Environ Earth Sci (2010) 61:173–186
DOI 10.1007/s12665-009-0334-8

ORIGINAL ARTICLE

Monitoring of the groundwater chemical status in the Azores archipelago (Portugal) in the context of the EU water framework directive

José Virgílio Cruz · Dina Pacheco · Raquel Cymbron · Sandra Mendes

Received: 6 April 2009 / Accepted: 20 October 2009 / Published online: 11 November 2009

Abstract A main challenge associated to EU Water Framework Directive corresponds to groundwater monitoring, both quantitative and chemical. The need for monitoring was also stressed by the Azores Water Plan. Monitoring of the chemical status of groundwater in Azores started in 2003 and has been progressively enlarged to all islands, totalizing 72 springs and 32 wells. A large number of parameters are analysed biannually, as major, minor and trace elements, pesticides and total hydrocarbons, as well as microbial indicators. Spring waters are mainly from HCO_3–Na type; instead water from wells is predominantly from the Cl–Na type, been differences attributed to their respective hydrogeologic framework. Springs discharge mainly from perched-water bodies, been influenced mainly from CO_2 in soils, silicate weathering, and seawater spraying and aerosols. Wells are in basal bodies, therefore subject to seawater intrusion influence, and 9% of Cl analyses made in wells exceed the standard value. Heavy metals, metalloids, hydrocarbons and pesticides all comply with standard values. Agriculture pollution also influences groundwater quality, as revealed by both NO_3 and PO_4 content, been the guide value exceeded respectively in 8 and 9% of the analyses. Despite the discontinuous variation of coliforms over time microbial indicators present an impact on water quality.

Keywords Groundwater monitoring · Groundwater quality · EU Water Framework Directive · Volcanic aquifers · Azores

J. V. Cruz (✉)
Department of Geosciences, CVARG,
Centre of Volcanology and Geological Hazards Assessment,
University of Azores, Apartado 1422,
9501-801 Ponta Delgada, Portugal
e-mail: jvc@uac.pt

D. Pacheco · R. Cymbron · S. Mendes
Directorate-Regional for Land Management and Water Resources, Av Antero de Quental, 9C, 2° Piso,
9500-160 Ponta Delgada, Portugal

Introduction

The Water Framework Directive (Directive 2000/60/CE), adopted on the 23rd of October 2000, is the main EU water policy instrument, associated to a rather demanding implementation strategy. According to the Water Framework Directive (WFD), groundwater should achieve the so-called "good status" by 2015, regarding quantitative and chemical aspects, and to reach this overall objective a proactive approach toward sustainable resource exploitation is defined. Therefore, several environmental objectives were pointed out to groundwater: to prevent or limit the input of pollutants to groundwater, to protect, enhance and restore all groundwater bodies, to implement measures to reverse any sustained and significant enrichment trend on the concentration of any pollutant introduced in groundwater due to human activities and to allow compliance for protected areas according to the respective standards and objectives.

In order to achieve the "good chemical status" the observation of several criteria is required, namely the inexistence of saline intrusion effects, the compliance regarding to EU quality standards and that the groundwater discharge to surface water bodies will not cause that these ones are not capable to attain their environmental objectives.

The challenges associated to WFD implementation are multiple and concerns about the deliver of the WFD goals remain present, recognizing that there is some way to go (Fürhacker 2008; Beunen et al. 2009). The type of leadership provided by the competent authorities is also criticized (Moss 2008).

This legislative act was later complemented by the Groundwater Directive (2006/118/CE), adopted on the 12th December, which came to force in order to develop principles to groundwater protection and sustainable development, especially in what concern to pollution prevention and control. The relevance and the history of the making of this Directive are reported by Quevauviller (2008).

Water monitoring is one of the key aspects of the WFD, and the Groundwater Directive is also partially focused in this practice, as a tool to evaluate groundwater quality and to provide data needed to identify and define measures to reverse upward trends in pollutants. Therefore, groundwater geochemistry plays an important role in what concerns WFD implementation, which is recognized as to demand a close integration between science and water policy (Quevauviller et al. 2005; Edmunds 2009).

Extensive reviews of the guidance for groundwater monitoring in the context of the WFD Common Implementation Strategy are provided by Quevauviller (2005) and Grath et al. (2007). Through the International Groundwater Resources Assessment Center, Jousma and Roelofsen (2004) reviewed groundwater monitoring programmes at international level and have shown the heterogeneous approaches been adopted worldwide. Recently, Jørgensen and Stockmarr (2009) discuss the Danish programme as an example of a country where groundwater is monitored for more than 20 years, resulting from the very high percentage of groundwater in drinking water supply, and provide a comparison with examples of other countries, stressing the rather low number of contributions in the international peer-reviewed literature. Nevertheless, examples can be found from EU member states, as for example Italy (Onorati et al. 2006), or from other countries, like Korea (Lee et al. 2007).

Monitoring of the chemical status of groundwater bodies, in the overall context of EU legislation, has been implemented at the Azores archipelago. The Azores archipelago is located in the North Atlantic Ocean, between 37° to 40°N latitude and 25° to 31°W longitude, and is made of nine islands of volcanic origin. It has a surface area of 2,333 km^2 and about 240,000 inhabitants (Fig. 1).

Groundwater is a strategic resource at Azores archipelago, playing an important role as the main water supply source and as ecosystem support matrix. However, and despite the environmental, social and economical value of groundwater, aquifers at Azores support an increase of pressure as already recognized in several studies. Groundwater pollution due to agricultural activities, salinization or lack of appropriate waste water drainage and treatment systems impact have been reported in the majority of the nine islands. As a result high contents of nitrogen species, as nitrate, derived from the application of synthetic and organic fertilizers, and from animal wastes leaching, as well as microbiology parameters and conservative indicators of mixing between fresh water and seawater as chloride, may cause failure to comply regarding EU and national water quality regulations.

A recent survey on the land use patterns at the Azores archipelago using LANDSAT 7 imagery have shown that about 56% of the surface area corresponds to agricultural occupation, mainly by pasture lands, exceeding by far the fraction occupied by forests and natural vegetation, that equals 22 and 13% respectively (DROTRH 2007). These conclusions enable to stress the potential magnitude from diffuse agricultural pollution sources.

The Azores Water Plan (AWP), that came to force on 23rd of April 2003, also recommends monitoring as a strategic priority, with the year 2006 as the deadline to implement a full monitoring scheme for all water bodies, including groundwater, according to WFD (DROTRH/INAG 2001).

To comply with WFD and AWP requirements, a monitoring network was defined according to the 54 groundwater bodies in the Azores, considering a phased approach. The main objective of the present paper is to describe the methodology and discuss results gathered with groundwater chemical monitoring at Santa Maria, São Miguel, Faial, Pico, Graciosa, São Jorge, Corvo and Flores islands.

Geological setting

Azores is a volcanic archipelago located according to a complex geodynamic setting, characterised by the proximity to the triple junction between the American, the African and the Eurasian plates (Fig. 1). The Middle Atlantic Ridge isolates Flores and Corvo islands, which are located west of the Ridge and lie on the American plate, from the other islands, which are spread toward the east, along a strip trending WNW-ESE and subject to a geodynamic control by tectonic structures.

