

Hydrogeochemical characteristics of a stratified aquifer and groundwater quality degradation, Sila Massif, Italy

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Abstract Hydrogeochemical surveys were carried out in eastern Calabria (Italy) for recognizing the groundwater flow domain, assessing the utilization level, and characterizing the degradation risks. Physical-chemical parameters of groundwater and surface water were determined. Waters draining crystalline and metamorphic rocks have Mg-HCO₃ to Na-Ca-HCO₃ compositions and low salinity (<0.20 g/L), whereas waters from sedimentary environments belong to the Ca-HCO₃ facies and have higher salinity (0.20 to 0.76 g/L). Waters interacting with evaporite formations show a dominant Ca-SO₄ composition, and high salinity (up to 2.9 g/L). The concentrations of toxic components are usually low, but in some samples nitrates and arsenic exceed the drinking limit. It is shown that quality degradation is due to anthropogenic activities, misuse of fertilisers, or discharge of untreated urban wastes.

Key words layered aquifer; geochemistry; contamination; water quality

INTRODUCTION

In recent times, there has been a tremendous increase in demand for freshwater due to population growth and intense agricultural activities. Many countries in the Mediterranean basin have experienced a water crisis on an unprecedented scale in recent years (Grenon & Batisse, 1989). In Italy more than 85% of the drinking water is extracted from aquifers, hence the monitoring, management and protection of groundwater quality is an economic and environmental objective (Onorati *et al.*, 2006). This water scarcity encompasses physical water shortages (quantity scarcity), rising groundwater salinity levels and water pollution. All these effects determine a shortage of good quality water (quality scarcity), and, consequently, physical, social, political and economic barriers to water access (access scarcity) (Pearce, 1994).

Population and development pressures, most notably agricultural demands, the growth in standards of living, tourism and urbanisation, have increased the demand for water resources. Unsustainable water management policies have been based on over-exploitation of groundwater in many Mediterranean areas and in other coastal areas of the world. The combined effect is very often a reduction of availability and quality, as an effect of seawater intrusion. In addition, increasing amounts of pollution, mainly agricultural and industrial, have caused a decline in groundwater quality and a threat to human health. Access to good quality water, or sometimes to any water at all, is difficult for many people and inter-regional/basin transfers are not possible in many cases (Grenon & Batisse, 1989). The primary objective of this work is the schematisation of the groundwater flow domain to assess the utilization level, the groundwater quality, as well as the degradation risks in Sila Massif, Italy.

STUDY AREA AND GEOLOGICAL SETTING

The study area is about 15 km² in extent and is situated near the villages of Cerenzia and Castelsilano, in eastern Calabria (Fig. 1). The altitude ranges from about 1000 m above sea level,

in the western part, to 50 m a.s.l. in the eastern portion. Vegetation cover is discontinuous; topsoils are almost absent apart from the southern part of the area. In the eastern margin of Calabria the crystalline and metamorphic rocks of the Calabrian orogenic edifice constitute the upper complex.

