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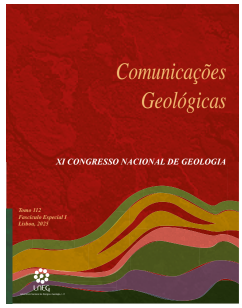
Characterization of saline waters from Ria de Aveiro (Portugal) for potential use in SPA treatments

Caracterização de águas salinas da Ria de Aveiro (Portugal) para potencial uso em tratamentos de SPA



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Abstract: This study aims to characterize the properties of the saline waters from an old saltpan at the Ria de Aveiro, and assess its potential use in skin treatments. Eight water samples were collected from two different areas of an open-air salt SPA, during four different climatic seasons between 2020 and 2021. Physichochemical parameters of the waters revealed an alkaline pH and high electrical conductivity (EC), mainly in the area where salt production takes place (Area 2). Chemical analysis revealead an enrichment in potentially toxic elements (PTEs), namely Cu and Cr^{6+}, in samples of Area 2, collected in the summer. MEV-EDE analysis of the total suspended matter (TSM) showed the presence of NaCl cubic particles, microorganisms (e.g., diatoms) and particles enriched in PTEs. The low concentrations of PTEs does not pose a risk to SPA users, allowing these waters to be used as a liquid phase in SPA treatments for skin diseases.

Keywords: saline waters, thalassotherapy, PTEs, SEM-EDS, Portugal.

Resumo: O presente estudo tem como objetivo caracterizar as propriedades de águas salinas de uma antiga salina da Ria de Aveiro e avaliar o seu potencial uso em tratamentos de pele. Foram colhidas oito amostras de água em duas áreas distintas de um SPA salino ao ar livre, em quatro diferentes estações climáticas, entre 2020 e 2021. Os parâmetros físico-químicos da água revelaram um pH alcalino e elevada condutividade elétrica (CE), principalmente na área onde ocorre a produção de sal (Área 2). A análise química revelou um enriquecimento em elementos potencialmente tóxicos (EPTs), nomeadamente Cu and Cr^{6+}, em amostras da Área 2, colhidas no verão. A análise do material total em suspensão (MTS) por SEM-EDS revelou a presença de partículas cúbicas de NaCl, microorganismos e partículas enriquecidas em EPTs. As baixas concentrações de EPTs não representaram qualquer risco para os utilizadores do SPA, permitindo a utilização destas águas como fase líquida em tratamentos de doenças de pele, em SPA.

Palavras-chave: águas salinas, talassoterapia, EPTs, MEV-EDE, Portugal.

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1. Introduction

The management and use of natural water resources requires knowledge of the water quality. For over 5000 years, SPA therapy has been used to improve health quality, such as leisure, and to recover the well-being of its users (Riyaz and Arakkal, 2011). The therapeutic effects of SPAs natural water baths on chronic skin and rheumatologic diseases have been known worldwide for centuries. According to Riyaz and Arakkal (2011), seas and oceans are fundamental resources for SPA therapies, being the Dead Sea reported as the one of the most important, recognized for thousand years for the "miraculous" curative and cosmetic properties. Thalassotherapy uses seawater to promote life quality by increasing well-being and health (Rodrigues *et al.*, 2022). According to Gomes *et al.* (2021), thalassotherapy combines the therapeutic and preventive use of sea products, with medical guidance. Compared to other more invasive treatments, *e.g.*, oral administration of tablets or capsules through the digestive tract, topical absorption of minerals, dissolved and combined in the thermal waters were used to relieve skin conditions, such as, psoriasis, eczema, irritation and itching, is less detrimental and more effective (Hamidizadeh *et al.*, 2017). Due to the presence of substances such as salts, mineral waters can aid in theraputical treatments of skin psoriasis and dermatitis (Khalilzadeh *et al.*, 2019; Jazani *et al.*, 2023). Studies have showed the effectiveness of salted waters use in the treatment of various diseases. Kim *et al.* (2020) showed its positive effects on fatigue recovery and muscle damage. Tognolo *et al.* (2022) reported the use of balneotherapy with therapeutic exercises as an effective strategy for patients with rheumatic diseases. Emine and Gulbeyaz (2022) registed improvements in the long-term life quality in patients with cancer.
The present study aims to (a) characterize the physicochemical parameters of the Ria de Aveiro saline waters; (b) quantify potentially toxic elements (PTEs) in waters andtotal suspended matter (TSM); (c) estimate risk to the SPA users; and (d) evaluate the Ria the Aveiro waters suitability for application in SPA treatments.

