Hydrogeochemical features of the Sardinian rivers

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ABSTRACT. — The physical-chemical parameters and contents of the main dissolved components, together with some minor elements, were determined in 35 waters from rivers flowing in Sardinia (Italy). Dominant Na-Cl, low salinity (<0.5 g/L) and high SiO_2 concentrations are observed in waters draining silicate environments, and dominant Na-Ca-Cl-HCO_3 and higher salinity (0.6 to 1.2 g/L) occur in waters from sedimentary environments. Waters draining areas that host Pb-Zn ores show higher SO_4 due to the oxidation of sulphide minerals. The main chemical composition does not change when waters are sampled at different climatic conditions; however, salinity and concentrations of the main ions increase at low-flow condition in the summer season. At high-flow condition, i.e. when the rivers have a high rainwater component, a decrease in many chemical species is observed due to dilution processes, but at the same time, an increase in the concentration of soluble species, such as nitrate, may occur.

RIASSUNTO. — I caratteri chimico-fisici, le concentrazioni dei componenti maggiori disciolti ed alcuni elementi minori sono stati determinati in 35 campioni dei principali corsi d'acqua della Sardegna. Le acque che drenano ambienti silicatici mostrano una composizione chimica a cloruro di sodio prevalente, bassa salinità (<0.5 g/L) e relativamente alta concentrazione in SiO_2. Le acque che drenano ambienti sedimentari hanno una composizione chimica a cloruro di sodio e bicarbonato di calcio prevalente, e salinità più alta (0.6 – 1.2 g/L). Le concentrazioni più elevate in solfato si osservano in acque che drenano aree minerarie con depositi ricchi in solfuri. Nei campioni d'acqua prelevati in diverse condizioni climatiche non si osservano variazioni nella composizione chimica principale, ma la salinità e la concentrazione degli ioni maggiori disciolti aumenta in condizioni di magra. In condizioni di portate elevate, ovvero quando le precipitazioni sono importanti, si osserva una diminuzione in gran parte delle specie chimiche dovuta a processi di diluizione, ma allo stesso tempo, può essere favorita la lisciviazione di specie solubili, come ad esempio il nitrato

KEY WORDS: *hydrogeochemistry, river water, Sardinia*

INTRODUCTION

Anthropogenic activities may have a relevant impact on the soil-plant-water system; the

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incorrect management of industrial, agricultural and urban wastes may cause a degradation in the quality of water, especially the surface water that is highly vulnerable. Considering that the demand of good-quality water is growing worldwide, the study of water resources is of primary importance in a sustainable development of our societies. In particular, the assessment of the water quality is of special interest in areas, such as the Sardinia island (Italy), where the quantity of water is limited by the occurrence of cyclical drought periods.

Sardinia is located in the Western Mediterranean Sea and extends on 24090 km². It shows variable climatic conditions, from semi-arid in the plain
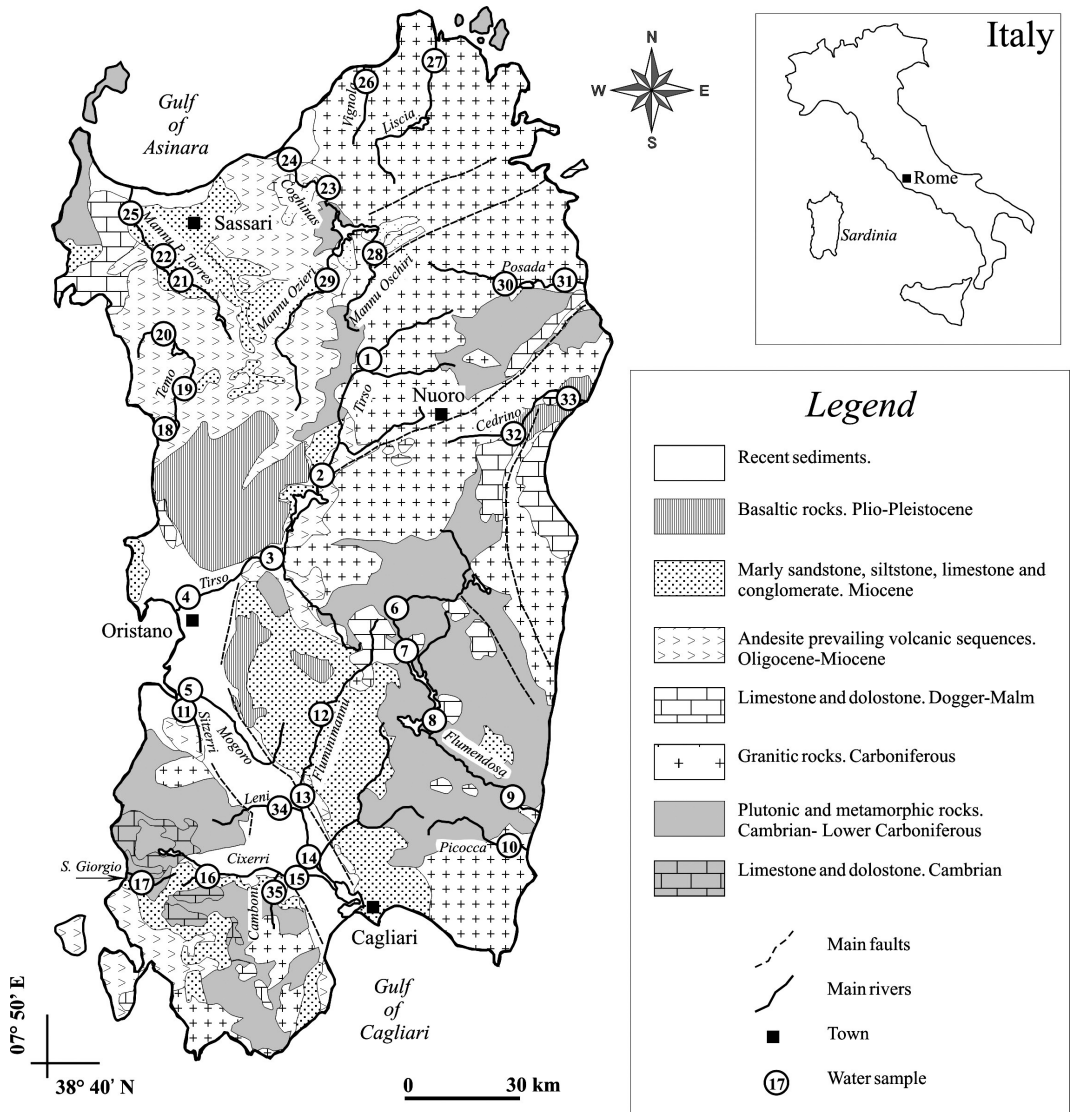

Fig. 1 – Map of Sardinia showing the main geology and hydrography (modified from Carmignani *et al.*, 2001a, b), and the location of the river water samples.

to semi-humid in the mountains. The mean precipitation is in the range of <500 to 1100 mm per year, with a mean of <50 to 90 rainy days; occasional heavy-rain events occur. The monthly mean temperatures range from 5°C in winter to 25°C in summer. The flow of rivers strongly depends on rainfall, and may vary by several orders of magnitude in a year, and from one year to the other. River water collected in artificial basins is the most important water resource in the region; it constitutes about 70% of the water supplied to about 1.6 million people for domestic, agricultural and industrial uses. Considering the importance of surface waters, this study was undertaken to evaluate the influence of climate on the quality and the chemical composition of waters in the main rivers of Sardinia.

Study area

The Sardinia region shows a large variety of rocks (Figure 1, Carmignani *et al*, 2001 b, c). A Paleozoic basement, made up of granitic and metamorphic rocks, extends from North to South in the eastern part of the island, and is interrupted by Tertiary rocks in the western part. Remains of Mesozoic carbonate rocks lay on the basement. A prominent structure, known as the Sardinian Rift, extends from North (the Gulf of Asinara) to South (the Gulf of Cagliari). The Sardinian Rift has been filled up with volcanic rocks (Oligo-Miocene andesite and ignimbrite, and Plio-Pleistocene basalt), and marine (Miocene carbonate, conglomerate and marl sequences) and continental (Plio-Pleistocene) sediments. The occurrence of diffused metal deposits (mainly Pb, Zn, Cu sulphide minerals) is particularly relevant in Sardinia. Sulphide ores and gossans were exploited intensively from 1880 to 1980. Mining activities contributed significantly to the social-economic development, also, they caused important landscape modification in the region. Most mines were closed in 1980-1990; residues of mining exploitation and processing have been left on site, frequently without an adequate disposal; they constitute potential sources of environmental contamination and may cause heavy-metal pollution in the aquatic system (Cidu and Fanfani, 2002).

