

Environmental issues in urban groundwater systems: a multidisciplinary study of the Paranhos and Salgueiros spring waters, Porto (NW Portugal)

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Abstract This study presents the results of a multidisciplinary approach, using hydrogeochemical, isotopic and ecotoxicological analyses, performed to assess the nature and suitability for use of Paranhos and Salgueiros spring waters (Porto city, NW Portugal). Based on the surface activities located along the course of the springs, 23 water samples were collected. All the samples were analysed for major element concentrations. The isotopic techniques employed included $\delta^2\text{H}$, $\delta^{18}\text{O}$ and ^3H . Standard acute bioassays with *Daphnia magna* were also performed. The hydrogeochemical analyses showed a nitrate and sulphate-enriched composition for these groundwaters, resulting mainly from urban drainage and sewer leakage. In the ecotoxicological analyses, no significant mortality was observed in any of the tests performed. The results obtained

in this study suggest that Porto urban groundwater could be suitable for irrigation uses.

Keywords Urban groundwater · Hydrogeology · Environmental isotopes · Ecotoxicology · NW Portugal

Introduction

Urbanisation changes drastically the hydrologic cycle of natural areas. Buildings, roads, sidewalks and parking lots make the land surface impermeable to the infiltration of precipitation, diminishing the natural recharge of the aquifer (Hirata et al. 2006). Due to the large number of anthropogenic contamination sources in cities, and the failure of the

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soil and vadose zone to attenuate them, groundwater can be degraded easily. This phenomenon is especially serious in cities located over water table aquifers, but is also present in urban areas that overlie semiconfined and confined aquifers. Most urban contamination originates from dispersed sources, such as in situ sanitation and sewer, which leads to increases in salinity, nutrient and pathogen groundwater concentrations (Zubair and Rippey 1999; Wakida and Lerner 2005). Urban aquifers are therefore vitally important, but very fragile, easily contaminated and could take a long time to be repaired and restored.

Apart from the more traditional disciplines such as structural geology and geomorphology, some interdisciplinary fields such as environmental geology, hydrogeology and engineering geology play a dominant role in urban geosciences (McCall et al. 1996). When integrated and mixed with a thorough knowledge of the regional and local geological conditions, these provide approaches more suitable to deal with issues related to human communities that make use of water and land at urban areas (Mulder et al. 2001). In addition, the increasing worldwide pressure under conditions of global anthropogenic and climatic change often requires an integrated multidisciplinary approach to address the scientific issues involving water resources. In agreement with this, environmental isotopes, such as $\delta^2\text{H}$, $\delta^{18}\text{O}$ and ^3H , should be used when assessing urban groundwater to provide information needed for the rational management of these water bodies. In fact, water in urban environments can develop isotopic “fingerprints”, which should be faced as unique tools used to (Clark and Fritz 1997; IAEA 1998, 2002): (1) identify the origin, age and dynamics of different water bodies; (2) determine the aquifers recharge; (3) evaluate mixing between surface waters and groundwater; and (4) define aquifer vulnerability to over-exploitation and pollution. Furthermore, according to a recent European Council Directive 2006/118/EC (OJEU 2006), aiming at the protection of groundwater, ecotoxicology knowledge should be taken into account for the evaluation of the chemical status of groundwater.

Although multidisciplinary and complex, the data required by current hydrogeological studies can be analysed and combined by taking advantage of databases properties, and particularly of geographic information system (GIS) databases (Gogu et al. 2001; Johnson 2009). A GIS is a powerful computer-based tool for integrating and analysing data obtained from a wide range of sources (Zaporozec 2004). In recent years, the use of GIS has grown rapidly in groundwater management and research. GIS is now widely used to create digital geographic databases, to manipulate and prepare data as input for various model parameters, and to display model output. These functions allowed primarily overlay or index

operations, but new GIS functions that are available or under development could further support the requirements of process-based approaches (Gogu et al. 2001; Jha et al. 2007).

The bedrock of Porto city is mainly granite, involving different hydrogeological compartments such as overlying sediments, weathered rock, the weathered-fissured zone, and fractured bedrock. *Paranhos* and *Salgueiros* spring waters are shallow groundwater that respond quickly to precipitation events and are particularly vulnerable to contamination. In this work, a multidisciplinary approach was applied to assess the nature and suitability for use of this groundwater. This approach combined major hydrogeochemical indicators with isotope techniques ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and ^3H) and ecotoxicological data, along with the integration of detailed geology and morphotectonics. This methodology was intended to enhance the understanding of urban groundwater systems in Porto city and can provide guidelines for the planning and management of water resources exploitation in an equitable, sustainable and ethical manner.

Regional setting

The history of Porto City dates back at least to the sixth century, since the days of Suevians, being one of the oldest cities in Europe. The conquest of the so-called *Portucale*, the previous designation for the Porto area, in 868 AD, is considered a major event of the most ancient history of Porto because this became the centre of the movement of the Christian's re-conquest of the Iberian Peninsula (de Oliveira Marques 1972). Porto City became an important metropolis since the twelfth century and nowadays is the capital of the second biggest urban region in Portugal, with an area of ca. 41 km² and a population of about 216,000 inhabitants. Porto city has been developed on granitic hill slopes of the Douro River (Fig. 1).

Porto urban area is located in a complex geotectonic domain of the Iberian Massif, on the so-called Ossa-Morena Zone and Central-Iberian Zone boundary (Ribeiro et al. 2007), alongside the Porto–Tomar–Ferreira do Alentejo major shear zone (Chaminé et al. 2003a, b; Ribeiro et al. 2007). The geomorphologic framework of this region consists of a littoral platform characterised by a quite regular planation surface dipping gently to the west, culminating around 120 m a.m.s.l., and on the east bounded by a series of hill ridges (250–300 m a.m.s.l. on the top). A regional tectonic control is the key for deeply incised river valleys, particularly Douro river valley, which interrupts the flatness of this morphological surface. The regional geotectonic setting of Porto urban area (e.g. Sharpe 1849;