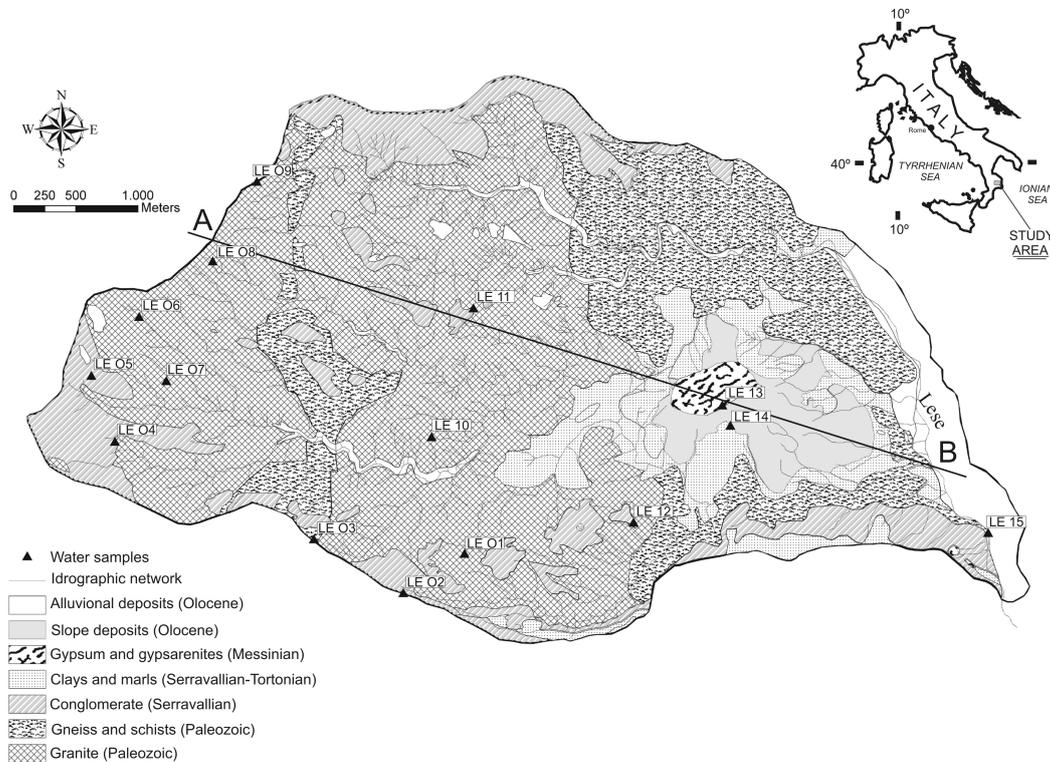


Fig. 1 Geological sketch map of the study area and location of water samples.

The Sila Massif represents the major morphostructural high of the Ionian margin of north-eastern Calabria; it is made up of rock units involved in the Hercynian and Alpine orogenys (Amodio Morelli *et al.*, 1976; Messina *et al.*, 1994). The Sila Massif comprises a complete Paleozoic section named the Sila unit, consisting of three different Paleozoic metamorphic complexes: the low- to very low-grade Bocchigliero complex, the greenschist- to amphibolite-facies Mandatoriccio complex and the granulite-facies Monte Gariglione complex, which is intruded by upper Paleozoic plutonic rocks of the Sila batholith (Messina *et al.*, 1994). The batholith is characterized by several intrusions ranging in composition from granite and granodiorite to gabbro and leucomonzogranite (Messina *et al.*, 1994). The Sila batholith is unconformably overlain by Mesozoic to Cenozoic sedimentary successions cropping out in the eastern and northeastern flanks of the Sila Massif including the Longobucco Group (Upper Triassic-Liassic through Toarcian), which is made up of continental red beds, overlain by carbonate shelf deposits, slope deposits, and deep-sea turbidites (Young *et al.*, 1986; Santantonio & Teale, 1987).

On the basement and the Meso-Cenozoic cover a Neogene-Quaternary succession constitutes the infill of the Crotona basin. Part of the Miocene succession crops out in the study area. The sedimentary cover consists of clastic and terrigenous sediments and evaporite strata. The basal sequence is composed of conglomerates passing upward to sands, sandstones, clays and marls and, in the upper part, by bio-siliciferous layers. These are unconformably covered by evaporite strata, overlain by a clastic succession of limestone breccias grading to gypsrudites, arenites and gypsum-bearing sandstones. These successions are overlain by deposits consisting of meter-scale blocks of limestone, gypsarenite breccias, and gypsarenite slumps (Roda, 1964).

The crystalline and metamorphic rocks of the basement are characterized by intense fracturing and by physical and chemical weathering features. These rocks constitute the main aquifer of the study area. In the central zone of the basin, the conglomerates and sandstones represent a second aquifer, confined by marls and clays at the top. In turn, this clayey-marly unit suspends a small aquifer hosted in the evaporite deposits.

In the Cerenzia area the mean annual rainfall is 1112 mm, with a dry season extending from May to September. Mean annual temperature is 8.8°C. The surface drainage network comprises several intermittent streams and the Lese stream, in the eastern part of the area, which is the only perennial watercourse. Several springs are the result of the shallow groundwater flow; the spring yield is generally low (<0.1 L/s), although many of them are perennial. Both the spatial distribution of the springs and their altitude confirm the hypothesized conceptual model. This hydrogeological model recognises a shallow unconfined aquifer, a semiconfined aquifer bounded by clay strata and, at the top of this, another water table aquifer, suspended by the clays (Fig. 2).

