

Article

Environmental Radioactivity, Ecotoxicology (^{238}U , ^{232}Th and ^{40}K) and Potentially Toxic Elements in Water and Sediments from North Africa Dams

Younes Hamed ^{1,2,3,*}, Yosra Ayadi ¹, Rihab Hadji ⁴ , Amina Ben Saad ¹, Matteo Gentilucci ⁵  and Elimame Elaloui ¹

¹ Laboratory for the Application of Materials to the Environment, Water and Energy (LAM3E), Faculty of Science of Gafsa, University of Gafsa, Gafsa 2112, Tunisia; ayadiyosraa@yahoo.fr (Y.A.); aminabensaad@yahoo.fr (A.B.S.); limam_aloui@yahoo.fr (E.E.)

² Department of Earth and Atmospheric Sciences, Science and Research Building 1, University of Houston, 3507 Cullen Blvd, Room 312, Houston, TX 77204, USA

³ TDS Company, Riyadh 11342, Saudi Arabia

⁴ Laboratory of Applied Research in Engineering Geology, Geotechnics, Water Sciences, and Environment, Setif 1 University, Setif 19000, Algeria; hadjirihab@yahoo.fr

⁵ School of Science and Technology, Geology Division, University of Camerino, 62032 Camerino, Italy; matteo.gentilucci@unicam.it

* Correspondence: hamedhydro.tn@gmail.com

Abstract: The natural radioactivity of ^{238}U , ^{232}Th and ^{40}K was measured in water and sediment samples collected from Sidi Salem dam (Tunisia) and Aïn Dalia dam (Algeria) in the Tuniso-Algerian transboundary basin. The samples were measured using a TERRA detector of gamma, beta, and alpha rays, and atomic absorption and gamma-ray spectrometry were used to analyze the levels of radionuclides and toxic elements, respectively. Potentially toxic elements (Fe, Pb, Zn, Ni, Cr, Cu and Cd) and associated health risks in surface water and sediment of dams were investigated in this present study. The concentrations of Fe, Pb, Zn, Ni, Cr, Cu and Cd in surface water ranged from 5.430 to 9.700 $\text{mg}\cdot\text{L}^{-1}$, 0.022 to 0.168, 0.018 to 0.142, 0.065 to 0.366, BDL to 0.0351, BDL to 0.071 and BDL to 0.048 $\text{mg}\cdot\text{L}^{-1}$, respectively. In the sediments, the concentrations of Fe, Pb, Zn, Cu, Ni, Cd and Cr were of the order of 136.7, 3.41, 3.22, 0.213, 0.182, 0.15 $\text{mg}\cdot\text{L}^{-1}$ and BDL, respectively. The mean radioactivity rates in the water samples were 1.72, 0.068 and 94.6 $\text{Bq}\cdot\text{L}^{-1}$ for ^{238}U , ^{232}Th and ^{40}K , respectively (Tunisia dam), and were 1.9, 0.09 and 131.43 $\text{Bq}\cdot\text{L}^{-1}$ for ^{238}U , ^{232}Th and ^{40}K , respectively (Algeria dam). The mean ^{238}U , ^{232}Th and ^{40}K radioactivity concentrations measured in the sediment samples were 2.67, 0.18 and 197.87 $\text{Bq}\cdot\text{kg}^{-1}$, respectively (Tunisian dam), and were 4.34, 0.27 and 287.61 $\text{Bq}\cdot\text{kg}^{-1}$, respectively (Algeria dam). The activity concentration of ^{40}K was higher than that of ^{238}U and ^{232}Th for the water and sediment samples. The activity concentrations follow the order $^{40}\text{K} > ^{238}\text{U} > ^{232}\text{Th}$. The cumulative impact of these radio-geochemical elements can cause immediate serious problems in the ecosystem due to their high potential toxicity to the environment and human health in this study area and can be transposable to any other similar region. A good knowledge of monitoring quality and quantity for transboundary water resources and international collaborations are essential to safeguard human health (women's breast cancer, thyroid cancer, neurological impact) and avoid conflicts, especially during climatic upheavals of drought.

Keywords: radioactivity; water quality; potentially toxic elements; health risks; potential toxicity



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1. Introduction

Natural radiation is a normal part of the environment that emanates from two main sources: cosmic radiation, which originates in outer space and passes through the atmosphere, and the decay of radionuclides (radioactive isotopes or radioisotopes) in the soil and the rock. Radionuclides undergo spontaneous disintegration into daughter nuclides with an associated emission of ionizing radiation in the form of alpha and beta particles, gamma

rays and other cosmic rays. Daughter nuclides may be stable or may themselves be radionuclides which also undergo radioactive decay. Rainwater, surface water and groundwater can contain radioactive elements (radionuclides). Radionuclides in water can be a concern for human health because several are toxic and/or carcinogenic. Radionuclides (^{18}O , ^2H , ^3H , ^{13}C and ^{14}C) are useful tools for determining the hydrodynamics of groundwater, the residence time, the intercommunication between the aquifers, the recharge rate of aquifers, the radioactivity rate disintegration, the water quality, the contamination source/rate and the age of groundwater in an aquifer or of sediment deposited at the bottom of a water body (dead zones of dams) [1–3].

Radionuclides of natural origins are normally present in different amounts in drinking water (rainwater, surface water and shallow/deep water). They are released from rocks that form the water reservoirs as happens with composition (anions, cations and different isotopes): erosion, transportation, sedimentation, dissolution and oxidation–reduction bring potentially toxic elements “PTEs” (Fe, Pb, Zn, Ni, Cr, Cu and Cd) and radioactive elements (e.g., ^{238}U , ^{232}Th , ^{226}Ra , ^{222}Rn and ^{40}K) from geological rocks into the water or introduce them in rainwater as atmospheric pollution [4–6].

