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ORIGINAL ARTICLE

Influence of different land uses on groundwater quality in southern Portugal

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Abstract In Alentejo region, southern Portugal, differences in groundwater samples from six groundwater bodies covered with different land uses were analysed based on the monitoring plan of the Alqueva multi-purpose project, created in the sequence of the construction of the Alqueva Dam on the Guadiana River, in South Portugal. For most of the groundwater bodies there is a statistical significant difference between magnesium, sulphate, chloride, and phosphate. All of these ions are strongly correlated with land use management. Groundwater, where land is covered by olive groves, has high levels of electric conductivity, calcium, potassium, sulphate, and phosphate. Dry land crops are correlated with calcium, magnesium, chloride and consequently, electric conductivity, phosphates and sulphate. Vineyards are strongly correlated with high sulphate and phosphate levels. This study clearly shows that different land uses within a certain groundwater body influence the water quality in a different way. Therefore, an appropriate soil management should be adjusted to each situation, taking into account the aquifer matrix and the overlying soil.

Keywords Groundwater · Land use · Groundwater quality

Introduction

Groundwater is an important natural resource and it represents a crucial component for the socio-economic development of a country. Natural processes, such as original quality of infiltrating waters, water-soil-rock interaction, lithology, hydrogeological conditions, tidal fluctuations, seawater intrusion, and anthropogenic activities, including agriculture, industry and urban development, are essential to determine groundwater chemistry evolution (Pacheco and Van der Weijden 1996, 2002; Pacheco et al. 1999; Adams et al. 2001; Rademacher et al. 2001; Guo and Wang 2004; Van der Weijden and Pacheco 2006; Aris et al. 2007; Lin et al. 2012). Natural groundwater quality is highly defined by the interaction of its physical and chemical components with the aquifer geologic context, since the contact time between water and rock is essential for its final natural quality (Duan et al. 2002; Pacheco and Van der Weijden 2012a, b; 2014a, b). Besides the natural processes, groundwater can also be influenced by the change in land use pattern (Basnyat et al. 1999; Roth et al. 1996, Stigter et al. 2006). This is particularly evident in areas with land use conflicts (Valle Junior et al. 2014). In sensitive hydrogeological settings, the effects of human activity can be determinant for the final groundwater quality and can even influence the natural geochemical processes (Pacheco and Szocs 2006; Pacheco et al. 2013). Chronic groundwater problems can be caused by widespread long-lasting and damaging inputs of pollutants due to unsuitable land use and poor land management (Lerner and Harris 2009). Depending on the type of aquifer, on its hydraulic parameters, on the length and characteristics of the

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flow path and on the pollutant characteristics (e.g. mass, volume, viscosity, miscibility capacity), the movement from the point of infiltration at the land surface to the point of discharge can be measured in hours, days, months, years, decades or even centuries (Lerner and Harris 2009). Agriculture practices can be a cause of diffuse pollution, which extends across the landscape and infiltrates to the groundwater through the whole outcrops of the respective aquifer (Lerner and Harris 2009). The uncontrolled use of pesticides and fertilizers, used to increase the agriculture production, has been reported to have a direct and negative impact on groundwater quality (Carpenter et al. 1998; Griffith 2002; Kolpin 1997; Matson 1997). Therefore, control and evaluation of groundwater quality is decisive to ensure its adequate use (Vijith and Satheesh 2007).

Climate changes will possibly reduce groundwater resources and worsen its quality in many regions before any land use and land management changes are being considered. Except for the littoral west, which is influenced by the Atlantic climate, the climatic conditions in southern Portugal are Mediterranean type. The precipitation occurs mainly during winter, when the temperatures are low, and very low levels of precipitation occur in summer, when the temperatures are high. Climate change projections for the Mediterranean region predict an increase in temperature, a decrease in precipitation and an increase on the occurrence of extreme events, with deep impacts on stream flows, water table levels and riverine ecosystems (Santos et al. 2014, 2015). On the other hand, the Mediterranean region faces an increasing water demand for agriculture and tourism (Treidel et al. 2012).

The Alqueva multi-purpose project (EFMA, in Portuguese) is located in Alentejo, a region with an area of approximately 30,000 km^2 (nearly a third of continental Portugal). The EFMA was conceived in 1957 as part of the Alentejo Irrigation Plan, but it was only implemented in 2002, after the construction of the Alqueva dam on Guadiana River, which created a lake with a length of 83 km, a surface of 250 km^2 and a total water volume of 4150 hm^3. It was created to hold a strategic position in the use of resources and to allow mainly the exploitation of existing agriculture potential in the region, aiming to achieve the following objectives: to establish a strategic water reserve to respond to current and future needs of the region; to ensure a regular water supply to the populations, industries and agriculture; to strengthen the capacity of existing reservoirs distributed throughout the territory; to provide a progressive change of the specialisation of agriculture in the south of the country, namely changing rain feed crops to irrigated crops, and also by changing the irrigation processes, where the wells that were erstwhile used for irrigation would be substituted by the water provided by this new artificial lake. Thus, the so-called cyclic recycling practices, which consist on the reuse of groundwater, is reduced. Finally, this project also intends to slow the desertification processes, to revert the depopulation of the region, to contribute to control the effects of climate change, creating at the same time potential for tourism compatible with environmental preservation and the expansion and enhancement of economic activities (in http://www.alqueva.com.pt/en/).

As part of that project, a monitoring plan to classify groundwater quality was implemented. The main purpose of this study was to perform a comparison between different land uses and to identify the impact of those surface occupations on groundwater quality for different groundwater bodies across the Alentejo region.

Study area, geology and hydrogeology of the region

The study area is located in southern Portugal (Alentejo region) and involves different groundwater bodies (Fig. 1) covered by different land uses, covering an area of 1200 km^2 of irrigation land. The climate in Alentejo region is Mediterranean type with very hot and dry summers with a frequent occurrence of droughts, sometimes in cycles of two to three consecutive years, as well as low levels of precipitation in summer. The maximum monthly average temperature is around 34 °C (in July) and the minimum is between 5 and 10 °C (in January) (SNIRH 2012). Among other characteristic of the Mediterranean climate is the water scarcity, where the majority of the great river's tributaries are temporary (Rosado and Morais 2010). During the dry season, these systems are characterised by the interruption of the superficial flow or total loss of water, while the wet season is characterized by the occurrence of flash floods (Gasith and Resh 1999). Even so, the flow continues underground on the majority of these hydraulic systems. During summer, the annual precipitation is about 4 to 5 % of the total and the rainy season occurs during late autumn, winter and early springtime. The mean annual precipitation in Alentejo region ranges from 450 to 1000 mm and it is irregularly distributed throughout the year and among different years. Therefore, the agriculture requires intensive watering due to high evapotranspiration during the productive cycle. The dry and wet cycles have a major role in the structure and functioning of Mediterranean ecosystems. In the south part of the country, the disrupting of the superficial river runoff during the hottest months interferes in the variation of water levels in reservoirs, usually followed by a decrease in water quality. On the other hand, flash flood events increase the nutrient and organic matter loads that reach downstream reservoirs (Silva et al. 2011).

