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The Quality Stability Assessment of a Thermal Spring Used for Therapeutic Purposes

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ABSTRACT

Thermal waters have a global distribution and find extensive therapeutic use. In Morocco, which boasts more than twenty high-quality therapeutic thermal springs, few studies have focused on the quality of these waters. In this context, the present study evaluated the water quality using physicochemical, bacteriological, and radioactive parameters for the Benkachour thermal spring waters in Morocco. The results indicate that all chemicals, bacteriological, and radiological parameters are below the standards, except for global beta activity and temperature, which makes it hyperthermal, with an annual average temperature of 50.54°C. According to the Piper diagram, the water type is chloride-sodium-potassium. On the basis on these results, it was concluded that thermalism in the Eastern region of Morocco, specifically Benkachour in Oujda, can contribute to sustainable tourist development at the national and international levels due to the quality of the parameters analyzed and can be an effective complementary approach in the treatment of low-grade pathologies. The data from this study can serve as a baseline for assessing future changes and defining standards for the quality of hydrothermal baths as well as balneotherapy worldwide.

Keywords: thermal waters, balneotherapy, hydrothermal treatments, water quality.

INTRODUCTION

In the early fourth century B.C., the earliest known medical text, the Corpus Hippocraticum, examined the concept of water from a scientific perspective. As history unfolded, individuals began to uncover the therapeutic qualities of water, including its ability to promote healing and protect against diseases (Melillo, 1995). While the Greeks played a pivotal role in the inception of balneotherapy, it flourished during the Roman Era when thermal baths became a customary health practice (Cilliers et al., 2006). Hydrology emerged as a genuine scientific discipline, and thermal treatments were prescribed with precise guidelines and subjected to medical oversight (Hakam et al., 2000; Pécastaings et al., 2009). Thermal medicine, presently recognized as a medical discipline, harnesses the healing properties of thermal water for therapeutic and rehabilitative objectives (Fioravanti et al., 2011). Its effectiveness has been extensively substantiated across various conditions, ranging from rheumatic ailments to cardiovascular disorders (Oyama et al., 2013). Additionally, numerous investigations have provided evidence of the impact of thermal water on skin conditions and its role in promoting skin rejuvenation (Liang et al., 2015). Specifically, some thermal springs with compositions and physicochemical qualities make them suitable for

therapeutic baths, having health benefits, or treating various illnesses (Pécastaings et al., 2009; Fikri et al., 2015). Morocco, home to more than twenty first-rate therapeutic thermal springs, has been the subject of several studies examining a selection of these thermal waters and their use as therapeutic baths in cosmetics formulations for their anti-irritant effects or to treat several skin diseases like psoriasis, atopic dermatitis (Lakhdar et al., 2006; Fikri et al., 2015; Fikri-Benbrahim, 2021).

The Moroccan's Eastern region possesses significant tourism resources, yet it remains isolated from national tourism circuits despite its diverse potential (including beach, spelunking, cultural, thermal, mountain, and religious tourism). Among the famous thermal stations in the region are the Fezouane and Benkachour stations, which have been known and frequented by locals for a long time. However, to the authors' knowledge, only a few studies (El Guerrouj, 1996) have delved into the physicochemical and microbiological quality of thermal waters in this region. These studies relied on a single sampling event that does not meet Moroccan standards (Article 55 of Law 36.15 concerning water) for the stability of the parameters examined in thermal waters to assess their quality. Furthermore, there has been no assessment of radioactive contamination in these studies. This study aimed to evaluate three aspects: (i) microbiological quality, (ii) identification of the physicochemical composition, and (iii) assessment of radioactive contamination.

MATERIALS AND METHODS

Study site

The Benkachour thermal station is in the center of the city of Oujda, which is part of the Angad plain and the Oujda Mountains. It is situated between the southern High Plateaus and the eastern Béni Snassen mountains. Geographically, Benkachour is located at coordinates: Longitude 01°50'00", Latitude 34°33'00", at an altitude of 580 meters, covering an area of one hectare, as represented in Figure 1.