Methods

In this study, the most important rivers and streams flowing in Sardinia were considered (Figure 1). Sampling of 35 surface waters was carried out in January 2003 at high-flow condition. In the Tirso, Mogoro, Flumini Mannu, Cixerri and S. Giorgio basins, sampling of water at 12 sites was repeated in June 2003 under low-flow condition. The location of water samples referred to the major rivers is shown in the maps reported in the Appendix 1 to 8; the schematic geology in the maps is derived from Carmignani *et al*. (2001b, c); the seasonal variability in precipitation (P) and temperature (T) at each basin is shown in the diagrams A, and refer to data collected in the period 1922-1992 (E.A.F., 1998).

At the sampling site, temperature, pH, redox potential (Eh), conductivity and alkalinity were measured; waters were filtered (0.4 µm) and acidified with suprapure HNO_3 for cation analyses. Anions were determined by ionic chromatography, main cations by ICP-OES and minor elements by ICP-MS. The ionic balance was always less than 5%, suggesting that the analyses are of good quality. Equilibrium calculations were made with the computer code WEB-PHREEQ (Parkhurst, 2001); the saturation index (SI) with respect to a mineral phase is equal to log(IAP/K); IAP = ionic activity product in the water, K = equilibrium constant at the water temperature.

Results and discussion

The physical-chemical characters and concentrations of the major and some minor components dissolved in waters from the Sardinian rivers are reported in Table 1. The water samples considered in this study have a large variability in flow rates: from 0.1 to 80 m^3 per second during the sampling carried out in January 2003. It should be noted that the highest flow was recorded at the Tirso (No. 3, Table 1, Appendix 6) sampled downstream of a large reservoir (Lake Omodeo); at this site the Tirso river receives the overflow water discharged from the reservoir; this operation normally occurs during the rainy season.

TABLE 1

Physical-chemical characters and dissolved (<0.4 μm) components in the Sardinian river waters sampled in January 2003; sample numbers with the label a indicate sampling in June 2003

No.	Name	Flow m³/s	T °C	pH	Eh mV	Cond. mS/cm	TDS g/L	Ca	Mg	Na	K	HCO₃	Cl	SO₄	SiO₂	NO₃	Br	F mg/L	Li	Rb	Sr	Ba μg/L
1	Tirso	0.8	11	7.5	470	0.32	0.19	14	8.7	36	1.7	56	65	20	12	9.2	0.23	0.18	1.8	1.3	75	12
2	Tirso	4	12	7.7	460	0.52	0.30	24	13	66	3.3	88	95	39	15	12	0.35	0.28	3.1	2.9	110	21
2a	Tirso	0.5	24	7.7	400	1.00	0.54	39	14	148	7.2	290	110	70	10	12	0.78	0.27	4.6	4.1	130	13
3	Tirso	80	11	7.9	470	0.46	0.26	34	15	42	2.1	110	70	35	12	7.2	0.25	0.17	2.5	1.2	120	30
3a	Tirso	10	14	7.6	500	0.62	0.33	29	14	67	5.6	130	90	43	14	6.0	0.38	0.18	2.8	2.5	130	30
4	Tirso	7	12	7.7	440	0.49	0.29	29	15	52	3.2	105	92	32	16	1.5	0.30	0.26	4.5	2.8	140	45
4a	Tirso	1	25	7.8	440	0.91	0.48	58	24	84	4.6	230	140	48	8	<1	0.48	0.30	5.9	1.8	270	42
5	Mogoro	2	13	7.9	460	0.81	0.50	70	22	79	7.0	230	120	65	25	16	0.40	0.30	5.4	6.9	350	71
5a	Mogoro	0.05	26	8.3	420	1.20	0.71	71	30	140	8.9	290	220	78	19	4.0	0.56	0.28	6.8	5.8	420	47
6	Flumendosa	7	9	7.6	490	0.15	0.08	10	4.3	12	1.2	34	20	12	8.4	3.1	0.07	0.20	0.9	0.5	35	21
7	Flumendosa	0.1	9	7.7	480	0.18	0.11	14	6.3	13	1.4	48	24	15	8.2	3.3	0.07	0.18	1.3	0.6	39	20
8	Flumendosa	0.1	11	8.2	490	0.81	0.53	74	48	42	1.8	220	87	160	5.5	5.2	0.30	0.33	9.5	1.5	280	30
9	Flumendosa	3	11	7.9	450	0.45	0.27	45	14	30	1.8	120	60	53	7.1	3.6	0.18	0.32	4.3	0.6	120	44
10	Picocca	2	10	7.1	490	0.31	0.17	14	7.5	34	1.5	32	67	23	11	4.1	0.23	0.39	2.4	0.5	62	44
11	Sitzerri	0.5	11	7.5	490	0.40	0.24	22	11	43	4.3	89	59	37	22	4.8	0.18	0.15	1.7	3.3	83	53
11a	Sitzerri	0.1	24	7.4	470	0.93	0.47	38	19	104	9.6	120	170	56	14	27	0.24	0.24	4.4	5.4	180	35
12	Flumini Mannu	0.1	9	8.2	470	1.30	0.78	102	37	106	12	380	180	140	12	15	0.63	0.39	20	2.4	740	62
12a	Flumini Mannu	0.05	22	8.1	430	1.70	0.98	130	53	140	10	430	220	200	7.7	1.9	0.35	0.35	29	1.9	1160	68
13	Flumini Mannu	0.2	11	7.8	470	1.80	1.17	135	62	200	11	360	360	210	9.1	25	1.20	0.45	14	1.3	880	65
13a	Flumini Mannu	0.1	24	7.8	460	2.00	1.11	130	60	190	10	340	340	200	9.4	27	1.10	0.33	16	1.3	990	67
14	Flumini Mannu	5	11	7.8	480	1.60	0.93	75	39	200	14	230	340	135	10	22	1.20	0.48	15	4.1	460	49
14a	Flumini Mannu	1	25	7.8	420	2.10	1.18	100	51	240	17	310	430	176	9.7	15	0.91	0.39	17	4.5	700	65