The study area is within the geologically complex Ossa-Morena Zone (OMZ), a part of the Iberian Peninsula hard rocks known as the Old Massif. The OMZ is formed by Palaeozoic metamorphic and igneous rocks. The

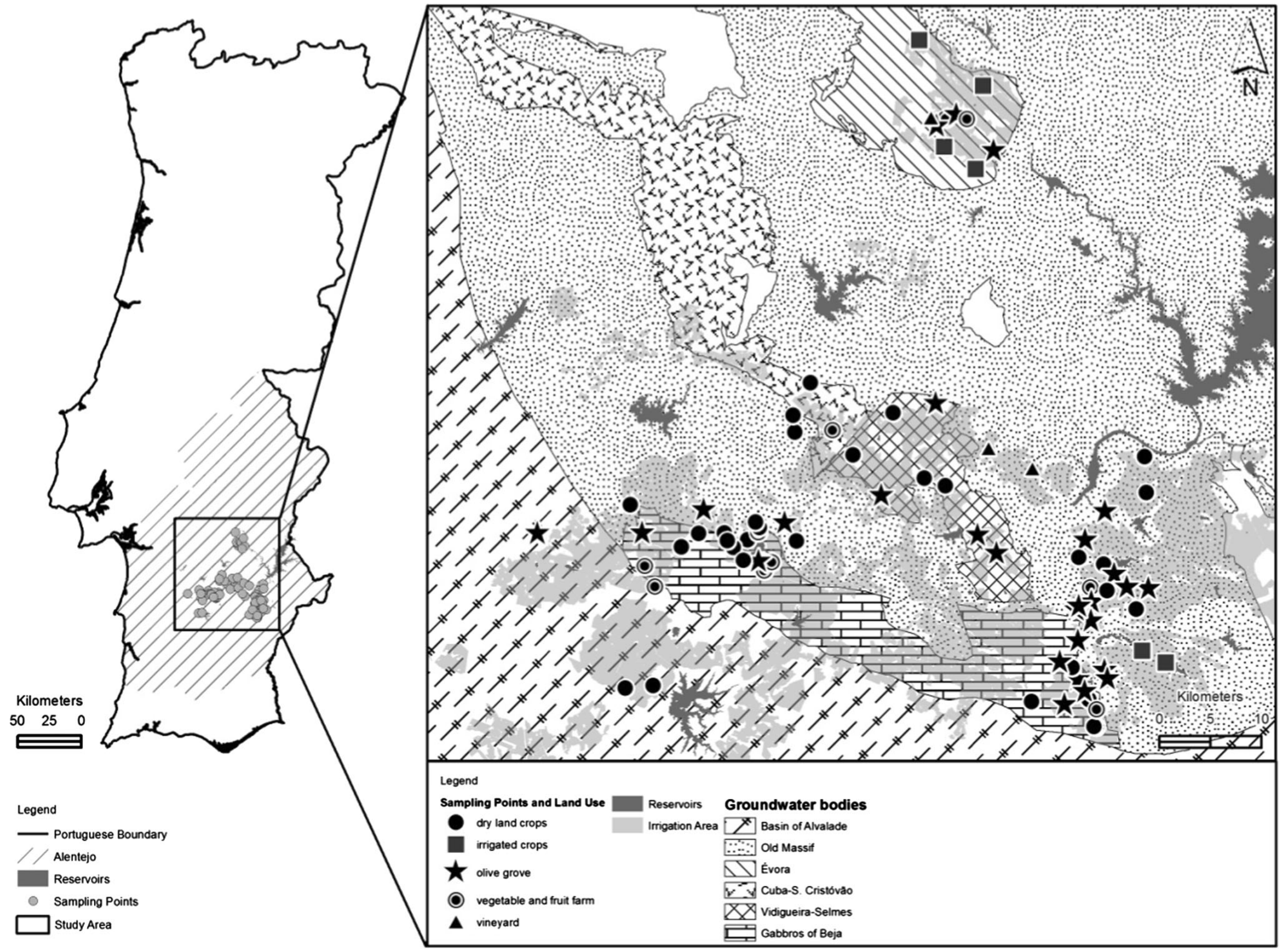

Fig. 1 Map of the study area in Portugal showing the location of the groundwater bodies and the sampling points with the corresponded type of land use

metamorphic rocks are represented mainly by schists, shales, greywackes, quartztites, gneisses, charnockites, amphibolites, metamorphised volcanic rocks, and metamorphic limestones, in a great complexity, affected in some places by strong structural features, making difficult the geological interpretation of the area. The lithology of the igneous rocks varies from granites to granodiorites, quartz-diorites, tonalitic rocks, diorites, gabbros, andesites, etc. (Chambel et al. 2007). Both the water volume and the natural water quality in the aquifers depend on the mineral composition of the rocks and on the fractured pattern and are also directly associated with the dimension of the weathering layers in the area: the most basic rocks (e.g. gabbros) have generally the most deep weathered layers (Chambel et al. 2007). On the western border of the Palaeozoic massif, the study also considered a sedimentary basin (Basin of Alvalade) deposited in Tertiary times over the metamorphic and igneous rocks of the Old Massif.

The study involved six groundwater bodies, four of them being defined as aquifers in hard rocks (Évora, Cuba-S. Cristóvão, Vidigueira-Selmes and the Gabbros of Beja aquifers), one defined as a low productivity hydrogeological hard rock sector (Old massif) and one (the Basin of Alvalade) a sedimentary basin deposited over the western border of the Palaeozoic massif. This last one, involving a sedimentary aquifer is here considered in its broader geologic sense, once the border considered in this study involves areas where groundwater is sometimes scarce and has normally natural chemical problems for its use (brackish water) and also areas of more productivity and better quality. Table 1 shows the more important lithologic types of these six groundwater bodies.

Table 2 shows the main hydrochemical differences between the aquifers and hydrogeologic sectors defined in Table 1. The main difference is between the hard rock aquifers and the hydrogeological sector (Old Massif) by one side and the Basin of Alvalade aquifer by other side. As can be seen in Table 2, the average of Electric Conductivity (EC) of groundwater in the Basin of Alvalade is more than three times the average of any other of the

Table 1 Lithologic types of the six groundwater bodies identified in the area of study (Almeida et al. 2000; Chambel et al. 2006, 2007)

Groundwater bodies	Lithologic types
Old Massif sector	Mainly schists and greywackes, and different kinds of igneous rocks, granites, granodiorites, quartz-diorites, tonalites, diorites, andesites, some gabbros, but also volcanic or porphyritic rocks
Évora aquifer	Gneisses, migmatites, granodiorites and quartz-diorites
Cuba-S.Cristóvão aquifer	Gabbrodiorites, granitic ortogneisses, a metapelitic-psamitic sequence, leptinites, black quartzites, metabasites and ortogneisses
Vidigueira-Selmes aquifer	Basic volcanites, granodiorites, gabbrodiorites, hornfels
Gabbros of Beja aquifer	Gabbros, diorites, serpentinites, meta-trondhejmites, meta-basalts, flasergabbros, amphibolites, piroxenites, dunites and peridotites
Basin of Alvalade aquifer	Conglomerates, clay, marls, sandy limestones, clay sandstones, coarse gravel

Not all of the described lithologic types for each of the groundwater bodies are represented in the area of study

Table 2 Main physical–chemical characteristics of the five aquifer systems and less productive sector (Old Massif Sector) identified in the study area

Groundwater bodies	*N*	pH (pH units)	EC (µS/cm)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	NO_3 (mg/L)
Old Massif sector	688	7.27	766	55	37	53	2.0	103	244	34	40
Évora aquifer	48	7.47	964	68	44	72	4.2	98	292	53	79
Cuba-S. Cristóvão aquifer	35	7.39	782	68	36	68	3.0	90	260	49	43
Vidigueira-Selmes aquifer	23	7.60	813	65	45	58	1.4	79	266	48	39
Gabbros of Beja aquifer	71	7.54	825	68	43	41	0.7	50	293	63	61
Basin of Alvalade aquifer	13	7.56	3171	104	116	273	7.3	824	387	80	32

Original data from ERHSA (2001)

aquifers, and this reflects mainly the sodium-chloride content of the waters of this aquifer, which are, in the border of the Basin, sometimes highly saline.