Several types of volcanic deposits outcrop on the nine islands. Santa Maria, Pico and São Jorge islands are made of basaltic rocks, where volcanic activity was mainly from the hawaiian and strombolian types, expressed by basaltic lava flows and pyroclastic rocks of the same nature. On the other islands, the volcanic rocks are chemically more evolved, ranging from basalts to trachytes. Large areas of islands such as São Miguel and Faial are covered by pumice fall deposits, ignimbrites and other types of

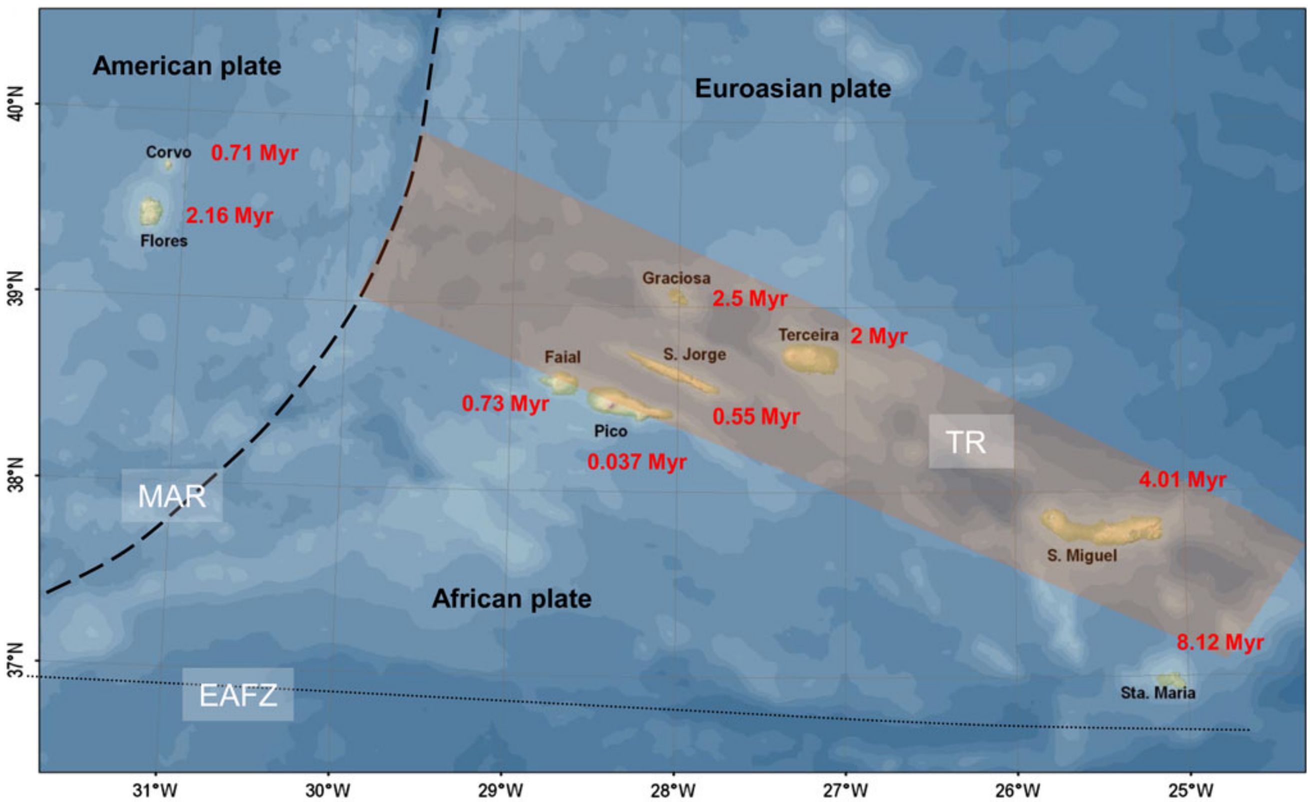

Fig. 1 Location of the Azores archipelago in the North-Atlantic Ocean and main tectonic features (*MAR* Middle Atlantic Ridge, *TR* Terceira Rift, *EAFZ* East Azores Fracture Zone). Maximum age for inland outcrops is presented

pyroclastic flow deposits and trachytic domes. Only at Santa Maria, the easternmost island of the archipelago, there are marine sedimentary units of Miocene age interbedded in the volcanic succession.

The maximum age observed on the archipelago is 8.12 Myr, at Santa Maria island (Abdel-Monen et al. 1975), and since settlement in the 15th century about thirty eruptions have taken place, the last of which was a submarine event that occurred near Terceira island in 1998–2000.

Water resources setting

Surface water

The average annual precipitation at the Azores is 1,930 mm, varying between 966 mm at Graciosa island and 2,647 mm at Flores, exceeding by far the average annual actual evapotranspiration, which is 581 mm. The average annual actual evapotranspiration also varies from one island to other, in the range between 502 mm (São Jorge) and 632 mm (Graciosa island; DROTRH/INAG 2001).

According to the classification defined by Thornthwaite (1948) the climate in São Miguel can be considered as humid to super-humid, and mesothermal with dry summers using the Kopen classification (Ricardo et al. 1977). Monthly average temperatures are higher in August, about 22°C in the coastal area and 15°C in the higher elevation areas, and the coldest month is February, with values between 14°C, in the coast, and 5°C in higher altitude zones (Ricardo et al. 1977).

Average annual precipitation at São Miguel, is equal to 1,722 mm (DROTRH/INAG 2001). The seasonal distribution is marked by a rainy season, and for example at Ponta Delgada, with an average annual precipitation of 958 mm, 76.3% of the total precipitation occurs between September and March. Monthly average precipitation is, in general, higher in January and the lowest measurements are made in July and August.

Average annual runoff at the Azores is 680 mm, with a range between 134 mm (Graciosa) and 1,371 mm (Flores island). Considering the island area it is possible to evaluate the average discharge, which is 322 $\times$ 10^6 m^3/year, varying between 8 $\times$ 10^6 m^3/year (Graciosa) and 1,731 $\times$ 10^6 m^3/year (São Miguel; DROTRH/INAG 2001).

Hydrogeology

Groundwater at Azores occurs in two major aquifers systems (Cruz 2003, 2004): (1) the basal aquifer system, which corresponds to fresh-water lenses floating on underlying salt water, and (2) in perched-water bodies. The basal aquifer system is in the coastal area, presenting generally a very low hydraulic gradient, and groundwater abstraction is from drilled wells. There are no evidences of a basal water lens continuity under the island, but it is possible in certain areas. Nevertheless, it is suggested that a hydraulic liaison occurs with the perched-water bodies at altitude, which eventually releases water to the basal unit. The perched-water bodies correspond to pervious units, with impermeable to very low permeable layers at the bottom and, where topographic conditions are favorable, are drained out by a large number of springs in the volcano slopes. Therefore, these aquifers at altitude correspond to confined layers or to leaky aquifers, which can lose water through aquitards bounding them from above. There is no evidence to support the hypothesis of the existence of dike-impounded aquifers (Peterson 1972), as in the Hawaiian conceptual model for volcanic islands; however this is not excluded with the present status of knowledge (Cruz and Silva 2001).

More than 1,000 springs and wells are spread all over the archipelago. In certain areas there are numerous hand-dug wells, which are not included in the survey for the Azores water resources planning (Cruz 2001). The distribution of springs in the archipelago is heterogeneous, with densities varying between 0.01 springs/km^2 at Pico and 0.72 springs/km^2 observed at Santa Maria island, resulting from climatic, geomorphologic and hydrogeological controls.

Specific capacity is on the range of 1.40×10^{-2}–266.67 L/s.m, with a median value of 32.29 L/s.m (Cruz 2001, 2004). The values shown a marked variability comparing wells from several islands and the highest specific capacity is observed at Pico and Graciosa, with wells drilled in recent basaltic lava flows, which generally are thin and fractured, presenting also frequently clincker levels interbedded.

