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Nitrate, sulphate and chloride contents in public drinking water supplies in Sicily, Italy

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Abstract Water samples collected from public drinking water supplies in Sicily were analysed for electric conductivity and for their chloride, sulphate and nitrate contents. The samples were collected as uniformly as possible from throughout the Sicilian territory, with an average sampling density of about one sample for every 7,600 inhabitants. Chloride contents that ranged from 5.53 to 1,302 mg/l were correlated strongly with electric conductivity, a parameter used as a proxy for water salinity. The highest values are attributable to seawater contamination along the coasts of the island. High chloride and sulphate values attributable to evaporitic rock dissolution were found in the central part of Sicily. The nitrate concentrations ranged from 0.05 to 296 mg/l, with 31 samples (4.7% of the total) exceeding the maximum admissible concentration of 50 mg/l. Anomalous samples always came from areas of intensive agricultural usage, indicating a clear anthropogenic origin. The same parameters were also measured in bottled water sold in Sicily, and they all were within the ranges for public drinking water supplies. The calculated mean nitrate intake from consuming public water supplies (16.1 mg/l) did not differ significantly from that of bottled water (15.2 mg/l). Although the quality of public water supplies needs to be improved by eliminating those that do not comply with the current drinking water limits, at present it does not justify the high consumption of bottled water (at least for nitrate contents).

Keywords Public water supplies · Nitrate · Sulphate · Chloride · Sicily

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Introduction

The deterioration of drinking water quality is a widespread problem in highly populated, arid and semi-arid regions. The climate in one such region, the Mediterranean (referred to as the Mediterranean climate), is characterized by long, hot and dry summer periods (from May to September) and a mild rainy winter season. The continuing population growth and intensive agricultural usage are substantially increasing water consumption. This problem is further exacerbated by the expansion of the tourist industry in Mediterranean coastal areas, which increases the water demand during the driest period of the year (Kondili and Kaldellis 2006).

The island of Sicily is in the central part of the Mediterranean Sea and has a long settlement history despite often experiencing water shortages. With more than 5 million inhabitants, it has one of the highest population densities in the region at 193 inhabitants per square kilometre. The average annual rainfall is about 600 mm, and ranges from less than 400 to about 1,200 mm. Some studies have found evidence for a decline of about 100 mm rainfall during the last century (Brunetti et al. 2004). Despite such negative trend, the effective meteoric recharge is still higher than the total water demand. However, the uneven distribution of the resource (Fig. 1c) and its very poor management in recent decades have led to occasional severe water shortages in many parts of the island. The main problems arise from the distribution network, some parts of which lose more than 50% of the transported water (38% on average), but there are also water quality issues due to salinization and contamination of some of the aquifers (Ferrara 1991; Aiuppa et al. 2003; D'Alessandro et al. 2011). Such problems mean that about 40% of households in Sicily to experience irregularities in water distribution, compared to an Italian national average of about 16%, and more than 63% have concerns about the quality