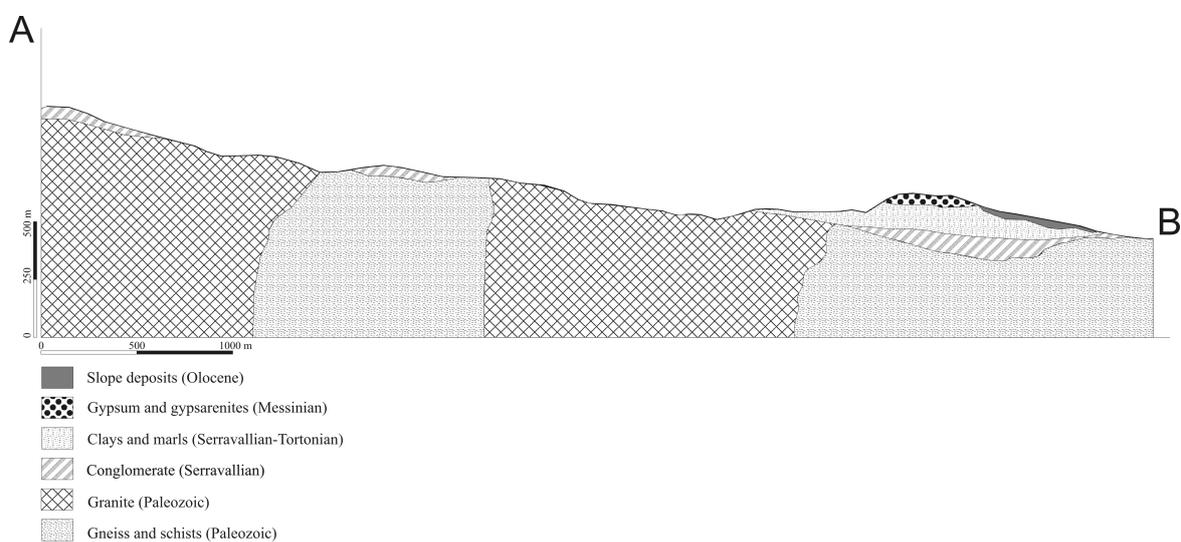


Fig. 2 Geological cross-section.

SAMPLING AND ANALYTICAL METHODS

Water samples were collected in September and October 2004 under low-flow conditions. The location of water samples is shown in Fig. 1. Some groundwater parameters, such as pH, redox potential (Eh), temperature, alkalinity and electrical conductivity, were measured in the field, while groundwater samples, suitably filtered and acidified, were used for laboratory analyses. Anions were determined by ion chromatography (HPLC Dionex DX-120), whereas cations were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, ARL3520) and inductively coupled plasma mass spectrometry (ICP-MS, ELAN DRC-e). The ionic balance was always within $\pm 5\%$, suggesting that the analyses were of reasonably good quality, as far as major dissolved constituents are concerned; both precision and accuracy were estimated at $\pm 10\%$ or better, using randomly duplicate samples and the standard reference solution NIST1643d.

RESULTS AND DISCUSSION

The analytical results of the water samples from the Cerenzia-Castelsilano area are reported in Tables 1 and 2. Water temperature ranges from 15 to 23°C, and reflects the air temperature during sampling. The pH is near neutral or slightly alkaline (6.4–8.2). The groundwater redox potential ranges from 90 to 320 mV, whereas the Lese stream has the highest Eh value (420 mV), indicating oxidising conditions, as expected for surface water.

Table 1 Physical-chemical parameters and concentrations of major dissolved components in waters.