2. Study area

A former saltpan at Ria de Aveiro (Portugal), located in Aveiro periurban area (Figura 1), was recently adapted to an artificial SPA with two distinct areas: Area 1, a limited artificial beach with tidal influence, used for saltwater baths and mud application in skin by its users; and Area 2, a recovered artificial saltpan, with salt production from March to October, used for direct application of salts and salted waters in shallow ponds (Almeida *et al.*, 2022). During this study, improvement works occurred in Area 1, in the beginning of 2021 summer, with inputs of allochthonous sand on the artificial beach margins to improve SPA artificial beach conditions.

Figure 1. Study area and surrounding environment (adapt. Google Earth Pro®, 2022).

Figura 1. Área de estudo e ambiente envolvente (adapt. Google Earth Pro®, 2022)

Ria de Aveiro is a temperate shallow coastal lagoon located on the NW of the Portuguese coast, separated from the sea by a sand bar, and connected to the Atlantic Ocean by a narrow artificial channel (Mil-Homens *et al.*, 2014). Dias *et al.* (1999) considered it as a lagoon with very complex and irregular geometry, characterized by narrow channels and the existence of mud flats and salt marshes (intertidal zones), with a maximum width x length of 10 x 45 km.

Ria de Aveiro has mixture of marine and fresh waters (Lopes *et al.*, 2008), with semi-diurnal tides decreasing with the distance from the mouth (Dias *et al.*, 2000). These authors classified Ria de Aveiro as a mesotidal lagoon, very well mixed, being the Vouga river the major source of freshwaters, with average flows of ~29 m^3/s. Morphologically, Ria de Aveiro has the characteristics of a typical bar-built estuary (Dias *et al.*, 1999).

The study area, geologically, its at the Aveiro Sedimentary Basin, deployed in the Lusitanian Basin, with local formations stratigraphically dated from the Quaternary, with a predominance of alluviums composed by silt, sandy and micaceous silt, silt with shells, muddy and coarse sands that are settle on the existing substrate (Teixeira and Zbyszewski, 1976).

The Ria de Aveiro is an important area that provides natural conditions for fishing, rice plantation, harbour, navigation, and recreation facilities. It is also a place where domestic, agricultural and industrial wastes have been discharged (Dias *et al.*, 1999). Between 1950s up to 1994 the water properties of the study area have been negatively affected over the years, by uncontrolled industrial direct discharges from the Estarreja Chemical Complex (ECC), the second largest Portuguese chemical area, located 10 km N of Aveiro urban area, that have caused a noticeable degradation in the quality of these waters (Lopes *et al.*, 2005). During this period, Ria de Aveiro received highly contaminated effluents from a Hg cell chlor-alkali chemical plant located in the ECC, what resulted in the accumulation of Hg and Pb in the lagoon waters and sediments (Pereira *et al.*, 2009).

For the present study, a total of eight saline water samples were collected in Areas 1 and 2 of the SPA area (Figura 1), in four different seasons between 2020 and 2021 (Table 1). Sampling sites were selected once are the areas were SPA users apply waters in the skin. Samples W1a and W1b were collected before the artificial beach recovery works (Area 1), and W1c and W1d immediately after and months later, respectively. Samples $W2a_1$ and $W2a_2$ were collected in the same sampling point of Area 2, but at different depths ($W2a_1$ at surface and $W2a_2$ at ~ 20 cm depth (bottom) of the shallow pond). The samples were collected at different periods to understand the influence of seasonal variation, despite the reduced number of samples.

Table 1. Samples ID, location, and sampling periods.

Tabela 1. Identificação das amostras, localização e períodos de amostragem.