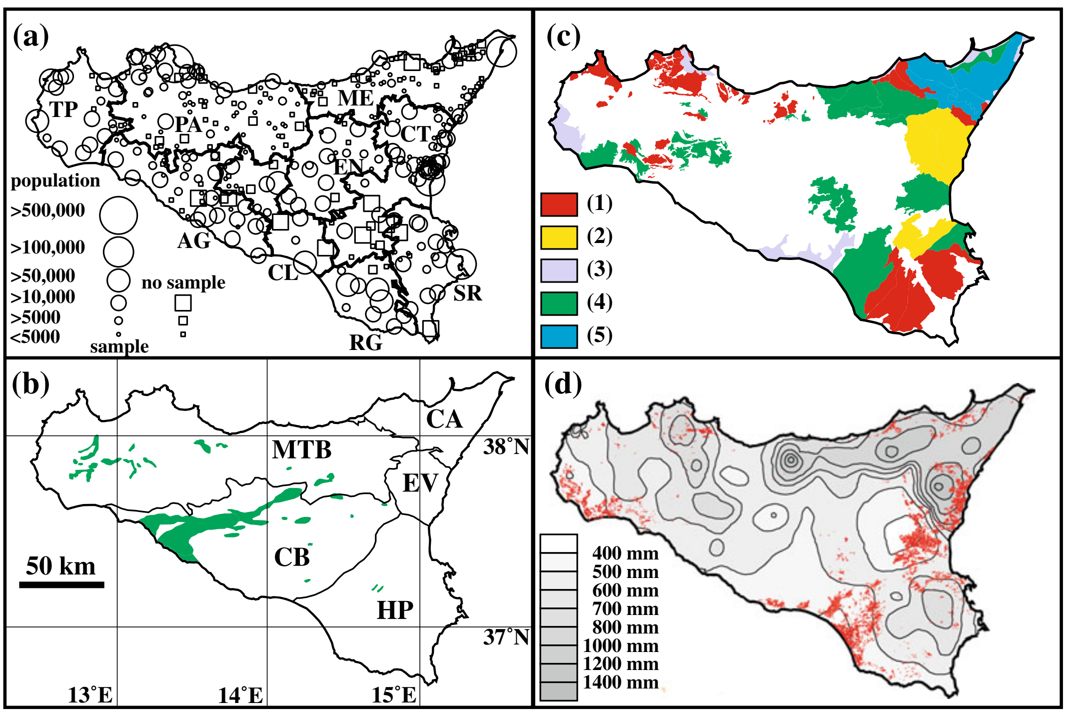

Fig. 1 Study area. **a** Administrative subdivision of Sicily into nine provinces (*AG* Agrigento, *CL* Caltanissetta, *CT* Catania, *EN* Enna, *ME* Messina, *PA* Palermo, *RG* Ragusa, *SR* Siracusa, *TP* Trapani) and population distribution; *symbol dimension* is proportional to the population of each municipality (*circles* represent municipalities where at least one sample was collected, while *squares* represent those where no sample was collected). **b** Geologic sketch (*HP* Hyblean Plateau, *CB* Caltanissetta Basin, *MTB* Maghrebian Thrust Belt, *CA* Calabrian Arc, *EV* Mt. Etna Volcano). Outcrops of evaporitic rocks are evidenced in *green*. **c** Map of the main aquifers: (*1*) aquifers in carstic and/or fractured carbonate rocks, (*2*) aquifers in volcanic rocks, (*3*) coastal aquifers in calcarenites, (*4*) aquifers in arenaceous rocks within big clastic sequences, (*5*) aquifers in metamorphic rocks (Regione Siciliana 2005). **d** Geographic distribution of rainfall heights in *grey tones* and map of groundwater vulnerability to nitrates of agricultural origin in *red* (Regione Siciliana 1998, 2005)

of tap water (compared to a national average of about 45%) (ISTAT 2003). These factors have led to a high consumption of bottled water; although this remains somewhat lower than the national average—about 82% of Sicilians state that they at least sometimes drink bottled water, compared to a national average of about 87% (ISTAT 2003).

Nitrate originating mainly from organic matter decay is generally a minor constituent ($\ll$10 mg/l) of unpolluted natural water (Nolan 1999). Dissolution of nitrogen-containing natural inorganic compounds rarely contributes to the chemistry of natural water (Holloway et al. 2001). The high rates of nitrogen fertilization, particularly on permeable soils with shallow water tables, result in the concentration of nitrate in groundwater being significantly higher than background levels in many agricultural areas. How nitrate influences human health is strongly debated (Powlson et al. 2008). The maximum admissible concentration (MAC) in most countries is within the range of 45–50 mg/l. Also, the World Health Organization (WHO) indicates a guideline value (GV) of 50 mg/l for drinking water (WHO 2004), which has been integrated into Italian national law as a MAC. A high nitrate concentration is always related to anthropogenic contamination, the main sources being fertilizers and human or animal bodily waste (Spalding and Exner 1993). Nitrate can be the main anionic species in both agricultural and urban areas. Recent scientific literature indicates that high concentrations of nitrate could even exert beneficial effects on human health (L'hirondel and L'hirondel 2002), but it remains an undesirable component because it is often accompanied by more dangerous constituents such as microorganisms and pesticides. Furthermore, the large input of nitrate can change the redox state of groundwater to favour the release of toxic elements from soils and aquifer rocks into the groundwater (Böhlke 2002) and cause eutrophication of surface water bodies fed by polluted groundwater (Howarth et al. 2000).

Sulphate and chloride are major constituents of natural water that are generally good tracers of the sources responsible for increases in salinity. Natural sources of sulphate and chloride are seawater and the dissolution of evaporitic rocks, and the main anthropogenic sources are urban, industrial and agricultural wastewater. Different origins of these contaminants have often been distinguished on the basis of their bromide-to-chloride ratio (Davis et al. 1998).

No health-based GVs have been proposed by the WHO for sulphate and chloride in drinking water (WHO 2004). However, concentrations in excess of about 250 mg/l for both anions can give rise to detectable taste in water. Therefore, the Italian national law set a GV of 250 mg/l for both parameters.

The present work was performed within the framework of a wider study to test the quality of drinking water distributed to public supplies in Sicily. In this paper, we report on four parameters (electric conductivity, nitrate, sulphate and chloride) measured in 667 samples collected throughout the Sicilian territory. Data on chloride and electric conductivity have been previously presented together with fluoride and bromide data (D'Alessandro et al. 2008), and are used here to make useful comparisons.

The nitrate content (in addition to other parameters) was also measured in the most widely consumed brands of bottled water on the Sicilian market, in order to compare nitrate intakes of the Sicilian population between public water supplies and bottled water.