In the Piper diagram of Fig. 2, and using only the average of all the water samples collected in each one of the systems in a previous study (ERHSA 2001), it's clear that the Basin of Alvalade is completely different from the other aquifers and hydrogeological sectors, showing mainly sodium-chloride waters, in contrast with the other systems, where bicarbonates are the main anions and where the cations are present in much more similar percentages.

Even so, it's possible to see that also the Gabbros of Beja have a slightly different average composition from the other aquifer systems, with higher bicarbonate and slightly higher calcium-magnesium content. This is due to the more basic rocks of this system, which also reflects in a deeper weathered layer (30–40 m), creating in the area some of the best agriculture soils in Portugal.

Materials and methods

Land use, sample collection and laboratory analysis

Seventy-nine wells distributed in a part of the irrigation area of EFMA Project were selected for this study during the monitoring program, according to the location defined in Fig. 1. During the monitoring program, an inventory of the land use around each sampling point was organized. Five major types of land uses were identified: irrigated crops, dry land crops (rain feed crops), vegetable and fruit farms, olive groves and vineyards.

The sampling campaign was performed between March 2010 and July 2013, with 2 to 3 collections per year for each well during the dry and wet seasons. The sample collection was performed according to the ISO-5667 for Water Quality Sampling. Most of the groundwater samples were collected from open wells, bore holes and hand pumped at various depths. The water collection was performed using a 3 L Van d'Orn bottle (Wild Co, Australia), to about one meter below the groundwater level, transferred to 1L polyethylene bottles and stored in portable refrigerators until they reached the laboratory. Water stored in the wells was not abstracted before taken the sample, except for the drilled wells, where this can have happened in some of them, depending on their storage capacity, and when water was abstracted using water pumps installed in the wells.

Twelve physical–chemical variables were chosen as more relevant for groundwater quality assessment: pH, electrical conductivity (EC), ammoniacal nitrogen (AN), total hardness ($CaCO_3$), cations (Na^+, K^+, Ca^{2+} and

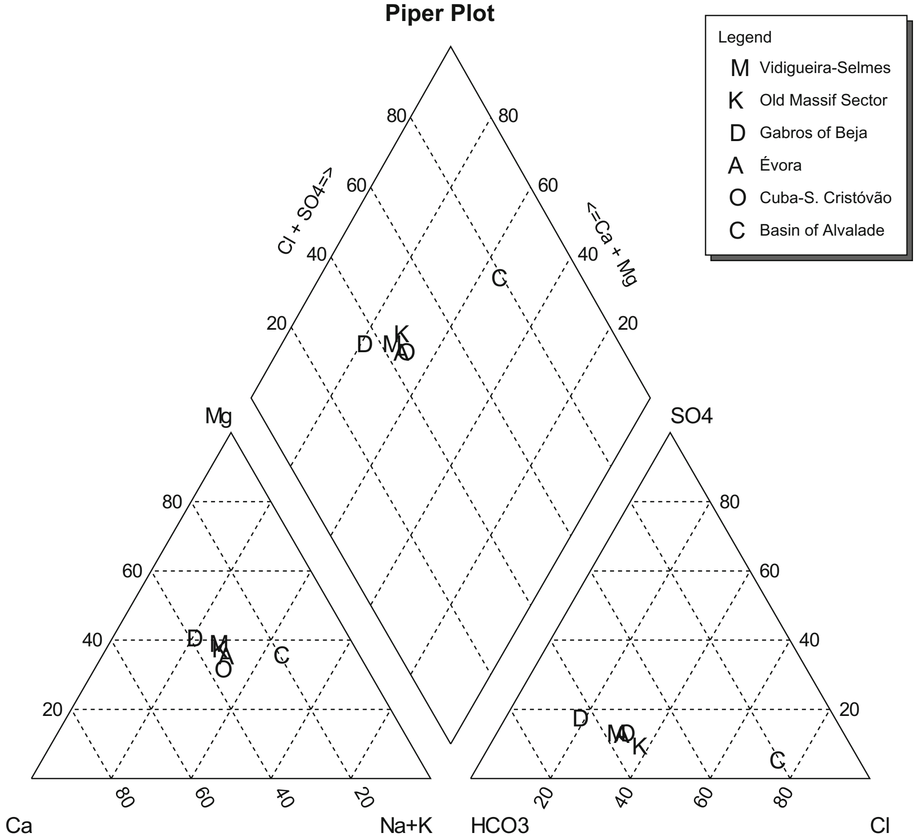

Fig. 2 Piper diagram of the different aquifers and less productive hydrogeological sector (Old Massif). Original data from ERHSA (2001)

Mg^{2+}) and anions (NO_3^-, SO_4^{2-}, PO_4^{3-} and Cl^-). In situ physical–chemical measurements (water temperature, pH and EC), were done using the in situ probe Troll 9500 Profiler XP (In-Situ Europe, UK). For major ions, the samples were acidified using 1 % HNO_3 to stabilize trace metals. The laboratory methods used to determine each variable and the respective reporting limits are summarized in Table 3.

Data and statistical analysis

To analyse differences between groups and because the data are not normally distributed, the non-parametric Kruskal–Wallis test was used. The Kruskal–Wallis test is the non-parametric analogue of a one-way analysis of variance (one way ANOVA), which does not make suppositions about normality. It assumes that populations have the same shape of distribution for the observations in each group. However, to be performed, the observations have to be ranked, just as most non-parametric tests. Therefore, the null hypothesis for the Kruskal–Wallis test involves that the samples are from identical populations (Hecke 2012).

The purpose of this study was to evaluate if the land use influenced groundwater quality. Therefore, the following null hypothesis and questions were established:

1. Concentration of individual chemical variables does not differ between groundwater bodies.
2. Concentration of individual chemical variables does not differ between land uses within the respective groundwater body.
3. Concentration of individual chemical variables does not differ between wet and dry season for land uses within the respective groundwater body.
4. Concentration of individual chemical variables related to anthropogenic activities does not differ between hydrological years for land uses within the respective groundwater body.

To further evaluate progression in groundwater quality before and after the EFMA project, the limits defined by the Decree Law 306/2007 from August 27th for water supply use, were used to detect how many cases were in infringement (Table 3). These data were then compared with data provided by the national water resources information system (SNIRH, in Portuguese) and previously published results (Chambel et al. 1999, 2007; Fialho et al. 1998).

A significance of 0.05, followed by a Bonferroni correction as post hoc test, was used to identify differences between groundwater bodies, land uses and annual and seasonal changes. The results are represented in tables and box-and-whiskers graphs.

