giulia Plain homogeneously both in terms of aquifer extensions and depths. Isotopic analyses were carried out at the University of Trieste on a VG Optima mass spectrometer. The oxygen isotopic composition ($\delta^{18}\text{O}$) was measured by means of a water–CO₂ equilibration technique at 25°C (Epstein and Mayeda 1953). The values are reported as per mil deviations from the VSMOW standard using the conventional δ notation (Craig 1961). The standard deviation of the measurements is about $\pm 0.02\text{‰}$ (2σ).

Table 1 Chemical and isotopic composition of groundwater samples from the Friuli Venezia Giulia Plain

Borehole ID	Type	Elevation (m a.s.l.)	Depth (m)	n _{in}	EC (µS/cm)	pH	TDS (mg/l)	Alk (mg/l)	TH (mg/l)	SAR	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Cl ⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	NO ₃ ⁻ (mg/l)	Water Type	SI _{tot}	SI _{Ca}	SI _{Mg}	SI _{sp}	SI _{an}	SI _{cat}	n _k	δ ¹⁸ O	Water Status
637	P	3	2	6	606	7.2	590	328	371	0.12	89.4	35.9	5.2	0.9	10.3	399	48.3	0.2	Ca-Mg-HCO ₃	0.08	0.14	-1.88	-2.13	-8.84	2	-7.30	2	
255	P	19	12	12	597	7.4	569	316	348	0.09	105.2	20.7	4.0	1.4	8.2	386	17.3	23.3	Ca-Mg-HCO ₃	0.23	0.36	-2.23	-2.48	-9.06	2	-6.81	2	
204	P	40	15	11	563	7.4	506	211	329	0.11	89.3	25.7	4.4	0.9	7.0	257	106.0	14.1	Ca-Mg-HCO ₃ -SO ₄	-0.16	0.10	-1.51	-1.76	-9.07	1	-8.44	2	
236	P	82	15	15	489	7.6	441	163	286	0.08	82.4	19.4	3.2	0.9	3.8	199	124.6	2.4	Ca-Mg-HCO ₃ -SO ₄	-0.16	0.14	-1.45	-1.70	-9.48	1	-8.63	2	
449	P	61	15	7	936	6.9	928	535	562	0.20	149.6	45.8	10.7	0.7	17.1	652	17.6	33.4	Ca-Mg-HCO ₃	0.12	0.21	-2.18	-2.43	-8.33	-	-	3	
610	P	20	15	8	605	7.4	556	265	343	0.14	87.2	30.4	6.1	1.8	11.2	324	53.9	42.3	Ca-Mg-HCO ₃	0.14	0.19	-1.83	-2.07	-8.73	2	-6.80	3	
613	P	30	17	8	626	7.3	578	268	366	0.09	94.9	31.2	4.0	1.1	8.7	327	72.7	38.0	Ca-Mg-HCO ₃ -SO ₄	0.04	0.16	-1.67	-1.92	-9.03	2	-7.61	3	
609	P	24	18	8	631	7.4	584	294	361	0.12	94.5	30.3	5.4	1.7	10.4	359	38.6	44.4	Ca-Mg-HCO ₃	0.21	0.25	-1.94	-2.19	-8.85	2	-7.33	3	
612	P	21	19	7	607	7.4	556	270	346	0.15	88.2	30.6	6.3	1.0	12.3	329	39.4	48.7	Ca-Mg-HCO ₃	0.04	0.15	-1.95	-2.20	-8.68	2	-6.82	3	
611	P	20	20	8	651	7.3	607	299	375	0.14	99.2	31.0	6.3	2.0	12.4	365	48.4	43.0	Ca-Mg-HCO ₃	0.16	0.23	-1.83	-2.08	-8.67	2	-7.01	3	
3776	P	51	20	9	588	7.4	568	303	352	0.07	97.4	26.5	3.2	1.1	8.0	370	13.6	47.8	Ca-Mg-HCO ₃	0.16	0.25	-2.38	-2.63	-9.18	-	-	3	
31126	P	28	20	3	260	-	212	115	148	0.07	44.5	9.0	2.0	0.6	2.8	140	7.4	5.2	Ca-Mg-HCO ₃	-1.78	-0.68	-2.81	-3.05	-9.81	1	-8.55	2	
1524	P	37	22	9	505	7.6	480	261	303	0.06	81.2	24.4	2.5	0.7	5.8	319	14.5	32.2	Ca-Mg-HCO ₃	0.20	0.26	-2.39	-2.64	-9.40	2	-7.66	3	
1357	P	34	23	12	348	7.9	325	186	200	0.05	49.5	18.5	1.6	0.3	3.6	227	7.1	15.2	Ca-Mg-HCO ₃	0.17	0.21	-2.83	-3.08	-9.94	2	-8.09	2	
624	P	60	25	5	506	7.5	447	178	289	0.09	77.5	23.3	3.5	0.9	5.3	218	107.0	11.5	Ca-Mg-HCO ₃ -SO ₄	-0.13	0.10	-1.54	-1.79	-9.30	1	-8.64	2	
639	P	25	25	8	639	7.3	592	310	373	0.09	101.6	28.9	4.1	1.7	12.2	378	24.5	40.7	Ca-Mg-HCO ₃	-0.02	0.17	-2.11	-2.36	-8.88	1	-7.02	3	
1298	P	17	25	14	589	7.4	567	302	353	0.07	95.7	27.6	3.3	1.0	9.3	369	24.7	34.7	Ca-Mg-HCO ₃	0.18	0.26	-2.12	-2.37	-9.09	2	-6.84	3	
1305	P	16	25	14	557	7.4	529	272	326	0.13	83.1	28.9	6.4	1.0	10.6	332	32.9	32.1	Ca-Mg-HCO ₃	0.15	0.20	-2.04	-2.29	-8.73	2	-7.19	3	
234	P	141	26	17	548	7.4	518	288	321	0.07	92.4	21.8	2.8	1.1	7.2	351	18.4	19.4	Ca-Mg-HCO ₃	0.08	0.27	-2.24	-2.49	-9.27	2	-7.03	3	
211	P	46	27	11	506	7.5	452	200	289	0.11	80.7	21.3	4.3	1.0	5.9	244	86.2	7.5	Ca-Mg-HCO ₃ -SO ₄	-0.33	0.04	-1.61	-1.86	-9.15	1	-8.64	2	
31055	P	32	27	10	298	7.9	265	137	167	0.07	50.4	10.1	2.2	0.9	3.4	167	6.2	6.4	Ca-Mg-HCO ₃	-1.73	-0.60	-2.86	-3.11	-9.67	2	-8.43	2	