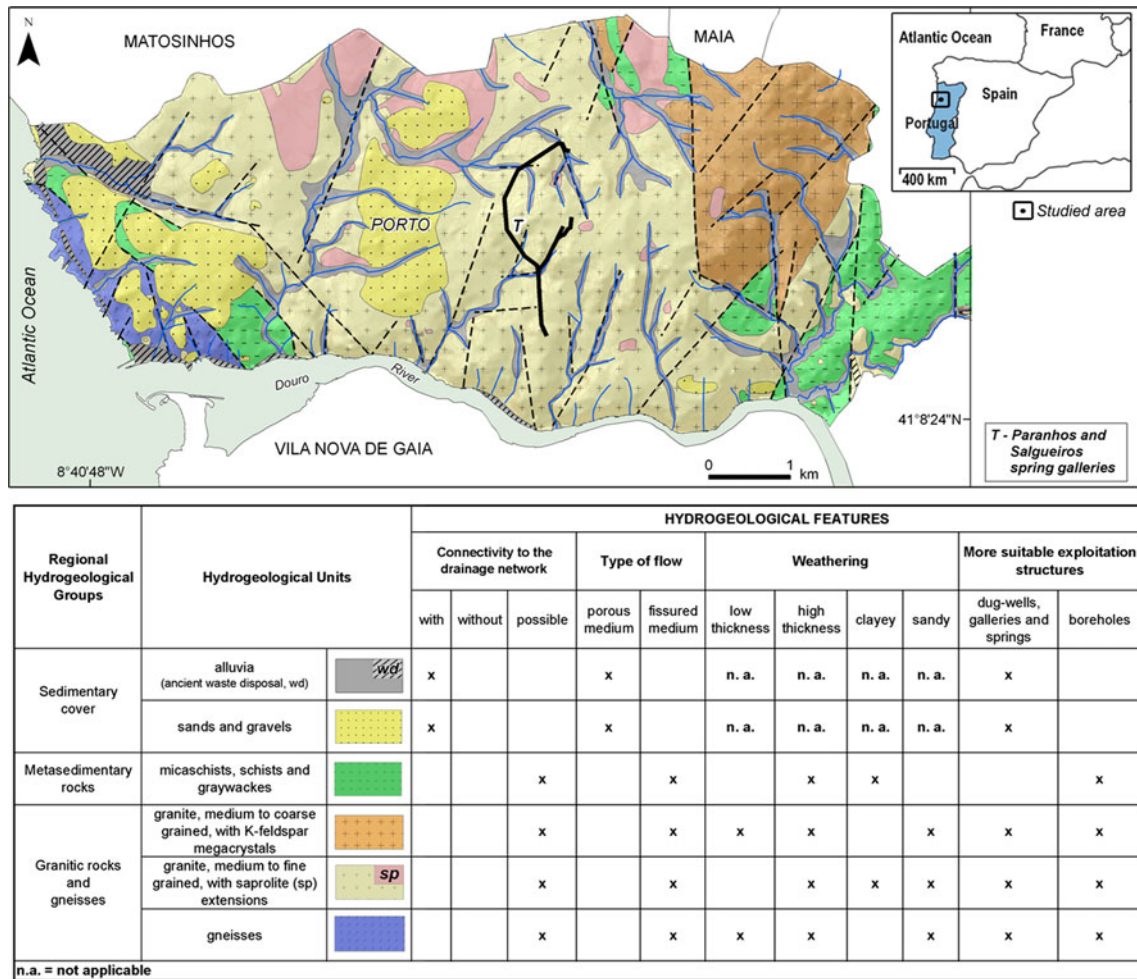


Fig. 1 Regional hydrogeological setting from Porto City (geological background revised from Carrington da Costa and Teixeira 1957; COBA 2003; Chaminé et al. 2003a). Regional hydrogeological units and related features in the Porto area (lower part of the figure)

Carrington da Costa 1958; Chaminé et al. 2003a, b; and references therein) comprises a crystalline basement complex of high-deformed and overthrust Late Proterozoic/Palaeozoic metasedimentary rocks and granites (essentially during Variscan orogeny). The bedrock is mainly composed of phyllites, micaschists and gneisses, whilst post-Miocene alluvial and Quaternary marine deposits dominate the sedimentary cover rocks. The igneous rocks include pre-orogenic and syn-orogenic Variscan suites, which occupy a large exposure of granitic rocks. The regional fracture network defines some preferential orientations: NNW-SSE and NE-SW are dominant, and more discreetly, ENE-WSW.

The regional hydrogeological units were defined applying the same lithological and structural criteria used to identify the regional geological units and correspond roughly to the main geological features (Fig. 1). Almost all aquifers of this region are in fissured hard rock and comprise a weathered material zone that may have a high

thickness. This layer seems to have an important role in the recharge of the aquifers underneath (Afonso 2003; Afonso et al. 2007a).

Methodology

This study followed a geoenvironmental approach in which a multitechnique methodology was applied with the aim of understanding and assessing the nature and suitability for human exploitation of these urban groundwater systems beneath Porto City, namely the Paranhos and Salgueiros spring galleries catchworks.

The underground area (ca. 3.2 km long and at a maximum depth of -20 m below ground level) was studied using the following tools (e.g. Struckmeier and Margat 1995; Assaad et al. 2004): subsurface geological and geotechnical mapping (scale 1/1,000), hydrogeological mapping and hydrological

techniques. Surface and subsurface geological fieldwork surveys were first carried out to identify major tectonic accidents responsible for groundwater circulation paths and to assess lithological and structural heterogeneities.

Subsequently, two fieldwork campaigns were performed: the first between April and July 2005 and the second from May to July 2006. A total of 23 sampling sites were then established and in situ determinations included temperature (°C), pH and electrical conductivity ($\mu\text{S}/\text{cm}$). Water samples were collected in each campaign, 3 on *Arca d'Água* masonry reservoirs, 14 along a granitic gutter pipe and 6 on the rock discontinuities, for hydrogeochemical, isotopic and ecotoxicological analyses. The hydrogeochemical analyses included major element concentrations, as well as nitrate, nitrite and ammonia, and they were acquired at “Centro de Estudos de Águas, IDT-IPP” (Porto, Portugal). The laboratory groundwater results were analysed with *AquaChem 5.1* software. Pearson's product moment coefficient (r) was used to assess possible linear relations between the physico-chemical variables assessed.

In what concerns isotopic methods, environmental isotopes (^{18}O , ^2H and ^3H) were measured at the “Instituto Tecnológico e Nuclear” (Sacavém, Portugal). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ determinations were carried out using a mass spectrometer SIRA 10 VG-ISOGAS, applying the analytical methods described in Epstein and Mayeda (1953) and Friedman (1953), respectively. The results are reported to the Vienna-Standard Mean Ocean Water (V-SMOW). The accuracy of the measurements was 1‰ for $\delta^2\text{H}$ and 0.1‰ for $\delta^{18}\text{O}$. The determinations of tritium (^3H) concentrations were carried out by electrolytic enrichment followed by liquid scintillation counting method (PACKARD TRI-CARB 2000 CA/LL). The detection limit of this equipment (liquid scintillation counter) is 0.5 TU. The associated error of the measurements is ± 0.6 TU, depending on the ^3H content of the water samples. The analytical method is described in IAEA (1976).