The Majerda transboundary basin, a prominent watershed in North Africa, extends from Eastern Algeria, near Souk Ahras, and stretches into Tunisia. Covering a vast expanse of approximately 23,175 Km^2 , with around 7700 Km^2 lying within Algeria’s borders, it plays a crucial role in the region’s water resources. The exploitation of uranium-rich ore deposits such as diapiric rocks in the Atlas of Algeria (Souk Ahras basin), together with nuclear development around the world, has increased the risk of anthropogenic radioactive pollution. Protection against such risks is essential. Aware of the importance of the problem, the Tunisian government has already launched a program that envisages the development of studies of the radiological environment in collaboration with the International Atomic Energy Agency (IAEA) and with the World Health Organization (WHO).

This study was initiated in the Tuniso-Algerian transboundary basin, known, in particular, for its richness in mines (e.g., phosphate-U, Pb/Zn, Fe), diapiric sediments (e.g., clay, limestone, gypsum, salt) and volcanic (magmatic and metamorphic rocks) deposits characterized by an average uranium content of 35 ppm. The main objective of this study was to perform in situ measurements of the natural gamma radioactivity and the geochemical analysis of ^{238}U , ^{232}Th , and ^{40}K and the potentially toxic elements (PTEs) Fe, Pb, Zn, Ni, Cr, Cu and Cd in the greatest dams in the Tuniso-Algerian transboundary basin (Sidi Salem dam in Tunisia and Ain Dalia dam in Algeria) and to estimate the naturally occurring radioactivity in the surface water and the sediment from the dead zones of the dams. A comparative study was performed with analyses from non-contaminated areas (Beni Haroun Dam, Algeria, and Sidi El Barak, Tunisia).

Human health exposure to a high concentration of background radiation (cumulative effect) may cause health risks. Radionuclides naturally present in the atmospheric environment, water resources (surface and groundwater), sediment or food above the international limit can provoke cardiovascular epidemics and other problems of excessive radiation dosing [7]. In the current study area, water quality deterioration has been reported, and the dependence of the inhabitants on the water supply available lacks security guarantees [8,9]. Many scientific reports have been conducted on the direct investigation of radioactivity levels in soil, water, food and sediment around the world, including in North African countries (Tunisia and Algeria) [10,11]. Human health requires a trace quantity (micro/nanograms) of certain elements for cellular metabolism. It is not that every geochemical element is harmful to life. Living organisms require varying amounts of metal or trace elements. Iron, cobalt, copper, zinc, molybdenum and manganese are required for human health. Excessive levels can be damaging to organisms. These elements exert their toxic effect by combining with one or more reactive groups essential for normal physiological functions [12,13]. There are no immediate harmful effects on health due to exposure to diapiric/metamorphic rocks, but in the long term, due to cumulative effects, everything is possible and plausible. Several countries in the world suffer from this type of problem, including Tunisia, Algeria,

Saudi Arabia, Kuwait, Iran, Qatar, Oman, Spain, Portugal, Niger and Nigeria [14,15]. In southern Tunisia, recent studies carried out by Hamed et al. [16], have shown high levels of radioactivity (e.g., U, Th, Ra, Rn, Cs) and PTEs (e.g., Cd, Pb, Zn, Fe, Cr, Sr, Li) exceeding the established standards in the phosphate-U/petroleum and geothermal basin known as the North Western Sahara Aquifer System (NWSAS) of the great transboundary basin of the North Africa–Southern Mediterranean Basin, divided between Algeria, Tunisia and Libya. The damage to human health is evidenced by an abnormal level of cancer disease in this phosphate-U-mining-polluted basin (Gafsa, Sfax, Gabes, Tozeur and Kebili), which affects all ages and both sexes. Therefore, the objective of this paper is to show the radiological effect and deduce the level of possible risk from the level of radioactivity and PTEs measured in surface water and sediments in the Aïn Dalia and Beni Haroun dams in Algerian territory (recharge zone) and the biggest dams of Sidi Salem and Sidi El Barak in Tunisian territory (discharge area).

2. Study Area

The Majerda Tuniso-Algerian transboundary basin is located in North Africa between Algeria (recharge area) and Tunisia (discharge area) (Figure 1a). This basin is characterized by specific geomorphology influenced by the Euro-African collision plates (Figure 1b). It is characterized by the existence of natural volcanic deposits (diapiric, magmatic and metamorphic rocks) in the north of the Atlas transboundary Tuniso-Algerian basin. The hydrographic network is a dendritic type; it is made up of a single permanent watercourse (Majerda River) belonging to the cross-border Majerda–Mallegue watershed, of which the upstream is in Algerian territory and the downstream is in Tunisian territory. The entire hydrographic network converges towards the Tunisian Mediterranean coast/Carthage Sea.