43	P	41	30	7	495	7.4	470	256	292	0.09	81.9	21.3	3.5	1.2	6.7	312	16.1	27.9	Ca-Mg-HCO ₃	-0.02	0.19	-2.33	-2.58	-9.22	2	-8.50	3	
202	P	41	31	12	484	7.6	425	167	278	0.09	76.6	21.1	3.4	0.8	4.6	203	106.6	7.3	Ca-Mg-HCO ₃ -SO ₄	-0.27	0.06	-1.54	-1.79	-9.37	1	-8.59	2	
206	P	33	31	11	589	7.4	537	245	346	0.08	90.2	29.3	3.3	0.8	8.1	299	76.2	29.3	Ca-Mg-HCO ₃ -SO ₄	-0.08	0.11	-1.65	-1.91	-9.13	1	-7.87	3	
31107	P	9	31	12	295	7.7	251	138	166	0.11	47.7	11.3	3.4	0.6	7.2	168	7.0	5.4	Ca-Mg-HCO ₃	-1.58	-0.57	-2.83	-3.08	-9.27	-	-	2	
219	P	27	32	11	643	7.3	591	296	371	0.14	98.4	30.3	6.3	1.8	11.5	360	48.3	32.4	Ca-Mg-HCO ₃	0.04	0.18	-1.83	-2.08	-8.71	1	-7.23	3	
209	P	50	33	11	604	7.4	546	235	348	0.14	96.0	26.3	5.8	0.9	9.3	286	100.6	19.7	Ca-Mg-HCO ₃ -SO ₄	-0.10	0.14	-1.51	-1.76	-8.86	1	-8.45	2	
212	P	44	33	11	585	7.4	527	237	341	0.08	89.7	28.4	3.3	0.8	8.0	289	79.2	26.5	Ca-Mg-HCO ₃ -SO ₄	-0.15	0.09	-1.64	-1.89	-9.14	1	-8.04	3	
588	P	111	33	5	617	7.2	575	317	357	0.15	104.6	23.1	6.5	0.9	4.8	386	14.5	34.8	Ca-Mg-HCO ₃	-0.16	0.15	-2.31	-2.56	-9.10	2	-6.25	3	
38	P	35	11	619	7.3	573	288	366	366	0.08	95.2	31.1	3.5	0.8	9.2	351	44.8	34.8	Ca-Mg-HCO ₃	-0.12	0.10	-1.87	-2.12	-9.05	1	-7.48	3	
638	P	24	35	8	643	7.1	600	330	368	0.10	108.7	23.4	4.4	0.8	15.9	402	13.3	31.6	Ca-Mg-HCO ₃	-0.35	0.07	-2.34	-2.59	-8.74	1	-6.52	3	
205	P	37	36	11	549	7.4	495	213	321	0.08	85.8	25.9	3.4	0.8	6.6	259	93.5	18.4	Ca-Mg-HCO ₃ -SO ₄	-0.11	0.12	-1.57	-1.83	-9.21	1	-8.33	2	
1303	P	21	36	13	663	7.3	621	300	386	0.12	102.8	31.2	6.1	1.5	10.5	366	53.7	47.9	Ca-Mg-HCO ₃	-0.02	0.15	-1.78	-2.03	-8.73	2	-7.12	3	
203	P	47	37	11	491	7.6	427	162	280	0.13	77.8	20.8	5.1	0.8	5.6	197	110.8	7.4	Ca-Mg-HCO ₃ -SO ₄	-0.21	0.09	-1.52	-1.77	-9.11	1	-8.73	2	
208	P	24	38	11	682	7.2	636	308	403	0.14	107.0	33.0	6.6	1.8	11.8	376	57.4	41.1	Ca-Mg-HCO ₃	0.03	0.17	-1.74	-1.99	-8.69	1	-7.34	3	
213	P	44	40	11	588	7.3	535	249	345	0.09	91.8	28.1	3.6	1.0	7.4	304	71.0	27.0	Ca-Mg-HCO ₃ -SO ₄	-0.13	0.11	-1.67	-1.93	-9.13	1	-7.70	3	
246	P	47	40	17	477	7.5	455	254	273	0.12	86.4	13.9	4.7	2.1	6.3	310	15.3	11.9	Ca-HCO ₃	0.06	0.33	-2.31	-2.56	-9.09	2	-6.76	2	
1322	P	18	40	12	414	7.6	395	223	239	0.07	66.9	17.4	3.2	1.2	5.0	272	11.8	15.7	Ca-Mg-HCO ₃	0.19	0.28	-2.54	-2.79	-9.45	1	-8.19	2	
1369	P	85	40	9	443	7.8	378	138	254	0.07	73.8	16.9	2.5	0.7	2.9	168	108.7	4.6	Ca-Mg-HCO ₃ -SO ₄	-0.33	0.07	-1.53	-1.79	-9.70	2	-8.90	2	
31012	P	18	40	4	367	-	306	163	214	0.09	62.9	13.8	2.9	1.4	4.4	199	9.3	12.4	Ca-Mg-HCO ₃	-1.37	-0.47	-2.61	-2.86	-9.45	-	-	2	
1523	P	42	43	9	408	7.8	381	215	241	0.04	62.5	20.7	1.3	0.4	4.4	262	8.4	21.6	Ca-Mg-HCO ₃	0.10	0.19	-2.69	-2.94	-9.79	2	-8.03	2	
218	P	50	44	10	566	7.3	509	254	319	0.18	81.8	27.8	7.4	1.1	12.4	309	43.8	24.1	Ca-Mg-HCO ₃	-0.21	0.04	-1.91	-2.17	-8.60	1	-7.34	2	
252	P	35	45	18	274	7.8	253	145	152	0.07	47.6	7.9	2.0	0.8	2.1	177	7.3	4.0	Ca-Mg-HCO ₃	-0.16	0.20	-2.80	-3.04	-9.92	2	-7.59	1	
269	P	55	45	30	599	7.3	592	315	357	0.11	91.3	31.2	4.8	1.6	7.4	384	30.2	37.2	Ca-Mg-HCO ₃	0.21	0.22	-2.07	-2.31	-9.02	2	-6.74	3	
618	P	20	48	8	581	7.4	538	270	329	0.20	83.4	29.2	8.2	1.9	13.5	329	39.3	33.6	Ca-Mg-HCO ₃	0.08	0.17	-1.97	-2.22	-8.52	2	-7.19	3	
1348	P	36	48	8	375	7.9	347	196	219	0.03	55.4	19.7	1.2	0.3	3.8	238	8.9	19.1	Ca-Mg-HCO ₃	0.09	0.17	-2.70	-2.95	-9.91	2	-7.35	2	
463	P	25	50	8	510	7.6	474	246	291	0.12	80.8	21.7	4.8	2.0	7.8	300	41.3	16.0	Ca-Mg-HCO ₃	0.33	0.35	-1.93	-2.18	-8.98	2	-7.24	2	
633	P	59	50	8	450	7.6	412	221	257	0.13	64.8	23.0	4.7	1.4	7.2	270	20.4	20.9	Ca-Mg-HCO ₃	0.08	0.17	-2.30	-2.55	-9.04	-	-	2	
634	P	59	50	7	552	7.5	492	243	300	0.27	77.2	26.1	10.8	0.9	15.1	297	43.2	21.4	Ca-Mg-HCO ₃	0.11	0.19	-1.96	-2.21	-8.35	-	-	2	
1527	P	54	50	9	456	7.7	409	228																				