Recharge rates range from 8.5 to 62.1%, and the highest values are observed at Pico, Terceira, Faial, São Miguel and Graciosa, especially in areas where the terrain is covered by recent basaltic lava flows and the soil is sparse. Groundwater resources estimates point to a total volume of about $1{,}580 \times 10^6$ m^3/year, distributed between 8.3×10^6 m^3/year at Corvo and the 582×10^6 m^3/year at Pico (Cruz 2001). Values above the median (101.3×10^6 m^3/year) are observed at São Miguel, São Jorge, Terceira and Flores islands.

Methodology

Despite the 98% contribution of groundwater sources to drinking water supply in the Azores (Cruz and Coutinho 1998), monitoring is relatively recent. This fact is contrary to the pattern identified by Jørgensen and Stockmarr (2009) for regions where groundwater contribution to water supply is important. From the conclusion drawn by these authors, the priority conceded to quality monitoring, at least in the Azores in the first stage, is a common feature of the groundwater monitoring programmes been implemented worldwide.

A phased approach was developed in order to implement a chemical monitoring network for groundwater bodies in the Azores archipelago. The main criteria adopted, due to financial constraints, was to couple surface and groundwater monitoring, in a holistic perspective, and therefore field work was initiated in 2003 and 2004 in islands, like São Miguel, Pico and Flores, where several surface water bodies in risk were identified, namely eutrophicated lakes, some of then classified as vulnerable zones according to EU Nitrates Directive (Directive 91/676/CEE), followed in 2006 by sampling in Corvo, Faial, Graciosa and São Jorge islands. Field work in Terceira island was only initiated in 2007, which results are no further discussed in the present paper.

To proceed to the selection of sampling points, springs both used for public water supply and presenting higher discharge rates were chosen, coupled with an analysis of the spatial distribution. For drilled wells the selection was based on the well yield and spatial distribution. Therefore, as a result of the referred criteria, the monitoring network in the archipelago is composed of 72 springs and 32 drilled wells (Fig. 2). Preliminary results have been reported by Cymbron et al. (2005, 2006) and Cruz et al. (2007).

The methodology consists in two sampling campaigns by year, one with a large spectrum of analysed parameters: temperature, pH, electrical conductivity, dissolved oxygen, Ca, Mg, Na, K, HCO_3, Cl, SiO_2, NO_3, NO_2, NH_4, PO_4, Al, Fe, Cu, Cd, Hg, Mn, Pb, As, other List I and List II from Directive 80/68/CE (pesticides, total hydrocarbons), coliform bacteria (total and faecal) and faecal streptococcus.

The remaining annual sampling campaign follows a minor number of determinations (temperature, pH, electrical conductivity, dissolved oxygen, NO_3, NO_2, NH_4, coliform bacteria (total and faecal) and faecal streptococcus). For drilled wells, chloride content was determined in the two sampling campaigns.

All the analyses were conducted at the INOVA laboratory (Institute for the Technological Innovation of Azores), which is accredited according to ISO 17025 using several methods according to parameters or species to be determined. Analytical methods were the following: atomic absorption spectrometry for major cations and trace metals, ion chromatography for major anions, molecular absorption spectrometry for silica, NO_3, NO_2, NH_4, PO_4 and total hydrocarbons, and chromatography for pesticides determination. Temperature, pH, alkalinity titrations and

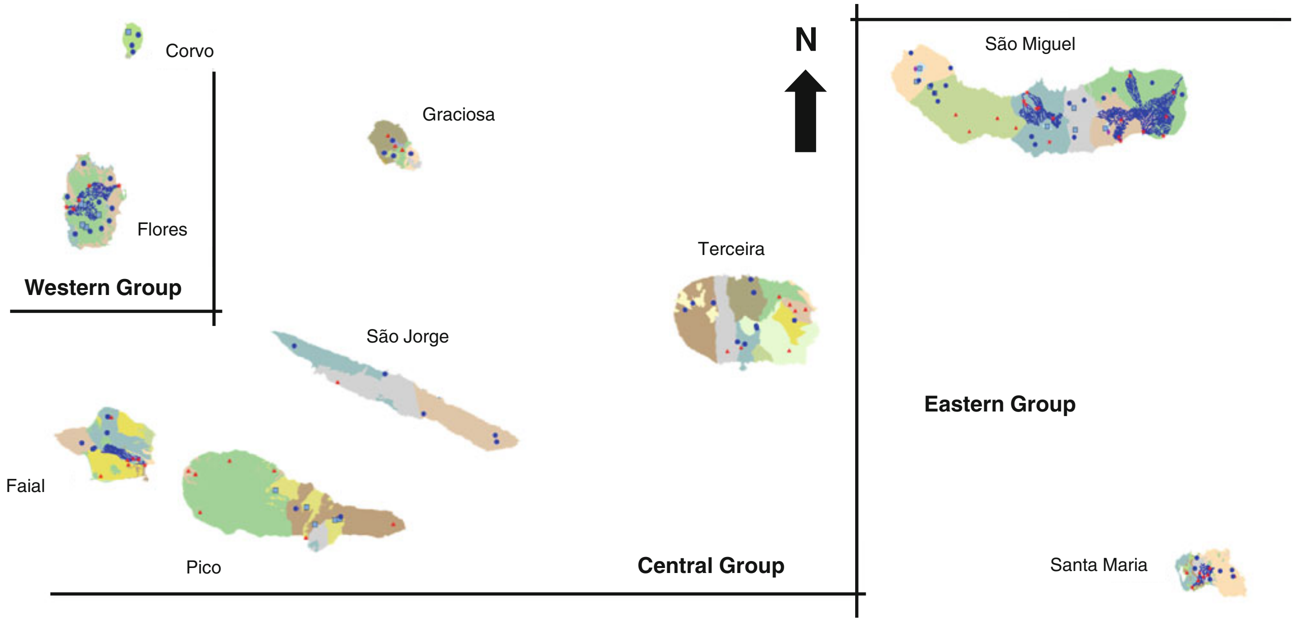

Fig. 2 Monitoring network for groundwater chemical status assessment on the Azores archipelago (*blue circles* springs, *red triangles* wells). In the background of the plot the 54 groundwater bodies in the Azores are represented, as well as the overall water quality monitoring scheme (*red stars* river water stations, *light blue squares* lakes)

electrical conductivity measurements were conducted in the field with specific portable equipment. For the coliform and faecal streptococcus determinations membrane filtration was used.

The major-ion composition statistical data (average; standard deviation; median; maximum; minimum), as well as results for master variables and PO_4 content, are reported in Table 1 for each island and for all the data set.

Hydrocarbons and pesticides are generally under the detection limits from the analytical methods, and therefore are not listed in Table 1. Heavy metals and metalloids are in compliance with standard values and frequently are also under the detection limits, reason for which are no further discussed in this paper.

Median values for pH point out to neutral to slightly alkaline waters (Table 1). At São Miguel, São Jorge, Flores and Corvo pH median values are lower than the median value calculated for all data set (7.30).

Electrical conductivity values depict a difference between springs and wells waters, as shown by statistical value: considering the data set, springs present an average conductivity equal to 202 μS/cm (median = 152 μS/cm), and wells have an average value of 983 μS/cm (median = 590 μS/cm), been this contrast attributed to their respective hydrogeologic framework. Springs discharge mainly from perched-water bodies and the low conductivity values are consistent with short residence times, as well as high water–rock ratio (Langmuir 1997), instead wells were drilled in basal water bodies, subject to an higher influence of sea-salts over groundwater chemistry due to seawater intrusion.

Data presentation and discussion

Hydrogeochemical outline

Groundwater geochemistry in volcanic regions is partially influenced by the dissolution of primary minerals on the volcanic rocks, depending on saturation state of primary minerals, by the precipitation of secondary minerals, by the aqueous chemistry of each element and by the acidic character of the environment (Aiuppa et al. 2000). Other factors correspond to rain chemistry, climate, rock type, residence time of water, rock division, temperature and pressure (Custódio 1989).