| No.	Name	Flow m³/s	T °C	pH	Eh mV	Cond. mS/cm	TDS g/L	Ca	Mg	Na	K	HCO3	Cl	SO4	SiO2	NO3 mg/L	Br	F	Li	Rb	Sr µg/L	Ba
15	Cixerri	1	11	7.7	500	0.78	0.46	48	22	87	5.6	152	150	61	9.3	10	0.50	0.32	3.6	2.7	140	98
15a	Cixerri	0.3	24	7.6	440	1.10	0.59	88	30	90	9.2	260	145	89	11	7.3	0.28	0.24	4.6	4.9	170	79
16	Cixerri	1	11	8.0	470	0.99	0.58	67	29	100	6.6	227	160	96	11	8.8	0.55	0.30	4.3	3.7	190	130
16a	Cixerri	0.5	27	8.2	400	1.10	0.62	78	34	89	11	350	150	72	8.1	1.2	0.28	0.20	4.4	7.0	160	80
17	S. Giorgio	0.1	11	8.0	490	1.10	0.75	104	46	77	8.4	182	112	304	8.0	8.1	0.40	0.36	7.5	7.8	160	33
17a	S. Giorgio	0.1	23	8.2	450	2.20	1.49	208	97	160	11	460	220	560	7.5	2.1	1.04	0.39	15	15	300	29
18	Temo	20	9	7.8	480	0.63	0.36	29	15	77	3.5	102	139	31	19	7.6	0.46	0.18	1.9	2.0	170	23
19	Temo	0.7	8	8.0	490	0.66	0.43	65	15	65	3.7	265	92	35	23	7.3	0.32	0.20	4.8	3.3	300	28
20	Temo	0.3	8	7.6	510	0.37	0.21	11	7.7	46	2.2	41	80	16	23	2.4	0.29	0.90	1.2	2.5	67	20
21	Mannu Uri	0.3	9	8.1	490	1.02	0.60	105	19	90	5.7	293	159	55	22	15	0.48	0.24	8.0	4.2	610	30
22	Mascari	0.5	10	8.1	460	1.05	0.64	108	21	94	8.1	358	138	69	22	20	0.48	0.36	19	8.0	630	30
23	Coghinas	10	10	7.6	490	0.44	0.25	19	9.3	54	3.8	67	90	23	14	5.9	0.30	0.21	4.1	3.2	90	16
24	Coghinas	11	9	7.5	500	0.47	0.27	22	10	61	3.8	78	98	24	15	5.9	0.31	0.28	10	4.3	110	21
25	Mannu P.T.	8	9	7.9	480	1.07	0.63	107	19	99	7.2	322	163	60	19	27	0.60	0.09	9.0	5.4	460	28
26	Vignola	0.3	9	7.4	460	0.29	0.17	8	7.1	39	1.9	33	65	17	15	3.1	0.23	0.12	2.4	0.8	50	9
27	Liscia	5	8	7.6	490	0.46	0.27	16	12	59	1.9	71	101	25	16	4.3	0.34	0.25	3.3	0.7	83	20
28	Mannu Oschiri	1	8	7.7	470	0.41	0.23	18	11	47	2.0	58	82	25	15	9.6	0.28	0.26	3.8	1.3	90	14
29	Mannu Ozieri	8	8	7.9	460	0.60	0.35	39	13	67	3.8	129	108	31	19	8.4	0.35	0.12	5.1	2.8	150	19
30	Posada	1	8	7.4	490	0.19	0.12	8	5.5	25	1.5	25	45	14	13	1.7	0.16	0.16	2.6	0.7	39	5
31	Posada	2	8	7.6	500	0.22	0.13	11	6.3	26	2.1	35	45	17	9.6	2.4	0.15	0.21	2.6	0.9	46	10
32	Cedrino	10	9	8.1	480	0.43	0.23	47	11	25	1.8	149	43	23	4.9	4.5	0.15	0.17	1.3	0.8	74	16
33	Oliena	1	8	7.8	480	0.38	0.22	28	13	32	2.3	90	55	30	17	17	0.20	0.29	2.8	1.4	89	25
34	Leni	0.2	9	7.8	480	0.57	0.35	29	16	63	4.0	138	113	44	7.8	28	0.37	0.30	4.4	1.5	140	29
35a	Camboni	0.1	24	7.8	490	0.68	0.35	35	18	66	3.3	170	100	29	15	<1	0.24	0.90	14	3.1	140	120
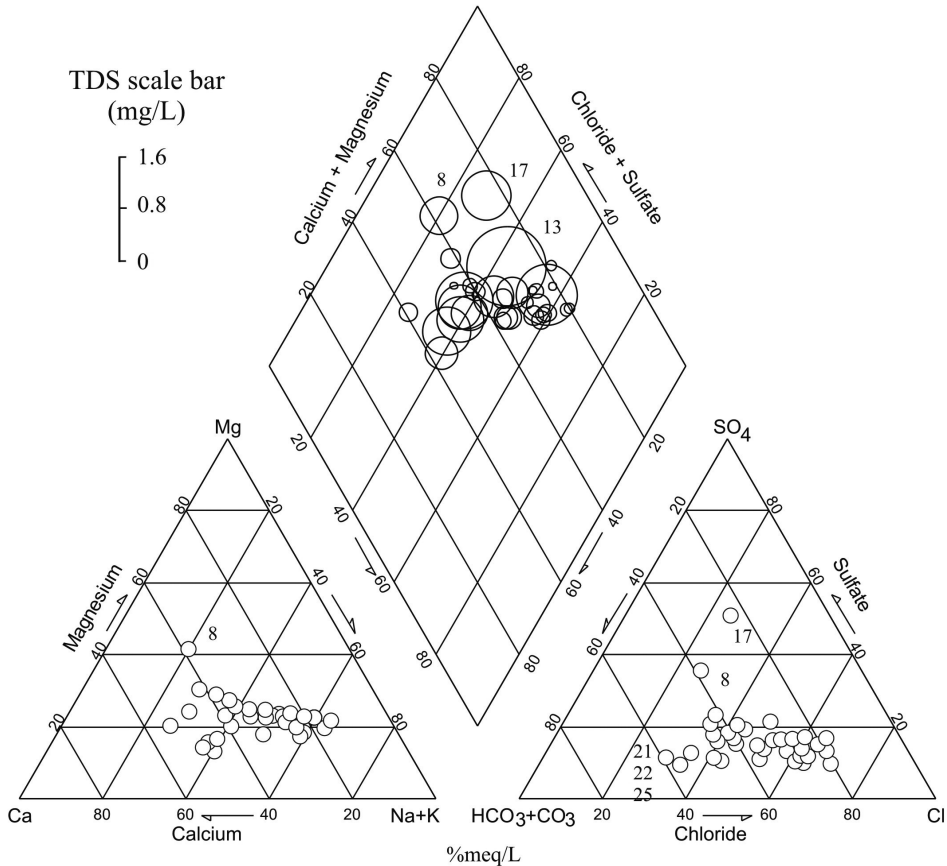
Fig. 2 – Piper diagram showing the main chemical composition of the Sardinian river waters sampled in January 2003.

Table 1 shows water temperatures in the range of 8 to 12 °C in January 2003 and 22 to 27°C in June 2003; temperatures in water reflect the air temperature during the different sampling seasons. The pH is near neutral or slightly alkaline (7.1-8.3). The redox potential (Eh) ranges from 420 to 510 mV: these values indicate oxidising conditions. Both pH and Eh values do not show significant variations at high- and low-flow conditions.

The conductivity (in the range of 0.2 to 1.8 mS/cm at high-flow) shows significant variations among samples depending on the dominant lithology in the catchments and on the size of the river basin. The lowest values are observed in the upper courses of rivers and in catchments dominated by silicate rock outcrops. Conductivity generally increases from the source to the mouth of rivers, and at the same site, it is higher in June 2003 at low-flow condition.

The Piper diagram shown in Figure 2 summarizes the water chemistry in the Sardinian rivers sampled in January 2003. Many waters show sodium-chloride composition and low salinity (TDS: 0.1 to 0.4 g/L), most of them drain granitic (e.g. No. 1, 10, 26, 27, 30, Table 1) and volcanic (e.g. No. 18, 20, 35, Table 1) rocks. A few waters have

calcium-bicarbonate composition and TDS 0.6 g/L (No. 21, 22, 25, Table 1, Figure 2), they flow on limestone formations (see Appendix 2). The other samples show an intermediate composition between sodium-chloride and calcium-bicarbonate and have higher salinity (TDS: 0.6 to 1.2 g/L); the highest salinity occurs in the Flumini Mannu (No. 13, Table 1, Figure 2) that receives water mostly flowing on marl-carbonate sediments of Tertiary age. The waters with TDS > 0.5 g/L are at equilibrium or supersaturated with respect to calcite (Figure 3).

Dissolved Mg is generally lower than Ca and Na. An important Mg contribution only occurs in the water sample No. 8 (Table 1, Figure 2); here a molar Ca/Mg ratio close to one is observed and is probably related to the weathering of Jurassic dolomite outcropping nearby (see Appendix 5). Sulphate is generally low in the studied waters, it is the dominant anion in the water of Rio S. Giorgio only (No. 17, Table 1, Figure 2). This sample is located downstream of an important abandoned mining area, near Iglesias (see Appendix 8); here the predominant sulphate character derives from the oxidation of sulphide minerals (mainly sphalerite, galena and pyrite), and from the weathering of mining wastes that may contain both primary sulphide minerals and secondary sulphates (Cidu *et al.*, 2005). A significant sulphate contribution is also observed in the Flumendosa water (No. 8, Figure 2); dissolved SO_4 in this water derives from the oxidation of pyrite disseminated in black schist of Silurian age (CARMIGNANI *et al.*, 2001a). All waters, including those with high sulphate concentrations, are undersaturated in gypsum; the more saline waters are less far from gypsum equilibrium than waters with low TDS (Figure 3).

The Stiff diagrams (reported in the Appendix 1 to 8, B) show that the main chemical composition of water at each site does not significantly change
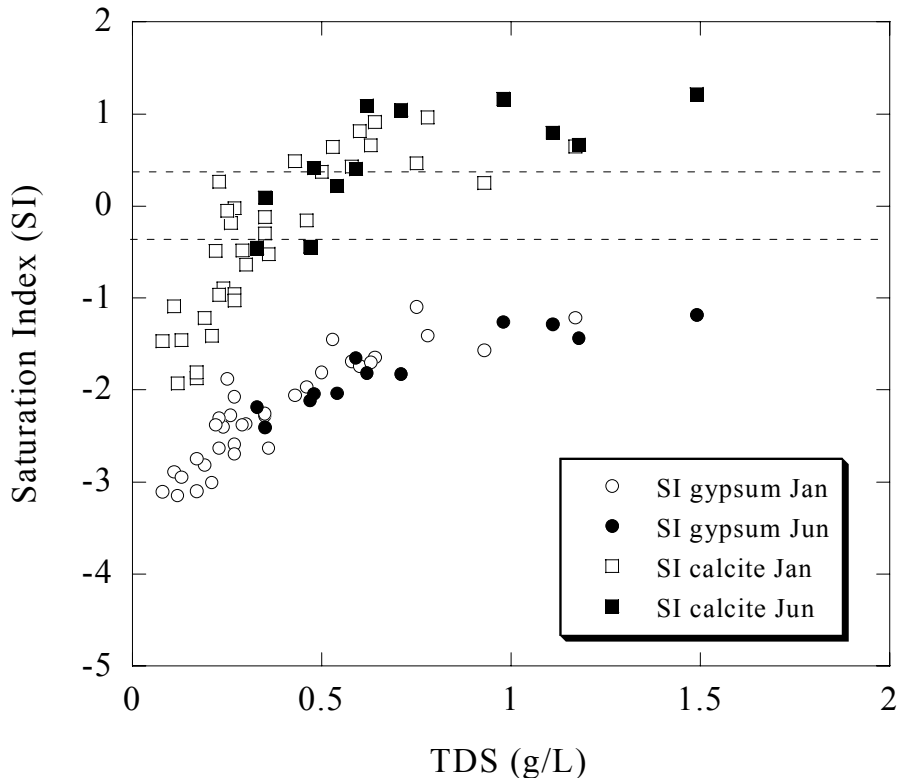