Table 1 continued

Borehole ID	Type	Elevation (m a.s.l.)	Depth (m)	n_{ca}	EC ($\mu S/cm$)	pH	TDS (mg/l)	Alk (mg/l)	TH (mg/l)	SAR (meq/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	Cl ⁻ (mg/l)	HCO_3^{-} (mg/l)	SO_4^{2-} (mg/l)	NO_3^{-} (mg/l)	Water Type	SI_{td}	SI_{ca}	SI_{ksp}	SI_{mi}	SI_{hd}	n_h	$\delta^{18}O$	Water Status
1374	P	95	60	6	512	7.9	431	136	288	0.11	83.3	19.4	4.2	0.8	4.1	165	149.0	4.6	Ca-Mg-SO ₄ -HCO ₃	-0.32	0.05	-1.38	-1.62	-9.36	2	-8.66	2
31002	P	41	60	8	640	-	551	285	373	0.08	113.9	21.5	3.5	1.0	7.9	347	18.4	36.4	Ca-Mg-HCO ₃	-0.68	-0.07	-2.18	-2.43	-9.11	2	-6.43	3
31101	P	3	60	6	427	-	335	157	216	0.43	58.5	17.0	14.4	1.0	25.6	192	13.8	13.1	Ca-Mg-HCO ₃	-1.58	-0.59	-2.47	-2.73	-7.97	2	-7.73	2
614	P	21	61	8	552	7.4	504	249	313	0.14	79.0	28.1	5.7	1.0	10.9	304	40.5	35.7	Ca-Mg-HCO ₃	0.09	0.17	-1.97	-2.22	-8.77	2	-7.14	3
620	P	30	62	8	492	7.6	434	176	282	0.06	70.4	25.8	3.2	1.2	5.2	215	101.5	13.3	Ca-Mg-HCO ₃ -SO ₄	-0.01	0.11	-1.61	-1.86	-9.48	2	-8.59	2
1520	P	76	62	10	528	7.6	486	265	305	0.04	80.2	25.4	1.7	0.4	6.4	324	13.7	34.2	Ca-Mg-HCO ₃	0.21	0.26	-2.42	-2.67	-9.53	-	-	3
608	P	24	63	8	618	7.3	580	301	356	0.13	92.7	30.2	5.7	1.7	11.4	367	14.2	36.9	Ca-Mg-HCO ₃	0.07	0.18	-2.00	-2.25	-8.77	2	-7.19	3
31067	P	64	65	7	407	-	336	175	229	0.13	66.4	15.3	4.7	2.0	5.7	213	34.2	15.9	Ca-Mg-HCO ₃	-1.44	-0.49	-2.47	-2.72	-9.16	2	-7.55	2
619	P	20	67	8	613	7.4	565	271	349	0.17	88.6	31.0	7.4	1.6	12.9	331	53.9	38.8	Ca-Mg-HCO ₃	0.26	0.25	-1.82	-2.07	-8.59	2	-7.31	3
237	P	95	70	12	514	7.5	467	211	286	0.18	78.2	22.0	4.4	9.3	25.8	69.2	16.2	16.2	Ca-Mg-HCO ₃ -SO ₄	0.00	0.19	-1.74	-1.99	-8.81	2	-7.65	2
1365	P	87	70	6	504	7.6	487	262	298	0.04	73.1	28.0	1.6	0.3	8.5	319	13.4	43.6	Ca-Mg-HCO ₃	0.04	0.13	-2.47	-2.72	-9.43	-	-	3
31004	P	43	70	4	494	-	424	223	293	0.08	85.2	19.4	3.0	1.0	6.0	272	11.2	28.0	Ca-Mg-HCO ₃	-0.98	-0.27	-2.49	-2.74	-9.30	2	-8.47	3
230	P	73	72	13	538	7.4	497	255	308	0.16	80.1	26.2	7.8	0.9	13.0	310	36.0	19.4	Ca-Mg-HCO ₃	0.07	0.18	-2.00	-2.25	-8.60	2	-7.18	2
235	P	123	80	17	337	7.7	318	182	187	0.10	61.4	8.3	3.2	1.6	3.1	222	8.8	6.0	Ca-HCO ₃	-0.23	0.22	-2.63	-2.88	-9.55	2	-7.43	2
746	P	39	84	5	460	7.7	429	234	265	0.08	70.9	21.4	3.1	0.9	6.1	285	17.2	24.1	Ca-Mg-HCO ₃	0.33	0.33	-2.35	-2.60	-9.28	-	-	2
35	P	125	90	8	591	7.4	544	276	345	0.09	86.9	31.1	3.8	2.3	10.3	337	33.7	39.3	Ca-Mg-HCO ₃	0.18	0.21	-2.02	-2.27	-8.98	2	-7.06	3
38	P	118	90	8	577	7.4	529	261	339	0.10	86.5	29.9	4.4	1.8	10.2	319	51.6	26.5	Ca-Mg-HCO ₃	0.04	0.16	-1.84	-2.09	-8.93	2	-7.43	3
169	P	101	90	9	487	7.7	455	254	290	0.05	75.3	24.6	2.0	0.3	4.9	309	13.2	25.5	Ca-Mg-HCO ₃	0.31	0.30	-2.45	-2.70	-9.58	2	-7.02	3
Fongtarini	P	140	90	2	477	8.0	401	215	270	0.04	65.6	25.9	1.4	0.4	4.5	263	18.9	22.1	Ca-Mg-HCO ₃	0.82	0.53	-2.33	-2.59	-9.75	-	-	2
240	P	76	91	11	498	7.5	459	235	291	0.09	73.4	26.2	3.5	1.2	7.5	286	35.4	25.2	Ca-Mg-HCO ₃	0.01	0.14	-2.05	-2.30	-9.15	2	-7.22	3
1528	P	124	91	9	548	7.6	531	279	327	0.12	83.9	28.4	4.8	0.2	7.0	341	17.2	48.4	Ca-Mg-HCO ₃	0.18	0.23	-2.33	-2.58	-9.07	2	-7.58	3
L	P	35	96	1	351	7.9	336	187	208	0.03	51.1	19.4	1.1	0.2	5.3	228	7.7	22.9	Ca-Mg-HCO ₃	0.74	0.44	-2.80	-3.04	-9.79	-	-	2
153	P	153	104	4	329	7.9	300	168	183	0.04	55.0	11.2	1.3	0.5	2.2	205	16.4	8.0	Ca-Mg-HCO ₃	0.13	0.34	-2.43	-2.68	-10.08	-	-	2
605	P	134	120	9	351	7.9	326	186	204	0.04	52.2	17.9	1.2	0.8	3.1	227	10.0	13.9	Ca-Mg-HCO ₃	0.57	0.41	-2.67	-2.91	-9.99	2	-7.33	2
230	P	142	126	10	543	7.5	493	231	319	0.07	82.4	27.5	3.0	0.8	7.8	282	61.0	28.9	Ca-Mg-HCO ₃	0.02	0.16	-1.78	-2.03	-9.20	2	-7.63	3
177	P	118	132	8	423	7.8	389	214	242	0.05	62.3	21.0	1.7	0.7	4.9	261	9.4	27.6	Ca-Mg-HCO ₃	0.28	0.29	-2.64	-2.90	-9.63	2	-7.95	3
225	P	197	135	17	524	7.7	477	190	305	0.11	84.3	22.8	4.3	0.7	8.8	232	110.8	8.4	Ca-Mg-HCO ₃ -SO ₄	0.24	0.32	-1.50	-1.75	-9.02	2	-8.38	2
1518	P	150	136	8	482	7.7	446	246	276	0.04	69.5	24.8	1.4	0.4	6.5	300	11.1	31.5	Ca-Mg-HCO ₃	0.10	0.19	-2.54	-2.80	-9.59	2	-7.17	3
601	P	154	150	8	427	7.7	395	224	248	0.03	66.1	20.1	1.0	0.3	3.9	274	9.1	20.4	Ca-Mg-HCO ₃	-0.07	0.14	-2.63	-2.88	-9.96	2	-7.59	2
171	P	224	176	9	575	7.7	534	280	339	0.05	81.2	33.1	1.9	0.4	9.1	341	16.7	50.7	Ca-Mg-HCO ₃	0.46	0.33	-2.35	-2.60	-9.34	1	-6.80	4
1315	SC	10	20	14	396	7.8	339	132	229	0.05	52.5	23.8	2.1	0.6	1.5	161	93.8	1.9	Ca-Mg-HCO ₃ -SO ₄	0.07	0.11	-1.72	-1.97	-10.05	2	-9.09	2
1319	SC	11	20	13	396	7.8	341	129	230	0.05	52.9	23.8	2.0	0.6	1.4	158	98.4	1.8	Ca-Mg-HCO ₃	0.10	0.13	-1.70	-1.95	-10.10	2	-9.08	2
1516	SC	48	20	10	643	7.6	607	327	366	0.16	117.2	17.9	7.1	3.1	10.1	398	30.4	23.3	Ca-HCO ₃	0.39	0.50	-1.95	-2.20	-8.71	2	-7.07	2
1525	SC	32	22	9	367	7.9	338	197	211	0.03	53.5	18.8	1.1	0.4	3.4	240	6.7	14.6	Ca-Mg-HCO ₃	0.17	0.20	-2.83	-3.08	-9.97	2	-8.19	2
1358	SC	24	25	9	418	7.8	389	221	241	0.04	60.6	21.9	1.6	0.5	5.1	269	8.3	21.3	Ca-Mg-HCO ₃	0.21	0.24	-2.77	-3.02	-9.87	2	-8.07	2
Ab. Zanin	SC	29	25	4	391	7.8	350	203	216	0.03	53.9	19.8	1.1	0.3	3.7	248	8.3	15.3	Ca-Mg-HCO ₃	0.41	0.32	-2.74	-2.99	-9.95	2	-7.90	2
1301	SC	5	30	11	418	7.5	388	220	239	0.09	65.3	18.3	3.6	1.0	5.7	269	12.0	14.1	Ca-Mg-HCO ₃	-0.02	0.16	-2.51	-2.76	-9.24	2	-6.99	2
cim_s_vito	SC	34	30	3	457	7.9	383	134	259	0.05	63.1	24.6	1.8	0.4	2.1	163	125.0	3.4	Ca-Mg-HCO ₃ -SO ₄	0.20	0.21	-1.55	-1.80	-9.98	2	-8.82	2
1302	SC	2	31	15	389	7.6	366	208	222	0.06	58.7	18.4	2.8	0.9	4.5	254	10.7	14.6	Ca-Mg-HCO ₃	0.22	0.17	-2.59	-2.84	-9.46	2	-7.15	2
torrate_35	SC	18	35	6	471	7.9	408	157	270	0.06	69.5	23.4	2.3	0.5	3.1	192	110.6	6.2	Ca-Mg-HCO ₃ -SO ₄	0.38	0.34	-1.56	-1.81	-9.70	-	-	2
1327	SC	6	37	14	499	7.5	472	264	288	0.09	82.3	20.0	3.9	1.1	7.1	322	15.4	18.7	Ca-Mg-HCO ₃	0.15	0.30	-2.34	-2.59	-9.12	2	-6.83	2
1300	SC	11	40	14	449	7.6	418	225	260	0.06	65.1	23.8	2.8	0.7	6.0	274	21.0	22.6	Ca-Mg-HCO ₃	0.19	0.22	-2.29	-2.54	-9.33	2	-7.19	2
1316	SC	12	40	10	417	7.8	364	142	240	0.07	56.6	24.0	2.5	0.6	2.2	173	102.3	3.3	Ca-Mg-HCO ₃ -SO ₄	0.11	0.13	-1.67	-1.92	-9.85	2	-9.01	2
1320	SC	11	40	14	591	7.3	572	314	344	0.11	103.9	20.7	5.3	2.3	9.4	383	18.5	27.1	Ca-Mg-HCO ₃	0.08	0.29	-2.21	-2.46	-8.88	2	-6.85	