Table 3 Methods used to determine the physical–chemical variables

Variable	Units	Limits[a]		Method
		MRV	MAV	
Temperature	°C	12	25	Thermometric analysis
pH	pH units	6.5–8.5	9.5	Electrometric analysis
Electrical conductivity	µS/cm	400	1000	Electrometric analysis
Ammoniacal nitrogen	mg/L NH_4^+	0.05	0.5	Indophenol blue method
Calcium	mg/L Ca^{2+}	100	–	Volumetric analysis
Chlorides	mg/L Cl^-	25	250	Volumetric analysis
Total hardness	mg/L $CaCO_3$	–	500	Volumetric analysis
Phosphates	mg/L PO_4^{3-}	0.4	–	Molecular absorption spectrophotometry
Magnesium	mg/L Mg^{2+}	30	50	Atomic absorption spectroscopy
Potassium	mg/L K^+	10	12	Atomic absorption spectroscopy
Sodium	mg/L Na^+	20	150	Atomic absorption spectroscopy
Nitrate	mg/L NO_3^-	25	50	Molecular absorption spectrophotometry
Sulphate	mg/L SO_4^-	25	250	Molecular absorption spectrophotometry

MRV maximum recommended value, *MAV* maximum admissible value

[a] Limits according Decree Law 306/2007, August 27th

Results and discussion

From a natural point of view, groundwater quality reflects basically the water–rock interaction inside the aquifer. Even so, the natural groundwater quality also reflects the contribution of the quality of original infiltrating water and the interaction between water and soil in the unsaturated zone.

The chemical compounds also change overtime. Normally they tend to increase with the water age inside the groundwater body (Morgenstern and Daughney 2012). The pH values increase overtime due to ongoing hydrochemical reactions (Morgenstern and Daughney 2012). Therefore, under the dominance of carbonate dissolution or hydrolysis of silicates and providing that no significant secondary precipitation occurs, the older the water is inside the groundwater body, the more alkaline it becomes.

Apart from the natural groundwater hydrochemistry, mainly dependent on the equilibrium between water and rock, there is the referred influence of anthropogenic activities.

The descriptive statistics for the physical–chemical parameters determined in the groundwater samples are summarized in Table 4. For each groundwater body, all the parameters exhibit a high distribution, suggesting a spatial variation, as indicated by the high standard deviation values. These differences can be explained by the different land covers within the same groundwater body, which might interfere with the groundwater quality, but also by geologic or structural differences inside the aquifer or groundwater body.

Concentration of individual chemicals and groundwater bodies

To test if the individual chemical concentrations were different for each groundwater body, the Kruskal–Wallis test was performed without discriminating land covers within each groundwater body. The test results for question 1 (see "Data and statistical analysis" section) rejected the null hypothesis (Table 5). Some chemicals occur naturally in groundwater but may be different from groundwater body to groundwater body due to the respective geology and weathering, and may occur at higher concentrations under certain land use. Interestingly, there were three parameters that were not different among the groundwater bodies, such as the ammoniacal nitrogen, phosphate and nitrate. Remarkably, these are some of the main variables related to land use management, mainly concerning fertilizers application.

For example, a comparison between two of the groundwater bodies, the Old Massif sector and the Basin of Alvalade aquifer, shows a difference of 0.50 in pH units (Table 4, Old Massif sector, mean = 7.58; Basin of Alvalade aquifer, mean = 7.05). This difference is easily justified by the mineralogical composition of each groundwater body, the Old Massif sector composed of shales, schists and other metamorphic or igneous rocks, while the Basin of Alvalade aquifer is a Tertiary sedimentary aquifer composed mainly by sandstone, conglomerate and gravel in the main productive units, formed by minerals much less sensitive to weathering than the ones of the other unities, like quartz. The low level of potassium in groundwater systems is due to its high capacity of cation exchange with the clay

Table 4 Descriptive statistics for the different groundwater bodies and the different land uses

Groundwater bodies and land uses		*N*	Variables and units					
			pH	Electric conductivity	Ammoniacal nitrogen	Calcium	Chloride	Total hardness
			pH units	µS/cm	mg/L NH_4^+	mg/L Ca^{2+}	mg/L Cl^-	mg/L $CaCO_3$
Groundwater body								
Old massif sector	Mean ± SD	254	7.58 ± 0.35	1042.1 ± *671.9*	0.13 ± 0.22	99.3 ± 34.7	133.7 ± 218.6	430.6 ± 157.3
	min–max		6.91–9.10	174.7–5410.0	0.05–2.76	12.0–231.0	14.8–1900	156.0–1357.0
Évora aquifer	Mean ± SD	109	7.55 ± 0.40	803.9 ± 282.1	0.12 ± 0.16	67.8 ± 23.1	71.5 ± 56.5	320.3 ± 85.2
	min–max		6.83–8.90	237.7–1778.0	0.05–0.70	31.6–137.0	6.0–324.0	181.0–562.0
Cuba-S. Cristóvão aquifer	Mean ± SD	22	7.54 ± 0.37	935.4 ± 353.5	0.09 ± 0.10	85.2 ± 20.6	66.5 ± 28.2	349.5 ± 89.2
	min–max		7.0–8.3	488.0–2090.0	0.05–0.47	47.0–118.0	9.0–130.0	186.0–449.0
Vidigueira-Selmes aquifer	Mean ± SD	70	7.52 ± 0.36	811.2 ± 183.0	0.16 ± 0.27	91.8 ± 27.4	103.6 ± 162.8	381.9 ± 80.1
	min–max		7.00–9.15	439.2–1416.0	0.05–1.76	5.0–130.0	29.4–1177.0	203.0–579.0
Gabbros of Beja aquifer	Mean ± SD	206	7.60 ± 0.33	808.6 ± 356.9	0.36 ± 1.70	88.4 ± 25.0	66.8 ± 79.2	383.9 ± 118.2
	min–max		6.67–8.86	252.1–2526.0	0.05–19.70	13.6–188.0	10.0–724.0	104.0–840.0
Basin of Alvalade aquifer	Mean ± SD	19	7.05 ± 0.64	500.7 ± 418.9	0.21 ± 0.30	50.8 ± 39.5	68.0 ± 56.3	311.4 ± 223.0
	min–max		6.09–8.20	72.8–1303.0	0.05–0.89	11.1–98.0	6.0–213.0	37.0–603.0
Land use								
Dry land crops	Mean ± SD	235	7.57 ± 0.33	1064.4 ± 718.7	0.34 ± 1.60	98.6 ± 35.9	131.6 ± 234.6	426.9 ± 161.0
	min–max		6.91–8.86	252.1–5410.0	0.05–19.7	12.0–231.0	9.0–1900.0	156.0–1357.0
Vegetables/fruit farm	Mean ± SD	130	7.54 ± 0.30	814.9 ± 254.4	0.12 ± 0.18	89.3 ± 27.5	61.1 ± 37.2	374.7 ± 89.8
	min–max		7.00–8.40	397.0–1807.0	0.05–1.28	26.0–158.0	11.0–237.0	181.0–586.0
Irrigated crops	Mean ± SD	43	7.63 ± 0.48	736.7 ± 156.3	0.12 ± 0.17	67.8 ± 16.8	56.1 ± 14.5	317.3 ± 56.4
	min–max		6.99–8.90	482.0–1097.0	0.05–0.66	48.0–113.0	28.6–75.0	247.0–422.0
Olive grove	Mean ± SD	242	7.55 ± 0.42	779.1 ± 299.0	0.11 ± 0.17	85.3 ± 29.6	85.2 ± 99.2	371.0 ± 136.6
	min–max		6.09–9.15	72.8–1712.0	0.05–1.58	5.0–181.0	6.0–1177.0	37.0–903.0
Vineyard	Mean ± SD	30	7.56 ± 0.40	978.5 ± 392.8	0.23 ± 0.51	75.5 ± 17.8	119.6 ± 89.6	378.9 ± 124.6
	min–max		6.83–8.30	527.9–1778.0	0.05–2.76	41.0–97.0	14.0–324.0	151.0–562.0