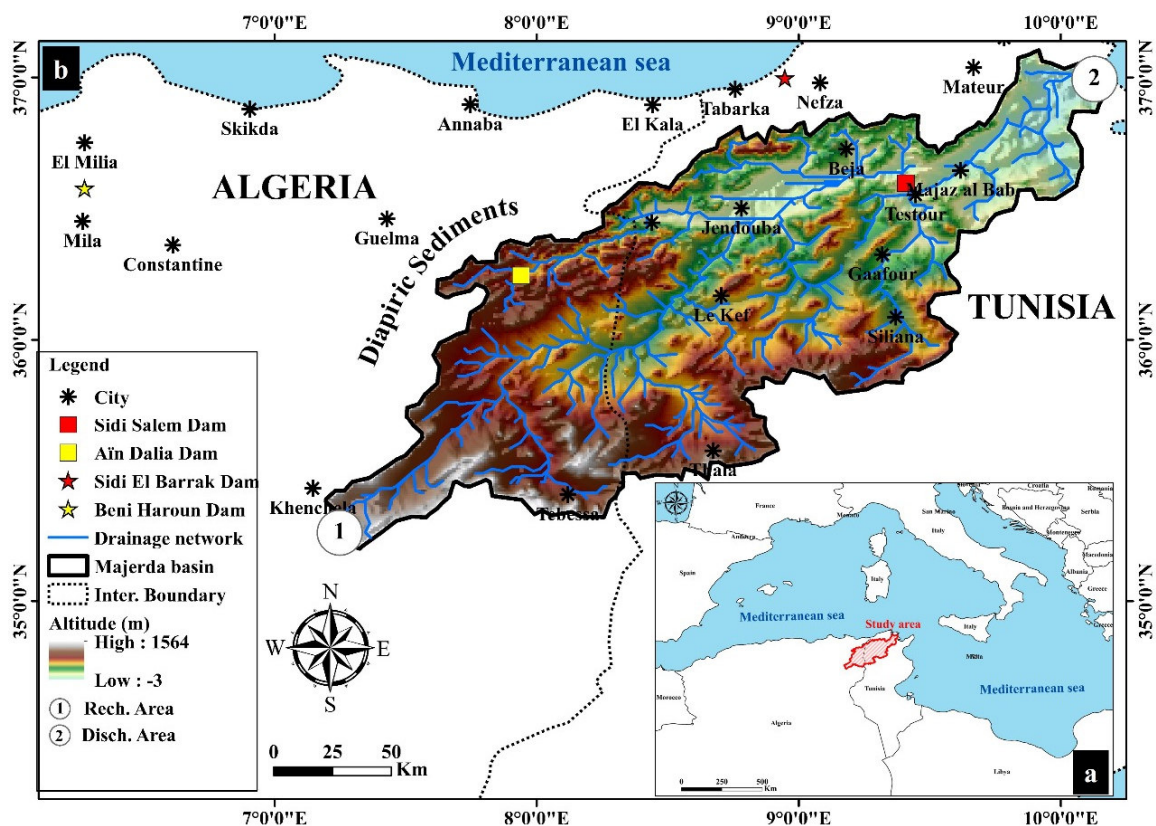


Figure 1. Geographic location of the study area (Majerda Tuniso-Algerian transboundary basin). (a) location of the study area vs. North Africa; (b) location of the study area vs. Euro-African collision plates.

In general, in the Southern Mediterranean Basin, dams are essential for sustainable water supply due to the unbalanced distribution and the irregularity of precipitation during the wet period of the year (September to April). During the wet period, the winter and spring, the reservoirs of dams store the water, while during the dry period of summer (May to August), the water is used for domestic and agricultural use and sometimes for industrial use. The Majerda Tuniso-Algerian transboundary basin falls within the sub-humid climatic zone, characterized by very high rainfall ($500\text{--}1200\text{ mm}\cdot\text{y}^{-1}$) and dry seasons, and it is located in the trough of the great collapse ditch of the Majerda [17]. The study area is characterized by a superposition of multi-layer aquicludes/aquitards [18] with the exception of the perched karstic carbonate (limestone and dolomite) units in NE Algeria and in NW Tunisia which are very vulnerable to this type of pollution by toxic and radioactive elements, or contamination is made possible by fracturation and surface and subsurface faults (decreasing the residence time). There are, therefore, significant surface reserves that are used in agricultural, domestic, industrial and tourist areas.

The Aïn Dalia dam is located in the town of Annaba on the Majerda River (Algerian part); its coordinates are 36.263439° N and 7.862016° E . It was built in 1956 to store surface water and protect cities against flooding. The Sidi Salem dam is located in the town of Beja (Testour) on the Majerda River (Tunisian part). Its coordinates are 36.590614° N and 9.396958° E . This dam was built in 1977 to also store surface water and use it during periods of shortage. The dimensions of the foot of this gigantic ancient dam are 73 m in height and 345 m in length. The principal objectives of this dam are the artificial recharge of aquifers and use in domestic, tourism and industrial activities in the coastal part of Tunisia via pipeline transfer (e.g., Bizerte, Tunis, Hammamet, Sousse, Monastir, Sfax).

3. Geological and Tectonic Setting

The study area is characterized by a specific geology: allochthone formations (Numidian Flysch/Nappe zone) and autochthone formations. These geological formations extend from the Triassic/diapir to the Quaternary (Figure 2a). Evaporitic Triassic sediments and metamorphic and volcanic rocks are the origin of the upwelling of PTEs and radioactive deposits (Figure 2b). The NW–SE and NE–SW major faults and fractures are responsible for the metallurgic mechanism and the rise of deep water during water/rock contact, as well as having equally important roles in the rechargeability of surface- and shallow-water reservoirs by rainwater (Figure 2c). The geological, geomorphological and tectonic evolution of the rocks forming the major tectonic units of the study area can be traced back some 500 million years to when they were located on different continents (Gondwana and Laurasia) [19].

In the study area, the slopes vary between 17 and 24% in the high-altitude zones (Tunisian–Algerian transboundary zone), between 0 and 5% in the discharge zone (Tunis Gulf) and between 6 and 16% in the flat area (Figure 2d). This variation in altitude and slope plays a crucial role in transporting contaminants (liquid or solid forms) from the transboundary territory (western part of the study area) to the Mediterranean Sea/Tunis Gulf (eastern part of the study area).

All these factors (e.g., geological factors, lithology, slope, drainage network, tectonic factors) are the principal parameters in aquifer vulnerability and in the cumulative impact of the potential toxicity caused by the PTEs and the radioactive nuclides in the study area.