Fig. 3 – Saturation index (SI) values for calcite and gypsum versus total dissolved solids (TDS) in the Sardinian river waters sampled in January 2003 (Jan) and June 2003 (Jun). The area within dashed lines indicates equilibrium conditions.
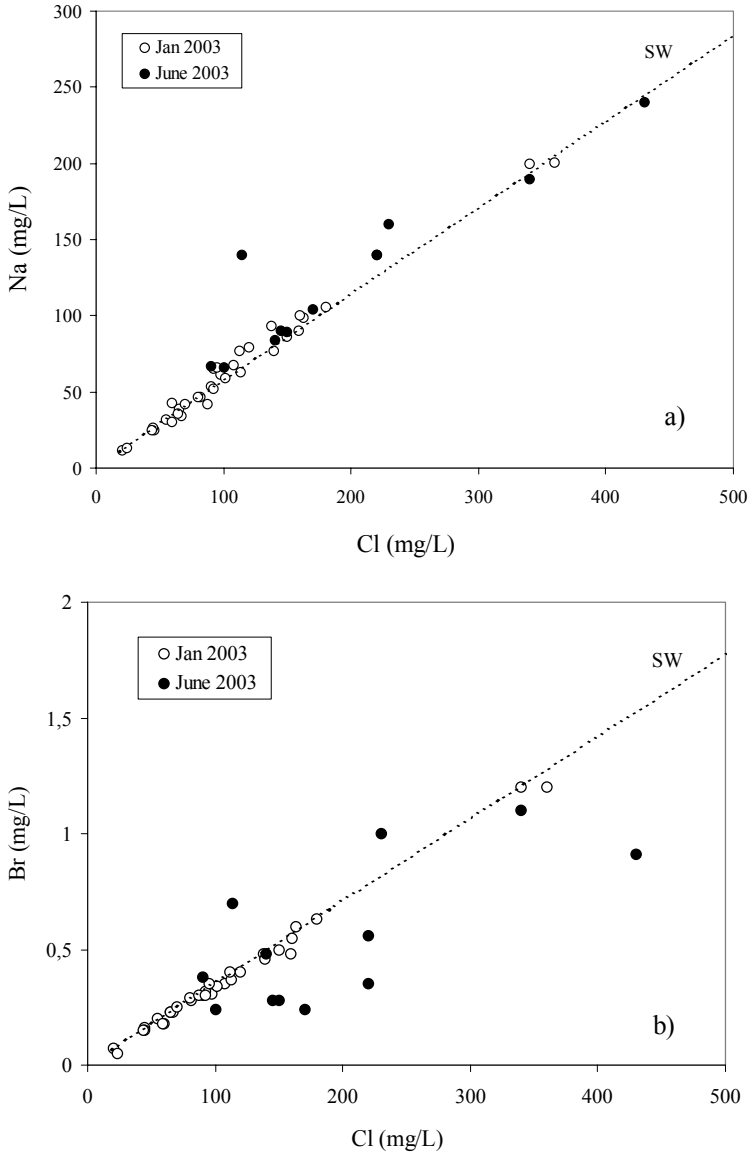
Fig. 4 – Plot showing dissolved sodium (a) and bromide (b) versus chloride concentrations in the Sardinian river waters. The dashed line indicates diluted seawater (SW).

when the water is sampled at different climatic conditions, but it can be observed that the concentrations of main ions generally increase in June 2003 at low-flow condition. This increase may be due to the low contribution of rainwater in June, to evaporation processes, and/or to the input of more saline groundwater into the rivers.

Figures 4a and 4b show that dissolved Na and Br are well correlated with Cl concentrations ($R^2=0.984$, and $R^2=0.993$, respectively; total
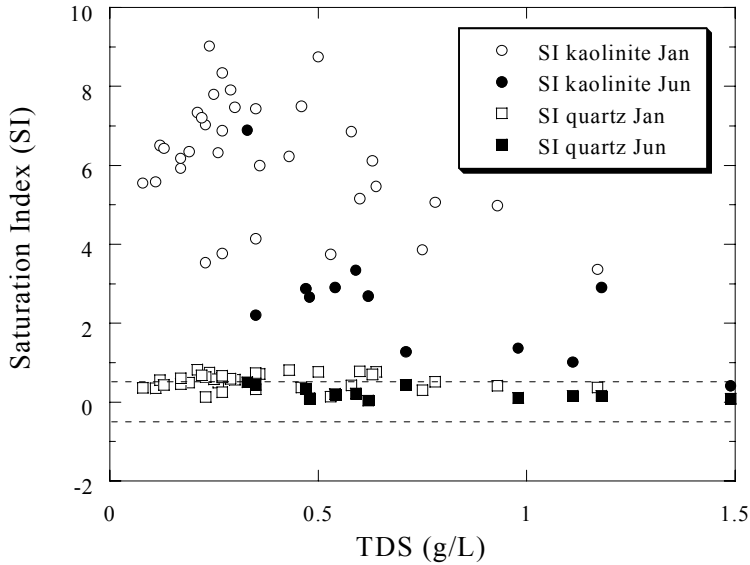
Fig. 5 –Saturation index (SI) values for kaolinite and quartz versus total dissolved solids (TDS) in the Sardinian river waters sampled in January 2003 (Jan) and June 2003 (Jun). The area within dashed lines indicates equilibrium conditions.
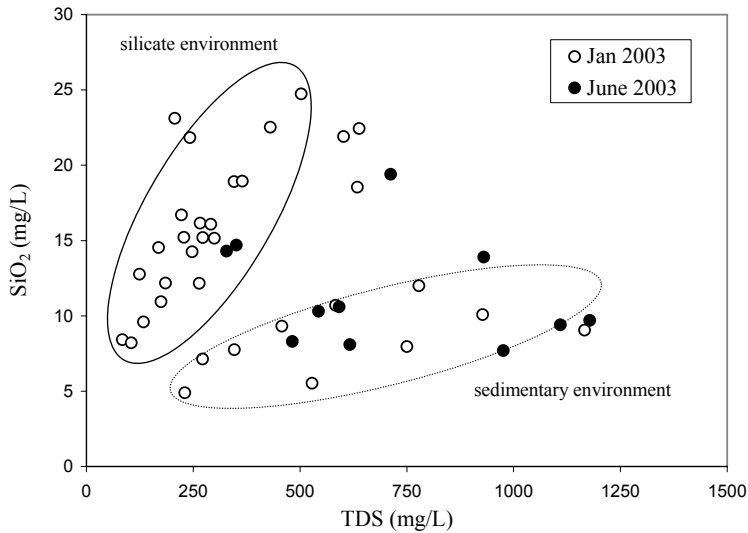

Fig. 6 –Plot showing dissolved silica versus total dissolved solids (TDS) in the Sardinian river waters.

samples = 47). The values of Na/Cl and Br/Cl ratios in waters sampled in January 2003 are very close to values observed in seawater. The Mg/Ca ratio close to the seawater value also occurs in the less saline waters sampled in January 2003. These observations indicate a high rainwater component in the waters sampled in January, and are in agreement with the following considerations. The

composition of rainwater in coastal areas of Europe strongly resembles diluted seawater; Na/Cl ratios in the rain remain similar to the Na/Cl ratio in seawater (Appelo and Postma, 1994); during the transport of marine aerosol, that in an island may represent an important source of salts dissolved in water, ion fractionation is not considered a relevant process (Mazor, 1997). Some waters collected in June 2003 at low-flow conditions (i.e. when the rainwater contribution is low) show Na/Cl and Br/Cl values that differ from the seawater ratios (Figures 4a and 4b), suggesting additional contributions other than rainwater and dissolution of marine aerosol, or hydrogeochemical processes other than evaporation of the river water. The Na/Cl higher than seawater is generally attributed to dissolution of Na-silicate minerals, such as albite, and/or to Ca-Na exchange reactions. Different processes may produce aqueous Br/Cl values different than Br/Cl in seawater, such as: halite dissolution; interaction of water with aqueous organic components or with organic matter present in the soil and in sediments (Edmunds, 2001); interaction of water with soils amended with pesticides and fertilizers, the latter may contain up to 500 ppm Br (Otero *et al.*, 2005); ion fractionation during the evaporation of water (Hounslow, 1995). Variations of Br/Cl in waters of

Sardinian rivers sampled in June 2003 are probably due to processes involving organic material and/or to drainage of cultivated soils.