Sample	Type	T (°C)	pH	Eh (V)	Cond. (mS/cm)	TDS (g/L)	Ca (mg/L)	Mg	Na	K	Alk	Cl	SO ₄	F	NO ₃	SiO ₂
LE01	s	21	7.3	0.16	0.32	0.14	18	5.2	8.3	1.5	87	7.1	8.2	0.2	0.8	18
LE02	s	21	7.3	0.15	0.93	0.31	48	8.2	36	3.1	140	29	47	0.3	41	29
LE03	s	20	8.1	0.10	0.81	0.35	41	16	24	6.2	207	15	40	0.3	2.2	19
LE04	s	15	6.4	0.20	0.37	0.11	14	3.6	14	1.4	55	13	11	0.2	4.7	38
LE05	s	16	6.5	0.17	0.50	0.18	39	2.9	8.9	0.9	103	11	11	0.2	<0.1	22
LE06	s	16	6.5	0.18	0.36	0.08	7.8	5.4	10	1.2	47	6.9	6.5	0.3	<0.1	21
LE07	s	18	6.6	0.32	0.38	0.14	12	8.8	12	1.8	63	13	25	0.2	2.7	24
LE08	s	20	6.8	0.17	0.91	0.27	38	18	28	3.2	124	38	25	0.2	68	18
LE09	s	21	6.6	0.14	0.67	0.15	18	19	16	2.7	48	21	23	0.2	83	23
LE10	s	18	6.6	0.16	0.46	0.16	7.8	11	23	1.6	79	15	24	0.6	3.9	38
LE11	p	17	7.5	0.08	1.25	0.40	74	12	22	1.9	233	22	40	2.0	0.3	26
LE12	s	22	7.2	0.12	0.81	0.35	75	5.5	15	2.1	193	25	38	0.8	0.8	27
LE13	s	23	7.7	0.10	1.91	0.76	93	37	74	3.0	267	35	256	4.7	<0.1	33
LE14	s	19	7.5	0.09	6.22	2.95	670	72	91	32	299	143	1640	1.3	8.1	16
LE15	f	23	8.2	0.42	0.68	0.27	39	10	20	3.5	145	16	33	0.7	<0.1	20

In the Type column: s = spring, w = well, r = river.

Table 2 Concentrations of dissolved trace components in waters.

Sample	Li	B	Al	Mn	Fe	Ni	Co	Cu	Zn	As	Rb	Sr	Mo	Cd	Sb	Ba	Pb	U	
	(µg/L)																		
LE01	4.8	9.2	4	1.9	80	<0.4	0.04	2.6	35	0.7	0.7	70	1.1	0.2	<0.1	11	5.8	1.7	
LE02	8.3	130	2	<0.5	200	<0.4	0.11	0.8	6.9	50	0.1	390	0.5	0.1	0.1	120	4.0	0.2	
LE03	18	35	13	<0.5	170	<0.4	0.08	0.9	4.5	7.0	7.8	400	2.7	<0.05	0.2	34	4.6	3.8	
LE04	13	16	3	1.4	60	<0.4	0.03	0.5	6.2	<0.2	0.3	90	<0.1	<0.05	<0.1	94	0.9	0.1	
LE05	6.1	12	<2	<0.5	160	<0.4	0.06	0.3	8.1	<0.2	0.2	140	<0.1	<0.05	<0.1	53	3.3	0.3	
LE06	7.0	7.7	19	0.8	40	<0.4	0.02	1.1	4.9	<0.2	0.2	32	<0.1	<0.05	<0.1	7.5	0.9	0.1	
LE07	5.6	10	13	1.4	60	<0.4	0.04	1.2	4.2	<0.2	0.2	90	<0.1	<0.05	<0.1	17	0.2	0.1	
LE08	7.3	190	5	<0.5	150	<0.4	0.07	1.2	4.0	<0.2	0.6	290	<0.1	<0.05	<0.1	43	1.8	0.8	
LE09	10	20	2	1.3	130	<0.4	0.2	0.9	20	<0.2	0.2	70	<0.1	<0.05	<0.1	3.4	0.8	0.1	
LE10	36	9.9	9	1.8	30	<0.4	0.02	1.5	12	18	0.5	70	1.1	0.1	<0.1	17	<0.1	0.3	
LE11	31	19	<2	30	330	<0.4	0.14	0.5	3.8	18	1.6	120	1.2	<0.05	0.2	19	<0.1	2.6	
LE12	8.9	20	2	70	410	<0.4	0.18	1.4	30	80	0.5	130	0.4	<0.05	0.1	16	<0.1	0.6	
LE13	59	310	<2	40	400	0.9	0.25	1.2	1.7	12	1.4	900	0.5	<0.05	0.1	50	<0.1	0.2	
LE14	95	540	3	2.9	2200	2.5	0.70	1.7	5.7	1.5	5.3	15000	21	0.1	0.3	14	<0.1	10	
LE15	4.9	46	2	2.4	150	<0.4	0.08	1.3	3.1	12	2.1	210	1.4	<0.05	0.1	52	<0.1	1.5	