For the ecotoxicological evaluation, standard acute bioassays with *Daphnia magna* (EPA 1993; OCDE 2000) were carried out at the Laboratory of Ecotoxicology of the Centre for Marine and Environmental Research and of the Institute of Biomedical Sciences of Abel Salazar of Porto University (Portugal), according to OCDE guidelines (OCDE 2000), as described in Guilhermino et al. (1996). Parent animals from a single clone (clone A, sensu Baird et al. 1989a) were cultured in groups of ten per 800 mL of ASTM hard water (ASTM 1980) with an organic additive (Baird et al. 1989b), and fed with *Chlorella vulgaris* (0.322 mg of carbon per daphnia per day). The photoperiod was 16 hL:8 hD and the temperature was $20 \pm 1^\circ\text{C}$. All bioassays were initiated with third to fifth brood neonates (<24 h old). The test medium was ASTM hard water without organic additive; the organisms were not fed

during the tests. The photoperiod and temperature were maintained as described above. As much as 20 animals were used per treatment, in groups of 5 per 100 mL of test solution. In each bioassay, five groundwater treatments and a control (100% ASTM hard water) were tested. Groundwater treatments were prepared by serial dilutions ($\leq 2\times$) of the original groundwater sample with ASTM hard water. For samples showing pH values below 7, two tests were simultaneously performed: one with pH correction and another without pH correction. The test period was 48 h. The measured effect was death, recognised by 15 s of immobilisation after stimulation by bright light. In all test vessels, pH, temperature, dissolved oxygen and conductivity were measured at the start of the test, and after 24 and 48 h.

This integrative methodology was further refined through the application of GIS techniques, which were important to help with the interpretation of the results. The database that is behind each of the layers can be updated at anytime if one of the parameters modified its characteristics, and thus new maps can be easily generated. These tools, together with the land use maps, and the data on contamination sources and groundwater quality will be useful for the future assessment of groundwater vulnerability to contamination.

Paranhos and Salgueiros spring waters: results and discussion

For more than six centuries, water was supplied to Porto City through fountains fed by numerous springs (e.g. Bourbon e Noronha 1885; D'Andrade Junior 1895; Cartado Mena 1908; Fontes 1908; Carrington da Costa 1938; Marçal 1968; Afonso et al. 2006, 2007b). Several underground galleries were excavated throughout the centuries to access the water from these springs. *Paranhos* and *Salgueiros* spring conduits were two of the main galleries (Fig. 2). These tunnels constitute a unique opportunity to predict the probable negative effects of surface water-groundwater interaction in the Porto City area.

Geological description of the site

The crystalline bedrock of the study area consists mainly of moderately deformed granitic rocks, representing the so-called Porto granite facies: two-mica, with K-feldspar and oligoclase-albite plagioclase, medium- to fine-grained, greyish in colour, changing to yellowish when weathered (Barata 1910; Rosas da Silva 1936; Carrington da Costa and Teixeira 1957; Almeida 2001; Begonha and Sequeira Braga 2002). The granite is crossed randomly by aplitic/pegmatic veins, which display much less weathering,

Fig. 2 Some aspects of the spring galleries catchworks: **a** *Arca d'Água* masonry reservoir (ca. XVI century); **b** junction of *Paranhos* and *Salgueiros* spring waters; **c** granitic gutter pipe; **d** seepage from an open sub-horizontal discontinuity



following the main regional tectonic systems. The local fracture network is intense and defines some preferential orientations: NNE-SSW to NE-SW, namely N20°E–N40°E, with a dip of 70°–80° towards NW. Several fault sets were also recognised with a mean orientation of NE-SW, N–S and a sub-horizontal set. Clayey sediments and sands with thicknesses less than 6 m (COBA 2003) constitute the alluvium deposits. The granitic substratum in this area is, generally, weathered to different grades, from fresh rock to residual soil in short distances, showing highly variable conditions and resulting in arenisation and kaolinisation, which may reach depths of more than 30 m (e.g. Begonha and Sequeira Braga 2002; Gaj et al. 2003). According to Begonha and Sequeira Braga (2002), kaolinite and gibbsite are the dominant secondary minerals, both in weathered rock and granitic saprolites. In addition, the spatial development of the weathered rock is completely irregular and unpredictable (Babendererde et al. 2004).

The local weathering grade and the discontinuities network are responsible for the highly variable permeability of the Porto jointed granitic rock mass. This fact results in

a very complex groundwater flow regime. In the less-weathered granite, the flow path is mainly related to the discontinuities set systems, whereas in the more heavily weathered material or soil-like granite, the ground acts more like a porous medium (Fig. 3).

Hydrogeochemistry

To understand how human activities may interfere with the chemical composition of these groundwaters, 23 sampling points were selected (see Fig. 3). The results of the physico-chemical analyses of local groundwater samples are presented in Table 1.

Sampled waters are mainly slightly acidic with a median pH value of 6.8 (pH values ranged from 5.1 to 7.9). Electrical conductivity (EC) measurements ranged from 369 to 604 $\mu\text{S}/\text{cm}$, indicating the presence of medium mineralised waters. The chemical signatures of these samples may be divided into two groups: (1) most of the waters from *Arca d'Água* masonry reservoirs and those flowing along the granitic gutter pipe are of $\text{SO}_4\text{-Ca}$ -type and (2) waters percolating through the rock discontinuities

Fig. 3 Hydrogeological map of the *Paranhos* and *Salgueiros* spring galleries catchworks. The sketch (*inset top right*) shows the location of *Paranhos* and *Salgueiros* spring galleries. The rose diagram (*inset lower left*) illustrates major discontinuity sets (surface geology information adapted and revised from Carrington da Costa and Teixeira 1957; COBA 2003 underground topography adapted from AES 2008)