Study area and methods

Sicily is the largest island in the Mediterranean Sea, and has a total surface area of 25,708 km^2. From a geological point of view it represents part of the south-verging branch of the Apennine–Maghrebian orogenic belt made up of a pile of nappes derived from the deformation of different Meso-Cenozoic domains resulting from the collision of the African and Eurasian tectonic plates. The main geolithological domains of the island are (Fig. 1b) (a) the Hyblean Plateau, representing the undeformed foreland that is made up of a thick succession of carbonate, clastic and volcanic rocks (Trias-Quaternary), (b) the Caltanissetta basin, a Neogene-Quaternary accretionary wedge composed of a thick sequence of sandstones, evaporites, marls and calcarenites, (c) the Maghrebian thrust belt, made up of a pile of allochthonous

Triassic-Eocene pelagic terrains (from limestones to clays) grading upwards into the Oligo-Miocene turbidites, (d) the Calabrian arc, formed by the remnants of Hercynian crystalline nappes (mainly composed of gneisses and phyllades) and (e) the active volcanic massif of Mt. Etna.

Sicily is one of the 20 regions (regioni) into which Italy is administratively subdivided. The Sicilian Region (Fig. 1a) is subdivided into nine provinces (province) that are further subdivided into municipalities (comuni). Sicily comprises 390 municipalities.

The typically Mediterranean climate of Sicily also features a rainfall with marked geographic differences. The median rainfall values measured from 1965 to 1994 at 180 meteorological stations (Regione Siciliana 1998) ranged from 380 to 1,200 mm, with a mean value of 600 mm for the whole island. The rainfall distribution map (Fig. 1d) shows that the rainfall was highest at high elevations, such as along the northern mountain chain (altitudes up to nearly 2,000 m) and at the Mt. Etna massif (~3,300 m). Intermediate rainfall values were measured in the mountainous areas of the western-central (altitudes up to 1,500 m) and south-eastern (~1,000 m) parts of the island. The rainfall was lowest along the entire southern coast and in the central-eastern part of Sicily, which are classified as semi-arid and sometimes arid areas (annual rainfall <400 mm).

The groundwater resources also have an uneven distribution (Fig. 1c). The most significant aquifers, which can be considered important water resources, were subdivided into the following five classes with decreasing water yields: (1) aquifers in carstic and/or fractured carbonate rocks, (2) aquifers in volcanic rocks, (3) coastal aquifers in calcarenites, (4) aquifers in arenaceous rocks within large clastic sequences and (5) aquifers in metamorphic rocks (Regione Siciliana 2005). Most of these aquifers are found in the part of the island with the highest rainfall, and there are very few aquifers in its semi-arid part (Fig. 1c).

Agriculture still represents an important part of the Sicilian economy, and more than 60% of the island is used for agricultural purposes. The predominant products derive from rain-fed crops (e.g. corn and fodder), which are associated with only limited use of fertilizers, but there is an increase in intensive agricultural practices that need intensive fertilization with nitrogen inputs of more than 200 kg/ha.

A regional map of groundwater vulnerability to nitrates of agricultural origin was constructed by cross-correlating all geographical data on geology, climate, aquifer vulnerability, soil characteristics and agricultural use (Regione Siciliana 2005). The most vulnerable areas are along the coastal area (Fig. 1d), which are also where the agricultural usage is most intensive (irrigated orchards and vegetables grown in the field or in greenhouses).

The distribution of drinking water in Sicily generally lacks central coordination, with administration organized at the municipality level. Of the 246 drinking water distribution systems in Sicily, 219 are managed directly by the municipalities and 187 serve the inhabitants of only one municipality. Each year 415×10^6 m^3 of water is distributed, 81% of which comes from groundwater sources, 15% from surface water and 4% from the desalinization of marine or brackish water.

To obtain significant information regarding the geographical distribution of the parameters under study in Sicily's drinking water, the following sampling protocol was planned:

- Samples of drinking water supplied by public companies to be collected in proportion to the population density, with an average of one sample for each 5,000 inhabitants in each municipality.
- One sample had to be taken from each municipality having less than 5,000 inhabitants, while the sample density was reduced for the largest cities.
- Thirty-six municipalities were excluded, either because they had less than 1,000 inhabitants or because of logistical difficulties (i.e. long distance from main roads or being on the minor islands surrounding Sicily).

Following these criteria, the collection of 960 samples from 354 municipalities was planned, but actually only 667 samples were collected from 251 municipalities. The overall final sampling density was one sample for every 7,635 inhabitants, and ranged from one in 5,449 inhabitants in the province of Enna to one in 9,896 inhabitants in the province of Trapani. Of the 103 municipalities where water samples were not collected, 10 exceeded 10,000 inhabitants (maximum ≈ 30,000) and 35 exceeded 5,000 inhabitants. The samples collected were representative of 87% of the total inhabitants and 76% of the total surface of the Sicilian region.

Samples were collected from April 2004 to June 2005, mainly from public fountains but also from the inlets of public aqueducts supplying private houses. Unfiltered water samples were stored in LDPE or PP bottles and analysed in the laboratory. Samples of bottled water were bought at commercial shops. The storage period, as deduced from the labelled bottling date, never exceeded a few weeks. Samples were stored in the laboratory until analysis in the bottle in which they were sold.