The contribution of volcanic rocks dissolution to groundwater composition was already characterized in studies made worldwide. A multivariate statistical analysis made over a database of about 250 chemical analysis of spring water discharging from perched-water bodies in the Azores depicted differences between aquifers of basaltic nature comparing to more evolved volcanic rocks, been the first more enriched in alkali-earth metals, despite the limited contribution of silicate weathering and the dilution effect provided by seawater salts influence (Cruz and Amaral 2004).

The projection of the major-ion composition in Piper-type diagrams shows that springs from São Miguel, São

Table 1 Results for master variables (temperature, pH, electrical conductivity) and major-ion composition in groundwater

Island	Temp (°C)	pH	Cond (μS/cm)	HCO_3 (mg/L)	NO_3 (mg/L)	PO_4 (μg/L)	SiO_2 (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)
Santa Maria													
Min.	14.2	6.10	138.0	26.00	1.40	20	10.00	4.10	20.00	18.00	0.90	3.40	4.00
Max.	21.3	8.60	4,200.0	220.00	75.00	515	58.00	248.00	1,270.00	587.00	24.10	197.00	84.00
Average	18.3	7.31	658.8	99.92	12.58	284	36.22	30.81	202.04	91.73	4.62	25.55	16.64
St.Dev.	1.6	0.69	1,034.7	68.02	10.51	137	13.27	63.43	375.83	149.04	5.80	50.08	20.14
Median	18.2	7.60	284.5	77.50	8.85	294	34.50	11.00	56.00	37.85	2.51	9.50	10.00
São Miguel													
Min.	9.1	6.00	27.0	9.60	0.27	13	4.70	1.90	11.00	6.60	0.70	0.90	0.90
Max.	23.0	8.00	533.0	196.00	116.00	851	68.00	44.00	85.00	100.00	101.00	21.00	26.00
Average	14.7	7.06	180.3	53.90	12.59	279	43.27	6.45	30.40	23.84	7.26	5.04	5.55
St.Dev.	1.8	0.51	108.9	36.57	21.79	199	13.09	6.01	22.31	15.35	12.41	5.00	5.02
Median	14.6	7.20	139.0	44.00	5.40	221	43.00	4.70	19.00	19.50	5.05	3.00	4.20
Graciosa													
Min.	13.0	7.10	284.0	85.00	1.80	191	31.00	8.10	51.00	37.00	4.50	8.80	13.00
Max.	24.5	8.70	4,700.0	108.00	26.00	558	40.00	107.00	1,589.00	483.00	117.00	115.00	107.00
Average	19.9	7.64	1,635.3	92.29	16.89	302	36.71	48.87	602.78	219.43	26.07	45.83	39.14
St.Dev.	3.5	0.46	1,393.8	8.96	6.89	125	2.93	40.16	503.34	163.68	40.56	36.77	31.50
Median	20.0	7.70	1,136.0	88.00	16.50	254	37.00	31.00	480.00	217.00	11.30	38.00	33.00
São Jorge													
Min.	14.9	6.40	117.0	40.00	2.60	66	19.00	2.40	11.00	15.00	0.80	3.10	4.20
Max.	18.1	7.50	843.0	260.00	31.00	803	59.00	32.00	162.00	117.00	11.00	40.00	15.00
Average	16.2	7.01	264.6	84.17	8.80	260	28.50	10.52	52.43	35.50	3.80	11.87	8.38
St.Dev.	1.1	0.37	245.6	86.79	7.85	312	15.42	10.85	63.87	40.17	3.90	13.92	3.75
Median	16.3	7.00	159.5	49.00	5.85	100	23.00	7.65	19.00	20.50	2.80	6.60	7.95
Pico													
Min.	12.0	7.00	73.0	31.00	0.30	153	2.70	1.70	11.00	8.80	1.70	1.70	3.60
Max.	16.6	8.40	2,340.0	245.00	5.70	1,407	53.00	80.00	614.00	374.00	16.00	50.00	29.00
Average	14.3	7.63	830.8	100.38	2.78	618	33.11	33.18	237.59	140.39	8.34	24.08	15.08
St.Dev.	1.1	0.39	658.6	64.96	1.27	382	13.20	26.11	191.50	120.56	5.05	17.03	7.38
Median	14.3	7.65	875.0	99.00	2.40	651	33.50	33.00	217.00	123.50	8.65	22.00	14.50
Faial													
Min.	11.9	6.70	79.0	24.00	1.80	28	28.00	1.60	13.00	12.00	2.20	1.40	1.40
Max.	17.9	8.00	1,359.0	165.00	6.30	460	59.00	45.00	364.00	236.00	14.00	39.00	25.00
Average	14.8	7.48	376.7	78.00	3.84	222	38.00	11.76	104.79	55.33	6.97	12.96	7.90
St.Dev.	1.8	0.35	409.9	58.76	1.81	152	8.77	14.41	120.03	73.00	4.05	15.57	8.09
Median	14.6	7.60	154.5	43.00	3.25	176	37.00	6.30	40.50	23.00	5.00	3.80	5.00
Flores													
Min.	12.9	6.10	101.0	16.00	0.30	70	18.00	2.50	16.00	11.00	0.90	2.30	3.30
Max.	17.0	7.70	246.0	76.00	3.80	430	59.00	321.00	46.00	27.00	4.80	8.30	13.00
Average	15.2	7.03	156.9	39.64	2.11	207	29.64	18.80	28.59	18.82	1.98	4.47	6.67
St.Dev.	0.8	0.45	41.6	16.52	0.95	108	12.33	67.51	9.22	5.00	1.26	1.90	2.83
Median	15.3	7.10	152.0	33.00	2.10	169	25.00	4.05	26.00	17.50	1.40	4.20	5.45
Corvo													
Min.	15.2	6.90	186.0	32.00	3.00	163	26.00	5.70	44.00	25.00	1.30	4.20	1.50
Max.	16.0	7.20	344.0	52.00	6.20	1,055	45.00	8.00	86.00	48.00	3.50	8.90	9.30
Average	15.7	7.08	246.0	42.33	4.23	512	34.33	7.07	59.67	34.00	2.63	5.77	4.27
St.Dev.	0.4	0.12	75.0	10.02	1.47	477	9.71	1.21	22.94	12.29	1.17	2.71	4.37
Median	15.8	7.10	208.5	43.00	3.50	317	32.00	7.50	49.00	29.00	3.10	4.20	2.00

Table 1 continued

Island	Temp (°C)	pH	Cond (µS/cm)	HCO_3 (mg/L)	NO_3 (mg/L)	PO_4 (µg/L)	SiO_2 (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)
Azores													
Min.	9.1	6.00	27.0	9.60	0.27	13	2.70	1.60	11.00	6.60	0.70	0.90	0.90
Max.	24.5	8.70	4,700.0	260.00	116.00	1,407	68.00	321.00	1,589.00	587.00	117.00	197.00	107.00
Average	15.8	7.21	405.1	68.06	10.28	305	37.80	18.11	127.45	58.64	6.70	13.40	10.49
St.Dev.	2.3	0.55	675.6	52.09	16.07	233	13.45	41.62	254.88	99.38	12.41	27.28	13.99
Median	15.3	7.30	186.0	48.50	5.55	240	38.00	5.90	42.50	23.00	4.50	5.70	6.50

Jorge, Pico and Faial corresponds mainly to HCO_3–Na type waters, despite a few samples been from the Cl–Na type or intermediate between these end-members in the anionic triangle (Fig. 3). In Santa Maria, Flores and Corvo spring waters are mainly from the Cl–Na type waters, while at Graciosa intermediate Cl–HCO_3 and HCO_3–Cl are dominant. Water composition from wells is more homogeneous, and is predominantly from the Cl–Na type. From the Piper plot is also possible to show that comparing the major-ion composition over the several islands studied, the major differences observable are mainly related to the magnitude of the seawater fraction in groundwater chemistry. Nevertheless, the influence of aquifer rock type over groundwater chemistry is suggested from statistical data depicted in Table 1, as median values for alkali-earth metals are higher in islands like Santa Maria, Graciosa and Pico where monitored aquifers are made essentially of volcanic rock of basic nature.