The water specific electrical conductivity (SEC) shows significant variations among samples (from 0.32 to 6.22 mS/cm at 20°C). The lowest values are observed in waters draining mainly crystalline and metamorphic rocks. Higher conductivity values, up to 1.9 mS/cm, were measured where groundwater flows in Miocene-Pliocene conglomerates and sandstones, locally with a not negligible clay fraction; SEC reaches the highest value (6.22 mS/cm) in the case of a groundwater flowing in evaporite rocks (sample LE14).

The main chemical composition of the waters is shown in the Piper diagram (Fig. 3). The waters draining mainly crystalline and metamorphic rocks show a dominant magnesium-bicarbonate to sodium-calcium-bicarbonate composition, and low total dissolved solids (TDS), less than 0.20 g/L. Waters interacting with Miocene sediments show a dominant calcium-bicarbonate composition and TDS in the range of 0.20–0.76 g/L. High TDS (up to 2.95 g/L) and calcium-sulphate composition is observed in the LE13 and LE14 samples, reflecting a prevalent water circulation in the evaporite formation. In particular, the LE14 sample exhibits a molar Ca/SO₄ ratio close to 1 due to gypsum dissolution.

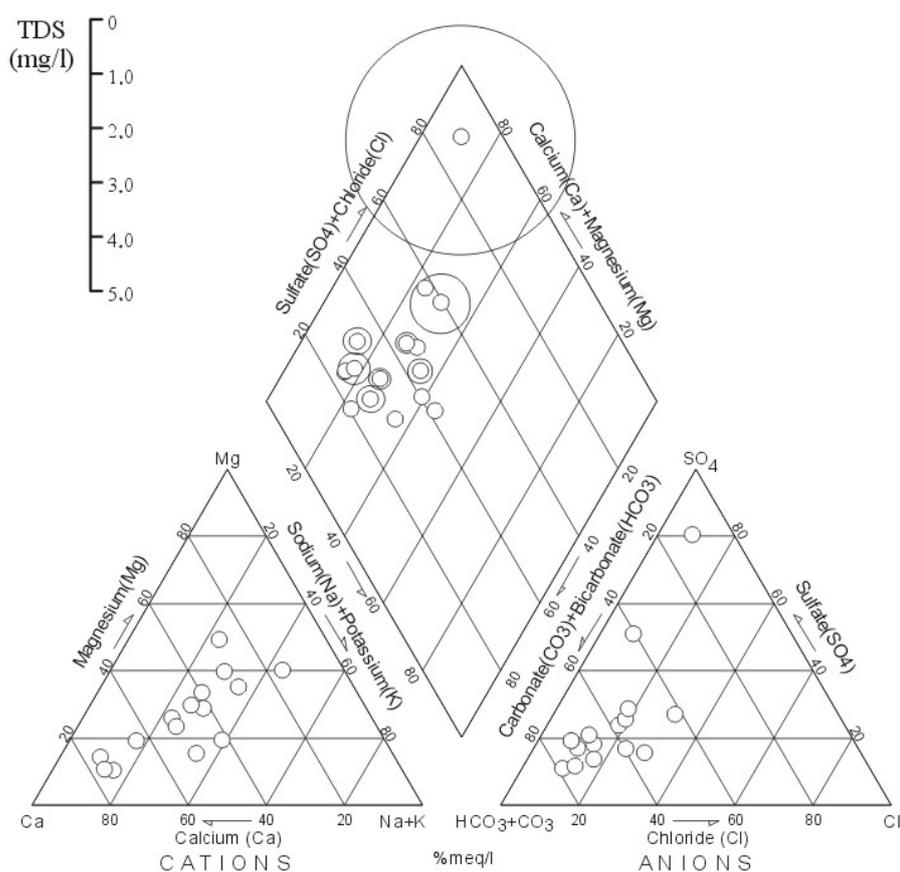


Fig. 3 Piper diagram of the sampled waters.