The market share of different brands in Sicily was estimated for 2004 from the sales data of the three largest sales networks. Two brands of bottled water, namely Vera and S. Benedetto, were obtained from two different sources. We assumed that each source represented half of the bottled water sold for each of these two brands. Altogether the analysed water samples represented more than 80% of the total bottled water sold on the Sicilian market.

Electric conductivity was measured with a laboratory conductimetre and referred to a temperature of 20°C. Nitrate, sulphate and chloride were analysed at the University of Palermo by a Dionex DX120 ion chromatograph with a suppressor and conductivity detector. A Dionex AS14 column and 1 mM sodium bicarbonate 3.5 mM sodium carbonate solution as eluent (1.2 ml/min) were used. Calibration standards were prepared with the same eluent matrix from concentrated standard solutions (1,000 mg/l). With a 25-μl introduction system, the detection limits were 0.05 mg/l for nitrate and sulphate, and 0.01 mg/l for chloride, with a precision of ≤3%.

Results and discussion

The analytical results are listed in Table 1 as statistical summary (the whole dataset is listed in Table S1 as supplementary file) and shown in Figs. 2 and 3 as binary correlation plots. The electric conductivity ranged from 199 to 4,620 μS/cm (20°C). Sixteen samples exceeded the GV of 2,500 μS/cm set by Italian law. The median values for the provinces ranged from 487 (Ragusa) to 699 (Trapani) μS/cm, except for the province of Catania (975 μS/cm). The chloride values ranged from 5.53 to 1,302 mg/l, with 31 samples exceeding the GV of 250 mg/l. The median values for the provinces ranged from 25.2 (Messina) to 86.5 (Trapani) mg/l. The sulphate contents ranged from 6.03 to 516 mg/l, with eight samples exceeding the GV of 250 mg/l. The median values for the provinces ranged from 18.3 (Ragusa) to 87.0 mg/l (Caltanissetta). The nitrate contents ranged from 0.05 to 296 mg/l, with 31 samples (4.7% of the total) exceeding the MAC of 50 mg/l, and 395 (59%) samples having concentrations lower than the GV (10 mg/l). The median values for the various provinces ranged from 3.38 (Enna) to 21.0 mg/l (Ragusa).

The results of analyses of the bottled water are reported in Table 2. The parameter values for all of the samples were below the corresponding MAC and GVs of the Italian national law, ranging from 126 to 1,840 μS/cm for electric conductivity, from 1.02 to 84.2 mg/l for chloride, from 1.33 to 101 mg/l for sulphate and from 1.19 to 31.1 mg/l for nitrate. The analytical results for the three ionic species were generally consistent with the data specified on the bottle labels. The measured and declared values are compared in Fig. 4. Four brands did not declare the nitrate content, and three of these had the highest contents (with values around 30 mg/l).

Binary correlation plots

Figure 2 shows binary correlation plots of the chloride, sulphate and nitrate contents against the measured electric conductivity for all of the collected water samples. Electric conductivity showed a strong positive correlation with chloride (Fig. 2a) but a much weaker correlation with sulphate (Fig. 2b) and almost no correlation with nitrate (Fig. 2c). The electric conductivity/chloride ratio was higher in many of the samples collected in the province of Catania (Fig. 2a) than in most of the other samples collected throughout Sicily. These samples were collected in the area around Mt. Etna and hence presumably derive from its