The influence of sea salts mixture toward groundwater composition is revealed by the close relation between conductivity and chloride ($r = 0.91$), as represented in Fig. 4. This plot also depicts the sharp difference between springs and wells, nevertheless the enrichment in chloride in springs is mainly due to sea-salts spraying, as expected from the rain composition in coastal areas and islands (Berner and Berner 1996). The close relation between Na and Cl ($r = 0.90$; Fig. 5) is also associated to the influence of sea-salts, and explain that these ions can account, respectively, 9.17–53.25% and 7.87–43.05% of the relative major-ion content in groundwater (in meq/L).

The higher proportion of wells been monitored in Graciosa and Pico comparing to springs also explains the higher median values for conductivity observed in these islands (Table 1). Nevertheless, with the exception of Corvo and Flores islands, the maximum value of conductivity observed in the other islands are always associated to samples collected in drilled wells with the exception of Flores and Corvo islands where water supply draws exclusively on springs.

Salinization in wells has been reported on having a negative impact on the quality of water supply, especially on those islands where groundwater abstraction on basal water bodies is crucial for populations (Cruz and Silva 2000), and the EU WFD and Groundwater Directive points out electrical conductivity as a marker of this process in order to define groundwater body chemical status. Chemically, chloride ion can be considered as a conservative marker of mixture between fresh water and seawater and the Portuguese water quality standards (PWQS) for groundwater been use as water source set a guide value equal to 250 mg Cl/L, similar to values proposed by EU Directive 98/83/CE and World Health Organization. From the data set only Serra das Fontes spring, located at Graciosa island, exceeds the 250 mg Cl/L guideline, due to an atmospheric source (seawater spraying and aerosols). Instead, in drilled wells the number of exceeding values is higher, corresponding to 9% of the 217 determinations made, resulting from marine intrusion. In wells been monitored in São Miguel and São Jorge values are always lower than the guide value, while at Santa Maria and Faial, respectively 20 and 22% of the Cl analyses made in wells reveal contents higher than 250 mg Cl/L. Instead at Pico 42% of Cl values exceeds the refereed maximum value allowed according the legislation.

The relationship between bicarbonate and chloride depicts two trends of groundwater chemical evolution. A group of springs and wells shows enrichment on HCO_3 independently of chloride, instead a group of wells reveals another trend, characterized by a parallel enrichment on both species (Fig. 6). The enrichment on HCO_3 can be derived both from CO_2 in soil and from silicate weathering and the lithologic control over alkali and alkali earths metals content was further discussed by Cruz and Amaral (2004).

Silicate weathering will also contribute with SiO_2 to solution and the HCO_3 versus SiO_2 plot reveals two groups of groundwater (Fig. 7). The majority of springs, as well as a few wells, depicts enrichment in silica and lower values

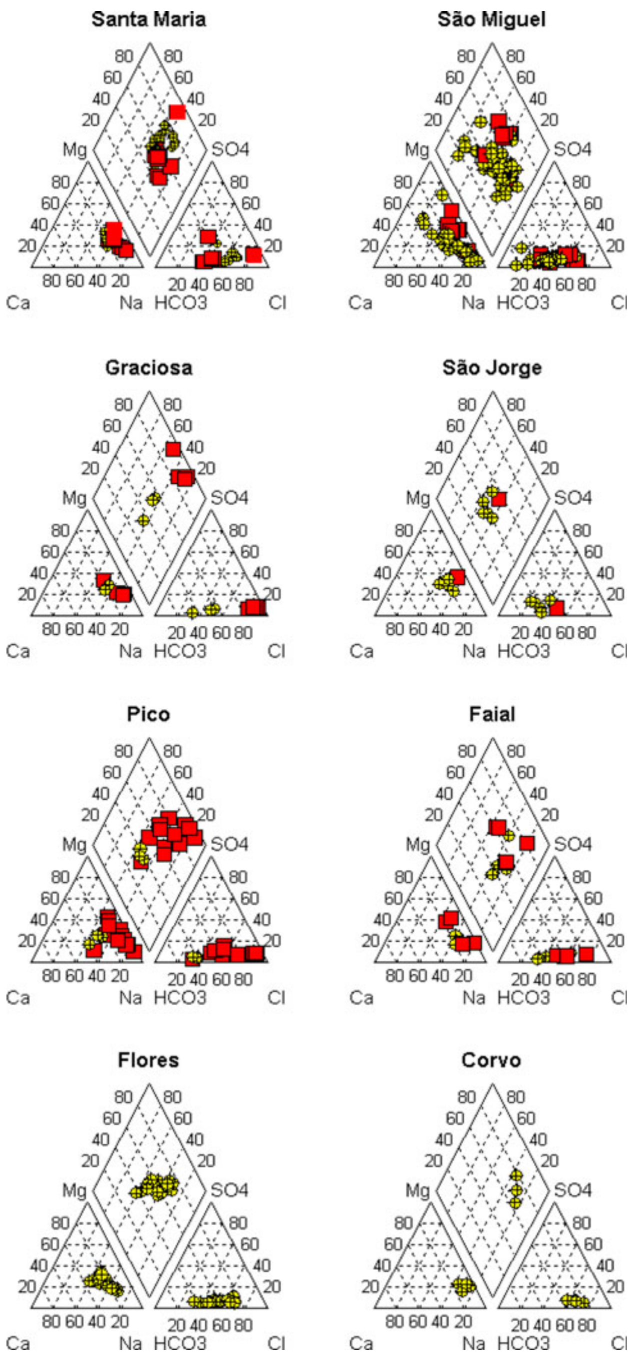

Fig. 3 Major ion composition represented by means of a Piper-type diagram (springs *yellow circles*, wells *red squares*)

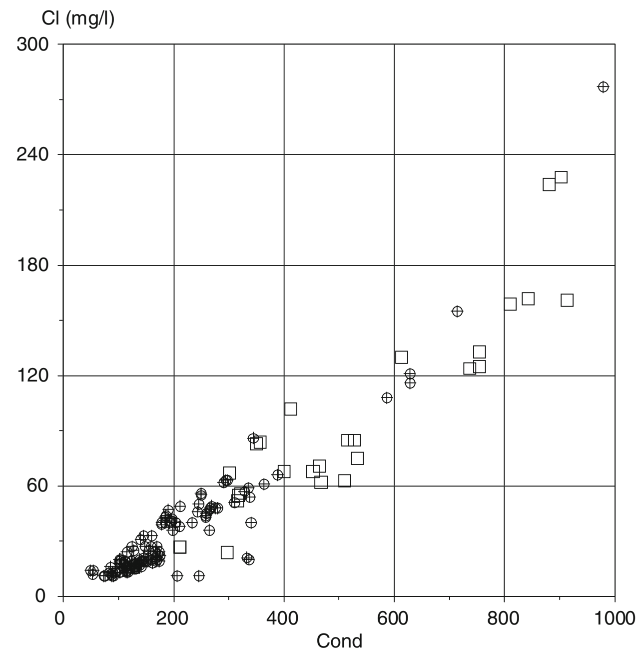

Fig. 4 Relationship between electrical conductivity (in µS/cm) and chloride content (in mg/L) in groundwater (*circles* springs, *squares* wells). For clarity both axis have been truncated and 13 wells presenting higher values are not plotted