In the studied waters, SiO_2 varies from 5 to 25 mg/L. All waters are supersaturated with respect to kaolinite, and at equilibrium with respect to quartz (Figure 5). The saturation index with respect to kaolinite in the waters sampled in January 2003 is much higher than in waters sampled in June 2003; this is likely due to the presence of Al in very fine material (< 0.4 μm) which is more abundant at high flow condition. Figure 6 shows dissolved SiO_2 concentrations versus total dissolved solids (TDS). It can be observed that SiO_2 generally increases as TDS increase, but two different trends can be recognised. The highest SiO_2 concentrations are observed in waters sampled in January 2003 at high-flow conditions; most of these waters drain granitic and volcanic rocks (i.e. dominant silicate environment). Considering that the weathering of silicate minerals is a very slow process, especially at low temperature, the high SiO_2 concentrations observed in those waters having a high rainwater component unlikely derive from dissolution of silicate minerals. It appears reasonable to presume that the SiO_2 measured in the water is likely present
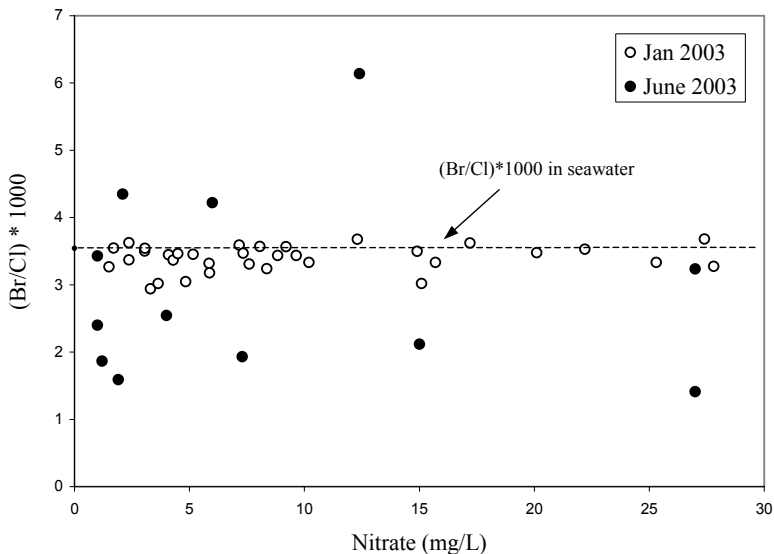

Fig. 7 – Plot showing the Br/Cl ratio versus nitrate concentrations in the Sardinian river waters.

W.H.O. guidelines and Italian regulations for drinking water, and water samples with dissolved concentrations above the Italian limits at high- and low-flow conditions

		WHO (1)	Italy (2)	water samples above limit	
				high-flow (Jan 2003) *(total samples: 35)*	low-flow (June 2003) *(total samples: 12)*
Cl	mg/L	-	250	No. 13 and 14	No. 13a and 14a
SO$_4$	mg/L	-	250	No. 17	No. 17a
Na	mg/L	-	200	none	none
NO$_3$	mg/L	50	50	none	none
F	mg/L	1.5	1.5	none	none

(1) World Health Organization (W.H.O. 2004).
(2) Italian regulations for drinking water (G.U.R.I. 2001).
 - not of health concern at levels found in drinking water; may affect acceptability of drinking water.

in very fine particles (<0.4 μm), or colloidal forms, that are not retained on the filter.

Concentrations of nitrogen-species in all samples are below the maximum values established by Italian regulations established for drinking water (G.U.R.I., 2001). Reduced nitrogen-species (NO$_2$, NH$_4$, not reported in Table 1) were always below 0.1 mg/L concentrations; this result is in agreement with the measured redox potential values indicating oxygenated waters. Nitrate (NO$_3$) dissolved in waters varies from <1 to 28 mg/L. Figure 7 shows

the Br/Cl ratio versus nitrate concentrations; taking into account the above considerations, those waters with Br/Cl ratio close to seawater are assumed to have an important rainwater component. It can be observed that relatively high NO$_3$ concentrations occur more frequently in January 2003 at high-flow condition; they are often measured in waters draining cultivated and farmed areas (e.g. No. 13 and 14, located in the Campidano plain) and are associated to relatively high K contents (see Table 1); in these waters, both nitrate and potassium
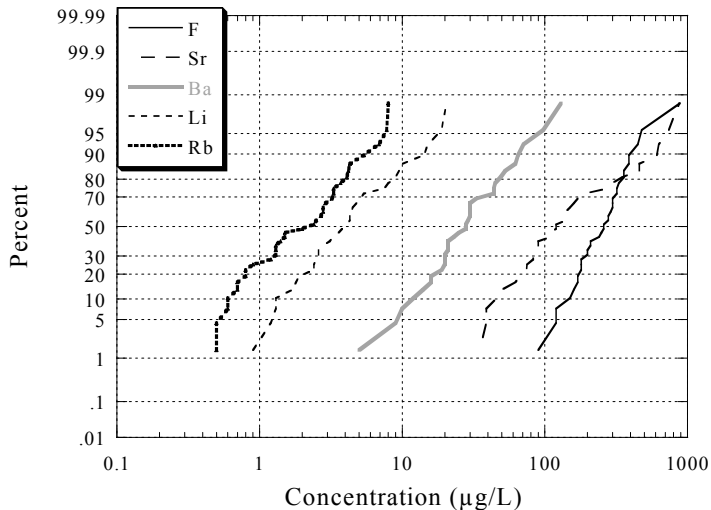

Fig. 8 – Frequency plots for Li, Rb, Sr and Ba concentrations in the Sardinian river waters sampled in January 2003.

derive in part from fertilizers and farming. Peak winter values exceeding 100 mg/L NO_3 concentrations have been observed in other rivers draining intensively farmed areas, such as East Anglia in the UK (Alloway and Ayres, 1997).

The concentrations of the minor components F, Li, Rb, Sr and Ba generally vary within one order of magnitude (Table 1). Figure 8 shows frequency plots for concentrations of these minor components in the river waters sampled in January 2003. Frequency curves for Li, Rb and Sr show similar shapes with low gradient, suggesting that the concentrations of these elements probably depend on their availability in the parent rocks (Drever, 1997). In particular, the highest Sr concentrations are observed in waters interacting with carbonate and marl sediments. The F and Ba curves show slightly higher gradient and might indicate that concentrations of these elements are controlled by the solubility of a mineral phase. In order to check this hypothesis the saturation indexes (SI) with respect to the fluorite and barite minerals were calculated, and the variation of SI values versus TDS is reported in Figure 9. It can be seen that many samples are at equilibrium or slightly supersaturated with respect to barite, and that the

saturation index of fluorite shows an increasing trend with increasing salinity; these observations suggest a possible solubility control for F and Ba concentrations in the river waters.

Table 2 reports the World Health Organization (W.H.O., 2004) guidelines and Italian regulations (G.U.R.I., 2001) for drinking water. The water samples with dissolved concentrations above the Italian limits, at high- and low-flow conditions, is also reported in Table 2. The only sample (No. 17) that shows dissolved SO_4 above the limits established for drinking water is the Rio San Giorgio draining the abandoned mines in the Iglesias valley (Appendix 8). The two samples having dissolved Cl above limits belong to the Fluminimannu (Appendix 7) where Cl derives from the interaction of water with marine-derived sediments. The waters having either SO_4 or Cl above limits are not used for domestic purposes.