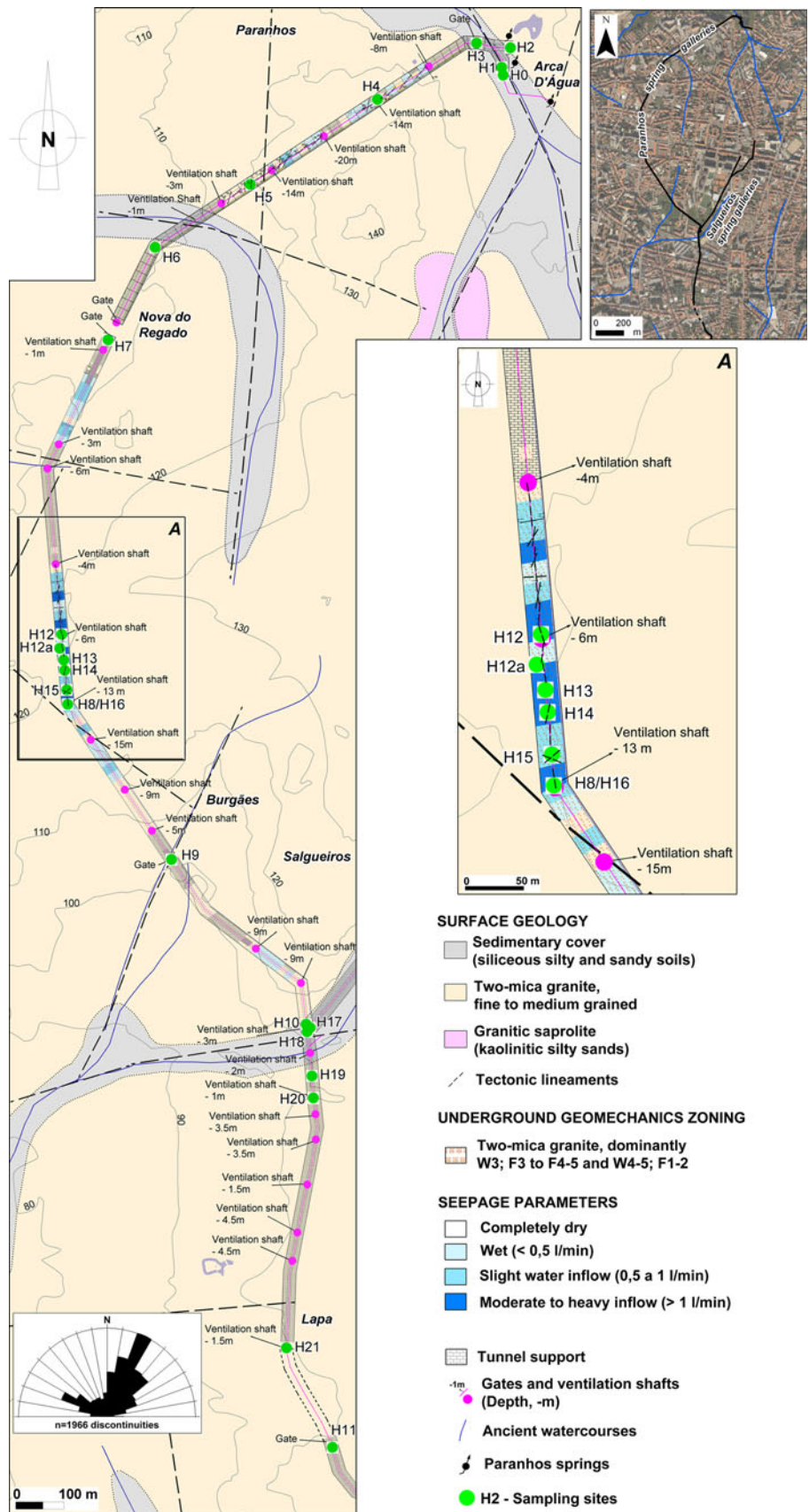


Table 1 Physico-chemical data for water samples collected during the fieldwork campaigns (2005 and 2006)

