

HYDROGEOCHEMICAL, ISOTOPICAL AND ECOTOXICOLOGICAL APPROACH TO THE PARANHOS SPRING GALLERIES CATCHWORKS FROM PORTO URBAN AREA (NW PORTUGAL)

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ABSTRACT

This multidisciplinary study presents the preliminary results of the hydrogeochemical, isotopical and ecotoxicological analyses performed to assess the nature and suitability for use of groundwater from the Paranhos' spring galleries catchworks. These springs constituted for more than five centuries one of the main water supplies to Porto city. For the characterisation of the underground area (ca. 3km extension and a -25m of depth), constituted mainly by granitic rocks, the following tools were applied: i) subsurface geological and geotechnical mapping and; ii) hydrogeological, isotopical and ecotoxicological techniques. Surface and subsurface fieldwork surveys were first carried out to identify major tectonic accidents responsible for groundwater circulation paths and to assess lithological and structural heterogeneity. Hydrogeological fieldwork campaigns were then performed, and in situ determinations included: temperature (°C), pH and electrical conductivity ($\mu\text{S}/\text{cm}$). Several sampling sites were subsequently established, based on the surface activities located on the course of the springs, and water samples were collected for hydrogeochemical, isotopical and ecotoxicological analyses. All the water samples have been analysed for major element concentrations. The isotopic techniques employed included d^2H and d^{18}O . For ecotoxicological evaluation standard acute bioassays with *Daphnia magna* were performed. For each sample, two 48h-LC50 bioassays were simultaneously performed: one with pH correction and the other without pH correction. In each bioassay, five concentrations of groundwater were prepared by dilution of the original sample with ASTM hard water.

The hydrogeochemical analyses showed a nitrate and sulphate-enriched composition for these groundwaters, probably resulting from intense urbanisation, sewer leakage and some agricultural practices. Concerning the ecotoxicological analyses, no mortality was observed in any of the tests performed. The results obtained in this study suggest that part of Porto urban groundwater could be suitable for irrigation uses, but additional tests must be carried out to verify its compliance with existing standards of water quality. Specifically, geoenvironmental and ecotoxicological studies are required to assess potential variations in water composition and toxicity associated with seasonal changes in climate and human activities.

KEYWORDS

Groundwater, Porto urban area, hydrogeochemistry, isotope hydrology, *Daphnia magna* bioassays

INTRODUCTION

This work is strongly connected with one of the most crucial water-related research issues at the turn of the millennium “Water and Society”, in particular with the “Land habitat hydrology in urban areas” a subject indicated by the UNESCO International Hydrological Programme (Aureli, 2002). Urbanization can have a profound effect on water resources and the hydrological cycle. The urban subsurface is a network of pipes, conduits, and other structures that provide pathways for the movement of urban-sourced contaminants into underlying aquifers. A consequence of such complexities is that urban groundwater resources are frequently prone to uncontrolled exploitation and to degradation resulting from indiscriminate effluent and waste disposal practices.

Faced with increasing worldwide pressure on water resources due to escalating demand, contamination and climatic change, it is becoming evident that integrated multidisciplinary approaches must be adopted to address the scientific issues related to water resources. In hydrogeological investigations of urban areas, chemical and isotopical analyses, as well as ecotoxicological assessment of waters collected from springs, dug-wells and boreholes can provide important information concerning the evaluation of mixing processes between surface waters and groundwaters. In fact, in urban areas, the chemical composition, and so the potential toxicity, of local groundwaters is often conditioned by human activities since the intense urbanisation and agricultural practices control the conditions occurring at shallow levels.

This multidisciplinary work presents the first results of the hydrogeochemical, isotopical and ecotoxicological studies employed to assess the nature and suitability for the use of groundwater from the Paranhos’ spring horizontal galleries catchworks. The importance of geology, palaeoweathering and climate on the hydrogeology to the Porto region are also highlighted.

GEOTECTONICAL AND HYDROGEOLOGICAL OVERVIEW

The Porto urban area is located in a complex geotectonic domain of the Iberian Massif, near the Porto–Coimbra–Tomar shear zone (Ribeiro et al., 1990; Chaminé et al., 2003). The crystalline bedrock of Porto city consists of granites in the eastern part and a gneisses-micaschists complex in the western part. A major fault zone — Porto-Coimbra-Tomar shear zone (Chaminé et al., 2003) — trending NNW-SSE, defines the boundary between these two major geological units. Variscan granitic rocks, representing the Porto granite facies and Ermesinde porphyritic facies, underlay the Porto site (s.str.).