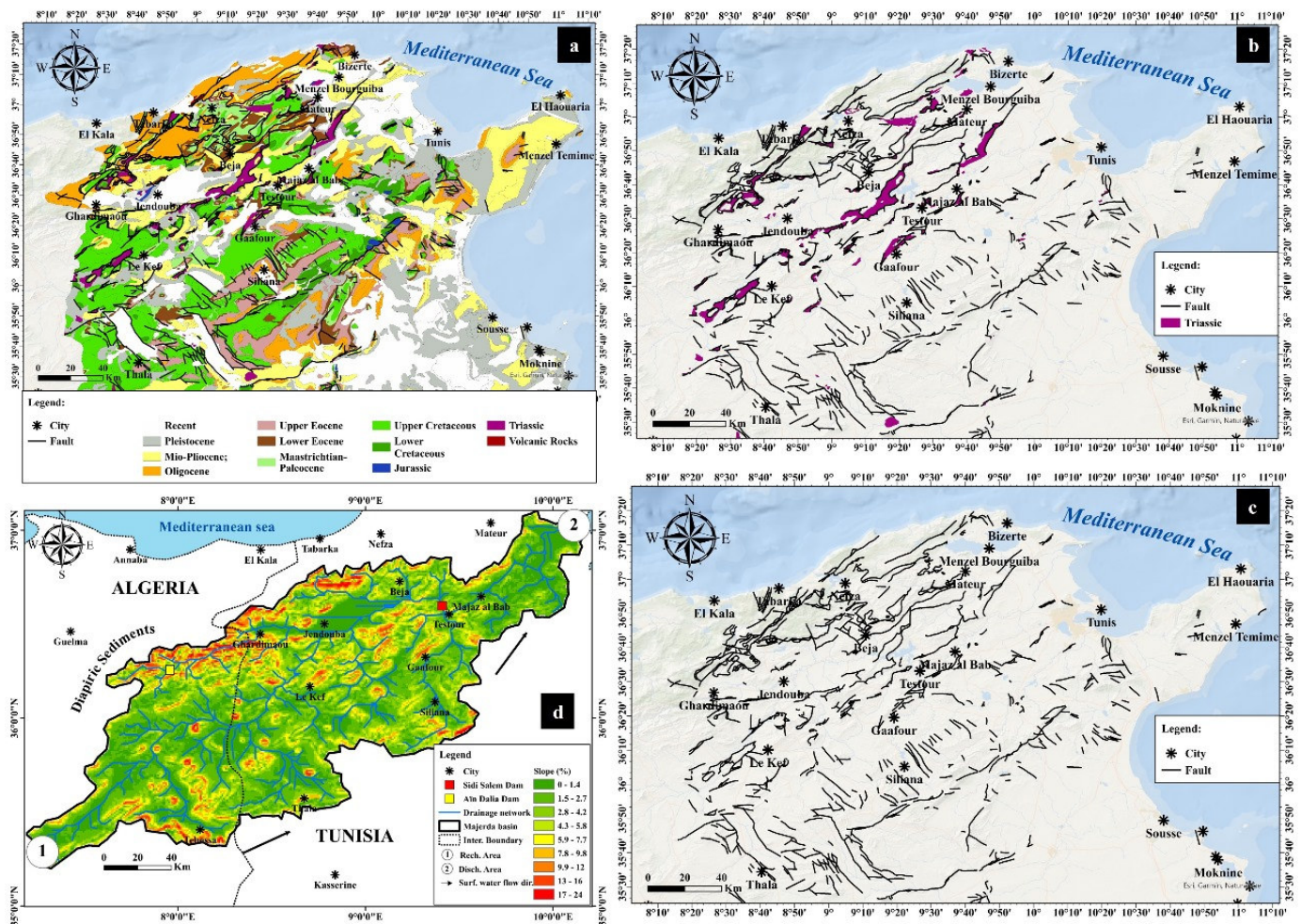


Figure 2. (a) Geological map (Numidian Flysch in the North is allochthone, and the rest is autochthone Fm.), (b) Triassic rocks (evaporitic sediments), (c) tectonic map and (d) slope map of the study area.

4. Materials and Methods

4.1. Sample Collection and Preparation

Twenty-four samples (16 surface water samples and 8 sediment samples) were collected during spring 2023 from the water (top and basal water parts of dams upstream) and sediment parts (top sediment parts of dams downstream) of two dams (Ain Dalia, Algeria, and Sidi Salem, Tunisia) in the polluted area and two other dams (Beni Haroun, Algeria, and Sidi El Barak, Tunisia) outside the pollution area; they were analyzed as a reference for geochemical comparison (Figure 3). Water containers were sampled and washed with chloric acid (0.1 M HCl) according to the international protocol of the WHO and the US Environmental Protection Agency. During our study, we did not perform dilution for liquid samples because the freshwater salinity from dams was less than $500 \text{ mg}\cdot\text{L}^{-1}$. But for samples with TDS greater than $500 \text{ mg}\cdot\text{L}^{-1}$, dilutions were performed to facilitate the detection of chemical elements using a spectrometer. In the field, the solid samples were placed in cellophane bags to avoid any kind of contact with open air (avoid air/sediment contact and biological and/or physical contamination). In the collection process, 1.5 L of water and 2.5 kg of sediment were collected, labeled and properly sealed. Before sample transportation, several parameters were measured in the field using a portable multiparameter instrument (pH, DBO_5 , DCO, T_p , dissolved oxygen, TDS, E.C, turbidity, color, smell and surface water depth). All the glass bottles were first washed according to the international protocol with sulfuric acid (diluted H_2SO_4) and then rinsed with distilled water and then with dam water to avoid any external physical and/or biological contamination (tempera-

ture, humidity, pressure and/or loss of radon or other isotopes). For this type of sampling, water samples should always completely fill the sample container leaving no space for gas to avoid any kind of gas exchange. The organic phase was separated into a separation funnel to avoid any error from the interaction between the organic and mineral composition in the water and in the sediment. During this sampling phase, careful documentation of important parameters such as location, date, time and weather conditions that could have an influence on the produced data was required in this study area. Among the precautions taken in this study, it was necessary to determine the weight of the empty vials on an analytical balance and measure the gamma radioactivity rate after calibration with known laboratory samples (standard reference samples analyzed by the IAEA).