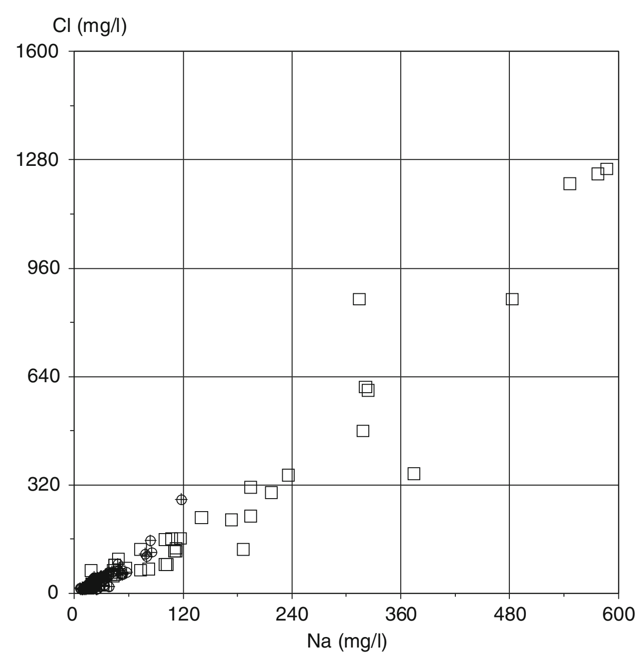

Fig. 5 Relationship between sodium and chloride content (in mg/L) in groundwater (*circles* springs, *squares* wells)

of HCO_3, instead most wells present also SiO_2 enrichment but higher bicarbonate content. This abnormal enrichment in bicarbonate, even exceeding the expected content considering mixture between fresh and seawater will be due to dissolution of volcanic-derived CO_2. Volcanic gaseous emanations in the Azores, both in fumarolic fields or of diffuse character through soil, present a CO_2-dominated composition, influencing water composition (Ferreira and Oskarsson 1999).

The contribution to groundwater composition derived from agriculture pollution can be shown by means of a SO_4

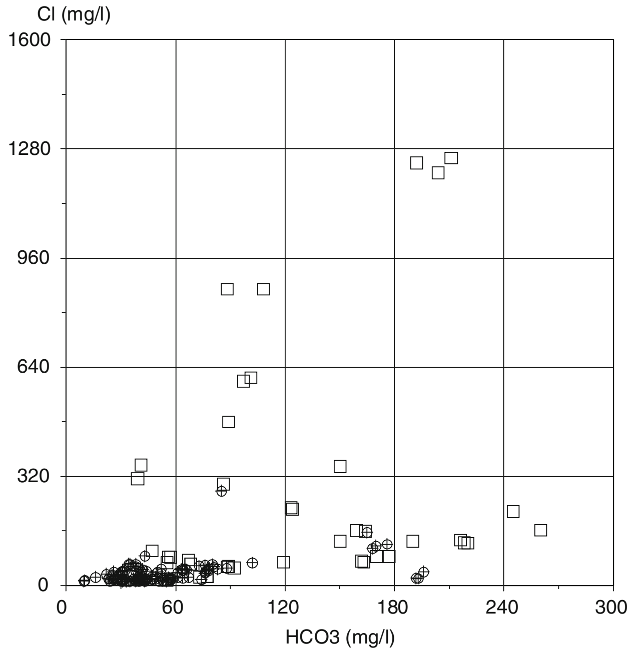

Fig. 6 Relationship between bicarbonate and chloride content (in mg/L) in groundwater (*circles* springs, *squares* wells)

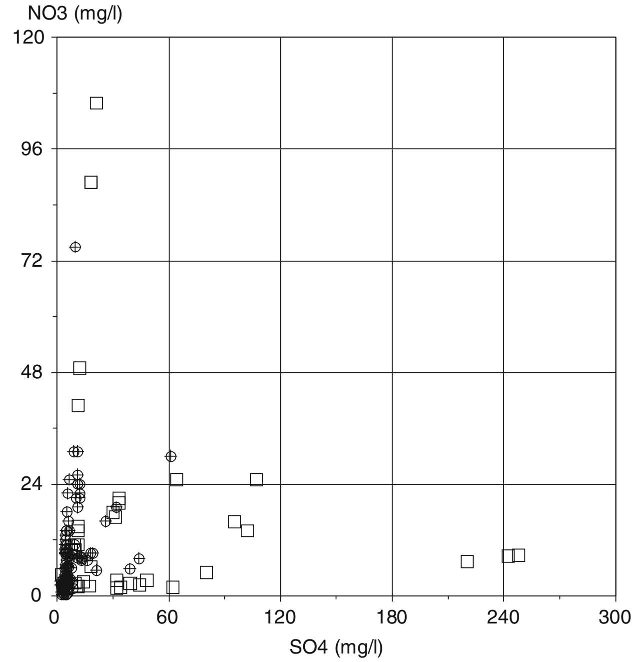

Fig. 8 Relationship between sulphate and nitrate content (in mg/L) in groundwater (*circles* springs, *squares* wells)

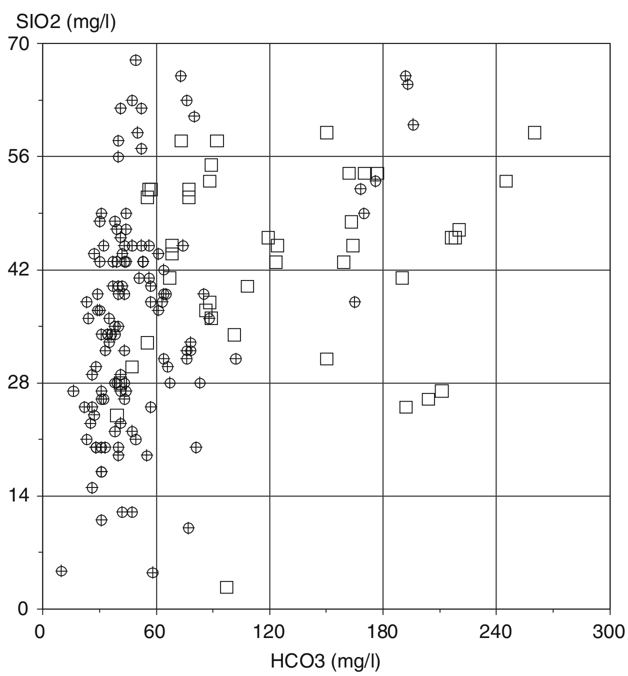

Fig. 7 Relationship between bicarbonate and silica content (in mg/L) in groundwater (*circles* springs, *squares* wells)

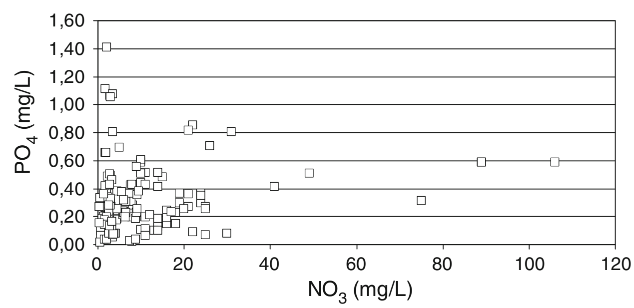

Fig. 9 Relationship between nitrate and phosphate content (in mg/L) in groundwater (*squares* represent all samples)

versus NO_3 plot, despite sulphate in solution can be derived both from agricultural practices or sea-salts mixing (Fig. 8). On the plot the majority of the springs depict NO_3 enrichment and a slight increase on sulphate content, derived from the application of synthetic and organic fertilizers, and from animal wastes leaching. The relation between agriculture practices and the nitrate dissolved in groundwater, as well as other pollutants, and the subsequent hydrogeochemical processes, have been worldwide studied and described in a large-scale overview (Houzin et al. 1986; Keeney 1989). Great emphasis has been given to fertilizers application but, nevertheless, the grazed pasturelands also imply high nitrogen leaching to groundwater due to animal wastes (Ryden et al. 1984; Burden 1986).