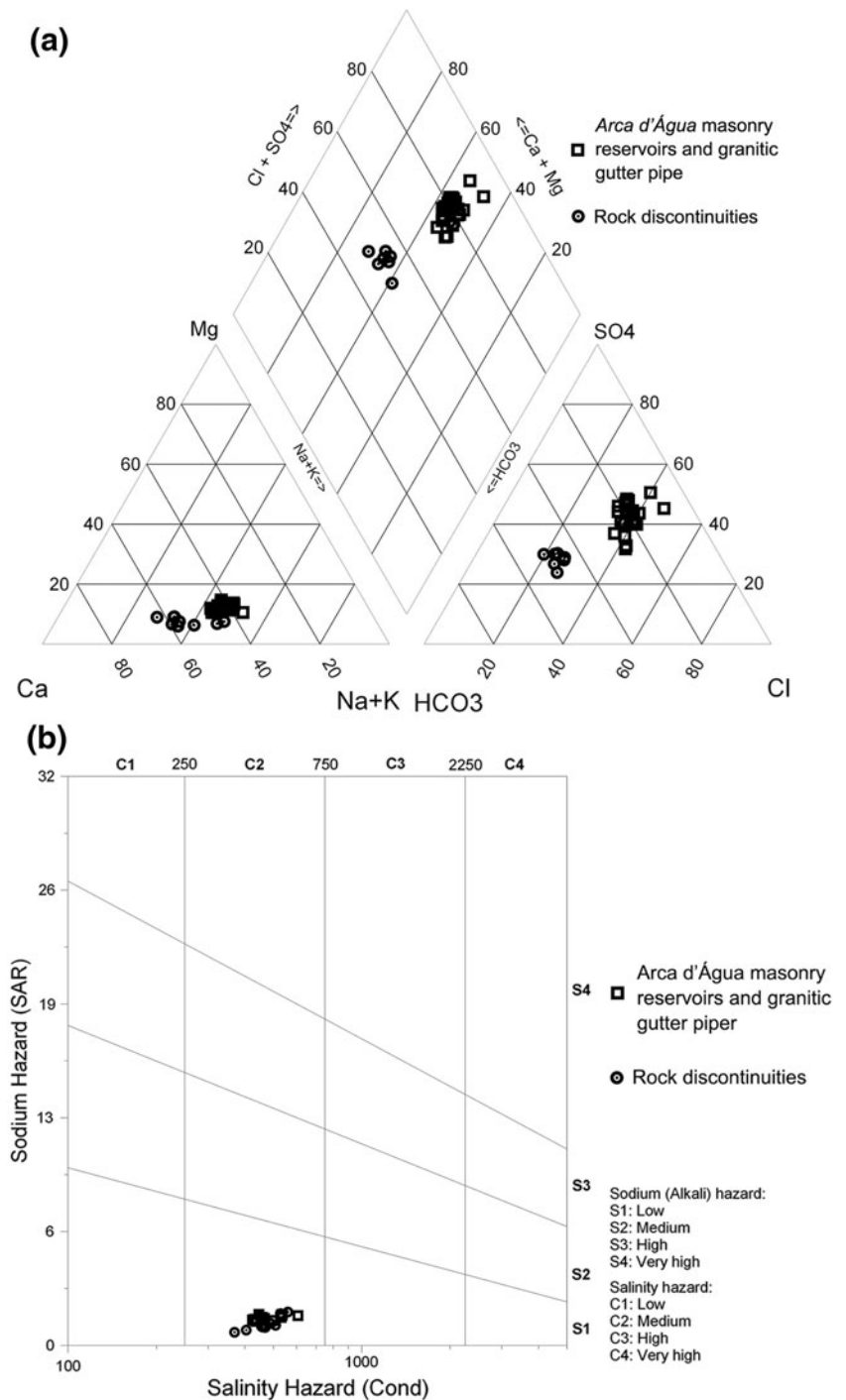
Sample ref.	Fieldwork campaign	Site description	EC (μS/cm)	pH	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	HCO ₃ (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	SiO ₂ (mg/L)	NO ₃ (mg/L)	NO ₂ (μg/L)	NH ₄ (mg/L)
H0	2006	ar	464	5.8	37	11	36	6.1	40	42	70	8.9	58	23	<0.04
H1	2005	ar	435	5.5	32	9.7	35	5.4	39	35	66	6.6	57	<13	<0.04
	2006	ar	457	5.5	34	10	33	5.8	35	37	62	8.3	67	<13	<0.04
H2	2005	ar	423	5.4	32	9.8	31	4.8	16	38	65	6.5	64	<13	<0.04
	2006	ar	445	5.1	38	15	29	4.9	13	41	54	9	72	<13	<0.04
H3	2005	g	435	5.7	32	9.9	35	4.8	33	37	71	6.9	60	<13	0.1
	2006	g	454	5.5	36	15	32	5.4	27	38	56	9	69	<13	<0.04
H4	2005	g	437	5.9	33	9.8	33	4.8	32	37	68	6.1	59	<13	<0.04
	2006	g	456	5.8	36	11	31	5.5	31	39	51	9.3	69	<13	<0.04
H5	2005	g	434	6.0	34	10	34	4.9	32	37	69	6.8	60	<13	<0.04
	2006	g	453	5.9	35	14	31	5.5	31	38	57	8.7	69	<13	<0.04
H6	2005	g	434	6.4	33	10	35	4.8	32	37	69	6.9	60	<13	<0.04
	2006	g	455	6.4	36	11	32	5.8	32	39	62	9.3	69	<13	<0.04
H7	2005	g	430	6.8	32	10	33	4.9	35	37	67	6.1	60	<13	<0.04
	2006	g	456	6.6	34	9.7	37	5.7	33	39	62	9.2	70	<13	<0.04
H12	2005	r	369	7.6	19	9.6	47	4.0	106	24	49	5.9	13	<13	<0.04
	2006	r	456	7.7	29	8.7	51	4.8	120	37	45	10	31	<13	<0.04
H12a	2006	r	469	6.7	27	9.5	49	4.6	98	33	47	9.5	62	<13	<0.04
H13	2005	r	490	7.0	35	24	56	3.9	129	37	55	6.0	35	145	0.81
	2006	r	560	6.6	49	14	45	4.6	47	50	68	10	100	<13	<0.04
H14	2005	r	405	6.6	23	18	51	3.4	97	27	48	6.2	36	<13	<0.04
H15	2005	r	530	6.8	47	13	47	4.1	48	47	68	7.3	86	<13	<0.04
H16	2005	r	460	7.9	29	20	57	3.5	106	31	54	8.4	49	<13	<0.04
	2006	r	509	7.8	31	11	52	4.1	104	35	52	13	63	<13	<0.04
H8	2005	g	430	7.4	34	11	34	4.9	33	37	69	6.8	61	<13	<0.04
	2006	g	456	7.3	35	11	38	5.8	33	39	53	9.6	70	13	0.12
H9	2005	g	434	7.7	31	9.8	32	5.0	35	37	68	6.3	59	<13	<0.04
	2006	g	457	7.5	35	9.8	37	5.8	34	39	54	9.6	70	16	0.14
H10	2005	g	434	7.7	32	9.6	33	5.0	34	37	69	6.2	60	<13	<0.04
	2006	g	457	7.4	35	12	37	5.8	33	39	53	9.5	70	16	0.11
H17	2006	g	604	7.5	48	16	47	10	73	57	78	11	71	<13	<0.04
H18	2006	g	526	7.6	41	11	39	7.7	53	50	61	10	70	<13	0.04
H19	2006	g	530	7.5	42	14	43	7.6	54	49	74	10	71	15	<0.04
H20	2006	g	534	7.2	42	14	35	7.5	55	51	52	11	72	<13	<0.04
H21	2006	g	529	7.1	41	15	35	7	51	50	72	12	73	<13	<0.04
H11	2005	g	497	7.9	35	11	39	6.1	49	43	76	7.4	63	24	<0.04
	2006	g	533	7.5	43	13	35	7.2	53	50	53	11	73	<13	<0.04
Median			456.0	6.8	35.0	11.0	35.0	5.0	35.0	38.0	62.0	8.9	64.0	n.d.	n.d.
Minimum			369.0	5.1	19.0	8.7	29.0	3.4	13.0	24.0	45.0	5.9	13.0	<13	<0.04
Maximum			604.0	7.9	49.0	24.0	57.0	10.0	129.0	57.0	78.0	13.0	100.0	145	0.81
Interquartile range			68.5	1.6	5.5	4.2	13.0	1.0	22.0	5.5	16.0	3.1	10.5	n.d.	n.d.

Site description: *ar* Arca d'Água masonry reservoirs, *g* granitic gutter pipe, *r* rock discontinuities, *n.d.* not determined

are mainly of HCO₃-Ca-type (Fig. 4a). Regarding the nitrate concentrations, this constituent displays a median value of 64 mg/L, with samples from the granitic gutter

pipe and the Arca d'Água masonry reservoirs much more enriched in NO₃ than the samples collected from rock discontinuities. All water samples were also analysed for

Fig. 4 Piper diagram (a) and Wilcox diagram (b) for water samples collected during the fieldwork campaigns



minor elements, such as nitrite and ammonia. Most of these samples present nitrite and ammonia values less than 13 $\mu\text{g/L}$ and 0.04 mg/L, respectively (see Table 1).