The regional geotectonical framework of Porto urban area (e.g., Sharpe, 1849; Barata, 1910; Rosas da Silva, 1936; Carrington da Costa, 1958; Chaminé, 2000; Almeida, 2001; Chaminé et al., 2003; and references therein) comprises a crystalline fissured basement complex of strongly deformed and overthrust Late Proterozoic/Palaeozoic metasedimentary rocks and granites. The Porto granite consists of two-micas, coarse grained, and greyish in colour, changing to yellowish when weathered. The granite is, generally, weathered to different grades, from fresh-rock to residual soil, showing highly variable conditions, resulting in arenisation and kaolinisation, which may reach depths of more than 100m (e.g., Begonha & Sequeira Braga, 1995; Begonha, 2001; Gaj et al., 2003; COBA, 2003).

The chemical palaeoweathering took place during the Cenozoic times under tropical/subtropical climate conditions (Araújo et al., 2003). The geomorphologic framework of the region corresponds to a wide flat area dipping gently to South and West.

The regional hydrogeological units described in Porto urban area are presented in figure

METHODOLOGY

This work presents the results of hydrogeochemical, isotopical and ecotoxicological studies, performed in order to consider the changes in the hydrological regime caused by urbanisation and to assess the nature and suitability for use of groundwater from spring galleries catchworks located in Porto urban area. For this purpose, the underground area (ca. 3km long and a -25m of depth) was studied using the following tools (e.g., Struckmeier & 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 heterogeneity.

Hydrogeological fieldwork campaigns were thereafter performed and in situ determinations included: temperature (°C), pH and electrical conductivity ($\mu\text{S}/\text{cm}$). Several sampling sites were then established, based on the surface activities located on the course of the springs, and 16 water samples were collected for hydrogeochemical, isotopical and ecotoxicological analyses. All water samples have been analysed for major element concentrations. The hydrogeochemical analysis were acquired at "Centro de Estudos de Águas / ISEP" (Porto, Portugal).

In what concerns isotopical methods, the techniques employed were $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in water, in combination with major and trace hydrogeochemical indicators. The vulnerability of groundwater source protection areas is also being assessed using environmental ^3H . In fact, the application of stable isotopic techniques, in co-ordination with major and trace element hydrogeochemistry could be extremely useful in delineating the downward infiltration and horizontal spread of urban recharge, which, in most cases, is a key question in aquifer management. The environmental isotopes (^{18}O , ^2H and ^3H) were measured at "Instituto Tecnológico e Nuclear / Departamento de Química" (Sacavém, Portugal). The ^{18}O and ^2H determinations were carried out using a mass spectrometer SIRA 10 VG-ISO-GAS applying respectively the Friedman (1953) and Epstein & Mayeda (1953) analytical methods. The results are reported in δ notation, which represents the relative deviations of the sample with respect to a standard value, defined by the following equation: δ (‰) = $[(R_{\text{sample}} / R_{\text{standard}}) - 1] \times 1000$, where R stands for the ratio $^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ in the sample and R_{standard} represents the same ratio determined in the standard. The accuracy of the measurements is 1‰ in deuterium determinations and 0.1‰ for oxygen-18. The Vienna - Standard Mean Ocean Water (V-SMOW) is accepted as the reference standard for ^2H and ^{18}O in water determinations. The tritium analyses are being carried out in all water samples using first an electrolytic enrichment method and after measured by liquid scintillation counting method (PACKARD TRI-CARB 2000 CA/LL). The detection limit of this equipment (liquid scintillation counting) is 0.5 TU. The associated error to the measurements varies with the tritium concentration in the samples, although usually is around 0.6 TU. The analytical method is described in I.A.E.A. (1976).