CONCLUSIONS

This study shows that the quality of the Sardinian river waters is generally good with respect to the parameters considered. The water quality, as well
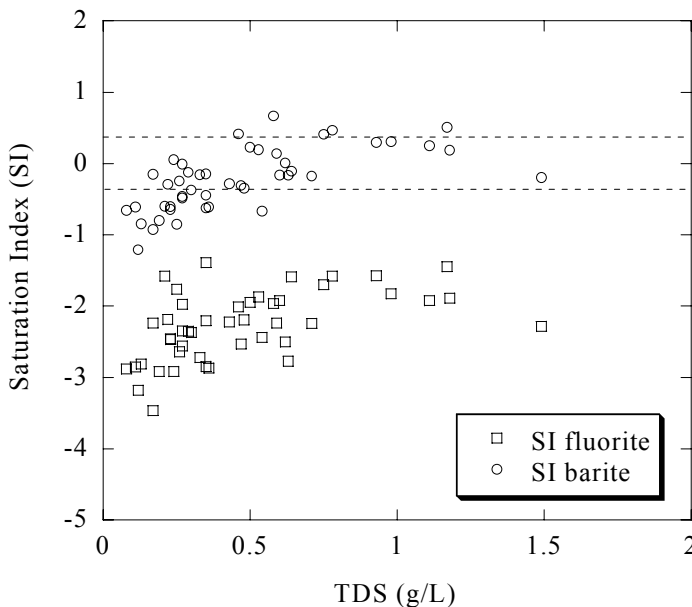

Fig. 9 – Saturation index (SI) values for fluorite and barite versus total dissolved solids (TDS) in the Sardinian river waters sampled in January 2003. The area within dashed lines indicates equilibrium conditions.

as the main chemical composition of rivers, does not change significantly when waters are sampled at high- or low-flow conditions; this observation apparently indicates that climate has a low influence on the water chemistry. Nevertheless, the amount of the rainwater component can be an important factor in some geochemical processes affecting the aqueous system, and therefore, climatic conditions should be considered when planning water sampling campaigns. A high rainwater contribution to the rivers leads to a decrease in the concentration of many chemical species due to dilution processes, but at the same time, may also lead to increase the concentration of soluble compounds, such as nitrate. Moreover, high-flow conditions often correspond to high suspended load that may comprise very fine particles unremoved by conventional filtration (usually 0.2 – 0.45 µm). The very fine fraction present in the water, especially in surface waters, should receive more attention because it may host different contaminants, such as adsorbed heavy metals, and it may contribute to their dispersion far away from contaminated sites.

REFERENCES

ALLOWAY B.J. and AYRES D.C. (1997) – *Chemical principles of environmental pollution.* 2nd edition, Blackie Academic and Professional, London, 395 pp.

APPELO C.A.J. and POSTMA D. (1994) – *Geochemistry, groundwater and pollution.* Balkema, Rotterdam, 536 pp.

CARMIGNANI L., CONTI P., PERTUSATI PC., BARCA S., CERBAI N., ELTRUDIS A., FUNEDDA A., OGGIANO G. and PATTA ED. (2001a) – *Note illustrative della carta geologica d'Italia alla scala 1:50.000, Foglio 549 Muravera.* Serv. Geol. It., 140 pp.

CARMIGNANI L., OGGIANO G., BARCA S., CONTI P., ELTRUDIS A., FUNEDDA A. and PASCI S. (2001b) – *Geologia della Sardegna – Memorie descrittive della carta geologica d'Italia.* Serv. Geol. It., **60**, 283 pp.

CARMIGNANI L., OGGIANO G., BARCA S., CONTI P., ELTRUDIS A., FUNEDDA A. and PASCI S. (2001c) – *Carta Geologica della Sardegna* – Scala 1:2.000.000. Litografia Artistica Cartografica, Firenze.

CIDU R., BIDDAU R. and SECCI G. (2005) – *Legacy at abandoned mines: impact of mine wastes on surface waters.* Proc. 9th Intern. Mine Water Congr. (J. Loredo and F. Pendàs Eds.), Oviedo, Spain, 247-252.

CIDU R. and FANFANI L. (2002) - *Overview of the environmental geochemistry of mining districts in south western Sardinia, Italy.* Geochem. Expl. Envir. Anal., **2**, 243-251.

DREVER J.I. (1997) – *The geochemistry of natural waters. Surface and groundwater environments.* 3rd edition, Prentice Hall, Upper Saddle River, New Jersey, 436 pp.

E.A.F. (1998) – *Nuovo studio dell'idrologia superficiale della Sardegna.* Ente Autonomo del Flumendosa (Scientific Responsible: Carlo Cao Pinna), Cagliari, Italy.

EDMUNDS W.M. (2001) – *Significance of geochemical signatures in sedimentary basin aquifer systems.* Proceedings 10th Water-Rock Interaction (R. Cidu Ed.), Balkema, **1**, 29-36.

G.U.R.I., Gazzetta Ufficiale della Repubblica Italiana (2001) – *Decreto Legislativo 2 febbraio 2001, n. 31.* In: Supplemento n. **52**, 3 marzo 2001. Istituto Poligrafico dello Stato, Roma, Italy.

HOUNSLOW A.W. (1995) – *Water Quality Data Analysis and Interpretation.* Lewis Publishers, New York, 397 pp.

MAZOR E. (1997) – *Chemical and isotopic groundwater hydrology: the applied approach.* Marcel Dekker, New York, 413 pp.

OTERO N., VITORIA L., SOLER A., CANALS A. (2005) – *Fertilizer characterization: major, trace and rare earth elements.* Appl. Geochem. 20, 1473-1488.

Parkhurst D. (2001) – WEB-PHREEQ: *aqueous geochemical modeling.* North Dakota State University, USA.