Nitrate concentration spans a wide range, from 0.1 to 83 mg/L, around a mean value of 9.9 mg/L. Although NO_3 concentration is usually less than 10 mg/L in the area, concentrations higher than the maximum admissible limit of 50 mg/L, established by Italian regulations for drinking water (GURI, 2001), are found in the three samples, LE02, LE08 and LE09. The concentrations of trace elements are usually low. However, the most saline water (sample LE14), of Ca- SO_4 composition, shows the highest concentrations of Li, Rb, Fe, Sr, Mo, Ba and U. In this sample, iron concentration is above the Italian drinking limit (200 $\mu\text{g/L}$). In all water samples, dissolved concentrations of Ni, Co, Cu, Zn, and the highly toxic elements Pb and Cd, are lower than the Italian drinking water limits, and often below detection limits. In contrast, high concentrations of arsenic, in the range 12-80 $\mu\text{g/L}$, are found in six water samples, including the Lese stream. These values are higher than the Italian limit of 10 $\mu\text{g/L}$.

The distribution of dissolved nitrate and arsenic are shown in two thematic maps (Figs 4 and 5), which have been drawn using the technique of the "inverse distance to a power" (Isaaks & Scrivastava, 1989). They are a simple way of representing georeferenced data and of characterising regional variability. Moreover, they allow identification of maximum and minimum values. The highest concentrations of nitrate and arsenic occur in waters sampled near Cerenzia and Castelsilano villages, as shown in Figs 4 and 5. Consequently, these anomalously high nitrate and arsenic values are probably related to anthropogenic activities, either discharge of untreated urban wastes or misuse of fertilisers in agriculture. The second hypothesis seems to be highly probable near Cerenzia village and in the southern part of the study area, where agriculture is mostly developed.

The anthropogenic control on the high contents of both nitrate and arsenic in the waters from the study area is also partly corroborated by the insignificant correlations of these two parameters with major components and some minor dissolved constituents (e.g. SiO_2 and F), which are chiefly governed by water-rock interaction processes.