Table 1 Statistical distribution of the analytical results

	Minimum	Percentiles					Maximum
		10	25	50	75	90	
Agrigento (76)							
Cond. (μS/cm)	350	413	461	562	643	796	1,701
Cl (mg/l)	12.8	20.5	28.2	39.9	58.6	87.2	265
NO_3 (mg/l)	0.07	1.91	4.50	7.22	11.7	38.2	98.3
SO_4 (mg/l)	9.29	26.6	39.1	51.2	76.1	119	373
Caltanissetta (30)							
Cond. (μS/cm)	282	347	482	576	705	869	1,499
Cl (mg/l)	13.4	24.3	29.9	46.0	62.3	90.7	148
NO_3 (mg/l)	0.10	0.70	1.94	9.00	24.4	36.5	134
SO_4 (mg/l)	8.26	19.7	37.6	87.0	134	202	516
Catania (165)							
Cond. (μS/cm)	249	529	768	975	1,165	1,492	2,140
Cl (mg/l)	12.7	34.5	47.7	72.2	90.4	118	212
NO_3 (mg/l)	0.05	2.84	4.06	5.66	16.4	31.2	277
SO_4 (mg/l)	11.2	32.0	42.0	57.9	71.4	128	243
Enna (36)							
Cond. (μS/cm)	228	306	363	549	798	1,208	2,510
Cl (mg/l)	10.5	12.4	16.0	28.3	93.8	156	498
NO_3 (mg/l)	0.10	0.36	0.58	3.38	17.0	23.7	127
SO_4 (mg/l)	10.5	26.2	34.0	55.8	110	181	326
Messina (71)							
Cond. (μS/cm)	199	309	371	549	696	789	1,294
Cl (mg/l)	9.83	12.9	15.6	25.2	34.0	46.8	92.8
NO_3 (mg/l)	0.05	1.71	3.66	7.15	15.4	21.9	35.4
SO_4 (mg/l)	6.20	13.7	32.7	42.6	69.0	131	163
Palermo (157)							
Cond. (μS/cm)	280	368	453	656	903	1,250	4,620
Cl (mg/l)	5.53	15.4	22.3	51.3	120	224	1,302
NO_3 (mg/l)	0.08	1.23	4.03	7.31	14.0	25.7	118
SO_4 (mg/l)	8.87	14.1	25.0	50.0	88.2	162	230
Ragusa (34)							
Cond. (μS/cm)	279	302	389	487	580	678	901
Cl (mg/l)	21.1	22.5	29.0	35.6	43.2	87.0	107
NO_3 (mg/l)	10.9	16.1	18.5	21.0	31.4	44.8	87.5
SO_4 (mg/l)	7.81	8.71	12.1	18.3	32.1	53.9	69.4
Siracusa (54)							
Cond. (μS/cm)	269	364	412	523	1,270	2,640	3,610
Cl (mg/l)	15.1	16.8	23.1	29.6	252	718	1,018
NO_3 (mg/l)	0.10	3.43	9.46	14.6	19.5	26.3	34.5
SO_4 (mg/l)	6.03	6.39	10.2	29.2	93.4	113	234
Trapani (44)							
Cond. (μS/cm)	336	512	570	699	819	973	1,078
Cl (mg/l)	12.4	36.9	51.9	86.5	142	180	212
NO_3 (mg/l)	0.10	1.16	4.40	15.3	41.4	87.8	296
SO_4 (mg/l)	11.1	18.3	24.8	58.2	93.1	120	179
Sicily (667)							
Cond. (μS/cm)	199	369	467	656	964	1,280	4,620
Cl (mg/l)	5.53	16.8	27.3	47.7	87.2	148	1,302
NO_3 (mg/l)	0.05	1.23	4.00	8.19	18.6	32.5	296
SO_4 (mg/l)	6.03	13.9	29.1	51.4	82.3	141	516

Data are shown for the whole Sicily and also subdivided per province (number of samples is indicated in parenthesis). Data of electric conductivity and chloride concentrations from D'Alessandro et al. (2008)
Cond. electric conductivity

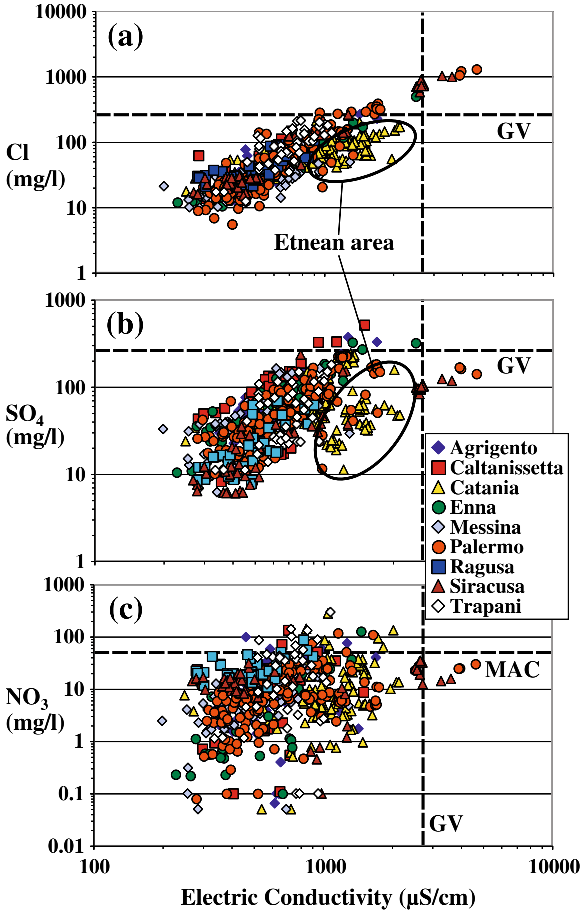

Fig. 2 Binary correlation diagrams of electric conductivity vs. **a** chloride, **b** sulphate and **c** nitrate contents. *Dashed lines* indicate the respective guideline value (*GV*) or maximum admissible concentration (*MAC*). Samples collected in the Etnean area have been evidenced by a *circle*