For the ecotoxicological evaluation, standard acute bioassays with *Daphnia magna* (OCDE, 2000) were carried out at the Ecotoxicology Laboratory from CIIMAR (Porto, Portugal). Parent animals were cultured in groups of 10 per 800 ml of ASTM hard water (ASTM, 1980) supplemented with an organic additive (Baird et al., 1989) and fed three times a week with the algae *Chlorella vulgaris* (0.322 mg carbon/daphnia/day). The photoperiod was 16 h L:8 h D and the temperature was 20 ± 1 °C. Experiments were performed according to the methodology described in (Guilhermino et al., 1996). In brief, all bioassays were carried out with animals from a single clone (clone A, sensu Baird et al. 1989a) and initiated with third to fifth brood neonates (<24 h old). Test medium was ASTM without organic additive;

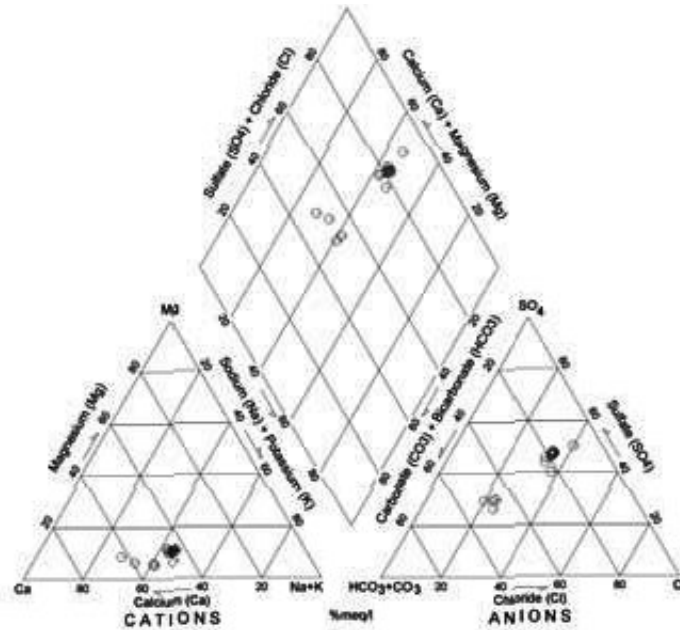
the organisms were not fed during the tests. Twenty animals were used per treatment, in groups of 5 per 100 ml of test solution in a glass flask. In each bioassay, five test solutions of groundwater, with a concentration factor equal or less than 2 between them, plus a control solution (100% dilution water) were prepared by dilution of the original sample with ASTM hard water. For collected samples showing pH values outside the range 7-9, two tests were simultaneously performed: one with pH correction and another without pH correction. Each test had a duration of 48 h. The measured effect was death recognised by immobilisation of the organisms during 15 s after stimulation by a bright light. Temperature and photoperiod were as described above. In all test vessels, pH, temperature, and conductivity were measured at the starting of the test, and after 24 and 48 h.

A MULTIDISCIPLINARY APPROACH

In general, integrated studies combining hydrogeochemical, isotopical and ecotoxicological techniques strongly contribute to quantitatively assess the changes in the hydrological regime caused by urbanization. They can also contribute to solve other problems, at a local scale, resulting from urban processes. Although little data and few case studies have been published, in which isotope and ecotoxicological techniques have been systematically applied in urban areas, various isotope techniques may have useful applications within this context. In this paper we put special emphasis on the fact that water resources and environmental assessment problems arising in urban areas range widely in scale (local investigation scale vs regional investigation scale). The area of application of environmental isotope geochemistry includes the assessment of recharge from leaking water mains and sewers, from in situ sanitation, from waste water and from influent surface water courses. On another hand, standard acute bioassays are widely used test methods for the toxicity assessment and monitoring of groundwater (EPA, 1993; Connon et al., 2003; Dewhurst et al., 2002). These tests provide rapid information on the degree of pollution present in the groundwater and the potential effect of that pollution on indicator or surrogate organisms. Typically, their result is the determination of the median lethal concentration (LC50), i.e., the concentration that causes a mortality of 50% of the tested organisms (Cooney, 1995) in the specific conditions of the bioassay.