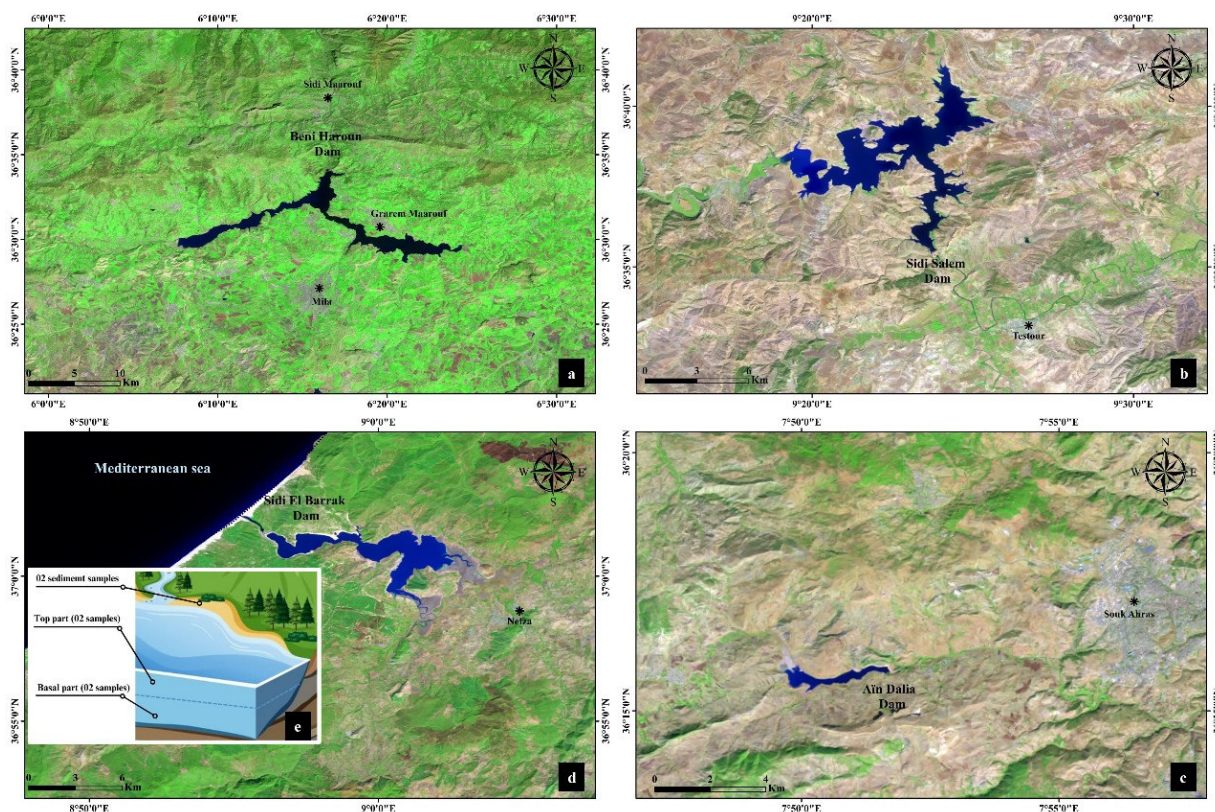


Figure 3. Location of Tuniso-Algerian dams (objective of sampling water and sediment). (a) Beni Haroun dam (Algeria), (b) Sidi Salem dam (Tunisia), (c) Ain Dalia dam (Algeria), (d) Sidi El Barek dam (Tunisia) and (e) sampling methods (water and sediment/dam). * means city.

4.2. Geochemical Analysis

A Terra detector (Pocket-type instruments, Ukraine-made/April-2021: battery life 800 h under no alarm condition and with 3 h under alarm condition, $-15\text{ }^{\circ}\text{C} < \text{temperature} < +45\text{ }^{\circ}\text{C}$ and relative humidity around 95%) was used for the gamma counting at the Faculties of Sciences of Gafsa Chemical Department/Laboratory for the Application of Materials to the Environment, Water and Energy (LAM3E) (Gafsa, Tunisia) and the Geo-laboratory (Sétif, Algeria). The measurement of activity concentrations of ^{238}U , ^{232}Th and ^{40}K was carried out with a gamma-ray spectrometer equipped with a broad-energy germanium (BEGe) detector. The radioactivity detector has a resolution of 8%. This detector, after calibration and testing in the laboratory with specific standards (liquid and solid) whose radioactivity rate is known (pure water, pure phosphoric acid and phosphate-U rock), was used in the field to measure the rate of total gamma and beta radioactivity as a precaution. When the limit is exceeded ($0.3\text{ }\mu\text{Sv}\cdot\text{h}^{-1}$), it triggers an alarm to announce radioprotection and take necessary measures in the study area. It determines the type of radioactivity and energy. Isotopic disintegration counting has been reported by numerous specialists in the

field of radioactivity [20,21]. The radioactive activity concentrations in the samples were determined using Equation (1).

$$C = \frac{A}{P_{\gamma}(M \text{ or } V)T_c \varepsilon} \quad (1)$$

where M is dried mass (solid sample in kilograms), V is water sample (volume in liters), P_{γ} is gamma emission probability, T_c is counting time and ε is detector efficiency.