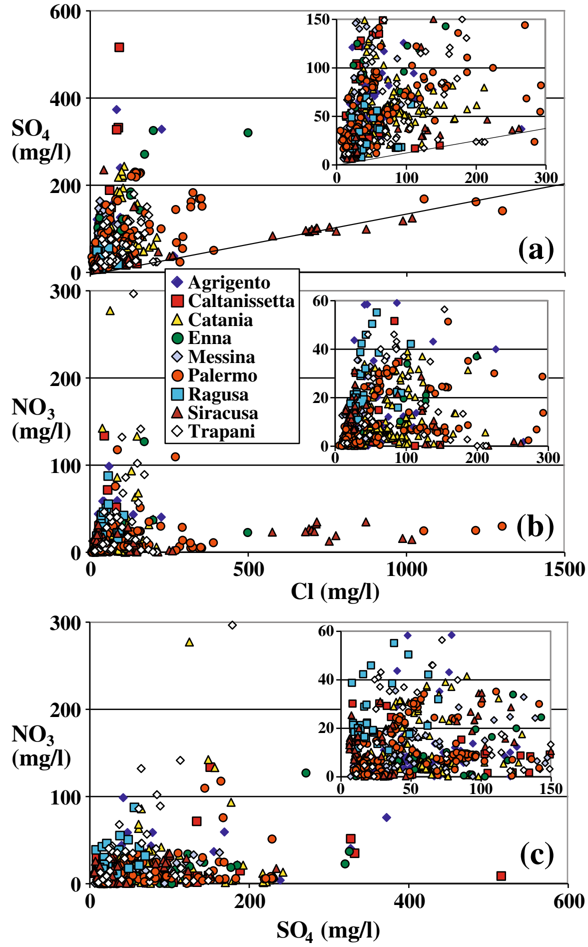

Fig. 3 Binary correlation diagrams of chloride vs. **a** sulphate and **b** nitrate and of sulphate vs. nitrate **c**. *Strait line* in (**a**) represents the chloride/sulphate ratio of seawater. *Insets* show the enlargement of the low concentration part of the plots

volcanic aquifers. Water in this area have on average a higher natural ionic content (D'Alessandro et al. 2011). While high salinity values in the rest of Sicily are mainly due to the presence of seawater or from dissolution of evaporite rocks, in the active volcanic area of Mt. Etna the main contributor to ionic content is bicarbonate deriving from the titration of magmatic carbon dioxide within the aquifers and to metals (mainly alkaline-earth elements) released by water–rock interaction processes (Aiuppa et al. 2003). Similarly, the Etnean groundwater shows electric conductivity/sulphate ratios that are higher than average (Fig. 2b) but fall within the large range of electric conductivity/nitrate ratios measured for the entire data set (Fig. 2c).

The samples with the highest conductivity were those with significant seawater contamination, as found previously (D'Alessandro et al. 2008). The same samples plot very close to the sulphate/chloride ratio of Mediterranean seawater in the binary correlation plot of Fig. 3a, while the remaining samples are enriched in sulphates with respect to the same ratio. A few samples collected in the provinces of Agrigento, Caltanissetta and Enna (central part of Sicily) exhibited very strong sulphate enrichment.

Table 2 Chemical composition of bottled water

Brand	%	El. cond. (µS/cm)	Cl (mg/l)	NO_3	SO_4
S. Maria	36	538	32.1	30.5	8.02
Vera[a]	12	271	2.91	4.32	19.4
Vera (S. Rosalia)[a]		388	13.3	2.63	16.0
Geraci	9	256	8.39	1.19	19.4
S. Benedetto (Popoli)[a]	5	512	6.76	3.50	23.3
S. Benedetto (Scorzè)[a]		301	2.94	7.85	4.00
Levissima	5	126	1.02	1.80	17.5
Mt. Cimone COOP	3	288	3.20	1.70	10.4
Auchan	3	619	8.86	2.11	37.6
Fiuggi	3	185	7.25	2.56	1.33
Ferrarelle	3	1,840	21.8	5.03	3.52
Rocchetta	2	301	8.01	1.41	7.55
Uliveto	2	1,189	84.2	7.43	101
Alisea	1	550	33.5	31.1	8.40
Ruscella	1	531	33.5	31.8	8.74
Norda	1	244	2.08	4.31	9.35

% indicative percent of the total bottled water sold on the Sicilian market, *El. cond.* electric conductivity
[a]Water of two different sources are sold under the same brand both for Vera and for S. Benedetto

The nitrate concentration was not significantly correlated with either the chloride (Fig. 3b) or sulphate (Fig. 3c) concentration.

Geographic distribution

The geographic distribution of the measured parameters was inspected by averaging values at the municipality level due to the occasional presence of large variations between single samples. The variability within each municipality was mainly dependent on the number and size of different utilized water resources. For example, the municipalities along the northern mountain chain and close to Mt. Etna that have access to exploit large water resources exhibited low CVs (coefficient of variation = standard deviation/mean), with values generally below 1 for electric conductivity, chloride and sulphate. In contrast, municipalities located in the most arid part of the island and far from large water resources generally exhibited larger CVs. The variability in the nitrate values followed a similar pattern but with some noteworthy exceptions. In areas with large water resources there were occasionally water samples with very low nitrate contents (possibly due to denitrification processes) and samples with high nitrate contents (probably due to local contaminations), which produced high CVs. In contrast, in the province of Ragusa, nitrate values exhibited low CVs (from 0.02 to 0.48) with generally elevated average values (from 15 to 55 mg/l), which is indicative of widespread contamination of the aquifers in that area. There were no measured nitrate values lower than 10.9 mg/l in this province.