From a hydrogeochemical point of view, most of the sampled groundwaters presented near-neutral pH values (median = 6.78), being the lowest rate 5.35 and the highest 7.9. In what concerns electrical conductivity, most of the samples presented medium electrical conductivities (median = 434 $\mu\text{S}/\text{cm}$), being the minimum value 405 $\mu\text{S}/\text{cm}$ and the maximum 530 $\mu\text{S}/\text{cm}$. Concerning chemical signatures, the studied groundwaters show a wide range; Ca^{2+} followed by Na^+ dominates cations and anions are dominated by SO_4^{2-} and Cl^- . Observing the Piper diagram of figure 2, one can conclude that most of the groundwaters are "mixed" $\text{SO}_4^{2-}/\text{Cl}^- - \text{Ca}^{2+}/\text{Na}^+$ waters.

Figure 2
Piper diagram for water samples collected from Paranhos spring galleries catchworks.

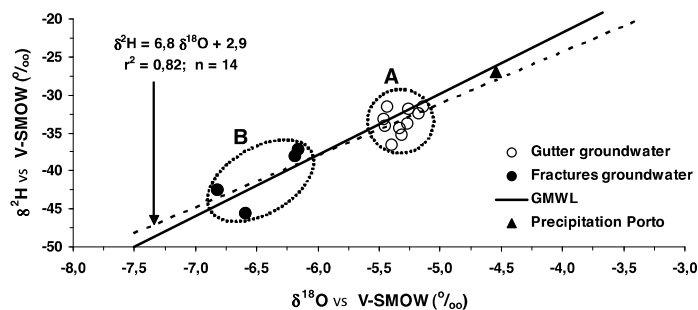


Besides major element concentrations, all water samples have been analysed for some minor elements, such as NO_3^- ; this constituent presented a median value of 60 mg/L, having minimum and maximum values of 35 mg/L and 86 mg/L, respectively.

Since one of the main goals of this study was to assess the suitability for use of groundwater from the Paranhos spring horizontal galleries catchworks, particularly the aptitude of these groundwaters for agriculture use, it was employed the Riverside diagram. This diagram deals with the Sodium Adsorption Ratio (SAR) and permits to evaluate the soil risk to salinization and alkalization. This approach led to the conclusion that all these waters induce a low risk to alkalization and a medium risk to salinization.

In what concerns the isotopic approach, in the diagram $\delta^{18}\text{O}$ vs $\delta^2\text{H}$ (figure 3) the isotopic composition of groundwater samples along the Paranhos spring galleries catchworks is presented. In this diagram two main water groups can be observed. The first one (A) presents an average isotopic composition of -5.33 ‰ and -33.5 ‰ in ^{18}O and ^2H , respectively; the second group (B) is composed by more depleted groundwater samples (by about 1 ‰ in oxygen-18 and around 7.5 ‰ in deuterium). 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 (LMWL: $\delta^2\text{H} = 6.8 \delta^{18}\text{O} + 2.9$; $r^2 = 0.82$) are also plotted.

Figure 3
 $\delta^{18}\text{O}$ vs $\delta^2\text{H}$ signatures of the groundwater samples from Paranhos spring galleries catchworks.



The first group (A) stands for groundwaters collected along gutter sampling points in the Paranhos spring galleries catchworks, presenting a homogeneous isotopic composition. This data distribution is pointing out to a single source for this group of groundwater samples. When compared the groundwater samples from group (A) with those from group (B), an isotopic depletion is found. In fact, the isotopic composition of the groundwater samples from group (B), collected from the granitic fractures could be ascribed to different causes, namely:

i) Contribution from a different aquifer system associated with a long circulation pattern, with recharge areas located at higher altitudes (at least 500 m higher than the recharge area of Paranhos system). This hypothesis is formulated assuming an isotopic fractionation gradient of $-0.20\text{‰} / 100\text{ m}$ in oxygen-18, which represents the mean isotopic gradient in Portugal (Carreira et al., 2005). From the chemical point of view, these waters are characterised by high electrical conductivity, and the highest HCO_3^- , Ca and K concentrations, which could be ascribed to a longer granite-water interaction process. From the geomorphologic point of view this hypothesis does not seem to be the most reliable;

ii) Existence of leakage waters from a local water reservoir (fed with water for public supply). In fact, in Porto urban area, the source of water supply is the Douro River, which presents a more depleted isotopic composition (data from Marques et al., 2003: $\delta^2\text{H} = -58.0\text{‰}$; $\delta^{18}\text{O} = -8.29\text{‰}$) when compared with the local precipitation in the area (Serra do Pilar Meteorological Station: weighted monthly average isotopic composition $\delta^2\text{H} = -26.9\text{‰}$ and $\delta^{18}\text{O} = -4.54\text{‰}$ in Carreira et al., 2005). The isotope depletion found in Douro River is related to the fact that the source of this river is located at 1700m a.m.s.l, on Urbion Mountains, near the city of Sória in the Spain interior (Loureiro et al., 1986). It should be stated that this group of groundwaters is characterised by the lowest NO_3^- and SO_4^{2-} contents. These waters are the only ones presenting NO_3^- values below the maximum admitted values (50 mg/L) for human consumption, corroborating this second hypothesis.