The PO_4 results range between 13 and 1,407 μg/L (median = 240 μg/L), been the maximum values observed at Pico and Corvo islands, resulting mainly from agriculture diffuse pollution sources. The NO_3 versus PO_4 plot shows a scattered pattern consistent with the weak correlation depicted ($r = 0.18$), nevertheless the majority of the

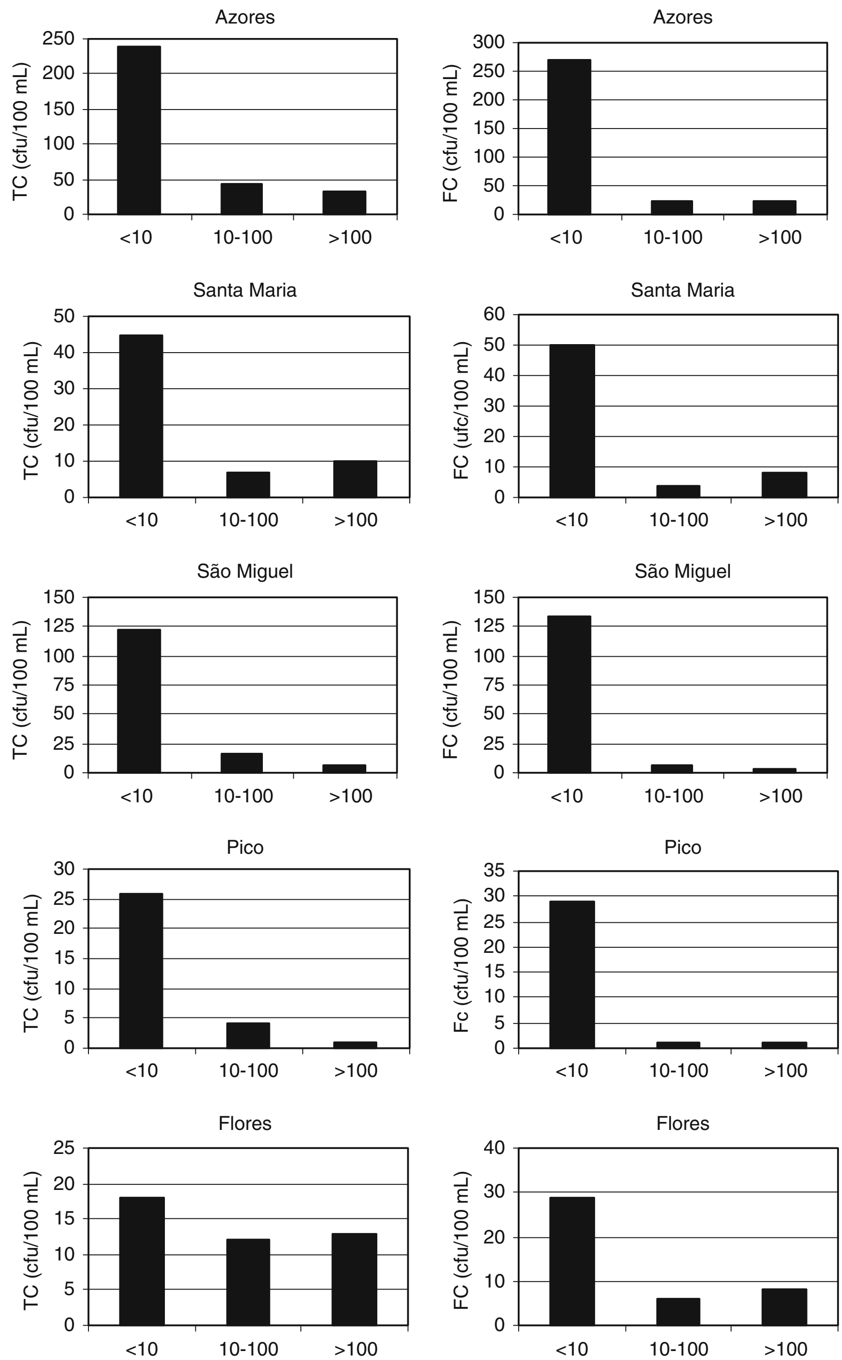

Fig. 10 Results of microbial indicators analysis represented by histograms for all data set and for islands where the number of determinations is higher

samples suggest a common enrichment on both species, which can be explained as been derived from an excess of nutrients on soil due to fertilizers overuse (Fig. 9). Most recent data on fertilizers application in the Azores shows that N and P elemental fertilizers corresponds, respectively to 0.13 and 0.019 kg/m^2 of the utilized agricultural area (1,028 km^2 in 2007), which in the first case is about 4 times higher than application in Portugal mainland (DROTRH/INAG 2001). The application of composed N–P and N–K–P fertilizers corresponds to 0.035 and 0.071 kg/m^2, respectively.

The PWQS set a maximum content of 50 mg/L for NO_3, which is exceeded only in Santa Maria (1.4% of the determinations in this island) and at São Miguel island (4.7% of the observations made in this island; 86% of the exceeding values been observed in a single drilled well not been use for public water supply). Following the WFD, the EU Groundwater Directive defined also 50 mg NO_3/L as a groundwater quality standard for chemical assessment status of water bodies. The PWQS permissible guide value (25 mg/L) is exceeded also in Graciosa (25%) and São Jorge (8.3%) islands.

PWQS defined a permissible value of 0.4 mg P_2O_5/L for phosphates in groundwater and considering the results gathered by the operation of the monitoring network been developed in the Azores 9% of the determinations exceed this guide value. The higher number of exceeding values occurs at Pico island (56% of the values determined in this island) and Corvo (33%), but on these islands the number of determinations were lower (respectively 16 and 3 analyses). In islands where the number of analyses his higher, depending on the beginning of samples collection, like São Miguel (72 analyses) and Santa Maria (36) values higher than the permissible guideline corresponds respectively to 12 and 0%.

Microbiological indicators

Results for total and faecal coliforms are represented according three classes for all data set and for islands with higher number of determinations (Fig. 10). This plot shows an high number of samples with total and faecal coliforms higher than 10 cfu/100 mL, especially in Flores island where a relative higher number of counts occurred.

From data on Table 2, that represents a synthesis of the results of microbial analyses, is possible to show at Graciosa and São Jorge counts are always positive (noted by <10 cfu/100 mL). Instead at the other islands zero counts range from 16 to 58% for total coliforms and from 27 to 58% for faecal coliforms, been the minimum values from Flores and São Miguel, respectively. Pico island depict the higher rate of zero counts for those microbial indicators (58%). Results for faecal streptococcus are lower in Pico island, instead the higher counts are from São Jorge, Flores and Corvo island.

Microbial contamination of groundwater can be associated to a diffuse source from grazed pastured lands, as described by Celico et al. (2004). It can be also derived from the absence of waste water drainage and treatment systems. In the Azores the territory is insufficiently covered by adequate sewage systems, which despite the improvement observed in the last decade is still insufficient, as only 46% of the population is actually covered by a waste water drainage system.