Table 1 continued

Borehole ID	Type	Elevation (m a.s.l.)	Depth (m)	n _{ab}	EC (µS/cm)	pH	TDS (mg/l)	Alk (mg/l)	TH (mg/l)	SAR	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	NH ₄ ⁺ (mg/l)	K ⁺ (mg/l)	Cl ⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	NO ₃ ⁻ (mg/l)	Water Type	SI _{tot}	SI _{sp}	SI _{shd}	n _s	δ ¹⁸ O	Water Status		
1293	SC	19	70	14	451	7.5	428	237	260	0.07	76.6	16.8	3.0	1.2	5.5	289	12.6	21.0	Ca-Mg-HCO ₃	0.00	0.24	-2.44	-2.69	-9.33	2	-6.99	2
cim_zoppola	SC	35	70	4	461	7.9	400	174	261	0.06	66.1	23.4	2.2	0.4	3.5	212	82.4	9.5	Ca-Mg-HCO ₃ -SO ₄	0.57	0.43	-1.70	-1.95	-9.66	2	-8.26	2
Scuola media_70	SC	15	70	5	413	7.9	353	134	235	0.06	57.6	22.2	2.3	0.5	2.0	164	102.2	2.6	Ca-Mg-HCO ₃ -SO ₄	0.23	0.22	-1.66	-1.91	-9.91	-	-	2
180	SC	40	80	9	426	7.8	372	161	247	0.04	60.0	23.3	1.4	0.4	3.2	196	79.5	7.8	Ca-Mg-HCO ₃ -SO ₄	-0.11	0.06	-1.74	-1.99	-9.90	2	-7.43	2
1296	SC	2	80	14	415	7.7	385	215	239	0.08	57.0	23.3	3.2	0.7	4.4	262	17.7	15.6	Ca-Mg-HCO ₃	0.32	0.25	-2.41	-2.66	-9.39	2	-7.43	2
1321	SC	2	80	14	514	7.5	482	250	297	0.14	69.7	29.9	6.3	0.8	10.1	305	35.4	24.1	Ca-Mg-HCO ₃	0.15	0.17	-2.06	-2.31	-8.75	-	-	2
1326	SC	1	80	14	513	7.5	473	246	294	0.15	68.7	29.7	6.9	0.9	12.6	300	32.4	20.6	Ca-Mg-HCO ₃	0.22	0.20	-2.10	-2.36	-8.62	2	-7.55	2
M	SC	30	80	4	373	7.9	326	156	207	0.04	48.7	20.7	1.4	0.3	2.1	56.1	5.9	5.9	Ca-Mg-HCO ₃ -SO ₄	0.19	0.20	-1.95	-2.20	-10.03	2	-8.51	2
Scuola media_80	SC	15	80	3	400	8.1	346	132	232	0.07	52.0	24.9	2.4	0.5	1.5	161	101.2	2.1	Ca-Mg-HCO ₃ -SO ₄	0.66	0.38	-1.70	-1.95	-9.98	2	-9.14	2
1378	SC	33	81	4	345	7.9	301	152	193	0.03	44.4	19.9	1.1	0.2	2.3	185	41.7	6.3	Ca-Mg-HCO ₃ -SO ₄	0.11	0.15	-2.10	-2.35	-10.13	2	-8.57	2
1306	SC	5	90	14	361	7.8	331	183	193	0.30	44.4	19.9	1.1	1.0	1.0	224	29.1	1.4	Ca-Mg-HCO ₃	0.37	0.24	-2.27	-2.52	-9.52	2	-8.29	2
1307	SC	8	90	14	444	7.6	405	203	261	0.08	61.5	26.1	3.5	0.7	2.8	248	52.8	8.3	Ca-Mg-HCO ₃ -SO ₄	0.04	0.11	-1.92	-2.17	-9.56	2	-8.27	2
1310	SC	9	90	14	372	7.8	330	158	211	0.13	47.2	22.6	5.2	0.8	1.0	193	58.6	0.7	Ca-Mg-HCO ₃ -SO ₄	0.19	0.15	-1.95	-2.20	-9.84	2	-8.67	2
1312	SC	10	90	13	483	7.5	457	249	285	0.07	69.5	27.1	3.1	0.8	5.4	303	25.7	20.1	Ca-Mg-HCO ₃	0.13	0.17	-2.19	-2.44	-9.35	2	-7.60	2
1325	SC	3	90	11	512	7.6	481	248	293	0.15	71.6	27.7	7.1	0.9	13.1	302	31.5	25.3	Ca-Mg-HCO ₃	0.47	0.32	-2.11	-2.35	-8.60	-	-	3
1361	SC	37	91	4	387	7.9	381	216	234	0.03	57.8	21.7	1.2	0.2	4.6	263	7.6	18.3	Ca-Mg-HCO ₃	0.71	0.47	-2.76	-3.01	-9.83	1	-8.04	2
339	SC	3	100	10	410	7.7	380	216	232	0.20	51.1	25.4	7.0	1.3	3.7	264	26.8	0.2	Ca-Mg-HCO ₃	0.44	0.25	-2.28	-2.52	-9.16	2	-7.74	2
1309	SC	3	100	14	372	7.7	340	173	204	0.22	45.6	21.8	8.6	1.0	0.9	211	51.9	0.2	Ca-Mg-HCO ₃ -SO ₄	0.26	0.16	-2.03	-2.27	-9.66	2	-8.62	2
1304	SC	20	110	14	540	7.5	507	258	313	0.14	79.2	28.0	6.9	1.2	10.6	314	36.0	30.2	Ca-Mg-HCO ₃	0.38	0.30	-2.02	-2.27	-8.71	2	-7.28	3
1328	SC	28	120	10	472	7.5	431	205	279	0.08	69.3	25.8	2.9	0.8	3.9	251	65.3	12.3	Ca-Mg-HCO ₃ -SO ₄	-0.06	0.09	-1.79	-2.04	-9.49	2	-8.23	2
338	DC	0	120	14	371	7.9	364	226	139	1.37	30.9	14.9	37.0	1.7	1.1	275	2.0	0.1	Na-Ca-Mg-HCO ₃	0.51	0.28	-3.75	-3.99	-8.96	2	-9.59	1
1297	DC	3	120	13	376	7.8	350	208	214	0.16	47.6	23.1	6.0	1.2	2.7	254	14.3	13.9	Ca-Mg-HCO ₃	0.39	0.25	-2.55	-2.80	-9.34	2	-7.50	1
1324	DC	3	120	10	469	7.5	435	241	276	0.08	67.6	26.1	2.9	0.7	6.3	294	0.2	0.1	Ca-Mg-HCO ₃	0.43	0.28	-2.48	-2.72	-9.30	2	-7.36	2
1299	DC	2	144	14	445	7.6	416	228	260	0.07	63.7	24.5	3.1	0.8	5.9	278	17.8	19.7	Ca-Mg-HCO ₃	0.21	0.20	-2.39	-2.64	-9.30	2	-7.01	2
1364	DC	14	150	4	373	7.7	359	225	177	0.62	44.1	16.2	19.0	1.4	0.8	274	0.2	0.1	Ca-Mg-HCO ₃	0.19	0.21	-4.57	-4.82	-9.39	2	-10.35	1
1317	DC	12	165	14	403	7.8	344	127	231	0.05	53.0	23.9	2.1	0.6	1.6	155	104.2	1.9	Ca-Mg-HCO ₃ -SO ₄	0.05	0.11	-1.68	-1.93	-10.03	2	-9.13	2
1380	DC	20	173	7	328	8.0	289	145	188	0.04	43.3	19.5	1.2	0.4	1.6	177	42.0	3.4	Ca-Mg-HCO ₃ -SO ₄	0.25	0.21	-2.11	-2.36	-10.24	2	-8.47	2
342	DC	20	174	14	401	7.9	347	127	233	0.06	53.1	24.4	2.0	0.5	1.7	155	105.9	1.5	Ca-Mg-HCO ₃ -SO ₄	0.08	0.12	-1.67	-1.92	-10.02	2	-9.18	2
1294	DC	11	177	14	426	7.6	393	211	246	0.08	58.7	24.2	3.4	0.8	5.5	258	28.2	12.9	Ca-Mg-HCO ₃	0.14	0.17	-2.19	-2.45	-9.28	2	-7.65	2
1345	DC	36	180	4	435	7.8	381	168	247	0.07	61.1	22.8	2.6	0.4	2.0	204	86.3	1.2	Ca-Mg-HCO ₃ -SO ₄	0.14	0.20	-1.70	-1.95	-9.83	1	-8.69	2
1323	DC	32	180	7	466	7.9	394	136	267	0.05	65.1	25.3	1.7	0.4	3.0	165	129.3	3.6	Ca-Mg-HCO ₃ -SO ₄	0.19	0.22	-1.52	-1.77	-9.85	2	-8.95	2
Doncal	DC	14	183	4	376	8.0	329	143	216	0.09	46.9	24.1	2.9	0.5	1.2	175	77.2	1.6	Ca-Mg-HCO ₃ -SO ₄	0.49	0.29	-1.85	-2.10	-9.99	2	-8.91	2
cava_riposo_183	DC	21	190	14	389	7.8	343	134	228	0.05	53.8	22.8	1.9	0.5	2.4	163	93.9	2.1	Ca-Mg-HCO ₃ -SO ₄	-0.08	0.06	-1.71	-1.96	-10.01	2	-9.07	2
1314	DC	18	190	7	391	8.0	338	141	225	0.06	51.1	23.7	2.1	0.4	1.7	172	83.3	3.2	Ca-Mg-HCO ₃ -SO ₄	0.39	0.27	-1.78	-2.03	-9.99	2	-8.92	2
torrate_190	DC	2	200	12	369	7.7	329	165	200	0.21	44.8	21.4	8.2	0.8	1.0	201	51.4	1.4	Ca-Mg-HCO ₃ -SO ₄	0.21	0.13	-2.04	-2.27	-9.66	-	-	2
1340	DC	17	200	7	421	7.8	414	255	143	1.57	35.9	12.9	43.0	4.6	1.2	311	0.5	0.3	Na-Ca-Mg-HCO ₃	0.47	0.33	-4.34	-4.59	-8.83	2	-10.32	2
1515	DC	10	200	7	340	7.9	330	208	173	0.49	39.7	17.9	14.8	1.2	0.9	253	0.7	0.8	Ca-Mg-HCO ₃	0.55	0.34	-4.05	-4.29	-9.41	2	-8.34	1
343	DC	12	220	9	385	7.7	330	141	214	0.16	47.8	23.0	5.5	0.6	1.4	172	77.7	2.7	Ca-Mg-HCO ₃ -SO ₄	-0.05	0.02	-1.84	-2.08	-9.68	2	-8.92	2
torrate_283	DC	18	283	1	334	7.7	308	193	153	0.39	35.5	15.6	11.0	1.0	0.5	235	6.4	0.5	Ca-Mg-HCO ₃	-0.02	0.06	-2.98	-3.23	-9.80	-	-	1

Ion concentration in mg/l, δ¹⁸O versus SMOW in ‰. Saturation indexes (SI) values calculated with Phreeqc (Parkhurst et al. 1980)

Aquifer characteristics: P phreatic, SC shallow confined and DC deep confined

Chemical water status according to the Italian Law (D.L. 1999 no. 152) where 1 excellent, 2 good, 3 satisfactory, 4 poor

Std. dev. standard deviation, min minimum, max maximum, n number of samples, - not determined