Sampling

Sampling was carried out monthly throughout the year 2021 at the Benkachour station. Samples

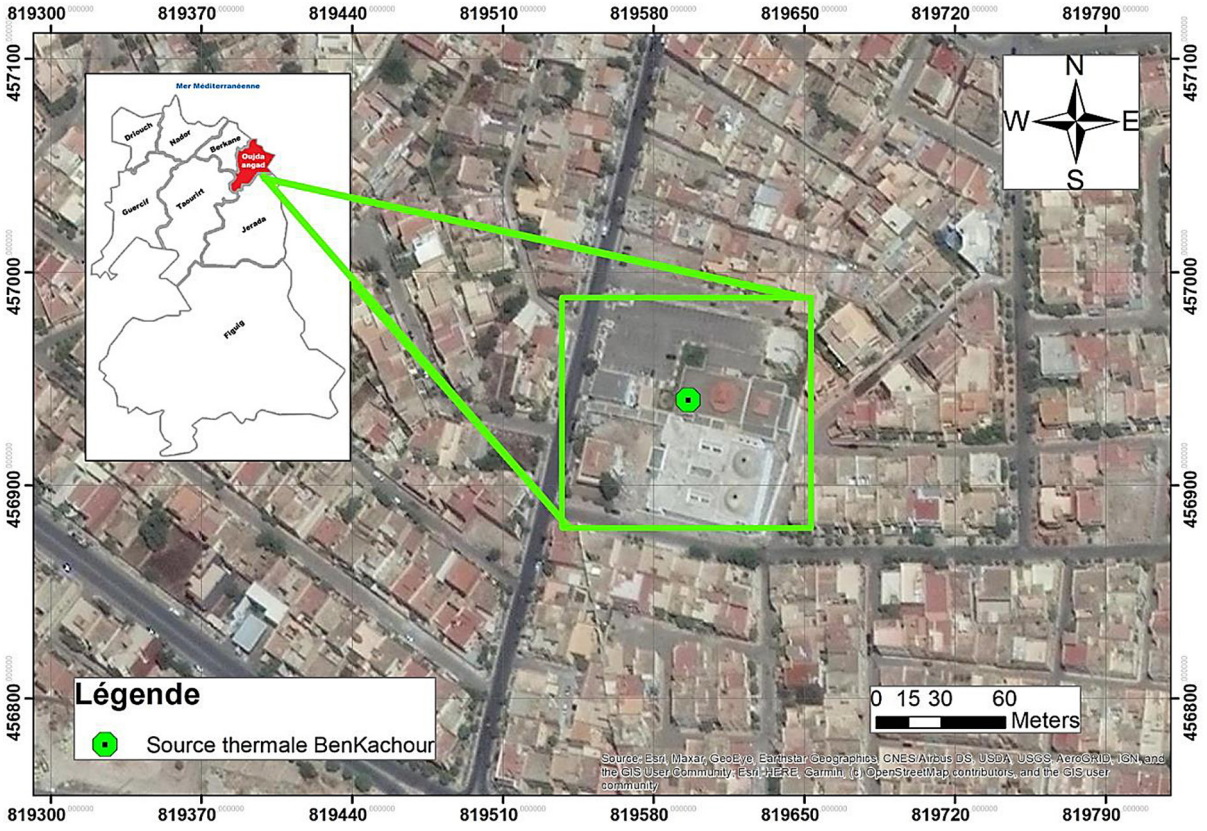

Figure 1. Location of the Benkachour Thermal Station, Oujda, Morocco

were aseptically collected in sterile bottles of 1000, 500, 250, and 50 ml, following the standards described in Rodier (Rodier et al., 2016). They were transported to the Laboratory of Hydrology and Thermalism in the Department of Biology and Environment at the National Institute of Hygiene (INH) in Rabat, Morocco, in isothermal containers at 4°C, and analyzed within eight hours of collection.

Physicochemical, microbiological, and radiological analyses

The physicochemical parameters studied for Benkachour water included on-site qualitative measurements and laboratory analysis. Temperature, pH, and conductivity were measured on-site and supplemented in the laboratory. The pH value was determined based on the method described in the Moroccan standard 03-7-009(2012), and the measurement of electrical conductivity of the Benkachour water was conducted according to the Moroccan standard NM03-7-011(2001). Nitrates were measured in the laboratory using spectrometry of molecular absorption and continuous-flow automated analysis based on electromagnetic radiation ranging from ultraviolet to radio waves with a wavelength of λ=415 nm. Major elements such as Na^+ and K^+ were determined using flame atomic emission spectrophotometry with a Perkin Elmer 430 spectrophotometer, while Ca^{2+} and Mg^{2+} were quantified using volumetric complexation with Ethylene Diamine Tetraacetic Acid (EDTA) described in Rodier (Rodier et al., 2016). Chloride (Cl^-) was measured through volumetric titration using the mercuric nitrate method, and HCO_3^- was determined through titrimetry, electrochemical method with a specific electrode, continuous-flow automatic analysis, and ion chromatography in accordance with the Moroccan water standards NM03-7-024 (1990).