Groundwater bodies and land uses		Variables and units					
		Phosphates mg/L PO_4^{3-}	Magnesium mg/L Mg^{2+}	Nitrate mg/L Na^+	Sodium mg/L K^+	Potassium mg/L NO_3^-	Sulphate mg/L SO_4^-
Groundwater body							
Old massif sector	Mean ± SD	0.35 ± 0.86	39.8 ± 22.8	82.0 ± 66.2	1.97 ± 1.65	28.9 ± 30.7	50.7 ± 40.3
	min–max	0.04–5.62	10.0–211.0	16.0–439.0	0.18–8.65	0.1–142.0	5.0–254.0
Évora aquifer	Mean ± SD	0.21 ± 0.24	45.2 ± 78.9	62.0 ± 40.9	3.93 ± 2.06	38.4 ± 52.2	75.6 ± 55.6
	min–max	0.04–1.16	11.0–587.6	5.0–241.0	1.00–6.72	0.25–215.00	5.0–293.0
Cuba-S. Cristóvão aquifer	Mean ± SD	0.32 ± 0.37	31.6 ± 10.8	53.6 ± 42.9	2.22 ± 1.48	42.9 ± 54.6	61.8 ± 25.6
	min–max	0.04–1.19	10.0–40.7	9.0–126.0	1.00–61.5	1.5–190.0	35.0–116.0
Vidigueira-Selmes aquifer	Mean ± SD	0.51 ± 1.54	32.0 ± 10.7	46.8 ± 30.5	1.49 ± 1.35	29.5 ± 32.3	46.7 ± 19.7
	min–max	0.04–9.73	13.1–56.3	7.0–132.0	0.24–5.01	0.2–122.9	10.0–117.0
Gabbros of Beja aquifer	Mean ± SD	0.33 ± 0.79	33.4 ± 13.1	52.6 ± 44.1	2.98 ± 9.03	37.4 ± 43.9	54.6 ± 61.5
	min–max	0.01–6.29	10.0–89.0	7.0–261.0	0.15–63.7	0.1–276.0	5.0–595.0
Basin of Alvalade aquifer	Mean ± SD	0.14 ± 0.09	23.4 ± 20.1	47.2 ± 42.0	1.75 ± 0.67	17.5 ± 21.0	64.4 ± 85.1
	min–max	0.04–0.37	4.9–52.3	2.0–100.0	0.47–2.60	0.6–97.5	5.0–250.0
Land use							
Dry land crops	Mean ± SD	0.49 ± 1.26	40.3 ± 23.8	80.9 ± 75.8	1.84 ± 1.88	33.5 ± 39.0	56.5 ± 40.5
	min–max	0.04–9.73	13.1–211.0	7.0–439.0	0.15–8.65	0.1–202.0	5.0–254.0
Vegetables/fruit farm	Mean ± SD	0.21 ± 0.45	33.5 ± 9.5	53.9 ± 26.3	4.45 ± 11.30	42.1 ± 49.0	60.4 ± 34.2
	min–max	0.04–3.94	10.0–72.1	11.0–126.0	0.16–63.70	0.1–276.0	5.0–178.0

Table 4 continued

Groundwater bodies and land uses		Variables and units					
		Phosphates mg/L PO_4^{3-}	Magnesium mg/L Mg^{2+}	Nitrate mg/L Na^+	Sodium mg/L K^+	Potassium mg/L NO_3^-	Sulphate mg/L SO_4^-
Irrigated crops	Mean ± SD	0.14 ± 0.07	34.1 ± 7.8	52.0 ± 20.6	4.20 ± 1.86	44.4 ± 59.3	43.5 ± 21.4
	min–max	0.04–0.36	24.9–50.2	11.0–72.1	1.00–6.48	0.28–215.0	5.0–114.0
Olive grove	Mean ± SD	0.27 ± 0.51	32.5 ± 14.4	57.9 ± 39.4	1.95 ± 1.5	29.0 ± 33.6	49.1 ± 61.1
	min–max	0.01–5.69	4.9–78.5	2.0–261.0	0.28–6.70	0.2–187.0	5.0–595.0
Vineyard	Mean ± SD	0.44 ± 0.97	75.8 ± 15.0	84.8 ± 58.1	2.02 ± 1.71	29.6 ± 38.2	87.7 ± 70.9
	min–max	0.04–4.41	21.7–77.9	22.0–241.0	0.40–5.85	0.2–124.0	21.0–293.0

Table 5 Kruskal–Wallis test results for differences between individual chemical concentrations between groundwater bodies

Variables for each groundwater body	*p* values
pH	0.005
Electric conductivity	<0.0001
Ammoniacal nitrogen	**0.648**
Calcium	<0.0001
Chloride	<0.0001
Total hardness	<0.0001
Phosphates	**0.597**
Magnesium	0.035
Sodium	<0.0001
Potassium	<0.0001
Nitrate	**0.238**
Sulphate	0.017

Numbers in bold represent the values that are not statistically different

minerals in the soil or inside the aquifer. On the other hand, potassium can be part of fertilizers; therefore, it is not a reliable cation to correlate with land use. The majority of representative natural chemical compounds in groundwater (Ca^{2+}, Na^+, Mg^{2+}, HCO_3^-) derives from the weathering of the silicate or carbonate minerals in the rocks like feldspars, plagioclases, biotite, amphiboles, calcite or dolomite. Cl^- is a special ion present in the aquifers, since it is more related to sea spray (so it is frequent in groundwater near the cost), but it can also be present in the aquifers by being trapped inside the rocks when the rock formations were formed under sea water or under saline lacks. SO_4^{2-} can be linked to metal minerals in the rocks, like pyrite (FeS_2) or arsenopyrite (FeAsS), which are present in many metamorphic rocks of South Alentejo.

Concentration of individual chemicals and land use

To understand how the different land uses can influence groundwater quality, each different land uses were identified inside each groundwater body. This was done using the information of the field reports filled by the sampling technician during the monitoring plan. The non-parametric test results showed that some variables were different among land uses, rejecting, this way, the null hypothesis 2 (see "Data and statistical analysis" section, Table 6). Based on the results, some variables were different for 3 out of 6 of the groundwater bodies, such as EC, calcium, phosphates, potassium and sulphate. The EC values were different among the Old Massif sector, Évora and Basin of Alvalade aquifers, which can be explained by the different natural composition of groundwater in these different geological environments (see Table 2).

One could not see the same result for the Gabbros of Beja aquifer, although there were the same land uses. This can be justified by the high rock dissolution and high grade of fracturing associated with gabbros weathering, allowing high permeability (Duque and Almeida 1998), which naturally increases the EC levels independently of the land cover.