Results

Geochemistry

Table 2 presents a univariate overview of the hydrochemical data of the study area divided as phreatic (P), shallow confined (SC) and deep confined (DC) groundwater samples, whereas hydrochemical and isotopic analyses as a function of the depth are reported in Fig. 3a and Whisker plots of major ion concentrations are reported in Fig. 3b. The dominant ion from the studied area is HCO₃ and five hydrochemical facies have been found: Facies 1: Ca–HCO₃; Facies 2: Ca–Mg–HCO₃; Facies 3: Ca–Mg–HCO₃–SO₄; Facies 4: Ca–Mg–SO₄–HCO₃ and Facies 5: Na–Ca–Mg–HCO₃ (Table 1). Facies 1 to 4 are distributed amongst the phreatic and shallow confined groundwaters, whereas the Na–Ca–Mg–HCO₃-type waters (Facies 5) have been recovered only down-gradient in the deep confined aquifers (Table 1) reflecting exchange reactions by water/clay-silt layer interactions (Hendry and Wassenaar 2000). Groundwater generally shows a decrease in conductivity and mineralisation with depth (Tables 1, 2). The mean temperatures for the studied groundwater samples are similar with a minimum value of 13.5°C for the phreatic to 14.7°C for the deep confined groundwater samples (Table 2; Fig. 3a). The EC data show a decrease in mean values from 509 μS/cm in the samples collected from the phreatic wells to 432 μS/cm and to 393 μS/cm in the shallow confined and deep confined groundwater samples. A similar trend of decreasing values is found for the TDS data in which there is a decrease from 466 to 355 mg/l from the phreatic to the

deep confined groundwater samples (Table 2; Fig. 3a). The pH values range from 6.9 to 8.0 (mean of 7.5) to 7.3 to 8.1 (mean of 7.7) to 7.5 to 8.0 (mean of 7.8) in the phreatic, shallow and deep confined groundwater samples, respectively (Table 2; Fig. 3a). Mean concentrations of HCO₃, Mg are generally similar with no observed differences between phreatic and confined groundwaters (Table 2; Fig. 3a). Potassium (from 0.8 to 1 mg/l) and Na (from 3.5 to 8.7 mg/l) concentrations increase with increasing depths of the confined groundwater (Table 2; Fig. 3a). Chloride concentrations range from 2.1 to 25.6 mg/l (mean of 7.7 mg/l) in the phreatic samples and from 0.9 to 13.1 mg/l (mean of 4.4 mg/l) in shallow confined groundwater and from 0.5 to 6.3 mg/l (mean of 2.2 mg/l) in the deep confined aquifers (Table 2; Fig. 3a). Nitrate concentrations range from 0.2 to 50.7 mg/l (above the maximum permissible level of the Italian law of 50 mg/l), with a mean of 23.7 mg/l, in the phreatic groundwater, from 0.2 to 30.4 mg/l (mean of 11.6 mg/l) in shallow confined groundwater and from 0.1 to 23.6 mg/l (mean of 4.1 mg/l), although only 15% of these groundwater samples have values of more than 4 mg/l, samples 1324, 1299 and 1294 of Table 1), in the deep confined aquifers (Table 2; Fig. 3a). Calcium concentrations range from 44.5 to 149.6 mg/l (mean of 79.2 mg/l) in the phreatic samples and from 41.4 to 117.2 mg/l (mean of 62.5 mg/l) in shallow confined groundwater and from 30.9 to 67.6 mg/l (mean of 49.5 mg/l) in the deep confined aquifers (Table 2; Fig. 3a). The distribution of SO₄ is highly variable from 0.2 to 149 mg/l and generally increases with increasing depth (Table 2; Fig. 3a). Sulphate concentrations decrease away

Table 2 Univariate overview of the groundwater samples

Parameter	Phreatic					Shallow confined					Deep confined				
	Min	Max	Mean	SD	<i>n</i>	Min	Max	Mean	SD	<i>n</i>	Min	Max	Mean	SD	<i>n</i>
Temp (°C)	11.6	15.7	13.5	0.9	86	11.7	17.7	14	1.4	43	12.3	19.3	14.7	1.9	20
EC (μS/cm)	260.3	935.6	509	114	86	306	643	432.7	74.4	43	327.9	469.2	393.3	40.4	20
pH	6.9	8	7.5	7.7	78	7.3	8.1	7.7	8	43	7.5	8	7.8	8.2	20
TDS	211.8	927.6	466.6	114.2	86	288.4	607.4	393.7	74.9	43	288.6	435.3	355.6	38.6	20
Ca	44.5	149.6	79.2	18.1	86	41.4	117.2	62.5	15.9	43	30.9	67.6	49.5	10.2	20
Mg	7.9	45.8	23.4	6.9	86	16.8	29.9	22.5	3.4	43	12.9	26.1	21.4	3.9	20
Na	1	14.4	4.1	2.3	86	1.1	11.1	3.5	2.3	43	1.2	43	8.7	11.8	20
K	0.2	4.4	1.1	0.7	86	0.2	3.1	0.8	0.5	43	0.4	4.6	1	0.9	20
Cl	2.1	25.6	7.7	3.9	86	0.9	13.1	4.4	3.2	43	0.5	6.3	2.2	1.7	20
HCO ₃	140.3	651.8	287.2	77.6	86	157.8	398.2	240.3	61.5	43	154.8	311.4	217	53.1	20
SO ₄	6.2	149	39.2	35.1	86	4.8	125	47.6	38.4	43	0.2	129.3	50.5	42.6	20
NO ₃	0.2	50.7	23.7	13.2	86	0.2	30.4	11.6	9.1	43	0.1	23.6	4.1	6.6	20
δ ¹⁸ O (‰)	-8.9	-6.25	-7.59	0.7	72	-9.14	-6.83	-8.05	0.7	38	-10.35	-7.01	-8.74	0.9	18

All values are in mg/l, unless otherwise indicated

SD standard deviation, *n* number of samples

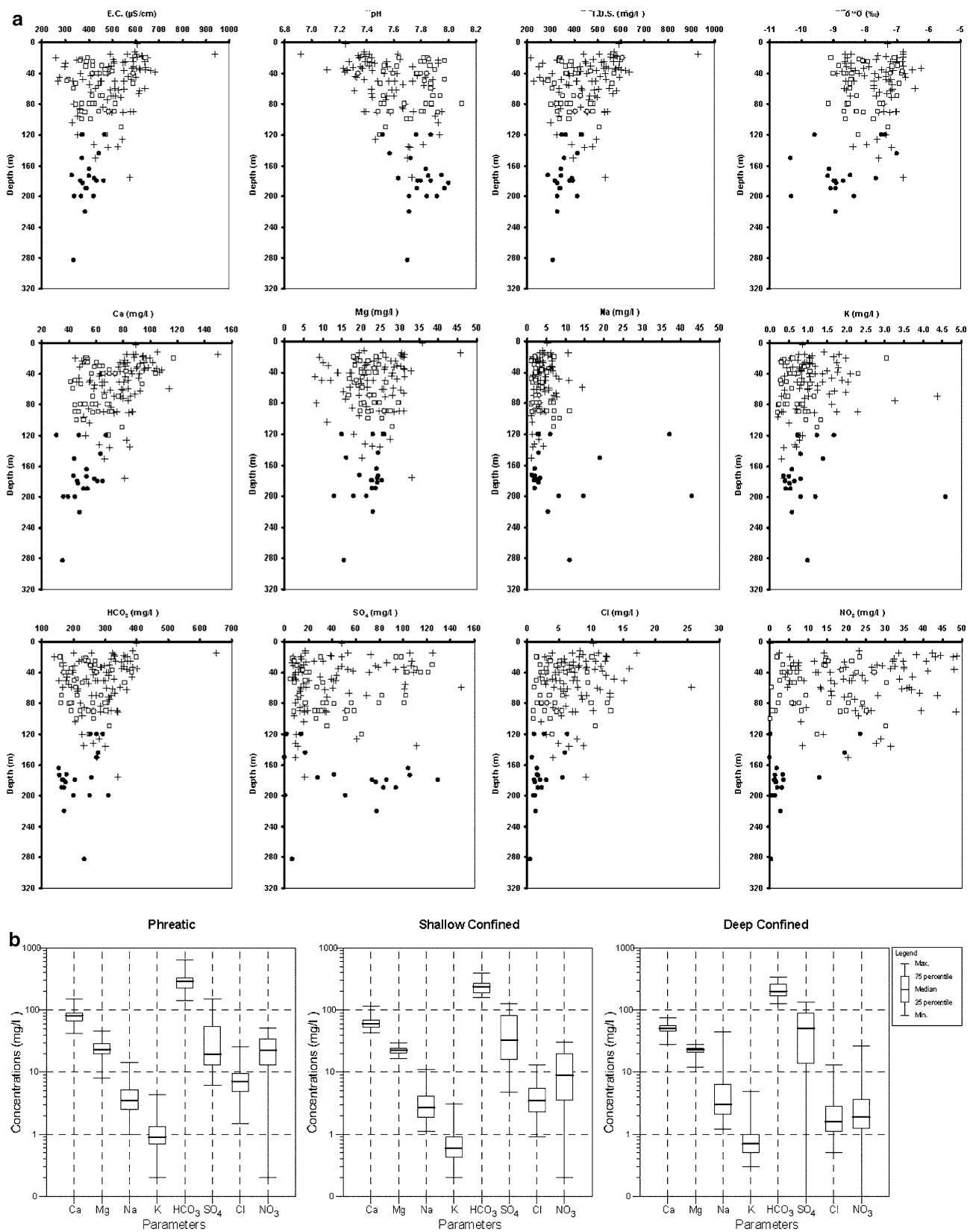


Fig. 3 a Evolution of hydrochemical and stable isotope parameters with increasing depth. (crosses phreatic, squares shallow confined, filled circles deep confined groundwater samples), b Whisker plots of the major ion concentrations

from the Tagliamento River, which has 130 mg/l of sulphate in its water at Pinzano, reflecting the gypsum outcrops in the Carnic Alps (Carniel 1999).