The determination of trace metal element pollutants (TMEP) such as Cu, Mn, As, Se, and Hg was performed using the electrothermal atomization atomic absorption technique. The study of pesticide residues was conducted through gas chromatography (GC). The microbiological study involved the enumeration of revivable microorganisms at 22°C and 37°C, fecal coliforms, *Escherichia coli*, intestinal *Enterococcus*, spores of sulfite-reducing anaerobes at +37°C and +55°C, *Pseudomonas aeruginosa*, fecal coliforms, fecal *Streptococcus*, *Salmonella*, *Legionella*, and *Legionella pneumophila* using filtration methods according to the ISO 9308-1, ISO 7899-2, ISO 6461-2, and ISO 6222 standards. Radiological control of total activity values for α and β elements was conducted at the National Radioprotection Center in Salé using the method of evaporation reduction of large volumes of filtered water with a gas detector according to NM 03.7.001 (2006).

Graphical and statistical methods

Data analysis was carried out in several steps using the RStudio software (version 2023.3.0.386). Firstly, descriptive statistics were performed for all variables using the "psych" package, providing clear information on data distribution and variability. Subsequently, a Principal Component Analysis (PCA) was conducted for all samples. PCA was selected as a powerful analytical tool in this research article due to its ability to uncover latent patterns within complex hydrochemical datasets. Lastly, to classify the studied water groups and identify their facies, well-known methods, namely the Piper and Schoeller diagrams were employed (Piper,1944; Schoeller, 1977).

RESULTS AND DISCUSSION

Statistical analysis of physicochemical parameters

Table 1 compares the physicochemical water quality parameters against the maximum acceptable value according to the Moroccan Standard NM 03.7.001 (MAV). The concentrations of physicochemical parameters of the Benkachour water show temperature values ranging from 48.5°C to 52°C, with an average temperature of 50.5°C. According to Verdeil (1982), these values confirm their hyperthermal nature, which has already been established in the work of El Guerrouj in 1996 (Verdeil, 1982; El Guerrouj, 1996). Furthermore, the pH values of the 12 samples showed results close to neutrality, with an average of 7.7. The electrical conductivity values are around an average of 5016 ± 99.7 µS/cm, confirming their hardness. The nitrate values in the samples recorded an average value of 6.41 ± 0.48 mg/l, which is higher compared to the values recorded in the works carried out at the Faculty of Sciences in Oujda in 1994 by EL Guerrouj, which showed a value of 2.89 mg/l (El Guerrouj, 1996).

Table 1. Descriptive Statistics for Physicochemical Parameters of Benkachour Water in 2021

Parameter	Unit	Minimum	Maximum	Mean ± SD	MAV*
pH	-	7.36	7.87	7.73 ± 0.18	6.5 < pH < 8.5
Temperature	°C	48.5	52.0	50.5 ± 1.3	Acceptable
Conductivity	µS/cm at 20°C	4740	5583	5016 ± 99.7	2700
Nitrates	mg/l	5.33	7.83	6.41 ± 0.48	50
Sodium	mg/l	886	944	912 ± 16.42	--
Chloride	mg/l	1304	1725	1439 ± 141	750
Bicarbonate	mg/l	317	325.3	319 ± 2.55	--
Calcium	mg/l	87.18	104.21	93.19 ± 3.81	--
Potassium	mg/l	8.1	9	8.55 ± 0.19	--
Sulfates	mg/l	48.9	98	82.5 ± 11.47	400

Note: * The maximum acceptable value according to the Moroccan Standard NM 03.7.001 (MAV).

The recorded concentrations of potassium, sodium, chlorides, bicarbonate, calcium, and magnesium are significant, explaining the high mineralization of the waters from the Benkachour thermal source. Additionally, the recorded sulfate value is 82.5 mg/l, which falls within the range of potability standards according to Moroccan standards (NM 03-7-001).

Principal component analysis (PCA)

According to the PCA, represented in Figure 2, of the Benkachour water, the variables were correlated to two principal components, which accounted for 55.21% of the Months (or variables) cloud total variability. This percentage is relatively high; thus, the first plane represents the data variability. This value is greater than the reference value that equals 49.65%. The dimension 1 opposes Months such as 8, 7 and 12 to Months such as 11 and 10. The group including Months 8, 7 and 12 shares:

- high values for the variables HCO_3^-, TAC and MS (variables are sorted from the strongest);
- low values for the variable pH;
- the group in which the Months 11 and 10 stand is sharing;
- high values for the variables Ca^{2+} and K^+;
- low values for the variables SO_4^{2-}, Mg^{2+} and Na^+;
- the dimension 2 opposes Months such as 1 and 9 to Months such as 8, 7 and 12.