Geochemical analysis was performed in the Sfax Tina City Laboratory (Sfax, Tunisia) to determine the concentration of toxic elements in solution in ppm or ppb ranges, using atomic absorption spectrometry (AAS). The accuracy of these analyses depends on the quality of the sample preparation; any contamination or incomplete dissolution of the sample can lead to erosion in the results. The ionic balance between the anions and the cations (% error) of geochemical analyses was less than 5%, which indicates that the error is very acceptable. In this part, we adopted GIS, remote sensing, mathematic modeling, Pearson's correlation matrix and principal component analysis (PCA) to explain the spatial distribution of the variables and the relationship between them.

4.3. Ecotoxicological and Radiological Parameter Risks

To evaluate the ecotoxicological and radiological risks and the danger to human health, some isotopic parameters were also calculated from the radioactivity measured on the ground in the study area and in the laboratory. The absorbed dose rate (D) due to the radioactivity concentrations (^{238}U , ^{232}Th and ^{40}K) was evaluated using Equation (2) according to international references [14,18].

$$\begin{aligned} D \text{ (nGy xh}^{-1}\text{)} &= C_U C_U + C_{Th} C_{Th} + C_K C_K \\ D \text{ (nGy xh}^{-1}\text{)} &= 0.462 C_U + 0.604 C_{Th} + 0.0417 C_K \end{aligned} \quad (2)$$

The parameters C_U , C_{Th} and C_K represent the radioactivity concentration ($\text{Bq}\cdot\text{kg}^{-1}$ and $\text{Bq}\cdot\text{L}^{-1}$) of solid and liquid samples from the study area, while $C_U = 0.462$, $C_{Th} = 0.604$ and $C_K = 0.0417$ are dose conversion factors [18]. The radium equivalent (Raeq) activity index was determined using Equation (3).

$$\text{Raeq} = C_U + 1.43 C_{Th} + 0.077 C_K \quad (3)$$

The external and internal radiation hazards (H_{ext} and H_{int}) were calculated using Equations (4) and (5).

$$H_{ext} = (C_{Ra}/370) + (C_{Th}/259) + (C_K/4810) \quad (4)$$

$$H_{int} = (C_{Ra}/185) + (C_{Th}/259) + (C_K/4810) \quad (5)$$

In this study, the annual gonadal equivalent dose (AGED) was calculated using Equation (6).

$$\text{AGED} \text{ (}\mu\text{Sv}\cdot\text{y}^{-1}\text{)} = 3.09\cdot C_U + 4.18\cdot C_{Th} + 0.314\cdot C_K \quad (6)$$

The ecotoxicological or health risk (H: effective dose) was calculated using Equation (7) [16].

$$H = R_a \cdot A_i \cdot C_f \quad (7)$$

R_a is the U, Th or K radioactivity concentration (in solid or liquid samples) ($\text{Bq}\cdot\text{L}^{-1}$); A_i is the annual intake (1 y^{-1}); and C_f is the ingested dose conversion factor for radionuclides ($\text{mSv}\cdot\text{y}^{-1}$).

The total annual effective dose HE ($\text{mSv}\cdot\text{y}^{-1}$) was calculated using Equation (8).

$$\text{HE} = \Sigma(R_a \cdot A_i \cdot C_f) \quad (8)$$

According to the international protocol of studying human health (age, sex, living area, exposition time), in our study, we adopted a subdivision according to different ages (for both sexes) in the study area for good precision. The conversion data/factors used in this study were adopted from the International Commission on Radiological Protection (ICRP) [22–24] for nine different age groups (Table 1).

Table 1. Total effective dose (HE) for surface water samples (Sidi Salem dam, Tunisia basin).

Age Group	0–1	1–2	2–7	7–12	12–17	17–25	25–45	45–65	>65
Upper side (mSv·y ^{−1})	1.22	1.59	1.83	2.14	3.66	4.45	5.12	6.34	7.04
Lower side (mSv·y ^{−1})	0.84	1.09	1.26	1.47	2.52	3.06	3.76	4.12	5.02
World standard value [24]	0.12 mSv·y ^{−1}								

5. Results

The radiological concentration activities for water and sediment samples (²³⁸U, ²³²Th and ⁴⁰K) are shown in Figures 4 and 5, respectively. In our study, we calculated the average of the top part (two samples/dam) and the basal part (two samples/dam) for the water samples and the average of the top part (two samples/dam) for the sediment (Figure 3e). The mean radioactivity concentration measured for the water samples in the upper part of the dam (Tunisia) is 1.74, 0.07 and 95.8 Bq·L^{−1} for ²³⁸U, ²³²Th and ⁴⁰K, respectively. The mean concentration measured on the lower side (basal part) of the dam was 1.70, 0.066 and 93.4 Bq·L^{−1} for ²³⁸U, ²³²Th and ⁴⁰K, respectively. The mean radioactivity concentrations follow the order ⁴⁰K > ²³⁸U > ²³²Th. The mean radioactivity concentration measured in the sediments collected on the upper side of the Sidi Salem dam (Tunisia) was 2.67, 0.18 and 197.87 Bq·kg^{−1} for ²³⁸U, ²³²Th and ⁴⁰K, respectively. Concerning the Algerian dam (Aïn Dalia), the mean concentration measured on the lower side of the water dam was 1.9, 0.09 and 131.43 Bq·L^{−1} for ²³⁸U, ²³²Th and ⁴⁰K, respectively. The mean radioactivity concentration measured in the sediments collected on the upper side of the dam was 4.34, 0.27 and 287.61 Bq·kg^{−1} for ²³⁸U, ²³²Th and ⁴⁰K, respectively. It was observed that the radioactivity measured in the sediments for ²³⁸U, ²³²Th, and ⁴⁰K was higher by a factor range of 1.57, 2.64 and 2.1, respectively, than what was measured in water samples from Sidi Salem (Tunisia). In the Algerian territory (Aïn Dalia dam), the radioactivity measured in the sediments for ²³⁸U, ²³²Th, and ⁴⁰K was higher by a factor range of 2.3, 3, and 2.2, respectively, than what was measured in water samples.