Pearson's correlation matrices (Swan and Sandilands 1995) were used to find relationships between two or more variables. Only correlations with $r \geq \pm 0.4$ are shown (Table 3). Samples showing $r \geq 0.7$ are considered to be strongly correlated, whereas samples with an r of 0.5–0.7 show moderate correlation at a significance level (p) of 0.05. Strong correlations exist among the major elements Ca, Mg, HCO_3 and EC for the phreatic groundwaters, and for Ca, Cl and EC for the shallow and deep confined groundwater samples (Table 3). These relationships clearly identify the tendency to follow a similar trend of evolution for the confined groundwaters. For the phreatic samples, a strong correlation exists between Ca and Mg, Ca and HCO_3 , Mg and HCO_3 , Mg and NO_3 , Na and Cl and HCO_3 and NO_3 (Table 3). For the samples collected from the shallow confined aquifer, a strong correlation exists between Ca and K, Cl, HCO_3 , NO_3 , between K and HCO_3 , Cl and HCO_3 , NO_3 and between HCO_3 , NO_3 (Table 3). The water samples collected from the deeper aquifers show strong correlations between Ca and Mg, Ca and Cl, Mg and Na, K (negative correlation), Na and K, Cl and NO_3 and a negative correlation between HCO_3 and SO_4 (Table 3). The major exchangeable ions present in the studied data set Na–Ca, Na–Mg and K–Na correlate positively with the phreatic and shallow confined groundwaters, whereas they have a negative correlation with the deep confined samples. It is therefore possible to postulate that the simultaneous increase/decrease in ions is largely the result of dissolution/precipitation reactions and concentration effects. The effects of ion exchange with fine, silty layers are brought to evidence by the negative correlations with the deep confined groundwater samples (Adams et al. 2001).

Environmental isotopes

The $\delta^{18}\text{O}$ of groundwater ranges from -6.25 to -8.90‰ (mean value of -7.59‰) in the phreatic groundwater samples, from -6.83 to -9.14‰ (mean value of -8.05‰) and -7.01 to -10.35‰ (mean value of -8.74‰) in the shallow and deep confined groundwater samples, respectively (Table 2; Fig. 3a). The most depleted groundwater samples (1340: -10.32‰ and 1364: -10.35‰) are collected from the southwest of the Friuli Venezia Giulia Plain (Table 1) amongst the deep confined groundwater samples. Stable isotopes in the Friuli Venezia Giulia River waters show different values according to the mean altitude of their drainage basins. The river water samples, collected from 2005 to 2006, range from -7.63 to -8.60‰ for the Natisone River (Boschin et al. 2006), from -7.68 to

-9.10‰ for the Isonzo River, from -8.23 to -9.31‰ for the Tagliamento River, from -7.09 to -9.98‰ for the Livenza River and from -7.94 to -9.78‰ for the Cellina River (CAMI 2007). Rainfall samples in Friuli Venezia Giulia monitored over a 2-year period for nine pluviometers and for 1 year for an additional four pluviometers, have $\delta^{18}\text{O}$ weighted mean values ranging from -7.09 to -10.39‰ , with an average value of -9.04‰ in the mountainous areas and from -7.45 to -7.78‰ for $\delta^{18}\text{O}$ in the Friuli Venezia Giulia Plain with a mean of -7.62‰ (Cucchi et al. 2007). The vertical isotopic gradient for the Friuli Venezia Giulia Region is 0.29‰ per 100 m, in accordance with previous findings for Friuli Venezia Giulia (Longinelli and Selmo 2003; Longinelli et al. 2006) and for neighbouring Slovenia and Croatia (Vreča et al. 2006) as well as for Austria (Kralik et al. 2006).

Geochemical contour maps

Hydrochemical zones provide useful information on plausible recharge sources and the chemical evolution of groundwater (Mahlknecht et al. 2006). Different hydrochemical zones were recognized and mapped in the Friuli Venezia Giulia Plain by Cucchi et al. (1999). However, the six zones previously mapped have been defined without differentiating the deep confined from the shallow confined groundwater samples and also without the statistical analysis approach used in this work. The general geographical distribution of the sub-surface groundwater samples (P and SC of Tables 1–3) is shown in Figs. 4 and 5 and is based on Kriging technique of the major ion distribution using ArcGIS by Esri. The deep confined groundwater samples have been not used to create these provinces because, as highlighted in the previous section, the geochemical characteristics indicate that they are separated from the sub-surface groundwaters and therefore have different physical and chemical signatures. The sulphate distribution map (Fig. 4a) reveals that the highest concentrations are found in the centre of the Plain, adjacent to the Tagliamento River, where maximum values of 100–125 mg/l are distributed throughout a NE elongate area—along the river course. The bicarbonate distributions (Fig. 4b) reach the maximum values of 339–460 mg/l in the northeast of the Friuli Venezia Giulia where the Isonzo River flows. The nitrate concentrations (Fig. 4c) have maximum values in two areas, one located in the northwest and the other in the central region close to the resurgence area. The maximum values in these two areas (from 34 to 43 mg/l) are close to the Italian limit of 50 mg/l for groundwater samples. Figure (Fig. 4d) shows the chloride distributions along the Friuli Venezia Giulia Plain. Chlorides in the area are higher in the east, where values between 6.4 and

Table 3 Pearson's correlation matrices for water samples collected in the deep confined aquifer

Phreatic												
	EC*	pH	TDS	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄	NO ₃	
Temp	0.41	-0.50	0.46		0.40				0.48		0.41	
	EC	-0.87	0.99	0.96	0.89	0.51			0.65	0.86		0.66
		pH	-0.88	-0.87	-0.70	-0.69	-0.69			-0.78	-0.79	
	TDS			0.95	0.90	0.48	0.48		0.62	0.91		0.68
		Ca			0.75	0.45	0.45		0.55	0.84		0.58
	Mg					0.75	0.45		0.59	0.80		0.71
		Na					0.42		0.84			
	K							0.42				
		Cl							0.42			
	HCO ₃									0.57		0.48
		SO ₄									0.57	0.72
NO ₃											0.48	
											0.72	
Shallow confined												
	EC*	pH	TDS	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄	NO ₃	
Temp						0.60						
	EC	-0.68	0.98	0.95	0.45		0.69	0.78	0.69			0.68
		pH		-0.75	-0.65		-0.49	-0.65	-0.71	-0.77		
	TDS				0.95	0.40	0.42	0.75	0.84	0.82		0.78
		Ca				0.40	0.42	0.75	0.72	0.73		0.70
	Mg								0.41			
		Na					0.62	0.41	0.44			0.44
	K							0.62	0.41	0.44		
		Cl							0.55	0.72		0.88
	HCO ₃									0.83		0.87
		SO ₄									-0.64	0.87
NO ₃											-0.53	
											0.44	
											0.88	
											0.87	
											0.87	
											0.87	
											0.87	
Deep confined												
	EC*	pH	TDS	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄	NO ₃	
Temp	-0.37			-0.67	-0.56	0.63	0.54	-0.40		-0.48		
	EC	-0.42	0.89	0.80	0.52			0.72				0.62
		pH		-0.54					-0.60	-0.51		
	TDS				0.55				0.72	0.59		
		Ca				0.85	-0.68	-0.51	0.77		0.46	
	Mg						-0.86	-0.72	0.58	-0.48	0.64	
		Na						0.88		0.64	-0.60	
	K									0.64	-0.55	
		Cl										
	HCO ₃										-0.89	
		SO ₄										
NO ₃												
												0.93

Samples strongly correlated ($r \geq 0.7$) are indicated in bold (see text for further explanations). All values in mg/l, unless otherwise indicated

11.9 mg/l are recorded. The magnesium distribution map (Fig. 5a) indicates highly variable data, with maximum values of 28–32 mg/l concentrated predominantly in an N–

S elongate strip approximately 20 km wide. According to the calcium distribution map (Fig. 5b), the higher Ca values are recorded in the northeast of the Friuli Venezia

Giulia Plain, where the Isonzo and Natisone rivers flow. Figure (Fig. 5c) illustrates the potassium distribution map, which highlights the maximum values located at the centre of the plain where three wells record values between 1.6 and 2.7 mg/l. The sodium distribution map is presented in Fig. 5d and indicates that higher values are located in the southernmost region of the studied area.