Calcium, besides being part of the mineralogy of many rocks, can also be applied as lime to adjust the soil pH in agriculture areas. Based on the results, there is a correlation between calcium levels and dry land crops, as it is observed for the Cuba-S. Cristóvão, Gabbros of Beja and Basin of Alvalade aquifers (Table 6). The same result was not observed for the Old Massif sector, probably due to its high variety of rocks with high natural calcium content, and also because most part of the good agriculture lands are in the previous groundwater bodies and not in the Old Massif sector.

Besides those variables that change naturally overtime, there are some that have a conservative nature; therefore, significant changes for the conservative variables within each groundwater body could be directly correlated with differences between land uses. Chloride has a conservative nature and its transport mechanism by rain and sea spray is the main natural source (Morgenstern and Daughney 2012). Even so, in some areas of South Alentejo, there are also indications of salt retained during the formation of the rocks, being it in Palaeozoic times for the metamorphic

Table 6 Results of Kruskall-Wallis test for the comparison of concentration of individual chemicals for each land use within the respective groundwater body

Groundwater body	Veg/fruit[a] olive[b] dry land[c] vineyard Old Massif sector	Veg/fruit olive irrigated[d] vineyard Évora aquifer	Veg/fruit dry land Cuba-S. Cristóvão aquifer	Olive dry land Vidigueira-Selmes aquifer	Veg/fruit olive dry land vineyard Gabbros of Beja aquifer	Olive dry land Basin of Alvalade aquifer
Land use for each groundwater body						
Variables						
pH	0.948	0.341	0.251	0.872	0.534	0.080
Electric conductivity	**6.8E−7**	**0.005**	0.088	0.228	0.278	**0.012**
Ammoniacal nitrogen	0.093	0.985	0.793	0.735	0.117	0.089
Calcium	0.472	0.742	**0.047**	0.482	**0.016**	**0.040**
Chloride	**0.020**	**8.65E−6**	0.088	0.929	0.409	0.162
Total hardness	0.711	0.824	0.144	0.305	0.176	**0.040**
Phosphates	**0.032**	**0.001**	**0.004**	0.541	0.383	0.453
Magnesium	**0.005**	0.407	0.347	0.732	0.395	**0.040**
Sodium	**0.001**	0.831	0.403	0.436	0.197	**0.040**
Potassium	**9.12E−5**	**0.029**	0.117	0.820	0.620	**0.040**
Nitrate	0.125	0.134	0.061	0.167	0.379	0.764
Sulphate	**0.005**	**0.001**	0.465	0.747	**0.049**	0.079

Numbers in bold represent the *p*-values that are statistically different

[a] Vegetables/fruit farm

[b] Olive grove

[c] Dry land crops

[d] Irrigated crops

rocks or in Terciary times for part of the sedimentary Basin of Alvalade aquifer, in this case by deposition of sea sediments (Costa et al. 2003) or salt concentrated in salt lakes during arid climate times, mainly in the border of the basin (Chambel et al. 2007).

Based on the results, along with the significant differences in the chloride levels, there are also differences in the sulphate and phosphate concentration (Table 6, Old Massif sector and Évora aquifer), indicating an agricultural source.

Sulphate levels are highly correlated with vineyards, vegetables and fruit plants, as can be seen for all the groundwater bodies covered by vineyards (Old Massif sector, Évora and Gabbros of Beja aquifers, Table 6) and vegetables/fruit farms (Old Massif sector, Évora and Cuba-S. Cristóvão aquifers, Table 6). Vegetables/fruit farms are also correlated with phosphate levels, which were different among 3 out of 6 groundwater bodies, except for the Gabbros of Beja aquifer. High levels of nitrate, sulphate, chloride and phosphorus can be related to fertilizer application such as ammonium sulphate, potassium chloride, potassium carbonate and other phosphorus compounds (Soveral Dias 1999). It is common to use those chemicals in vineyards. Vineyards play an important role transferring the total phosphorus to the water, since this element is not very mobile (Yang et al. 2009). Phosphorus is a macronutrient essential for the life of all living cells and is directly absorbed by the plants in the form of orthophosphate (PO_4^{3-}), which in turn is present in many fertilizers (Bowatte et al. 2006). Excessive use of these fertilizers may cause soil saturation, leading to an increase in phosphorus transport through runoff by soil particles or through drainage, and consequently, transferred to groundwater.

In regions where sewage systems are lacking or do not cover the entire municipality, Cl^- in groundwater may also be derived from leachates of domestic effluents (Pacheco 1998; Pacheco and Landim 2005). The incorrect management of fertilizer applications as well as domestic effluents could lead to the increase of sulphate, phosphorus and chloride levels, contaminating groundwater but, in this region, with very low concentration of population, the problem of domestic effluents can happen just in specific points and can't be considered at general level in the study area.

Magnesium ion is stable overtime (Morgenstern and Daughney 2012), therefore the significant differences observed could be directly correlated with land uses, since some fertilizers can also contain magnesium in their composition. Both in the Old Massif sector and in the Basin of Alvalade aquifer, significant differences between land uses within the groundwater bodies were detected for magnesium levels, and both of them were correlated with dry land crops (Table 6: magnesium levels, Kruskal–Wallis test, p value = 0.005; Table 4: Old Massif sector, mean = 39.8 ± 22.8; Basin of Alvalade aquifer, mean = 23.4 ± 20.1).

Differences in nitrate levels at any of the groundwater bodies were not detected (Table 6). One of the reasons could be the fact that nitrate, in spite of conservative, is not very stable and can vary for several reasons. It is also known that nitrates vary seasonally (Glavan et al. 2013).

Concentration of individual chemical variables and seasonal variations

It should not be forgotten that there is a strong interaction between groundwater and surface water. Many rivers and streams are fed by springs, which make these rivers permanent throughout the year, even when there is no rainfall. The rivers, in turn, may at some point of their journey contribute to recharge the aquifers (influent rivers). Thus, the poor quality sometimes occurs in surface waters can be transmitted to groundwater and vice versa (Ribeiro 2009). By taking into account the average of physical–chemical parameters, the differences between wet and dry seasons can be masked. Therefore, the seasonal behaviour of each component was investigated (question 3, see "Data and statistical analysis" section). It is already known that during the wet season, surface water quality is primarily controlled by inorganic (mineral) contents and this non-anthropogenic form of pollution achieves high concentration in surface tributaries. Dissolved oxygen and pH represent the high importance of the surface runoff of nitrate, phosphorus and particulate organic matter. On the other hand, during the dry season, the system is mainly controlled by dissolved oxygen, pH and temperature (Serafim et al. 2006). In this study, the null hypothesis was true for the Vidigueira-Selmes and for the Basin of Alvalade aquifers, where none of the parameters was influenced by wet and dry seasons at any type of land use (data not shown). Nevertheless, only a few variables were subject to changes with wet and dry seasons, such as pH, for vegetables/fruit farms at the Old Massif sector, and at the Gabbros of Beja aquifer for olive grove and dry land crops. The same tendency was observed for vegetables/fruit farm at the Gabbros of Beja aquifer, although this difference was not significant (Kruskal–Wallis test, $p = 0.053$). These differences could not be correlated with any specific land use. Electric conductivity was also seasonally influenced for some land uses, but once again, it could not be correlated with any land use in particular (Kruskal–Wallis test, Old Massif, olive grove, $p = 0.003$; Évora aquifer, vegetables/fruit farm and vineyards, $p = 0.030$ and $p = 0.045$, respectively). The irrigation practices generally cause an increase in salts, due to alternating evapotranspiration cycles (Stigter et al. 2006). Therefore, some of the differences between land uses could be masked and not detected.