The group including Months 1 and 9 stand shares:

- high values for the variable SO_4^{2-};
- low values for the variable HCO_3^-;

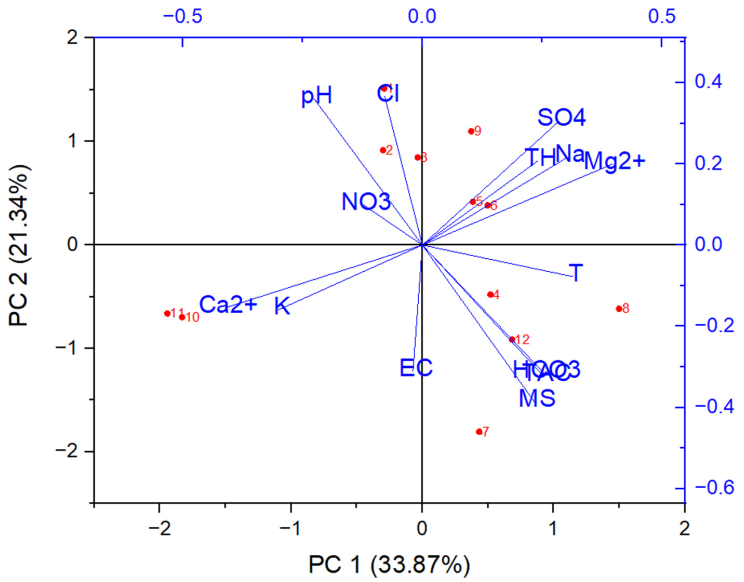

Figure 2. Months and variables factor map (PCA)

- the group including Months 8, 7 and 12 stand shares;
- high values for the variables HCO_3^- TAC and MS;
- low values for the variable pH.

The hydrochemical classification of water

Water classification according to the Piper diagram

The Piper diagram (Figure 3) has shown the predominance of sodium chloride in the water of Benkachour, giving it chloride-sodium-potassium facies. Thus, the excess of sodium, chloride, and bicarbonate suggests the presence of both carbonate formations and saline series based on sodium chloride (NaCl) in the subsurface of the region.

Classification of water by Schöller-Berkaloff

The Schöller-Berkaloff diagram (Figure 4) indicates that the water has higher values of chloride and sodium. These results partially align with those of the Piper diagram (Figure 3), which also indicates chloride-sodium-potassium facies.

Trace metal elements

The concentrations of trace metal elements in the Benkachour water (Table 2) are below the standards for drinking water. Some elements recorded elevate values like copper, manganese, which record values of 1.1 and 0.1 mg/l, respectively. but it remains below the concentration recommended by the Moroccan drinking water standards. These elevated levels could result from rock degradation or possibly originate from certain volcanic formations in the region (Tarik et al., 2023). According to the Moroccan standard NM 03.7.001 for human drinking water, water from the Benkachour plant complies with toxic substance standards.

Pesticides

The water from Benkachour recorded very low levels of pesticide residues (Table 3), which do not exceed the maximum concentrations prescribed by specific Moroccan standards for drinking water (NM03.7.001). This indicates the absence of agricultural pollution.

Microbiological parameters

The results of the bacteriological analysis represented in the Table 4 shown the absence of total coliforms, *Escherichia coli, Enterococcus intestinalis*, sulfite-reducing anaerobe spores, *Pseudomonas aeruginosa*, fecal streptococci, Salmonella, and Legionella, which are responsible for water