Regarding the results of the ecotoxicological evaluation of Paranhos groundwater, within all test vessels pH, temperature, and conductivity variation was always lower than 1 unit. Mortality recorded in control solutions was less than 5%. No mortality was recorded at the lowest concentrations of groundwater tested in any of the tests performed, whereas occasional lethality, always below 10%, was recorded at concentrations greater than 50% effluent (figure 4). The low mortality observed within the groundwater concentrations tested, occurred usually in the tests without pH correction, and was no longer observed in the corresponding pH corrected tests. These results are in good agreement both with the low pH values registered at some sample sites and the high sensitivity exhibited by *Daphnia magna* to acidic environments (Peters, 1987). The results obtained so far do not discard, however, the possible occurrence neither of more subtle effects on organisms, such as changes in growth and/or reproduction, nor of seasonal patterns of toxicity, eventually associated with climate changes and/or human activities. Additional bioassays will therefore be carried out to assess these potential variations.

CONCLUDING REMARKS AND OUTLOOK

Preliminary hydrogeochemical analyses showed a nitrate and sulphate-enriched composition for these groundwaters, probably resulting from intense urbanisation, sewer leakage and some agricultural practices. Environmental isotopic techniques were indispensable for the study of the impact of urbanisation on geohydrological processes ascribed to Porto urban area. Although rainfall values of tritium tend to return to pre-bomb levels, environmental tritium remains a unique tool in assessing groundwater mean residence time, mobility and vulnerability to pollution. The ^3H results will be presented and discussed in future papers due

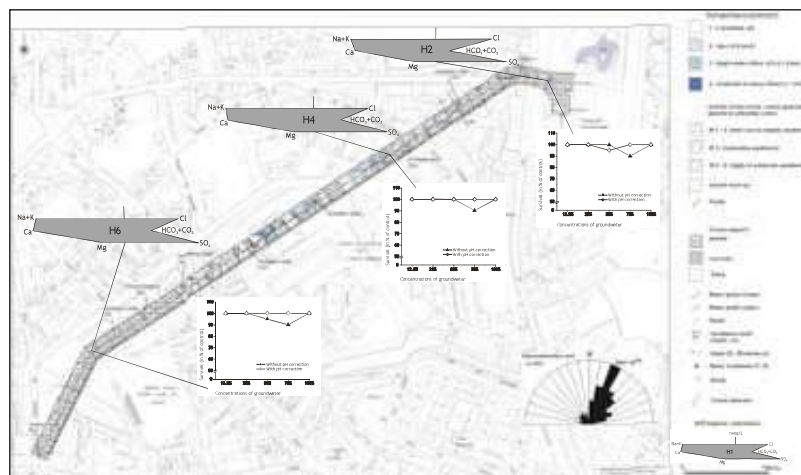
to logistical constrains, in order to assess the vulnerability of groundwater sources. The ecotoxicological evaluation showed no relevant mortality, suggesting a low toxicity potential for the Paranhos groundwater.

The results obtained in this study suggest that part of Porto urban groundwater could be suitable for irrigation uses, but additional tests must be carried out to verify its compliance with existing standards of quality. Specifically, geoenvironmental and ecotoxicological studies are required to assess potential variations in water composition and toxicity associated with seasonal changes in climate and human activities.

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Figure 4
Hydrogeological mapping of one of the Paranhos spring galleries catchworks (Jardim de Arca d'Água — Rua Nova do Regado sector). Hydrogeochemical groundwater composition at three sample sites (Stiff diagrams above the tunnel profile) and corresponding ecotoxicological results (scatter diagrams below the tunnel profile) are shown. The structural diagram (inferior right) shows the main discontinuities sets orientation (n=344).



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