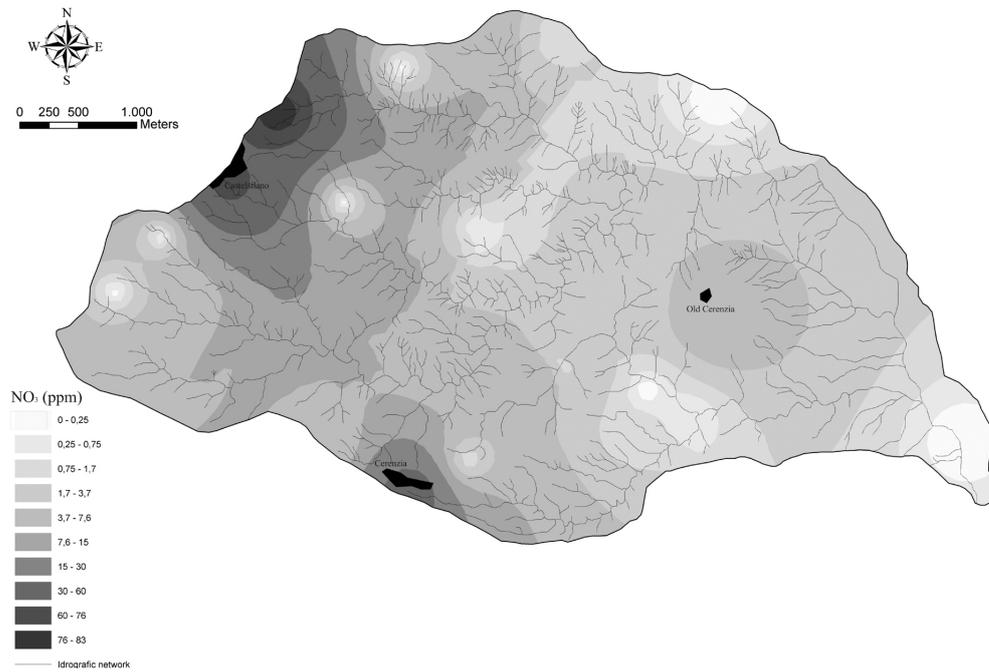


Fig. 4 Map of nitrate concentrations in the Cerenzia-Castelsilano area.

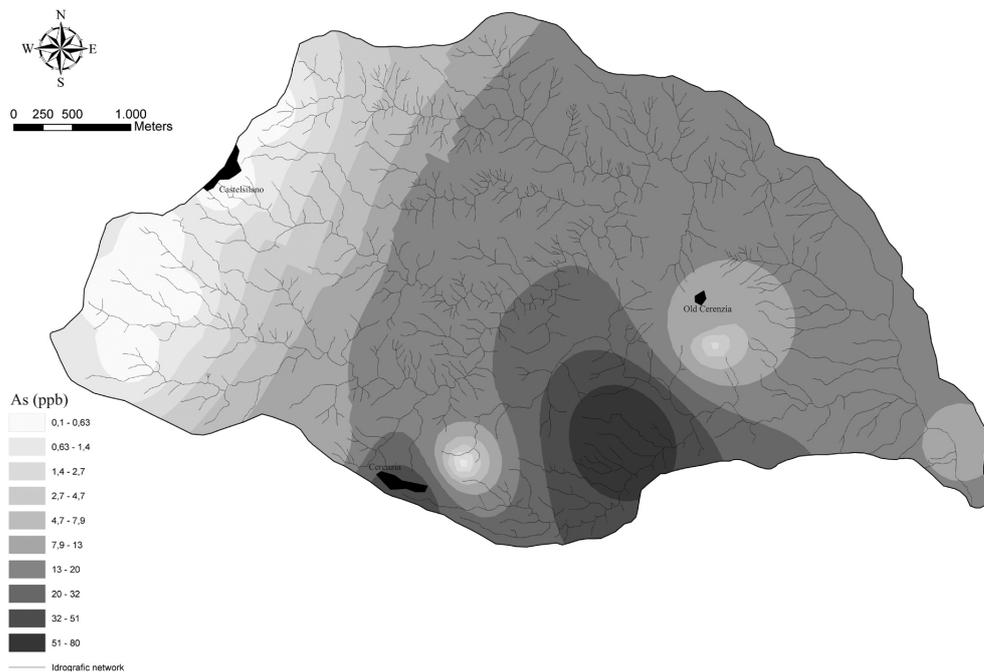


Fig. 5 Map of arsenic concentrations in the Cerenzia-Castelsilano area.

CONCLUSION

The hydrogeological survey carried out in the Cerenzia–Castelsilano area (southern Italy) permits recognition of the presence of a stratified aquifer system, comprising a shallow unconfined aquifer, a semiconfined aquifer bounded by clay strata and, at the top of the latter, another water table aquifer, suspended by the clays.

Groundwater interacting with crystalline and metamorphic rocks has low salinity (< 0.20 g/L) and variable Mg-HCO₃ to Na-Ca-HCO₃ composition, whereas groundwater discharged from

sedimentary rocks have somewhat higher salinity (0.20 to 0.76 g/L) and belong to the Ca-HCO₃ facies. Completely different chemical characteristics, namely high salinity (up to 2.9 g/L) and Ca-SO₄ composition, are instead acquired by groundwater interacting with evaporite rocks. Nitrate and arsenic contents are generally low, apart from some samples exceeding the drinking limit. Local degradation in water quality is due to anthropogenic activities, either discharge of untreated urban wastes or mis-use of fertilisers in agricultural practices.

Acknowledgements This paper benefited by the comments and suggestions of Dr Alyssa Dausman. The Authors are grateful for article improvement which was possible thanks to her review.

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