The results of the concentrations of the PTEs (Fe, Pb, Zn, Ni, Cr, Cu and Cd) in the surface waters of the two reservoirs of the Majerda River (contaminated area of the study area: Aïn Dalia and Sidi Salem dams) are presented in the Section 6.3. The concentrations of Fe, Pb, Zn, Ni, Cr, Cu and Cd in surface water range from 5.430 to 9.700 mg·L^{−1}, 0.022 to 0.168, 0.018 to 0.142, 0.065 to 0.366, BDL to 0.0351, BDL to 0.071 and BDL to 0.048 mg·L^{−1}, respectively. The average concentration of toxic elements follows the trend Fe > Pb > Zn > Ni > Cr > Cu > Cd. This result indicates the dominance of Fe, Pb and Zn in surface water samples from the Aïn Dalia dam (Algeria). The average concentration level of Fe (7.565 mg·L^{−1}) is much higher than the standard values (0.3 mg·L^{−1}); it is almost 25,217 times higher. Cu (0.0225 mg·L^{−1}) was found to be below the WHO-recommended limit of 2.00 mg·L^{−1}. Ni (0.086 mg·L^{−1}), Cr (0.061 mg·L^{−1}) and Cd (0.009 mg·L^{−1}) were slightly above the WHO-recommended levels of 0.07, 0.05 and 0.003 mg·L^{−1}, respectively, for drinking water [24]. Pb (0.218 mg·L^{−1}) was found to be above the WHO-authorized limits of 0.01 mg·L^{−1}. In the sediments, the concentrations of Fe, Pb, Zn, Cu, Ni, Cd and Cr are of the order of 136.7, 3.41, 3.22, 0.213, 0.182, 0.15 and BDL, respectively.

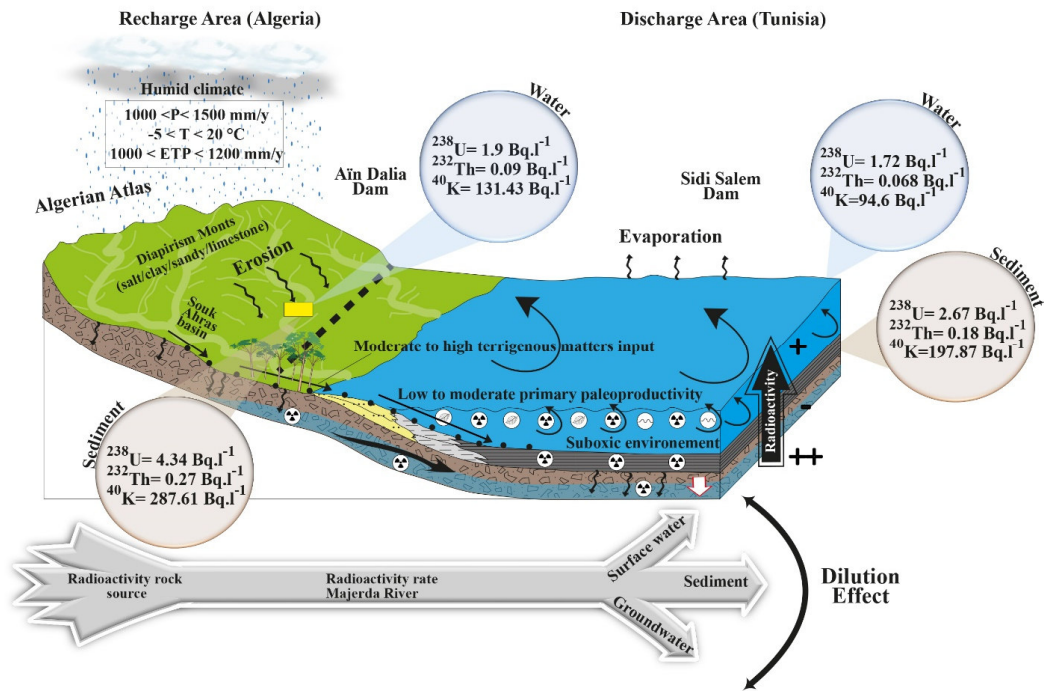


Figure 4. Conceptual model showing the hydrodynamics of surface water during wet climate in the study area (contaminated area of Ain Dalia and Sidi Salem dams).