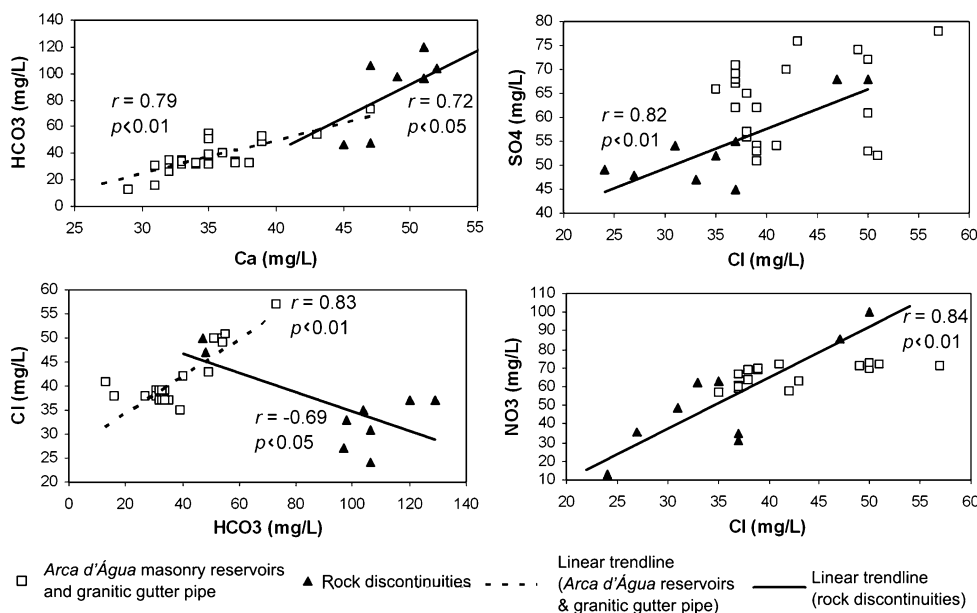
According to the analysed parameters and the Portuguese legislation, these waters are not potable for human consumption. The drinking-water guideline limit for nitrate (50 mg/L) was exceeded in 87% of the samples.

Although their risk to salinisation is medium (Fig. 4b), these waters may be suitable for irrigation purposes.

Concerning the irrigation guidelines limits imposed by the Portuguese law, these waters have EC and SAR (sodium adsorption ratio) values below those limits, 1,000 $\mu\text{S/cm}$ and 8, respectively. Nevertheless, since the majority of the samples exceed 50 mg/L for nitrate, this means that more sensitive cultures can be affected by these high levels of nitrate.

To better understand the hydrochemical relationships of these waters, several correlations were established. Figure 5 indicates that: (1) samples from rock discontinuities

Fig. 5 Scatter diagrams on some hydrogeochemical parameters for water samples collected during the two fieldwork campaigns. Pearson correlation coefficient (r) and its respective significance level are indicated for each studied linear relationship



present higher concentrations of Ca and HCO₃, whereas those from *Arca d'Água* masonry reservoirs and the granitic gutter pipe show, in general, higher concentrations of Cl, SO₄ and NO₃; (2) Ca and HCO₃ seem to have the same source for all these studied samples; (3) HCO₃ and Cl seem to present different origins along the rock discontinuities; (4) Cl, SO₄ and NO₃ appear to have the same source in discontinuities, but different genesis in *Arca d'Água* masonry reservoirs and granitic gutter pipe.

Since granitic rocks dominate the local geological environment, the presence of some of the Ca can be explained by ion exchange processes between clay minerals (e.g. kaolinite) and groundwater (Na and K are retained by the clays, and Ca is released). Regarding HCO₃, this parameter may be ascribed, partially, to the hydrolysis of plagioclases from the granitic rocks, but its origin on the oxidation of organic matter cannot be excluded (e.g. Foster 1997).

In the waters from *Arca d'Água* masonry reservoirs and granitic gutter pipe, the atmospheric transport of sea spray should be regarded as a possible source of Cl, due to the proximity of Porto City to the Atlantic Ocean. According to Lorrai et al. (2004), after the deposition of seawater salts in the soil zone, cyclic dissolution/evaporation processes could be responsible for ion concentration in the unsaturated zone as well as in the shallow aquifers. The presence of sulphate and nitrate may be attributed to agricultural fertilisers, since there are several public gardens and backyards above the *Paranhos* and *Salgueiros* spring galleries. These contaminants infiltrate throughout the soil and may easily reach the shallow groundwater.

In the waters circulating in rock discontinuities, two samples present different geochemical signatures from the

waters of the same group. These two outliers could be attributed to a mixing process of infiltrated meteoric waters with a different underground flow path. The lower bicarbonate concentration in these two water samples could be explained by local granitic heterogeneities, inducing a slighter water–rock interaction (e.g. plagioclase hydrolysis). In the waters from rock discontinuities as a whole, wastewaters should be considered as typical sources of Cl, NO₃ and SO₄. Leakage from sewerage systems could also be an important factor, since most of these infrastructures may be deteriorated and so they are not leakproof (see Eiswirth 2002; Barrett 2004; Taylor et al. 2004; Burn et al. 2007).

Concerning the isotopic approach, representative analyses of groundwater samples are presented in Table 2.

Figure 6 shows the diagram $\delta^{18}\text{O}$ versus $\delta^2\text{H}$, where two main groundwater clusters have been identified. One of the groups (A) stands for groundwater sampling points collected along the granitic gutter pipe and in *Arca d'Água* masonry reservoirs (spring chambers). This group of waters presents a homogeneous isotopic composition, with average values of -5.3 and -33.2‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. The other group of waters (B), collected from the rock discontinuities is characterised by more depleted $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (by about -6 and -39‰ , respectively), presenting a heterogeneous isotopic composition.

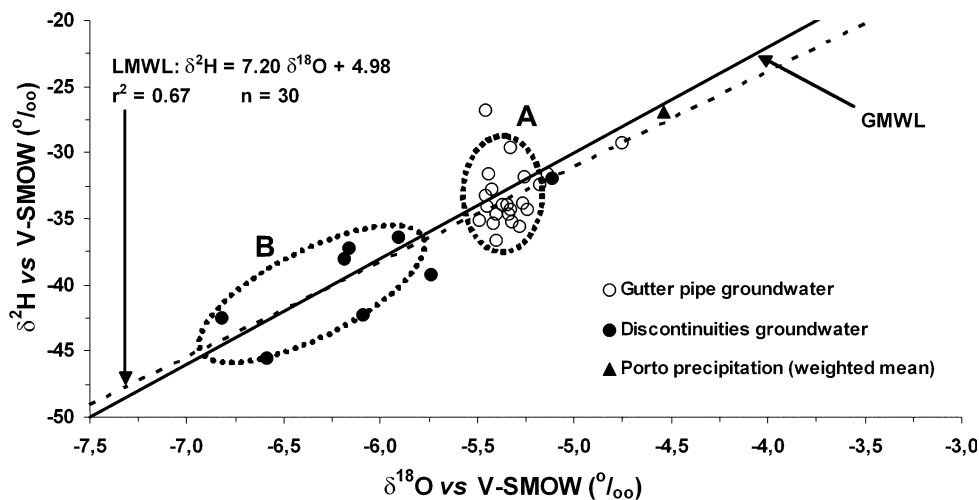
The observed isotopic depletion in groundwater from group (B) could be attributed to the fact that they could be ascribed to random precipitation events, resulting into a direct infiltration of meteoric waters along the fractured granitic rocks. Studies performed in Portugal, within the monthly precipitation survey, have demonstrated that the isotopic composition of daily rain events can range