Discussion and conclusions

As a general rule, water-rock interaction processes affecting the geochemical composition of water appear to be time and exchange surface dependent (Barbecot et al. 2000). Considering the temperatures generally encountered in the catchments areas, the stable isotopes of water can generally be considered as conservative and not being affected by exchanges with either soil or rock (Barth 2000; Négrel and Petelet-Giraud 2005). In the case of complex aquifers, characterised by non-homogeneous water circulation, the combination of stable isotope data and geochemical ion distribution provides information on the

down-flow groundwater evolution. The shallower groundwater samples indicate a wider range of $\delta^{18}\text{O}$ values as well as greater standard deviation values (Fig. 6), which suggest that these waters have not mixed sufficiently to homogenise variations in isotopic composition of recharge waters or that they have fast recharge rates (Cartwright and Weaver 2005). While there is a general homogenisation of the $\delta^{18}\text{O}$ values with depth, the deep confined groundwater shows more depleted values for confined groundwater with increasing depth ($\delta^{18}\text{O} = -8.74\text{‰}$) as described previously for other parts of the Padanian Plain (Zuppi and Sacchi 2004; Pilla et al. 2006) as well as for many groundwater systems internationally (Weaver and Bahr 1995; Purtschart et al. 2001; Vaikmae et al. 2001; Grasby and Chen 2005). The large variations between isotopic signature of phreatic and shallow confined waters in comparison to the deep confined groundwater (Fig. 6), as well as the marked depletion in the $\delta^{18}\text{O}$ values of the deep confined groundwater samples in relation to the sum of the total ions (Fig. 7), points to complex groundwater circulation models that have probably substantially changed during the varying temperature regimes of the Holocene-Pleistocene (in

Fig. 4 Contour maps of selected geochemical component distribution in the Friuli Venezia Giulia Plain. **a**, **b**, **c**, **d** refer to SO_4^{2-} , HCO_3^- , NO_3^- , Cl^- , respectively

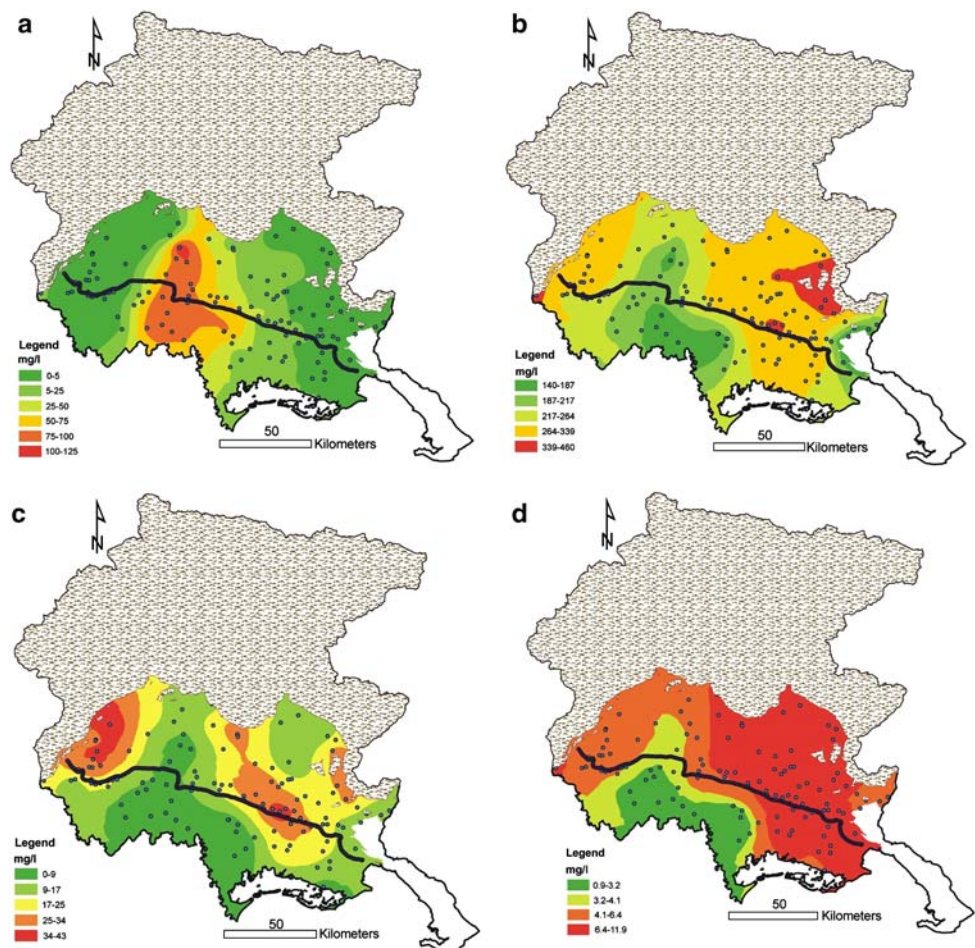
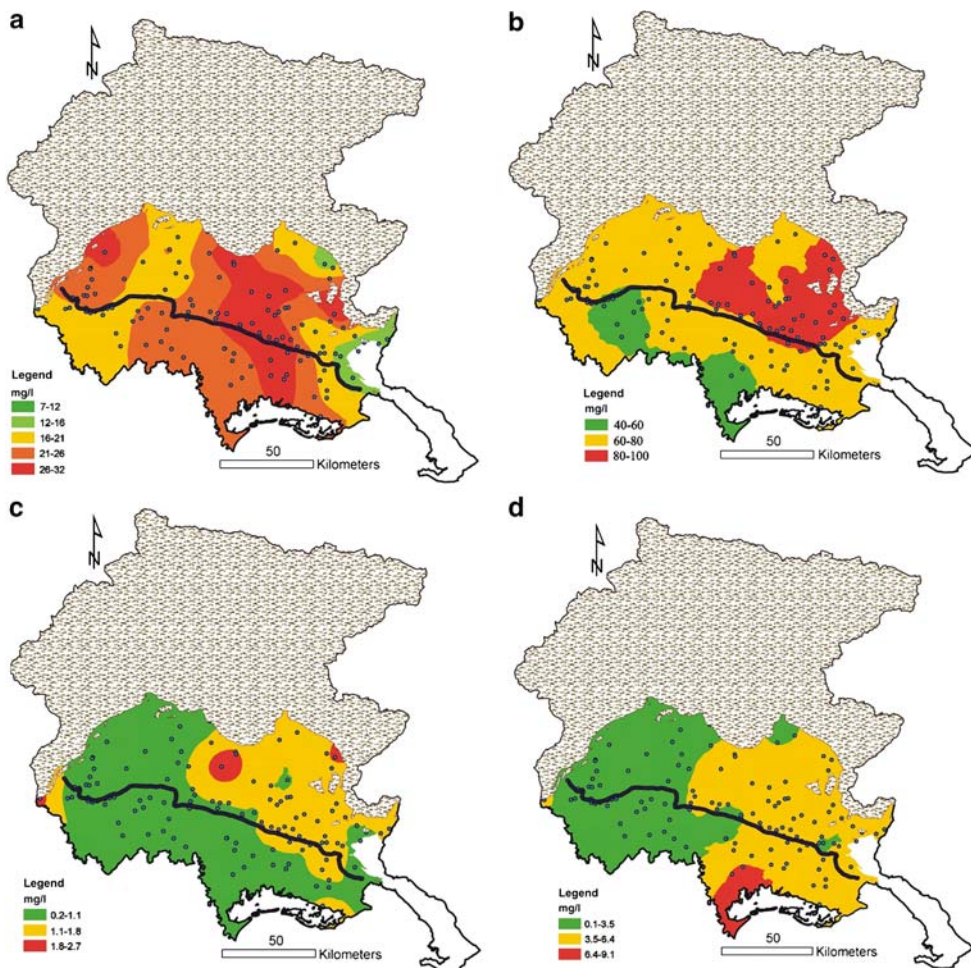


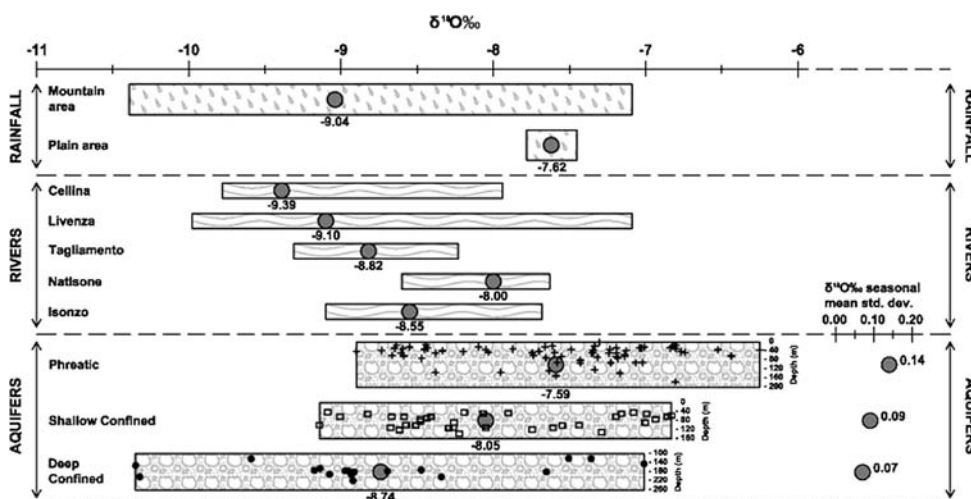
Fig. 5 Contour maps of additional geochemical component distribution in the Friuli Venezia Giulia Plain. **a**, **b**, **c**, **d** refer to Mg^{2+} , Ca^{2+} , K^+ , Na^+ , respectively



particular during interglacial and glacial periods, where ice sheets covered the study area). Significant late Quaternary sea-level fluctuations, associated with alternating cooler and wetter periods would have changed the hydraulic gradients and partially or completely disconnected the deeper parts of the aquifer systems from the more active

surface circulations as found in the neighbouring Veneto region (Zuppi et al. 2004). The deep confined waters are characterised by essentially passive hydrodynamic conditions with almost no cross-transfer with the polluted shallower groundwaters. The $\delta^{18}O$ values indicate that there is very little continuity between the aquifers and that