Sample ID	Area	Period
W1a, $W2a_1$, $W2a_2$	1, 2	Spring 2020
W1b	1	Winter 2021
W1c, W2c	1, 2	Summer 2021
W1d, W2d	1, 2	Autumn 2021

3. Analytical techniques

Water physicochemical parameters (pH, Electrical Conductivity (EC), Temperature (T), and Dissolved Oxygen (DO); Table 2) were determined in situ, using a multiparameter probe, model HANNA HI 98494. Sampling occurred during CoViD19 pandemic restriction periods, what lead to the inability of in situ measurments in 2021 winter and autumn samples. In the laboratory, one liter of each water sample was filtered under pressure until filtration stopped, using weighted GN-6 Metricel® 0,45 µm fibre filters to access the Total suspended matter (TSM). Filters were placed in Petri dishes and oven dried at 40 °C until analysis, and TSM was calculated as follows: $TSM = [(CF + SM) – CF] / V$, where, CF is the clean filter, SM is the suspended matter deposited on the clean filter, and V is the volume, that corresponded to 1 L of the water filtered.

The water samples chemical composition was obtained by visible light spectrophotometry, using an Hanna Instruments® Spectrophotometer, considered the most rapid, simple, low-cost, and easily miniaturized equipment for small volume samples, when compared to other chemical analysis methods (Yang *et al.*, 2020). A Scanning Electron Microscope (SEM), model VEGA LMU, operating in high and low vaccum of image acquisition through secondary and back-difused electron detectors, was used to determine the morphology and size of the individual particles contained in the filters. Particles semi-quantitative chemical characterization was achieved by elemental chemical analysis using an Energy Dispersive Spectrometer (EDS). A mix of protocols was used to access the identification of individual inorganic insoluble particles (Wu *et al.*, 2016). All analyses were performed at GeoBioTec/University of Aveiro.

4. Results and Discussion

Physicochemical parameters are presented in Table 2. Water samples revealed an alkaline pH (7.65 to 8.48), similar to thermal waters studied by Hamidizadeh *et al.* (2017), and EC ranging 44.31 to 200 mS/cm. Highest EC values were recorded in samples from Area 2, as expected, resulting from the much higher salinity in these ponds. Waters T ranged 9.96 – 24.08 °C, and DO, from 2.30 to 10.35 ppm. The winter and autumn water samples parameters could not be measured, but lowest temperature and highest DO would be expected. Samples registed lowest and highest temperature values that corresponded to the spring and summer periods, respectively. The highest DO was found during spring, in agreement with the seasonal characterization by Sharma and Tiwari (2018), with the DO decrease during summer season in agreement with the law of gases solubility. Area 2 samples presented higher TSM content (85.7 – 695.5 mg/L), than Area 1 (29.4 – 48.4 mg/L), as expected given Area 2 higher salt content (Table 2).

Table 2. Physicochemical parameters, and TSM content.

Tabela 2. Parâmetros físico-químicos e teor de MTS.

	W1a	W1b	W1c	W1d	W2a$_1$	W2a$_2$	W2c	W2d
pH	8.29	-	7.96	-	8.48	7.65	7.72	-
EC	44.3	-	53.1	-	107.2	196.6	200	-
T	10.94	-	23.07	-	9.96	17.84	24.08	-
DO	10.35	-	7.43	-	6.72	1.54	2.30	-
TSM	43.6	48.4	44.4	29.4	314.5	85.7	695.5	249.8

EC – Electrical Conductivity (mS/cm); T – Temperature (°C); DO – Dissolved Oxygen (mg/L); TSM – Total Suspended Matter (mg/L); "-" not determined.

The SEM-EDS analysis of the TSM particles revealed the presence of cubic NaCl particles, salts deposited in organic and inorganic particles, reflecting the saline environment of the sampling areas (Figura 2). Results were in line with sediment samples collected in same locations and temporal periods (Almeida *et al.*, 2022), both by microorganisms and Potentially Toxic Elements (PTEs) enrichment.

Elemental concentration of saline water samples is presented in Table 3. Water chemical analysis revealed Ca, and Zn maximum concentrations of 326, and 2.24 mg/L, respectively, indicating an enrichment in these elements. Bromine, Fe, and I water content reached 0.13, 0.09, 0.4 mg/L, respectively, with higher concentrations in Area 2. Ca and Cu, and Fe and Zn presented lower, and higher content, respectively, when compared with Hamidizadeh *et al.* (2017) thermal waters study. According to these authors, after daily bathing in the Dead Sea for weeks, Br, Ca, and Zn increased significantly in the serum of psoriatic patients. Additionally, this study results, according to the medicinal waters classification (Ziemska *et al.*, 2019) were considered below guidelines, which inferred a minimum I, Br, and Fe content of 1, 5, and 10 mg/L, respectively. Sample W2c showed a significative increase of Cu and Cr^{6+} (1.16 and 0.218 mg/L, respectively; Table 3 in bold), suggesting a potential PTEs enrichment by evaporation in this shallow pond (< 20 cm water depth), with low Ca content (below detection limit - bdl).