Table 2 Isotopic data from the fieldwork campaigns (2005 and 2006)

Sample ref.	Fieldwork campaign	Site description	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	^3H (TU)
H0	2006	ar	-5.24	-34.3	0
H1	2005	ar	-5.18	-32.4	2.8
	2006	ar	-5.49	-35.1	0
H2	2005	ar	-5.27	-33.8	2.1
	2006	ar	-5.42	-35.4	0
H3	2005	g	-5.46	-33.2	2.5
	2006	g	-5.37	-34	0
H4	2005	g	-5.32	-35.2	1
	2006	g	-5.28	-35.6	1.5
H6	2005	g	-5.33	-34.3	3.6
	2006	g	-5.43	-32.8	1.4
H7	2005	g	-5.45	-34.1	3
	2006	g	-5.34	-34.6	2.2
H12	2005	r	-6.82	-42.5	2.8
	2006	r	-5.11	-31.9	0
H12a	2005	r	-6.59	-45.5	3.3
	2006	r	-6.09	-42.3	2.2
H13	2005	r	-6.19	-38	4.4
	2006	r	-5.91	-36.4	2.3
H16	2005	r	-6.16	-37.2	4.5
	2006	r	-5.74	-39.2	2.5
H8	2005	g	-5.44	-31.6	2.1
	2006	g	-5.33	-29.6	1.2
H9	2005	g	-5.14	-31.6	2
	2006	g	-4.75	-29.3	1.2
H10	2005	g	-5.4	-36.6	2.4
	2006	g	-5.35	-34	1.6
H17	2006	g	-5.46	-26.8	1.4
H11	2005	g	-5.26	-31.8	3
	2006	g	-5.4	-34.7	1.2

Site description: *ar* Arca d'Água masonry reservoirs, *g* granitic gutter pipe, *r* rock discontinuities

Fig. 6 $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ signatures of the groundwater samples from *Paranhos* spring galleries. The Global Meteoric Water Line (GMWL: $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$ in Craig 1961) and the Local Meteoric Water Line were plotted as reference (LMWL: $\delta^2\text{H} = 7.2\delta^{18}\text{O} + 4.98$; $r^2 = 0.67$; $n = 30$)



between -11.85 and 0.37 ‰ for oxygen-18 and between -80.4 and 12.8 ‰ for deuterium (Carreira et al. 2006).

On the other hand, groundwater from group (A) seems to be mostly meteoric waters that have infiltrated mainly along the granitic weathering zones. These weathering zones have an important influence on the extent to which recharge reaches underlying aquifers, presenting a homogeneous isotopic composition due to a continuous recharge all over the time. In fact, this group of groundwater presents an isotopic composition that approaches the long-term mean isotopic composition of precipitation at Porto meteorological station ($\delta^2\text{H} = -26.9$ ‰; $\delta^{18}\text{O} = -4.54$ ‰, Carreira et al. 2006).

Two different patterns can be observed between groundwater ascribed to the granitic gutter pipe and *Arca d'Água* masonry reservoirs and the rock discontinuities in the ^3H content in the sampled groundwater (see Table 2). In fact, groundwater from rock discontinuities present higher ^3H concentrations (≈ 2.7 TU) than other groundwater, with a mean ^3H concentration of 1.7 TU, indicating a faster circulation path. Further, the arithmetic mean at Porto meteorological station presents a weight annual mean of 4.5 TU (Carreira et al. 2006).

Besides, one can also identify a decrease in the ^3H values between the 2005 and 2006 campaigns. The highest

tritium values are ascribed to the first fieldwork campaign, varying between 1.0 and 4.5 TU. In contrast, in the second fieldwork campaign, tritium ranged from 0.0 to 2.5 TU (Fig. 7).

The decrease in tritium values between the two fieldwork campaigns can be explained taking into account the climatic features that occurred in the region. During the year 2005, Portugal was under a severe dry period where the amount of precipitation was about 25–30% of the previous records (IM 2005). One possible explanation for the high tritium values measured during the dry period (2005) could be attributed to a regional circulation, related to an earlier recharge at a time where the ^3H values in precipitation were higher. The waters from the gutter pipe are mainly supplied by percolation of water through the granite's weathering zone. Weathering zones are characterised by slower flow paths ascribed to a porous media, in contrast to the faster water circulation along the rock discontinuities.

On the other hand, the decrease in the tritium activity found in 2006 (in all water samples) can be attributed to the presence of older groundwater entering the system due to the lack of precipitation during the preceding years (see Fig. 8). This hypothesis seems to be corroborated by the extremely low ^3H content in samples from the spring

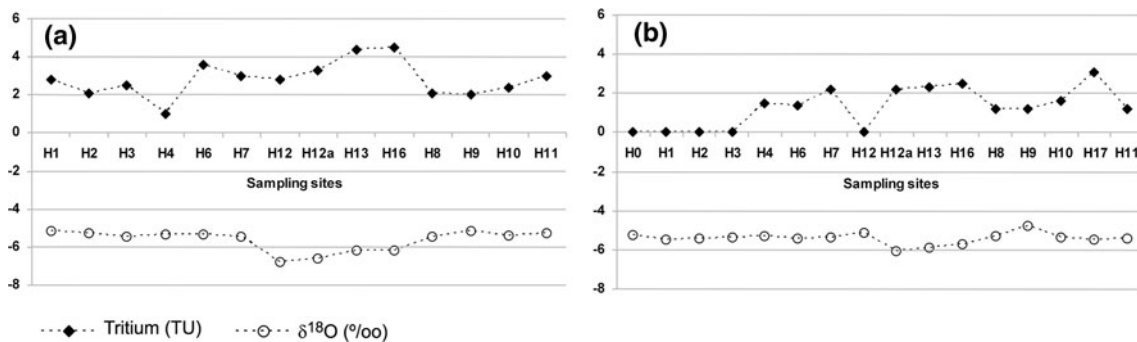


Fig. 7 Evolution pattern of ^3H and $\delta^{18}\text{O}$ contents along spring collection chambers for 2005 (a) and 2006 (b) fieldwork campaigns