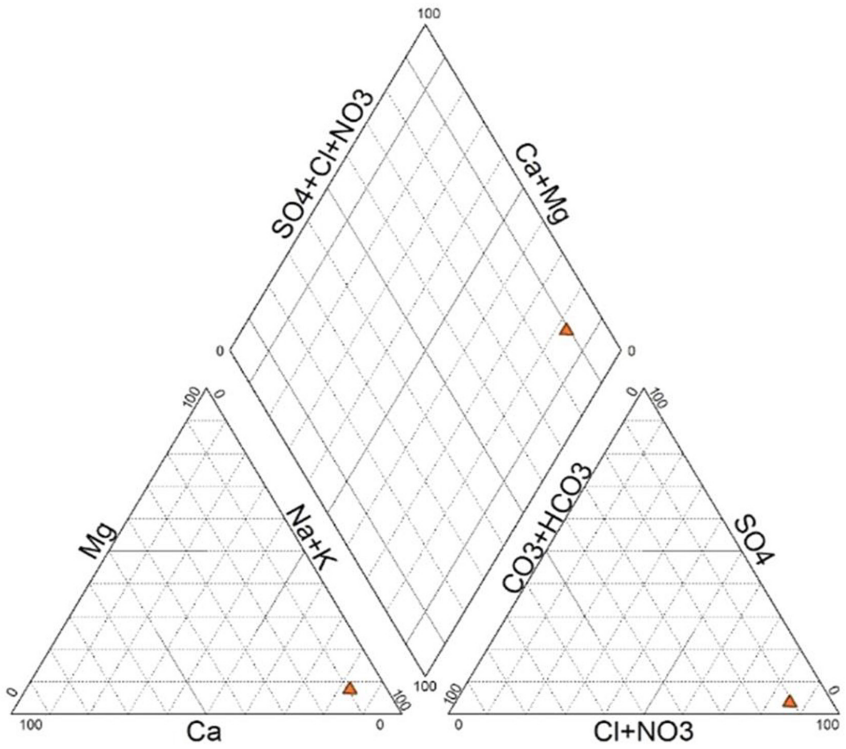

Figure 3. Piper diagram of the Benkachour water

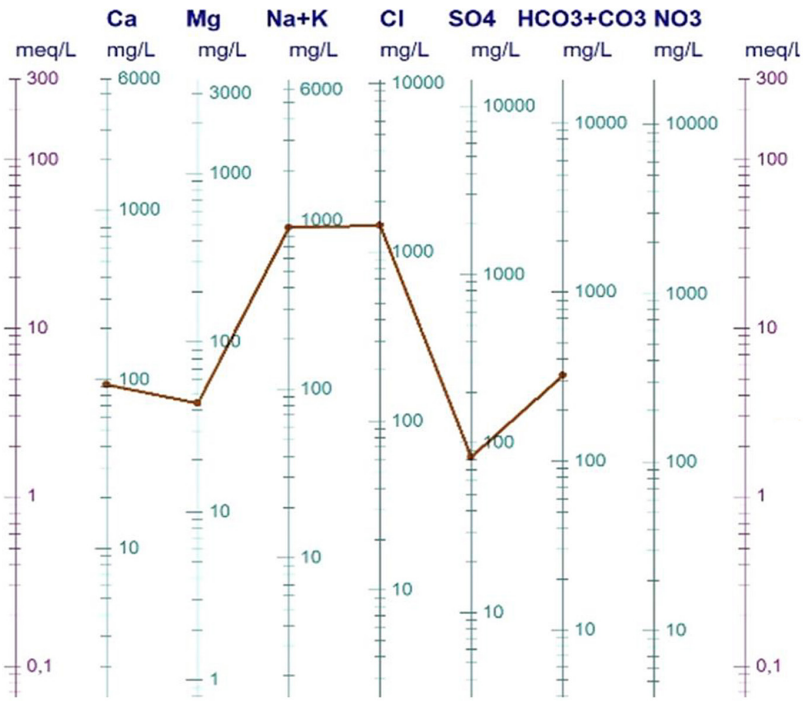

Figure 4. Schöller-Berkaloff diagram of the Benkachour water

Table 2. Trace metal element pollutants values in the Benkachour waters

Trace metal elements	Unit	Values	MAV*
Pb	mg/l	0.0067	0.01
As	mg/l	0.0092	0.01
Cu	mg/l	1.1	2
Mn	mg/l	0.1	0.5
Se	mg/l	0.0069	0.01
Hg	mg/l	0.0002	0.001

Note: *the maximum acceptable value according to the Moroccan Standard NM 03.7.001 (MAV).

non-compliance. Furthermore, these results confirmed the presence of revivable microorganisms at 22°C and 37°C but within the permissible limits according to Moroccan standard NM 03.7.001 related to human consumption. This allows concluding that the water from this site is well protected against contamination by microorganisms. This is not the case in several studies conducted worldwide on various thermal stations, which revealed the presence of several pathogens, sulfite-reducing anaerobes, *Pseudomonas aeruginosa*, *E. Coli*, and *Legionella* (Germinario et al., 2012; Antolín et al., 2006).