Table 3. Elemental concentration of saline water samples (mg/L).

Tabela 3. Concentração elementar de amostras de água salina (mg/L).

	W1a	W1b	W1c	W1d	W2a$_1$	W2a$_2$	W2c	W2d
Br	bdl	0.13	0.03	0.04	0.01	0.10	0.10	0.05
Ca	168	315	284	283	224	326	bdl	283
Cu	0.08	0.51	0.10	0.16	0.31	0.16	**1.16**	0.17
Cr^{VI}	0.007	0.010	0.003	0.005	0.050	0.003	**0.218**	0.053
Fe	0.03	0.08	0.08	0.08	0.04	0.09	0.08	0.03
I	bdl	0.1	bdl	0.1	0.4	bdl	0.3	bdl
Mn	0.2	0.4	0.3	0.2	0.6	0.3	0.5	0.2
Zn	1.68	2.15	1.89	1.92	2.17	2.24	1.53	2.14

a)

b)

c)

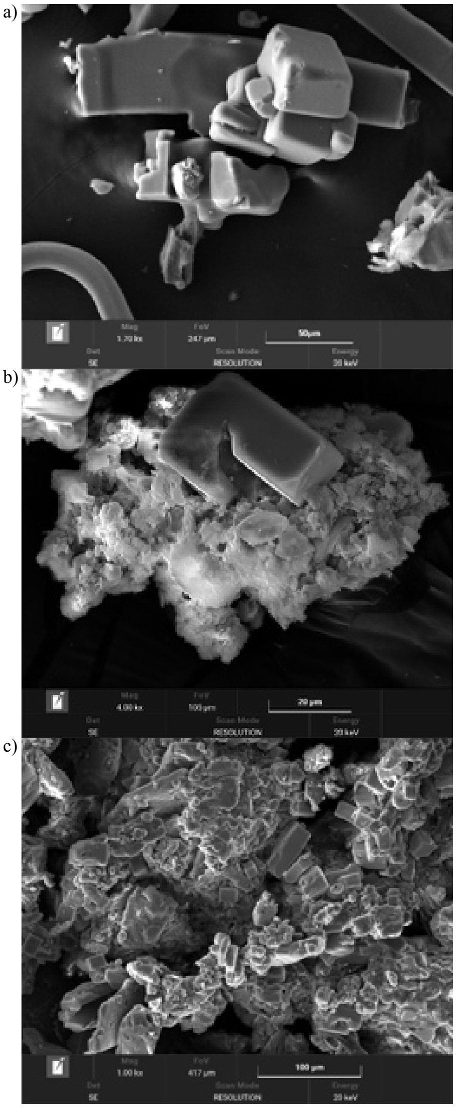

Figure 2. SEM-EDS images of suspended matter from saline water samples: (a) salt cubic particles (NaCl); (b) salt particle deposited on an agglomerate of organic (e.g., diatom) and inorganic material (e.g., quartz and particles enriched in Al, Fe); (c) salt agglomerates associated with organic and inorganic material enriched in PTEs.

Figura 2. Images de MEV-EDE da matéria total em suspensão nas amostras de água salina: (a) partículas cúbicas de sal (NaCl); (b) partícula de sal depositada sobre um aglomerado de material orgânico (por exemplo, diatomáceas) e inorgânico (por exemplo, quartzo e partículas enriquecidas em Al, Fe); (c) aglomerados de sal associados a materiais orgânicos e inorgânicos enriquecidos em EPTs.

5. Conclusions

Water samples revealed alkaline pH and high electrical conductivity. Morphological properties of the total suspended matter were typical of saline environment conditions. Despite the chemical analysis showed a Cu and Cr^{6+} enrichment, those were low PTEs concentrations that does not pose a risk to humans, making these waters suitable for SPA therapies. In general, samples from Area 1 were the most suitable for this thalassoterapy, due to better properties, such as lower PTEs content. Results were in agreement with sediment samples collected at the same periods and locations at Ria de Aveiro lagoon. Studies are being conducted to use these waters in peloids maturation processes, using sediments from the same sampling site.

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