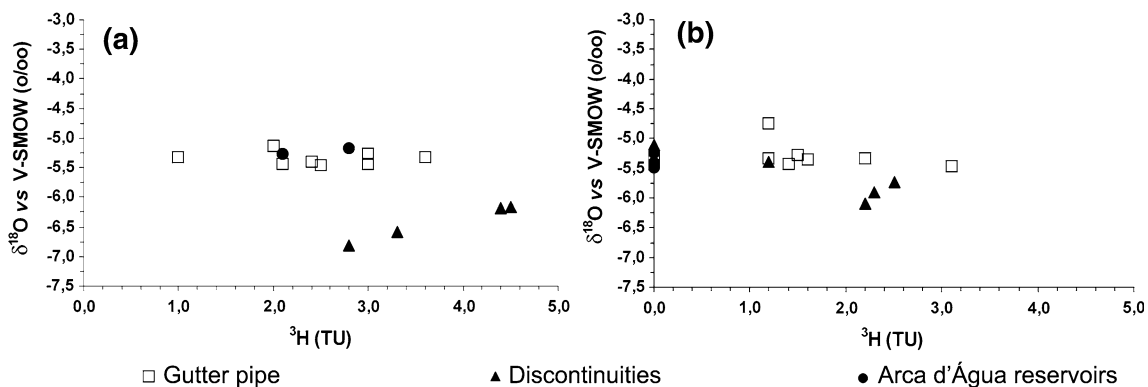


Fig. 8 $\delta^{18}\text{O}$ versus ^3H scatter diagrams for water samples collected during 2005 (a) and 2006 (b) fieldwork campaigns

chambers (below detection limits) and the present tritium content in the regional precipitation (4.5 TU).

Ecotoxicological evaluation

For the standard acute bioassays with *D. magna*, the results showed that within all test vessels, pH and temperature variation was always lower than 1 unit, whereas dissolved oxygen was always above 60%, so fulfilling the test validation criteria (OCDE 2000). Mortality recorded in control solutions varied between 0 and a maximum of 5%. No significant mortality was observed in the test solutions for any of the bioassays performed. Occasional lethality, below 10%, was recorded in some of the bioassays, as for instances for samples collected in sites H12, H16 and H21 (Fig. 9). Low mortality, always equal or below 25%, was observed in samples with pH values below 7 (H2 and H6, Fig. 9), within the two highest groundwater concentrations tested. This mortality was not observed in the corresponding pH-corrected tests. These results are in good agreement with the high sensitivity exhibited by *D. magna* to acidic environments (Peters 1987). Furthermore,

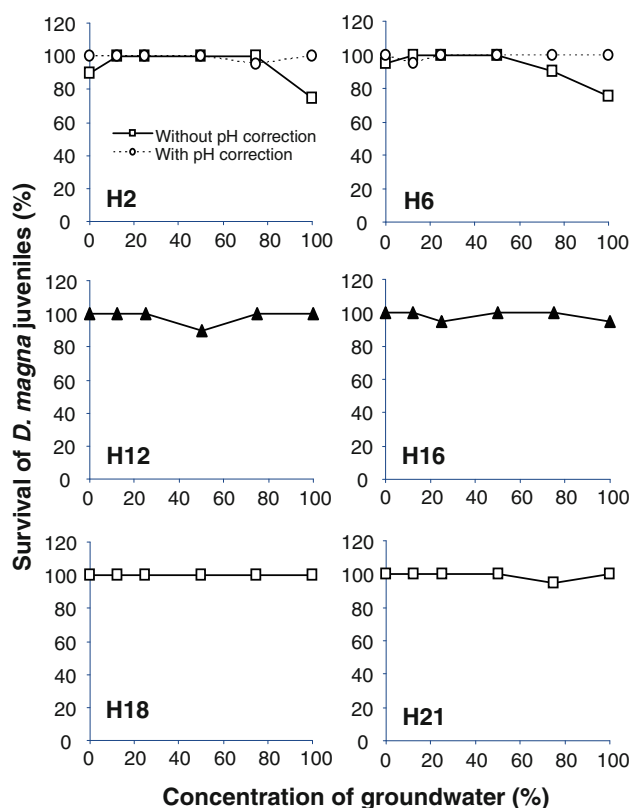


Fig. 9 Results obtained for six of the standard acute bioassays performed with samples from *Paranhos* and *Salgueiros* groundwater, collected during the 2006 campaign in the *Arca d'Água* masonry reservoirs, the granitic gutter pipe (*white symbols*) and the rock discontinuities (*black symbols*)

although high, the concentrations of nitrates found in this groundwater were well below those reported to be lethal for cladoceran species. Indeed, median lethal concentration (LC50) values of 374 and 462 mg/L were found in laboratory exposures of *Ceriodaphnia dubia* and *D. magna*, respectively, to nitrates (Scott and Crunkilton 2000). Overall, the results suggest a low toxicity potential for these groundwaters, eventually compatible with its use for irrigation purposes. The results obtained so far do not exclude, however, the possible occurrence of more subtle effects on organisms, such as changes in growth and/or reproduction, or alterations at the biochemical level. Future ecotoxicological work will thus concentrate on the study of possible sub-lethal effects induced by the exposure to these groundwaters.

Concluding remarks and outlook

This methodology proved to be valuable in expanding our understanding of the Porto urban groundwater systems. Hydrogeochemistry and isotopic methods were essential to identify and characterise these groundwaters. Geochemical signatures indicate that the quality of the groundwater, namely the nitrate and sulphate-enriched composition, may be ascribed to urban drainage and a damaged sewage system. Nevertheless, these results suggest that the studied groundwater may be suitable for irrigation purposes. The application of stable and radioactive isotope techniques has been extremely useful in recognising two different groundwater groups with different flow paths, delineating the downward infiltration and horizontal spread of urban recharge, which, in most cases, is a key question for the management of aquifers. One of the groups stands for groundwater sampling points collected along the granitic gutter pipe and in *Arca d'Água* masonry reservoirs (spring chambers). This group presents a homogeneous isotopic composition. The other group stands for groundwater collected from the rock discontinuities, presents a heterogeneous isotopic composition and is characterised by more depleted $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values. The first group seems to be mostly represented by meteoric waters that infiltrated mainly along the granitic weathering zones, whilst the second group is related to meteoric waters that infiltrated along the fractured granitic rocks.

Paranhos and *Salgueiros* groundwater may receive contaminants from several sources, which comprise a complex mixture of pollutants. The standard acute bioassays performed provide a useful method of assessing potential lethal effects of these complex mixtures on an ecologically relevant microcrustacean species, representative of primary consumers in food chains. The future collection of groundwater from dug wells and boreholes and

the application of stable isotope ratios of N, S and C, in coordination with major and trace element hydrochemistry and ecotoxicological assays, will provide important information on the evaluation of mixing processes between surface waters and groundwater. In addition, this can be exceptionally useful to identify the origin of a wide range of possible anthropogenic sources that can contaminate these urban aquifers. In urban areas, groundwater is cyclically replenished directly by precipitation and by surface water percolation downwards through the subsoil. The investigation of the source of the recharge processes is essential for the development and management of groundwater resources in urban areas.

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