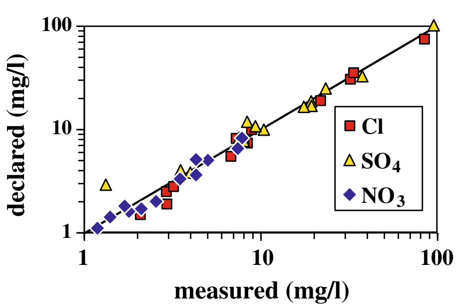

Fig. 4 Binary correlation diagrams of measured vs. declared in the label values of chloride, sulphate and nitrate in the analysed bottled water samples. The *line* represents the 1/1 ratio

Figure 5 shows the distribution of the 251 average values for those municipalities in which at least one sample had been collected. The values of electric conductivity (Fig. 5a) and chloride concentration (Fig. 5b) were highest along the northern and eastern coasts of the island. As previously discussed by D'Alessandro et al. (2008), seawater intrusion is the main reason for these high values. These parameters were lowest along the northern mountain chain, which is also the part of Sicily with the highest rainfall (Fig. 1d). The area of Mt. Etna represented an exception,

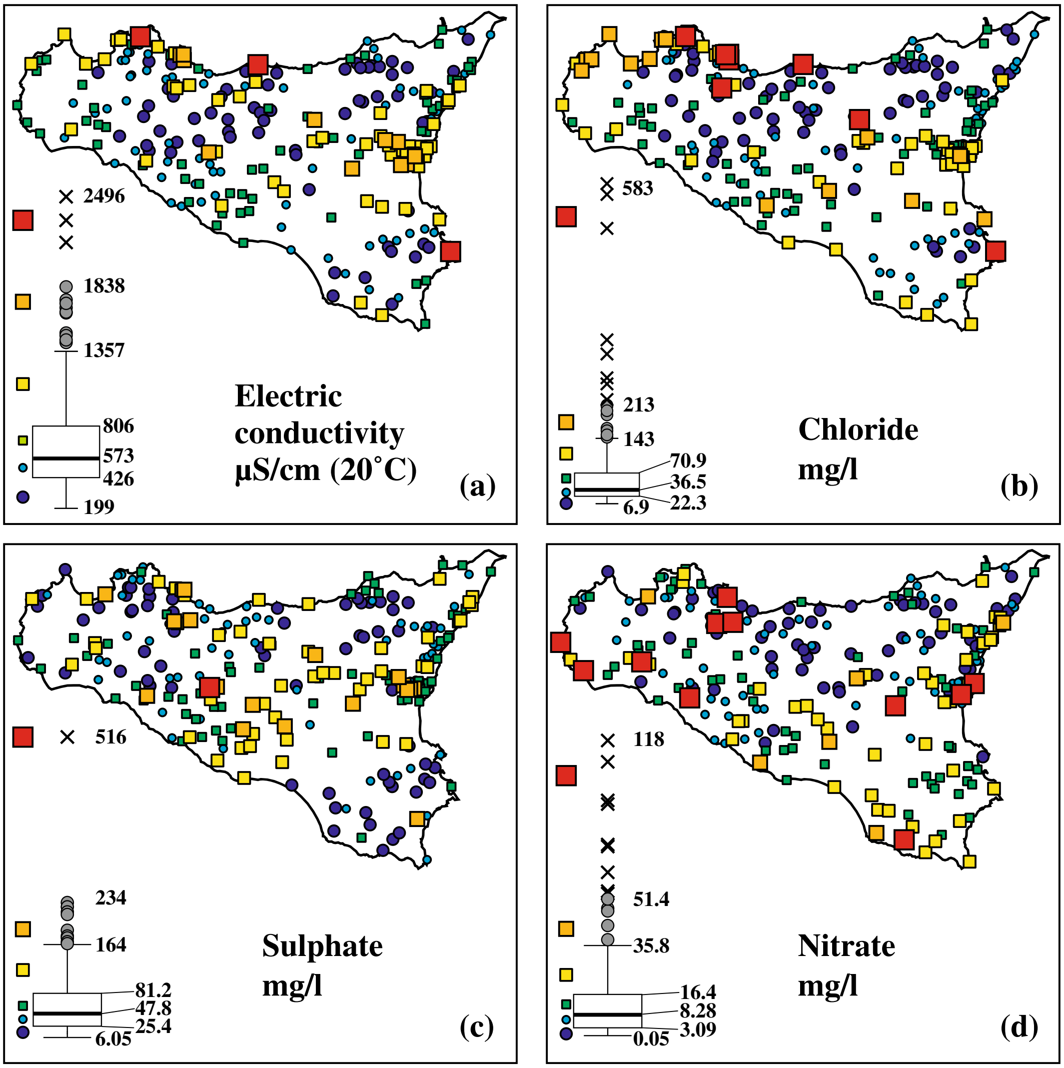

Fig. 5 Geographic distribution of electric conductivity (**a**), chloride (**b**), sulphate (**c**) and nitrate (**d**) in the sampled water (average values on a municipality level). *Symbols* are drawn on the basis of the *box and whiskers* diagram in which the *thick line* is the median value, the *box* is the interquartile range, the *lower whisker* is the minimum value and the *upper whisker* is the maximum non-outlier value; the *grey circles* are outliers (>upper quartile + 1.5 times the interquartile range), and the *crosses* are extremes (>upper quartile + three times the interquartile range)