W.H.O., World Health Organization (2004) – *Guidelines for drinking-water quality,* third edition. Vol.1, World Health Organization, Geneva.
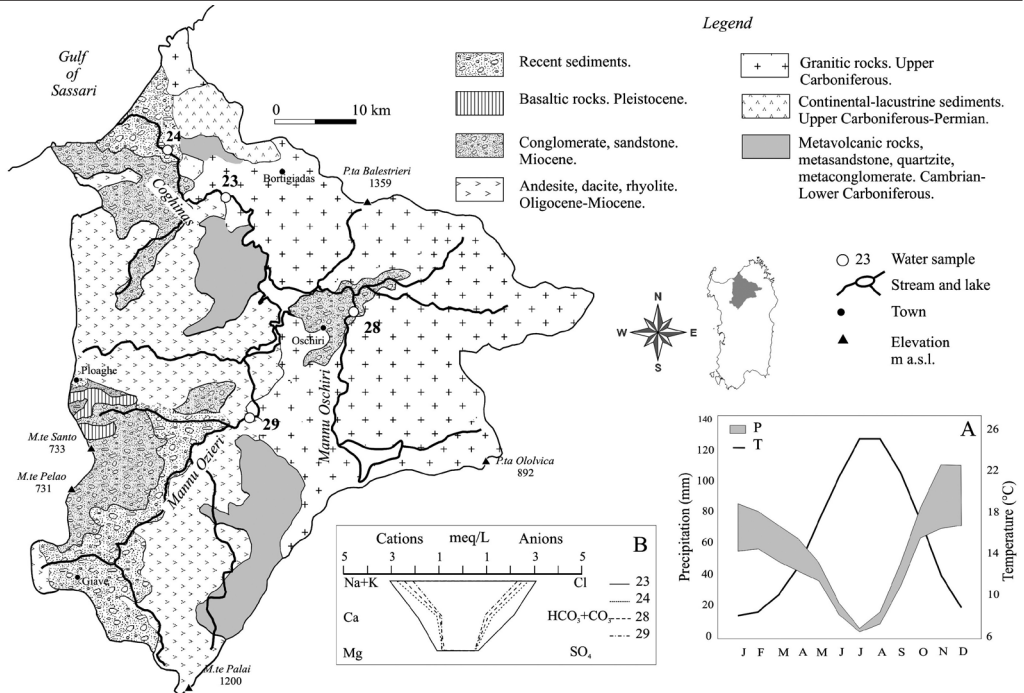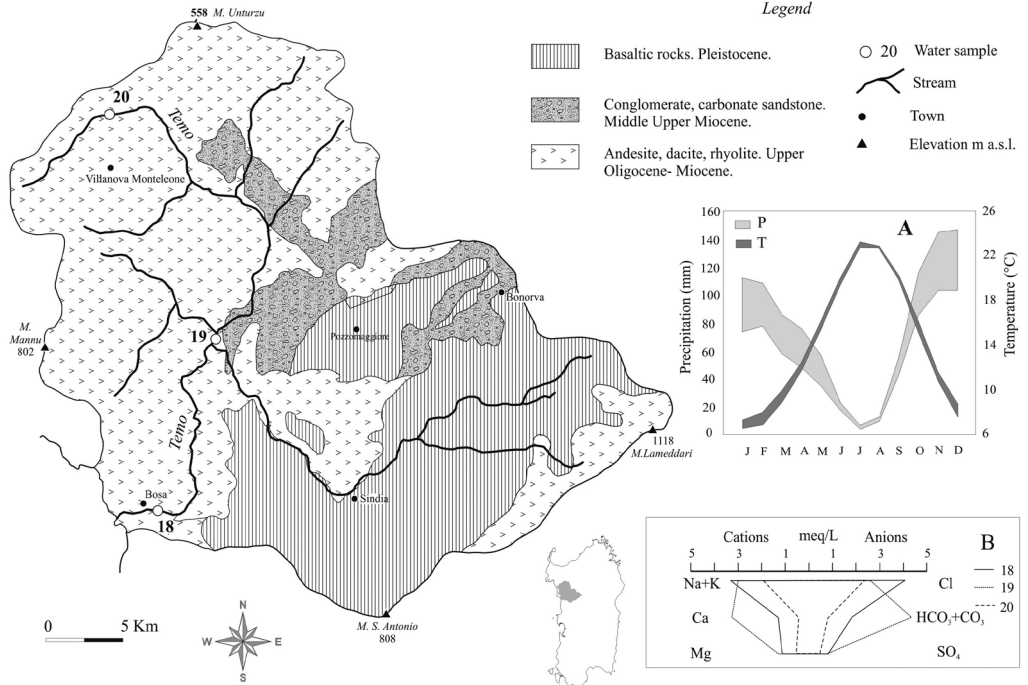
Geological sketch map and location of water samples in the Coghinas basin. The monthly mean of precipitation (P) and temperature (T) reported in diagram A refer to data collected at the S. Maria Coghinas (10 m a.s.l.), Coghinas (66 m a.s.l.), Oschiri (202 m a.s.l.) and Chilivani (220 m a.s.l.) stations. The Stiff diagram (B) shows the chemical composition of waters.
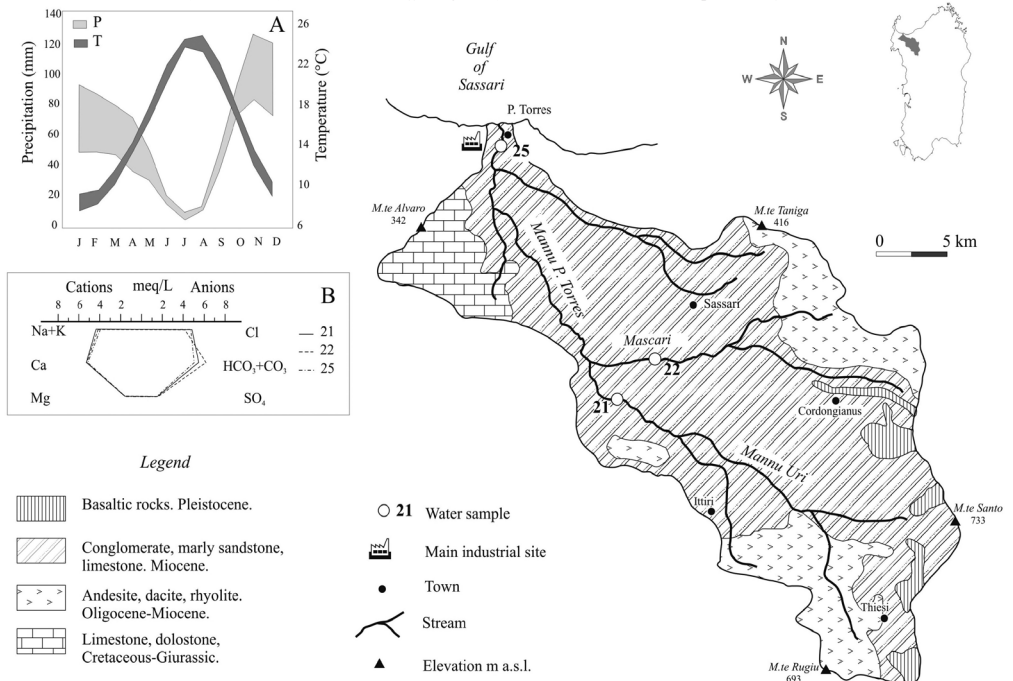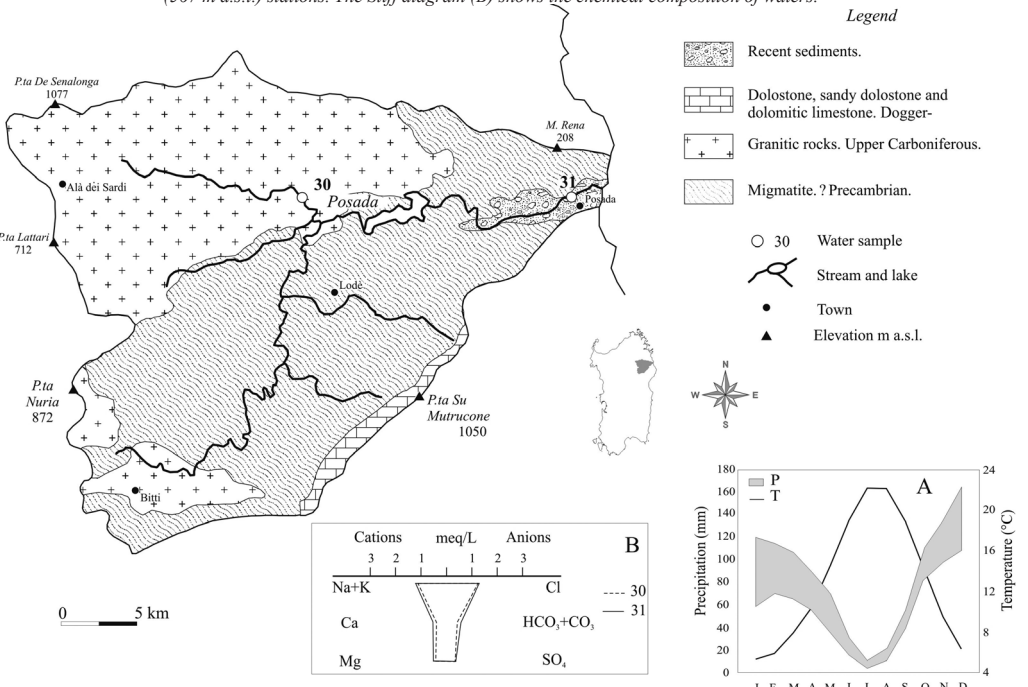

Geological sketch map and location of water samples in the Mannu Porto Torres basin. The monthly mean of precipitation (P) and temperature (T) reported in diagram A refer to data collected at the Porto Torres (2 m a.s.l.), Uri (150 m a.s.l.), Sassari (224 m a.s.l.) and Thiesi (472 m a.s.l.) stations. The Stiff diagram (B) shows the chemical composition of waters.
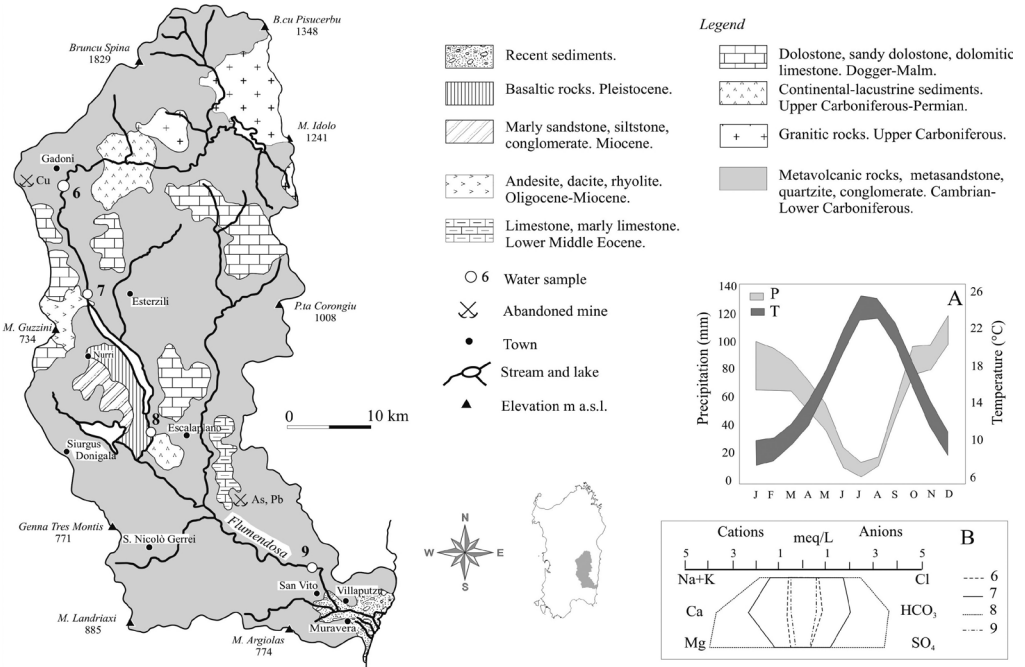
Geological sketch map and location of water samples in the Temo basin. The monthly mean of precipitation (P) and temperature (T) reported in diagram A refer to data collected at the Bosa (6 m a.s.l.), Reinamare (300 m a.s.l.), Bidighinzu (334 m a.s.l.) and Villanova Monteleone (567 m a.s.l.) stations. The Stiff diagram (B) shows the chemical composition of waters.
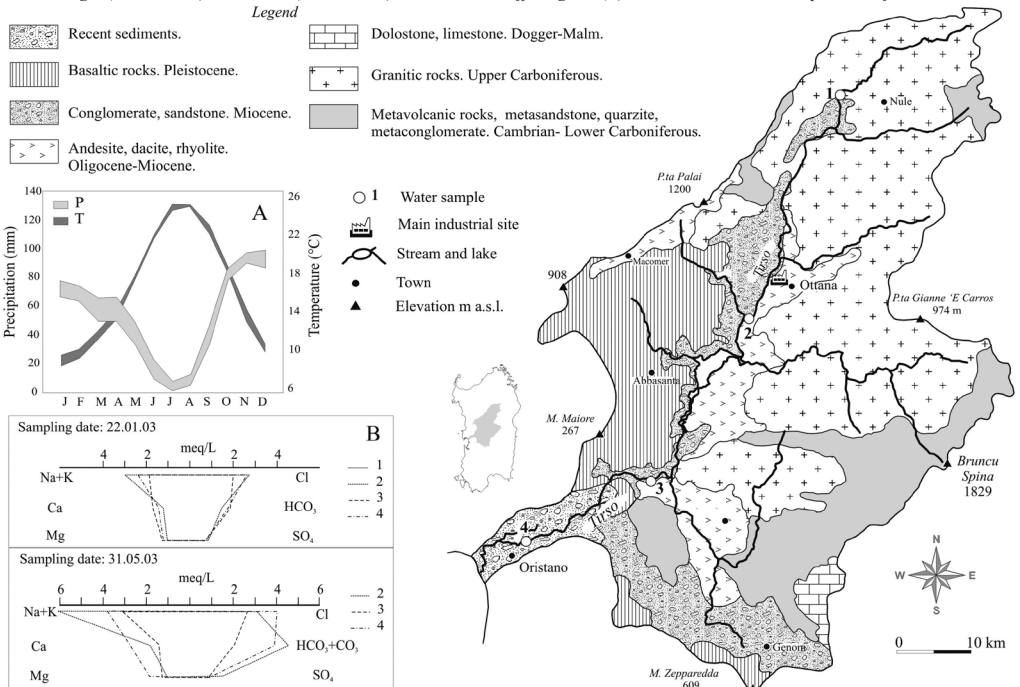