The pattern of variation of total and faecal coliforms over time shows a discontinuous distribution (Fig. 11). This heterogeneity can be derived from soil washing in response to rain episodes, according to a mechanisms similar to the one proposed by Naclerio et al. (2008) to explain a similar pattern.

Table 2 Results from microbial analyses (minimum and maximum values)

Island	TC (cfu/100 mL)	FC (cfu/100 mL)	FS (cfu/100 mL)
Santa Maria			
Min.	0	0	0
Max.	>2,000	740	53
São Miguel			
Min.	0	0	0
Max.	>2,000	740	10
Graciosa			
Min.	<10	<10	<10
Max.	510	100	60
São Jorge			
Min.	<10	<10	<10
Max.	11,000	2,500	270
Pico			
Min.	0	0	0
Max.	>1,000	390	6
Faial			
Min.	0	0	0
Max.	130	60	60
Flores			
Min.	0	0	0
Max.	>10,000	5,200	210
Corvo			
Min.	0	0	0
Max.	11,000	5,200	270

TC Total coliforms, *FC* faecal coliforms, *FS* faecal streptococcus

Conclusions

The WFD is associated to a rather demanding implementation strategy, been groundwater monitoring one of the main challenges. When WFD came to force, the Azores government launch the preparation of the Azores Water Plan (AWP), following the framework provided by the first, which came to force in year 2003. An example of the interrelationship of both documents is the stress given to the need for monitoring and evaluation of groundwater body status.

Despite financial and operational constrains, associated to the fragmentation of the territory in nine islands, chemical monitoring of groundwater was initiated in year 2003 and progressively extended to all islands. Besides the determination of chemical parameters microbial indicators were also analysed in all the 72 springs and 32 wells that make the network.

Major-ion composition reveal a sharp difference between springs and wells, that can be attributed to their

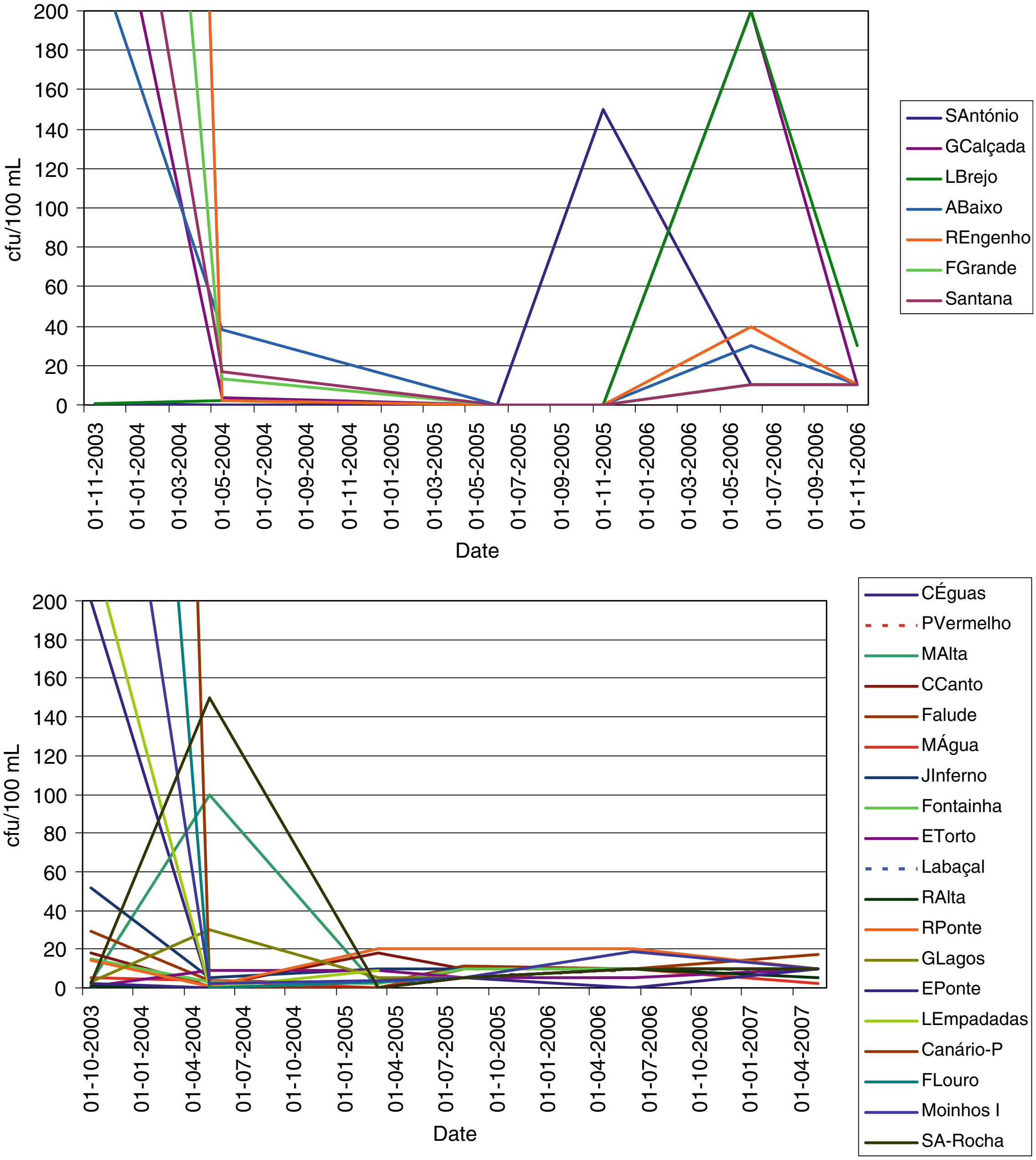

Fig. 11 Time-series for total and faecal coliform counts in springs from Santa Maria (*top*) and São Miguel (*bottom*)

respective hydrogeologic framework, as springs discharge mainly from perched-water bodies, therefore been influenced by silicate weathering, an atmospheric source associated to seawater spray and aerosols and biogeochemical processes in soils. In opposition wells are in the basal groundwater bodies, and water composition is chemically influenced by seawater intrusion. Especially in wells salinization present a negative impact on the groundwater quality, and EU and Portuguese water quality regulations are exceeded in 8% of the analyses made.

Groundwater pollution due to agricultural activities is shown by NO_3 and PO_4 content in waters, resulting in failure to comply regarding to EU and national water quality regulations in certain points. Fertilizers overuse as well as animal wastes leaching in grazed pasture lands explains these abnormal values. Despite the discontinuous distribution over time of total and faecal coliform microbial contamination of groundwater can be also due to a diffuse source associated to grazed pastured lands, Nevertheless, an unsatisfactory coverage of the territory by sewage systems may also resulting in some cases in failure to comply regarding EU and Portuguese water quality regulations.

Heavy metals and metalloids, as well as hydrocarbons and pesticides, are in compliance with standard values and generally under the detection limits, the later suggesting a small use of pesticides in agriculture. The low industrialization in the Azores contributes to the very low content of other pollutants been analyzed, as shown by the gross value added to regional product by industrial activities, including energy generation, which is equal to 10.3% (2007), compared to contribution from agriculture (11.3%).

Despite priority given to chemical status, a new challenge is now foreseen in the Azores, as the quantitative monitoring of groundwater bodies should be implemented in a second phase in order to fully comply to EU WFD and Groundwater Directive.

Acknowledgments The authors wish to acknowledge the financial support from the EU INTERREG IIIB program to the AQUAMAC I and AQUAMAC II projects.

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