Fig. 6 $\delta^{18}O$ range and mean values for the Friuli Venezia Giulia rainfall, rivers (from Boschini et al. 2006 and CAMI 2007) and groundwater samples (this study)



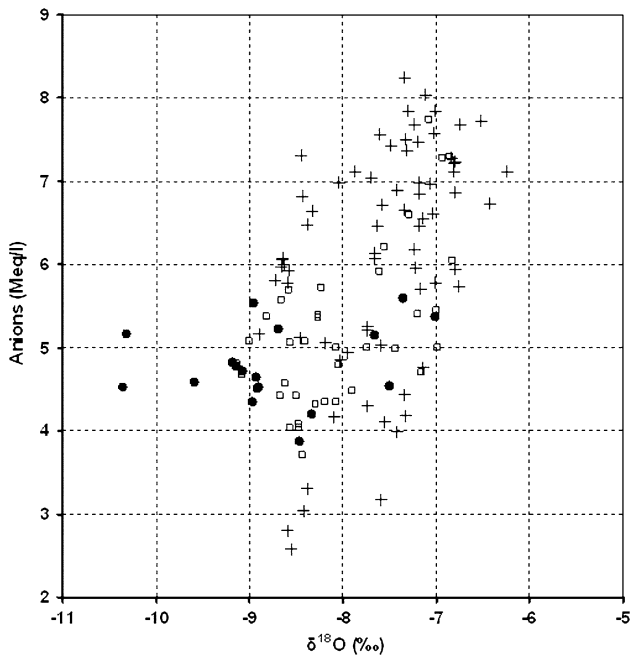
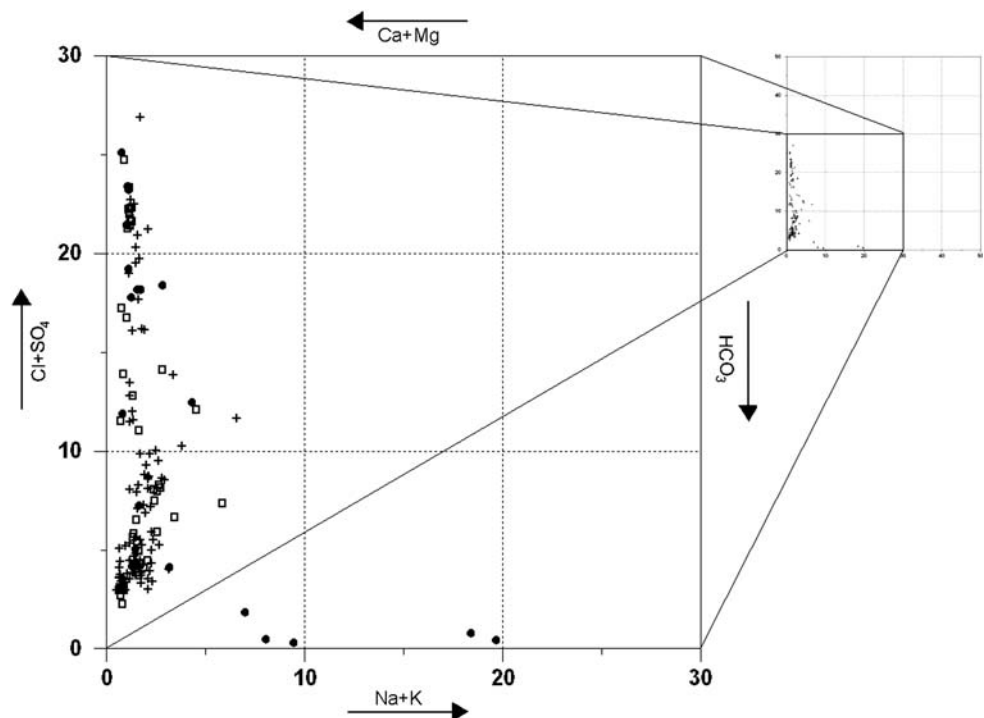


Fig. 7 Stable isotope $\delta^{18}\text{O}$ ratio relative to the total anions expressed in Meq/l, (crosses phreatic well samples, triangles shallow confined well samples and circles deep confined well samples)

the deeper aquifers may be, at most, only partially recharged by the present rainfall and the infiltration of local rivers. In addition to lower $\delta^{18}\text{O}$ values, the deep confined groundwater samples are characterised by relatively high Na–K values as highlighted by the Ludwig–Langelier diagram (Fig. 8). These deep confined waters have

Fig. 8 Major ion water composition according to the Ludwig–Langelier diagram (crosses phreatic well samples, triangles shallow confined well samples and circles deep confined well samples)



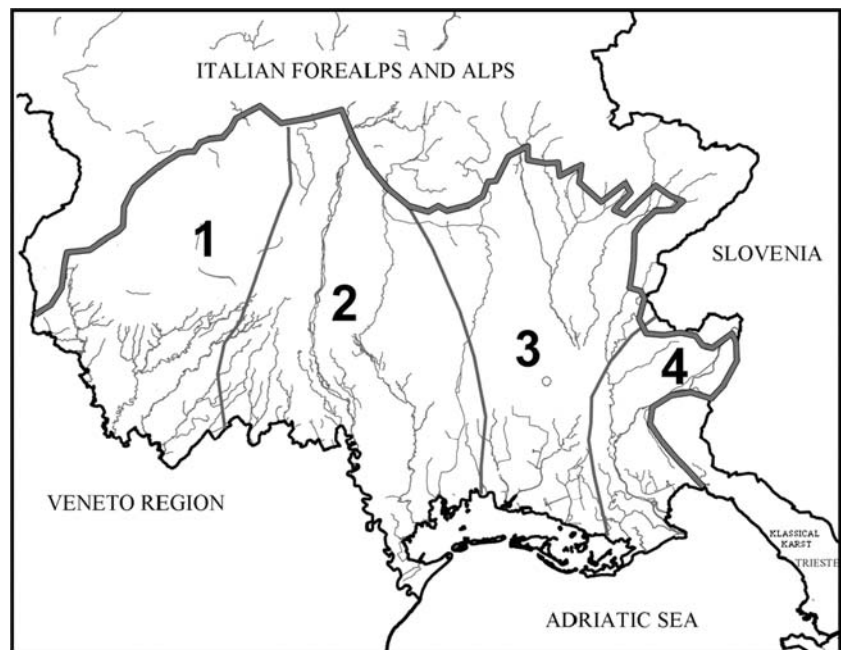
chemical characteristics that are distinct from water samples recovered closer to modern recharge areas, suggesting that the ion exchange between the deep confined groundwater and the silty-clay layers is therefore partially responsible for the groundwater chemistry variations with depth (Figs. 3a, 8). In addition, mineral saturation calculations indicate that the shallow and deep confined groundwaters are unsaturated with respect to gypsum, anhydrite and halite, whereas dolomite and calcite reach saturation in the great majority of the samples (Table 1). The phreatic groundwater samples have values that range from unsaturated to oversaturated for dolomite and calcite, whereas these samples are always unsaturated with respect to gypsum, anhydrite and halite (Table 1).

Four different hydrochemical zones have been recognised and mapped in the Friuli Venezia Giulia Plain, based on the chemical and isotopical information of the sub-surface (phreatic and shallow confined) groundwaters (Figs. 3a, 9).

Zone 1 The *Cellina-Meduna* Province groundwaters are characterised by depletions in $\delta^{18}\text{O}$ values, high bicarbonate (217–460 mg/l) and nitrate (due to intensive agricultural activity) ion (17–43 mg/l) and very low sulphates (0–50 mg/l) and potassium (0.2–1.1 mg/l) concentrations. The large difference in stable isotope data indicates that in this province the sub-surface groundwater is characterised mostly by river infiltrations (Cellina and Meduna rivers have depleted values in comparison to local rainfall, Fig. 6).

Zone 2 The *Tagliamento River* Province sub-surface groundwaters are strongly influenced by the Tagliamento

Fig. 9 Geochemical provinces of the Friuli Venezia Giulia Plain



River. This zone is characterised by very high concentrations of sulphates (50–125 mg/l) and chlorides (6.4–11.9 mg/l) and low bicarbonate (140–217 mg/l) and nitrate ion concentrations (0–17 mg/l).

Zone 3 The province between the *Torre* and *Natisone* rivers is characterised by high concentrations of nitrates (17–43 mg/l) due to intense agricultural activity and high calcium values (60–100 mg/l).

Zone 4 The *Isonzo River* Province is characterised by $\delta^{18}\text{O}$ values similar to local rainfall, high bicarbonate (217–460 mg/l) and chlorides (6.4–11.9 mg/l) concentrations. The isotopic data are similar to local rainfall and imply that the sub-surface groundwater is mainly recharged by local rainfall.

The difference in water chemistry and stable isotope data between the sub-surface and the deep confined groundwater provides clear indications of the potential vulnerability of the groundwater resource to surface contamination from a variety of sources, such as agricultural practices, discharge from urban areas and small-scale industries located in the region. To date, groundwater with high nitrate and chloride contents is distributed patchily in the phreatic and shallow confined groundwaters, and there is little or no apparent evidence that fertilizers and pesticides have contaminated the deep confined groundwaters. Since the groundwater contributes to the surface water, shallow and deep aquifer vulnerability to overpumping and/or contamination may result in increased risk to water resources throughout the entire catchments' region.

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