Geological sketch map and location of water samples in the Posada basin. The monthly mean of precipitation (P) and temperature (T) reported in diagram A refer to data collected at the Orosei (10 m a.s.l.), Torpè (24 m a.s.l.), Galtellì (40 m a.s.l.), Lodè (345 m a.s.l.), Nuoro (545 m a.s.l.) and Alà dei Sardi (663 m a.s.l.) stations. The Stiff diagram (B) shows the chemical composition of waters.
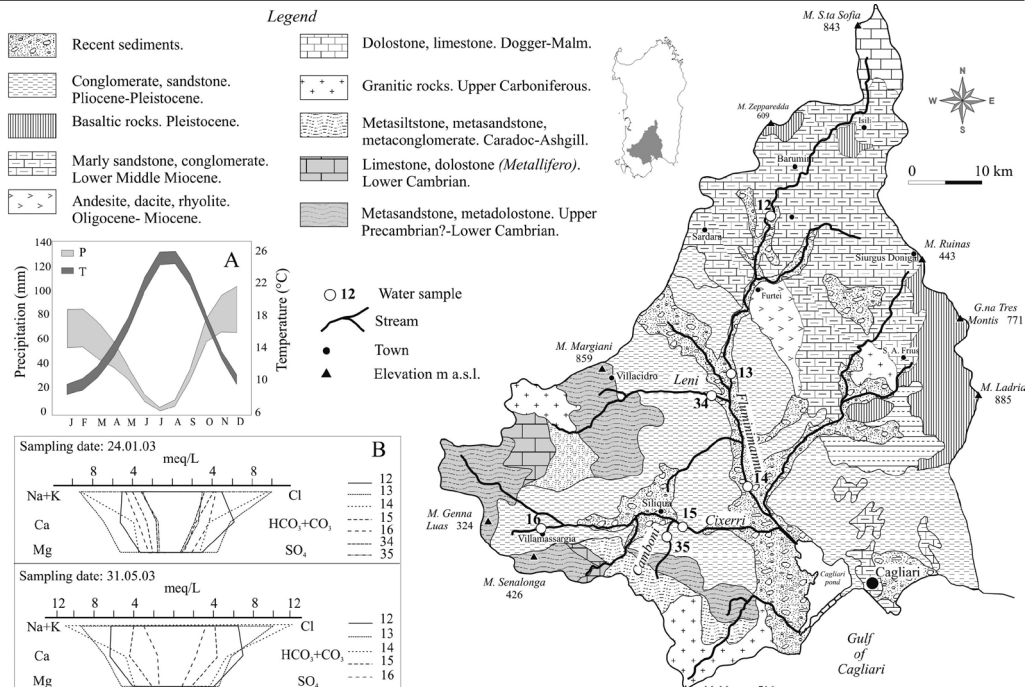
Geological sketch map and location of water samples in the Flumendosa basin. The monthly mean of precipitation (P) and temperature (T) reported in diagram A refer to data collected at the Muravera (19 m a.s.l.), Escalaplano (338 m a.s.l.), Villanovatulo (347 m a.s.l.), Armungia (366 m a.s.l.), and Seulo (797 m a.s.l.) stations. The Stiff diagram (B) shows the chemical composition of waters.
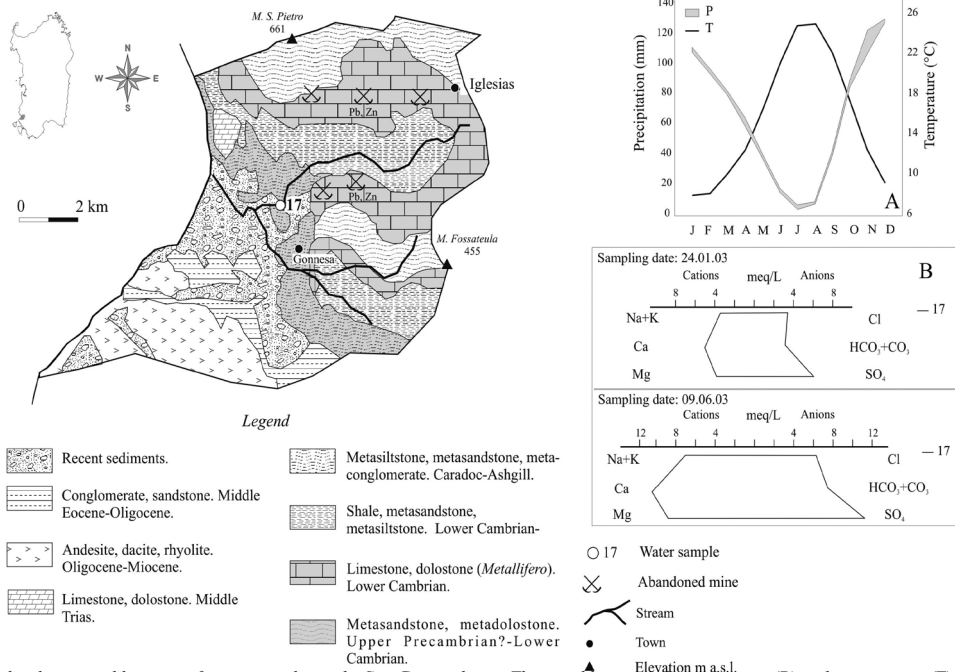

Geological sketch map and location of water samples in the Tirso basin. The monthly mean of precipitation (P) and temperature (T) reported in diagram A refer to data collected at the S. Giusta (10 m a.s.l.), Oristano (12 m a.s.l.), Busachi (50 m a.s.l.), Tirso Rifornitore (184 m a.s.l.) and Benettutti (406 m a.s.l.) stations. The Stiff diagram (B) shows the chemical composition of waters.

Appendix 7

Geological sketch map and location of water samples in the Fluminimannu and Cixerri basins. The monthly mean of precipitation (P) and temperature (T) reported in diagram A refer to data collected at the Decimomannu (15 m a.s.l.), Villasor (22 m a.s.l.), Siliqua (53 m a.s.l.), Villamar (108 m a.s.l.), Villamassargia (154 m a.s.l.), Lunamatrona (162 m a.s.l.), Iglesias (193 m a.s.l.), and Villacidro f.c. (213 m a.s.l.) stations. The Stiff diagram (B) shows the chemical composition of waters.

Appendix 8

Geological sketch map and location of water samples in the San Giorgio basin. The monthly mean of precipitation (P) and temperature (T) reported in diagram A refer to data collected at the Monteponi (190 m a.s.l.) and Iglesias (193 m a.s.l.) stations. The Stiff diagram (B) shows the chemical composition of waters.