Concentration of individual chemical variables and anthropogenic activities

In mainland Portugal the diagnosis and characterization of groundwater quality done by the Management Plan of Hydrographic Basins (PGBH 2012) clearly showed that there are concentrations of nitrates from agricultural sources in some aquifer systems, surpassing in many cases the parametric value of 50 mg/L (SNIRH 2012). The increase of nitrate concentration in groundwater is a result, in most cases, of diffuse sources related to intensive use of fertilizers in agricultural activities. The nitrogen compounds are found in soil in several states, in a dynamic equilibrium. In the presence of abundant organic matter and aerobic conditions, the processes of ammonification and nitrification cause mineralization of organic nitrogen to nitrate, which is the final and stable product of these reactions. Nitrate ion is very soluble in water and is absorbed by the soil, and it is easily leached by percolating water to the saturated zone (Ribeiro 2009). The leaching process of nitrogen occurs during wet periods of the year and after harvesting. Because nitrogen is not actively absorbed by the plants when precipitation exceeds evapotranspiration, during those periods the fertilizers and mineralized crop biomass residues are responsible by the nitrogen leaching to groundwater (Glavan and Pintar 2010; Rusjan et al. 2008).

The leaching process of nitrate, from soil to groundwater, can be significantly reduced by good management practices. Even so, it will take many decades or even centuries for most nitrate concentrations to drop significantly, even if the nitrate leaching is stopped immediately (Lerner and Harris, 2009). Therefore, during the 4 hydrological years, a control of nitrate, phosphate and ammoniacal nitrogen levels was performed, and differences along the years were calculated (question 4, "Data and statistical analysis" section).

Although a significant difference in nitrate content in all the groundwater bodies, except for the Old Massif sector and Gabbros of Beja aquifer (Kruskal–Wallis, $p < 0.0001$, for both), the maximum levels achieved at the end of the hydrological year 2012/2013 were lower in all the groundwater bodies, compared with the first hydrological year studied (Fig. 3). The reduction of nitrate levels could be explained by the fact that groundwater recycling is no longer in practice. Because of

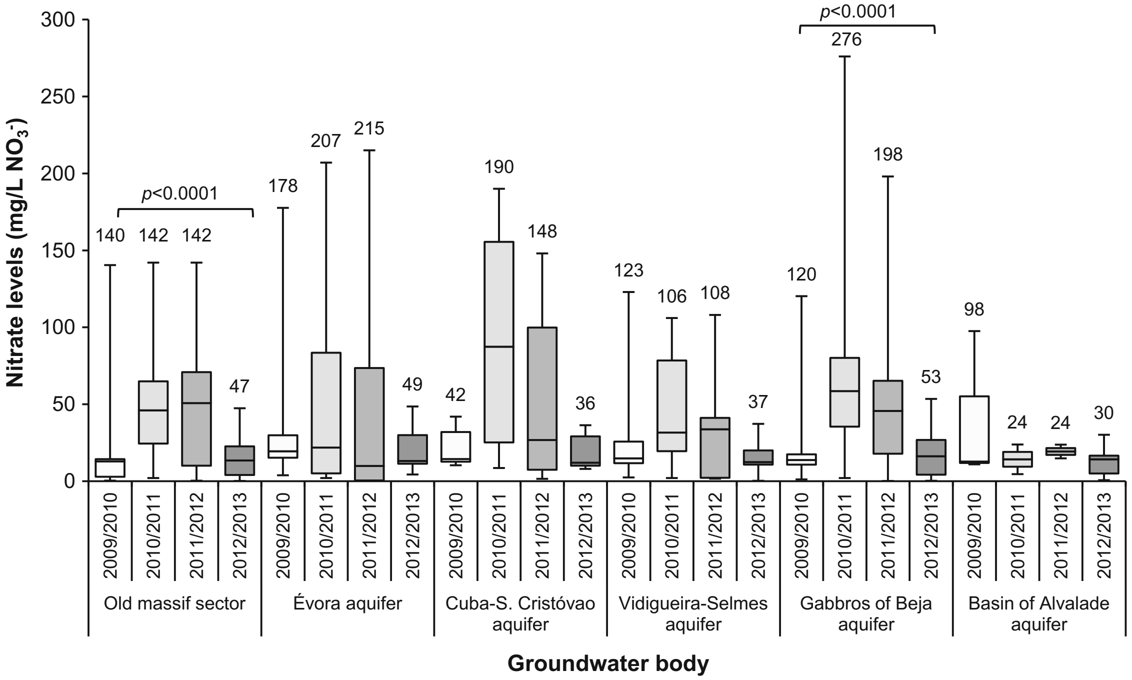

Fig. 3 Differences in nitrate content in different hydrological years for the studied groundwater bodies. *Numbers* above upper whisker represent maximum levels reached

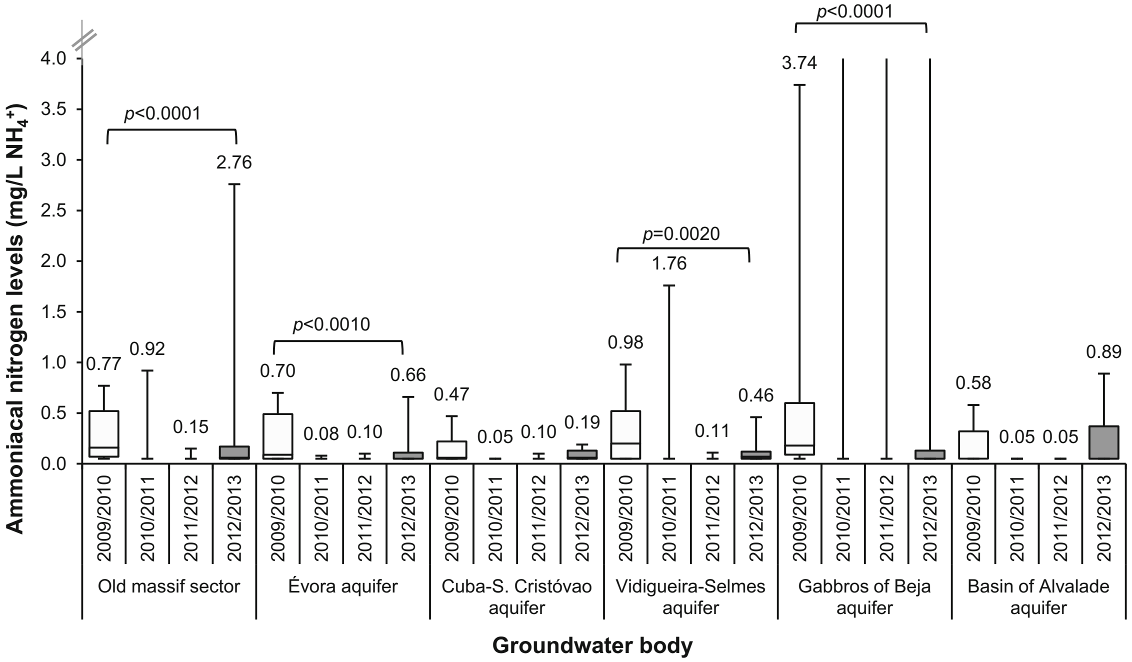

Fig. 4 Differences in ammoniacal nitrogen content in different hydrological years for the studied groundwater bodies. *Numbers* above upper whisker represent maximum levels reached

the EFMA project, groundwater that was used before for irrigation is no longer used and it was substituted for water from the artificial lake, with approximately ten times less nitrate content (average of 33.07 ± 39.98 mg/L NO_3^- in groundwater from 2009 to 2013 for all wells studied, and 3.40 ± 7.00 mg/L NO_3^- in the surface water of the dam lake from March 2003 to September 2009, $n = 237$).