showing relatively high electric conductivity and chloride values despite being one of the areas of highest meteoric recharge. As stated in "Binary correlation plots", this depends on the intense water–rock interaction within the aquifers of the volcano being enhanced by the dissolution of huge quantities of magmatic carbon dioxide (Brusca et al. 2001). Furthermore, a significant proportion of the chloride dissolved in the Etnean aquifers derives from the open-conduit degassing of the volcano mediated by meteoric recharge (Aiuppa et al. 2006). Intermediate-to-high values of electric conductivity and chloride content were found also in the semi-arid central part of the island. This area is also characterized by the widespread presence of evaporite rock outcrops (Fig. 1b) whose dissolution contributes to increased salinity of the groundwater. Both the climate and geology of the central part of Sicily also explain why the sulphate contents of water are highest there (Fig. 5c). The coastal areas show intermediate-to-low sulphate values, indicating that seawater is not a major contributor of this ion. The relatively high values in the Etnean area are justified (similarly to chloride) by the contribution of volcanic degassing to the sulphate content of the local groundwater (D'Alessandro et al. 2003; Aiuppa et al. 2006).

The geographical distribution of nitrate in public water supplies (Fig. 5d) closely mimics the regional map of groundwater vulnerability to nitrates of agricultural origin (Fig. 1d). The worst nitrate pollution, with values often exceeding the MAC, all occurred in the most vulnerable areas.

Comparison of nitrate in public supply and in bottled water

Whilst the nitrate contents in public drinking water supplies occasionally reached very high values (up to 296 mg/l), only 4.7% of the samples exceeded the MAC set by the national law. Furthermore, 59% of the samples had concentrations below the GV of 10 mg/l, and the median value was 8.9 mg/l. For comparison, none of the bottled water samples exceeded the MAC, with a maximum value of 31.8 mg/l and a median value of 3.9 mg/l. Although this appears to indicate that the quality of bottled water is higher than that of public water supplies in terms of nitrate contents, considering the probable human nitrate intake from both sources suggests that the differences are not significant. The average nitrate content of the public water supplies weighted for the population of the different municipalities was 16.1 mg/l, while the average for bottled water weighted for their respective share of sales was 15.2 mg/l. These comparable values are due to more than one-third of the bottled water sold in Sicily having relatively high nitrate contents (about 30 mg/l).

Whilst the quality of Sicilian water supplies needs to be improved by excluding water resources polluted by nitrate, the present situation probably does not justify the high consumption of bottled water in Sicily (at least considering only the nitrate intake). Apart from being expensive, consuming bottled water is also detrimental to the environmental since two-thirds of the total comes from outside Sicily and requires transportation over hundreds or even thousands of kilometres, possibly on trucks, and thereby significantly contributes to atmospheric pollution. Furthermore, the use of bottled water, being sold almost exclusively in plastic bottles that are recycled only in minimal part (<10%), is associated with the problem of disposing the empty containers. Finally, it has to be underscored that the European legislation on water quality often poses more stringent limits for the water distributed by public supplies than for bottled water and recent studies evidenced the presence on the European market of bottled water whose regular long-time consumption could have adverse effects on human health (Misund et al. 1999).

Conclusions

This study further highlights the high variability in the quality of public drinking water supplies in Sicily. The water quality is highest close to the major groundwater resources of the island, which are mainly located along the northern mountain chain where geological (thick permeable sequences) and climatic (higher rainfall) factors support the formation of large aquifers. In contrast, the water quality is lowest along the southern coast and the central-eastern part of Sicily, where geological and climatic conditions do not allow for the presence of significant aquifers. Furthermore, in this area the widespread presence of evaporite rock contributes to deterioration of the water quality by increasing the salinity of the groundwater. Anthropogenic activities are a further factor contributing to groundwater quality deterioration, and its impact is stronger along the coast where agricultural activity is most intensive and the population density is highest. The high levels of water consumption in this area, especially for irrigation, has produced both nitrate pollution and seawater intrusion into the coastal aquifers. This problem is increasing and is also extending to areas with major water resources, such as the Mt. Etna area, as shown by 4.7% of the 667 collected samples showing nitrate contents higher than the MAC.

Nevertheless, the estimated average nitrate intake for the Sicilian population did not differ significantly between public water supplies

(16.1 mg/l) and bottled water (15.2 mg/l). This small difference (at least for nitrate) does not justify the high consumption of bottled water, which is both expensive and environmentally damaging.

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