Radiological parameters

Table 5 represents the analyses of Albha and Beta Global radioactivity in the Benkachour water; the value of global alpha activity follows the Moroccan standard 03.07.001, but global beta activity is over the Moroccan standard. Beta activity is mainly caused by ^{40}K and short-lived daughters of ^{238}U, ^{234}Th, and ^{234}Pa (Forte et al., 2007).

CONCLUSIONS

Natural thermal waters have been used for centuries in treating various pathologies due to their therapeutic effects. Today, a renewed interest in these waters is driven by a desire to return to natural remedies. Indeed, their properties, like thermal and chemical effects, make them suitable for various clinical situations. Still, these thermal establishments are exposed to various contamination risks by various pollutants, and health risks have become major health risk concerns. Environmental impact studies should be conducted before

Table 3. Values of pesticide molecules in the Benkachour waters

Pesticide molecules	Concentration (µg/l)	MAV*
Alachlore	< 0.01	0.1
Endrine aldéhydique	< 0.01	0.1
Aldrine	< 0.01	0.03
Alfa-HCH	< 0.01	0.1
Bêta-HCH	< 0.01	0.1
Bifenox	< 0.01	0.1
Captane	< 0.01	0.1
Carbaryl	< 0.01	0.1
Chlorfenviphos-Ethyl	< 0.01	0.1
Chlortal-diméthyle	< 0.01	0.1
Cyperméthrine	< 0.01	0.1
Dieldrine	< 0.01	0.03
Heptachlore	< 0.01	0.03
Lindane	< 0.01	0.1
DDT	< 0.01	0.1
Parathion éthyle	< 0.01	0.1
Propazine	< 0.01	0.1
Perméthrine	< 0.01	0.1
Carbendazime	< 0.01	0.1
Malathion	< 0.01	0.1

Note: *the maximum acceptable value according to the Moroccan Standard NM 03.7.001 (MAV).

Table 4. Results of bacteriological analyses of water from the Benkachour thermal spa

Parameter	Average (12 months) ± SD	MAV*
Microorganisms revivable at 22 °C (1 ml^{-1})	0.17 ± 0.00	100/ 1 (ml)
Escherichia coli 100 ml^{-1}	0.00 ± 0.00	00
Enterococcus intestinalis 100 ml^{-1}	0.00 ± 0.00	00
Spores of sulphite-reducing anaerobes +37 °C 50 ml^{-1}	0.00 ± 0.00	00
Pseudomonas aeruginosa 100 ml^{-1}	0.00 ± 0.00	00
Microorganisms revivable at 37 °C 1 ml^{-1}	0.25 ± 0.00	20/ 1 (ml)
Fecalcoliforms 100 ml^{-1}	0.00 ± 0.00	00
Fecal Streptococci 100 ml^{-1}	0.00 ± 0.00	00
Spores of sulphite-reducing anaerobes + 55 °C 50 ml^{-1}	0.00 ± 0.00	00
Salmonella 1 (l^{-1})	0.00 ± 0.00	00
Legionella 1 (l^{-1})	0.00 ± 0.00	00
Legionella pneumophila 1 (l^{-1})	0.00 ± 0.00	00

Note: * The maximum acceptable value according to the Moroccan Standard NM 03.7.001 (MAV).

Table 5. Radiological parameters of the Benkachour waters

Parameters	Unit	BENKACHOUR water	MAV*
Global alpha activity	Bq/l	0.05	0.1
Global beta activity	Bq/l	1.27	1

Note: * The maximum acceptable value according to the Moroccan Standard NM 03.7.001 (MAV)

exploiting thermal springs to prevent these health risks. In the conducted case study, the stability of the quality of natural thermal-mineral waters in Benkachour demonstrated that this water is hyperthermal, with chloride-sodium-potassium facies. Bacteriological analyses showed the absence of pathogenic microorganisms in these waters. Furthermore, the radioactive analysis of the waters from the station revealed compliance with the Moroccan standards NM 03.7.001 except for global beta activity. The data obtained in this study can be used as a baseline for evaluating future changes and setting standards for hydrothermal bath and balneotherapy quality in the world.

This study has demonstrated the stability of the quality of the parameters studied in this site according to the Moroccan standards. The potential benefits of this thermal spring are perhaps due to a combination of factors, of which thermal and chemical effects are the most important. However, standardized protocols and in vitro studies should be conducted to consider these waters for therapeutic purposes to confirm the cause-and-effect relationship.

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