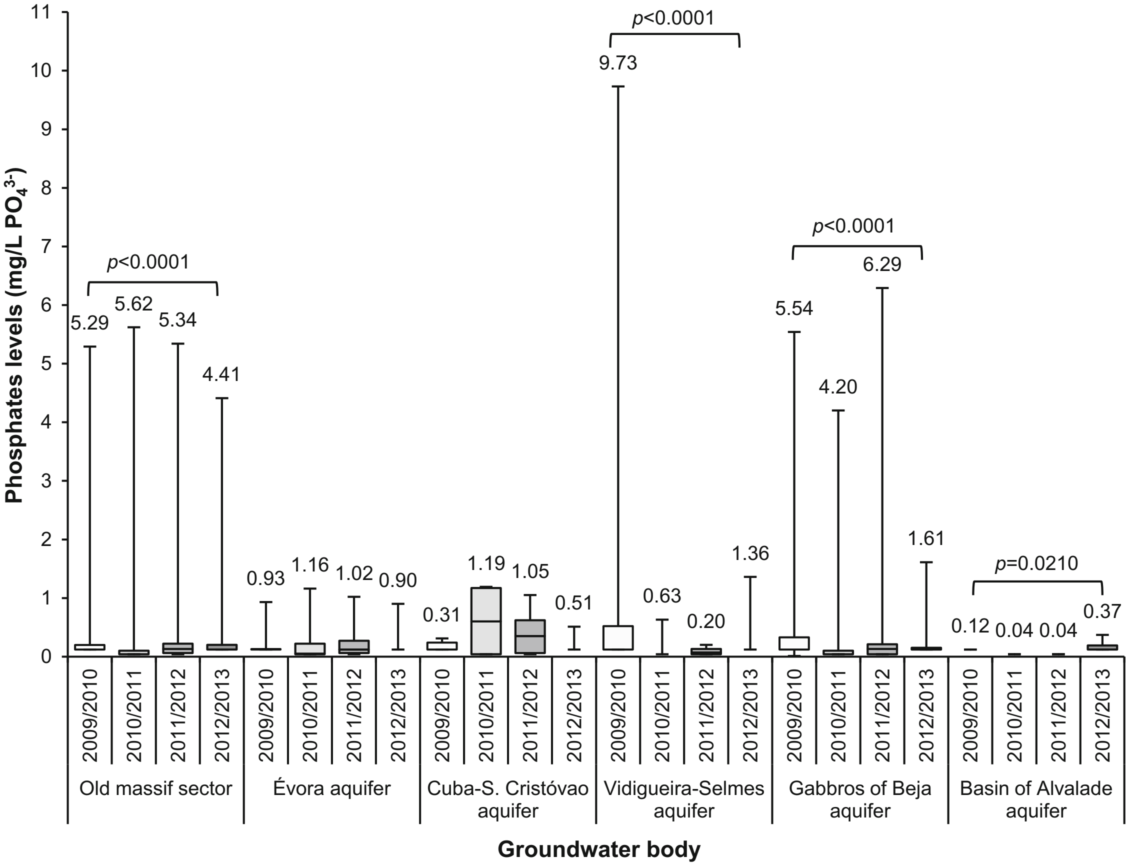

Fig. 5 Differences in phosphate content in different hydrological years for the analyzed groundwater bodies. *Numbers* above upper whisker represent maximum levels reached

Oppositely, differences along the 4 hydrological years for ammoniacal nitrogen levels were statistically different for the Old Massif sector, Évora, Vidigueira-Selmes and Gabbros of Beja aquifers (Kruskal–Wallis test, $p < 0.0001$, $p < 0.001$, $p = 0.002$, $p < 0.0001$, respectively). However, basically for all the groundwater bodies, the maximum levels at the end of the monitoring plan were higher than on the previous year (Fig. 4). Ammoniacal nitrogen is an indicator of organic contamination. Therefore, organic sources such as agricultural waste or seasonal dieback vegetation (Burkartaus and Stoner 2008) could have led to an increase of levels of ammoniacal nitrogen on its own.

During the 4 hydrological years, phosphate levels were significantly reduced in the Old Massif sector, Vidigueira-Selmes and Gabbros of Beja aquifers (Kruskal–Wallis test, $p < 0.0001$ for all, Fig. 5). Nevertheless, besides the high variability, by the end of 2012/2013 the levels were lower compared with the previous years, except for the Basin of Alvalade aquifer. The concentration of total phosphorus in groundwater is not related to the geology, due to the scarcity of this compound in igneous and metamorphic rocks, requiring other sources, including anthropogenic activities and degradation of organic matter (Menezes et al. 2014). The high value detected during the hydrological year of 2012/2013 was observed at a dry land crop field and perhaps it was a particular situation. The monitoring plan must continue to screen this situation.

Mitigation measures

According to Foster et al. (2002) the types of agricultural activity responsible for the most severe cases of diffuse contamination of groundwater are those related to large areas of monoculture. Traditional shifting cultivation, extensive grasslands and agro-ecosystems usually have a lower probability of subsurface contamination (Menezes et al. 2014). Therefore, an appropriate soil management should be adjusted to each situation, taking into account the aquifer matrix and the overlying soil. Furthermore, seasonal monitoring is of particular importance in the southern semi-arid areas of Portugal, where streams are temporary, with discharges ranging from zero to high volumes during the dry and wet seasons, respectively. Consequently, tributaries are subjected to a great variability in the hydrologic regime and experience wide variability in physical, chemical and biological parameters, affecting the reservoir's function downstream (Morais 1995; Morais et al. 2004).

With the EFMA project the use of groundwater is highly reduced in this area; so, the increase in mineralisation due to groundwater recycling is no longer in practice. Thus, a dilution of certain physical–chemical parameters is happening.

To avoid the continuous contamination of groundwater in this new area of irrigation, some planning is necessary:

- The use of the manual of good agriculture practices
- The control of the additives that the soil really needs, being it fertilizers, pH correctors or others
- The control of the excess of irrigation water, namely using software to control the water quantity during irrigation according the needs of humidity in the soil;

The last point focus technology that is more and more used in South Portugal, where water is scarce and the need to control water quantity for irrigation is also an economic goal of the more modern farmers.

Final remarks

This study clearly showed that different land uses within a certain groundwater body influence the water quality.

It is shown that, in spite of the original differences in the chemical content of natural groundwater bodies in this region, where for example chloride is highly variable between mainly hard and sedimentary rocks, the influence of fertilizers in agriculture seems to have a major role in the final content of specific ions.

In fact, in most of groundwater bodies there is a statistical significant difference between magnesium, sulphate, chloride, and phosphate. All of these ions are strongly correlated with land use management. Groundwater where land is covered by olive groves has high levels of EC, calcium, potassium, sulphate and phosphate. Dry land crops are correlated with calcium, magnesium, chloride and, consequently, EC, phosphate and sulphate, and, vineyards are strongly correlated with high sulphate and phosphate levels.

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