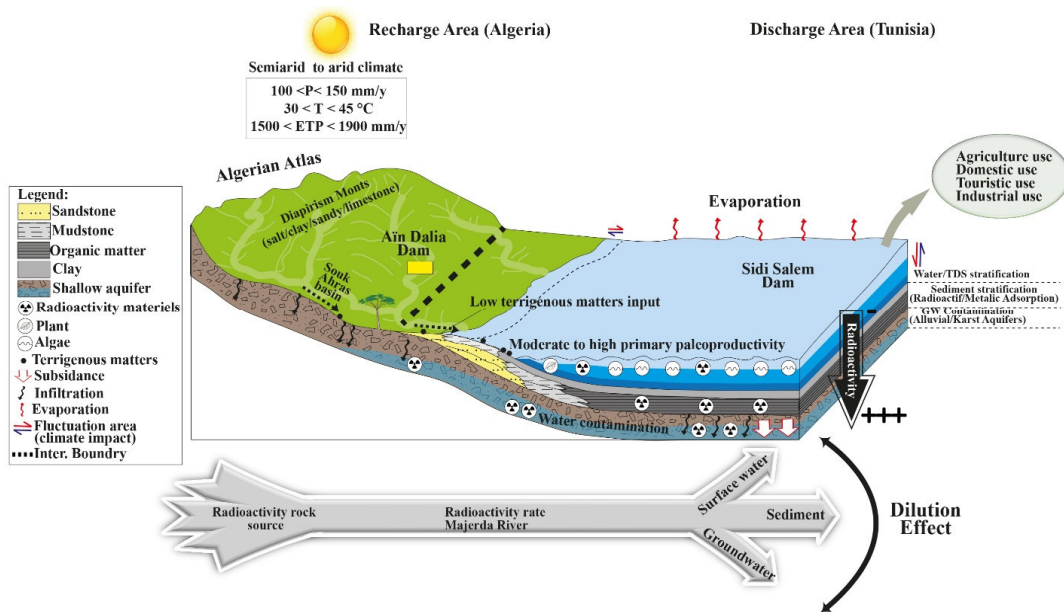


Figure 5. Conceptual model showing the hydrodynamics of surface water during the period of dry climate in the study area (contaminated area of Ain Dalia and Sidi Salem dams).

6. Discussion

6.1. Spatial Distribution of the Radioactivity in the Study Area

The results are not surprising since sediments will transfer part of the radionuclide contents to the water, and the Algerian area (Souk Ahras area: recharge area) is where diapirism (sediment upwelling) originates this natural radioactivity. The estimated radiological impact parameters are presented in Table 2. The absorbed dose rate ($nGy \cdot h^{-1}$) for sediment samples was below the world standard limit value (Table 2).

Table 2. The sediment radiological parameters in the study area. Absorbed dose rate (D); radium equivalent (Raeq); external and internal radiation hazards (Hext and Hint); annual gonadal equivalent dose (AGED).

Location/Country	D (nGy·h ⁻¹)	Raeq (Bq·kg ⁻¹)	Hext	Hint	AGED (μSv·y ⁻¹)
Ain Dalia dam/Algeria	14.12	36.79	-	-	104.53
Sidi Salem dam/Tunisia	9.59	18.16	-	-	71.13
World standard value [24]	57.00	370.00	1.00	1.00	1.00 Sv·y ⁻¹

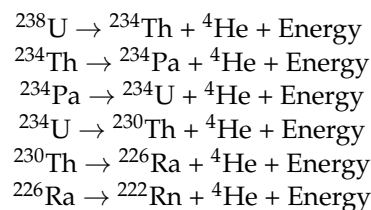
The AGED is less than the world limit of 1 Sv·y⁻¹ [18]. The calculated absorbed dose for water was used to further calculate the total annual effective dose HE (mSv·y⁻¹) as shown in Table 2. The total annual effective dose obtained for all different age groups was below the permissible reference limit [20]. Radioactivity contamination may be dangerous because of the cumulative effect in the long term, depending on the socio-economic activities in this transboundary basin and also on the future regional and global economic and climatic scenario in the North Africa basin and its relationship with the atmospheric Mediterranean circulation and with the global atmospheric circulation of the North and South Atlantic Ocean (impact of anthropogenic activities during rainstorms, windstorms and/or sandstorms).

Ain Dalia dam (recharge area, Algeria) and Sidi Salem dam (discharge area, Tunisia) reveal significant variations in radioactivity levels. The results indicate that the highest radioactivity concentrations were observed in the lower parts of the dams (sediment parts) which can be attributed to the organic matter and clay mineral adsorption of the radionuclides [16]. The dead area (stagnation and compact zone in the bottom part) of the dam is composed of stratified/compacted sediments. In this part, there is a dependence on the drainage network input from the mount's erosion (clay, gypsum, sand, limestone/dolomite). That is why the nearest dam (Ain Dalia) to the sources of the natural diapiric radioactivity sediments (e.g., salt, gypsum, clay, sandstones) from the Algerian Atlas is very enriched by these natural diapiric and metamorphic radioactivities. The decrease in the radioactivity rate from the Algerian territory to the Tunisian territory is due to the geochemical process (contact air/water/rock interactions) in many effluents of the drainage network of the Majerda Tuniso-Algerian transboundary basin and due to the bioaccumulation/complexation during the residence time of water and sediments [25,26].

This radioactive distribution can be influenced by the tectonic activity (major faults and fractures), rock types, aquifer intercommunications, residence time, climatic/meteorological parameters and direction of the rain/wind, which can transport the radioactive particles and disperse them in different directions in the Majerda basin from the Algerian Atlas to Tunis Gulf (approximately within a radius of 300 km with a wind speed which oscillates between 20 and 100 km·h⁻¹ which depends on regional and global climatic and meteorological conditions). The tectonic impact has a good role in the rechargeability/contamination of shallow karstic water reservoirs by these PTEs and radionuclides and in the intercommunication between the different water reservoirs in the study area [27,28].

These dams (Sidi Salem and Ain Dalia) show significant radioactivity variability in an analysis of surface water and sediments. High levels of total radioactivity are generally in the range of 0.21 μSv to 0.28 μSv in the sediment in Ain Dalia dam, and the total radioactivity increases with the water depth. From this recharge area (Algerian area) to Sidi Salem dam (Tunisian discharge area), the levels of the total radioactivity are generally in the range of 0.2 μSv to 0.23 μSv in the sediment, and the total radioactivity increases with the depth also. There is a cumulative impact on the water and on the soil. These higher values are mainly recorded in specific areas such as the cities of Tebessa, Souk Ahras, Annaba, Jendouba, El Kef and Beja, which are associated with the mining and ore industry and also with the presence of diapiric and metamorphic rocks in the high altitude of this transboundary basin (1500–2800 m) [29–33].

These radioactive values are often observed in regions close to the surrounding mountainous areas, where the geological characteristics and the agriculture/industrial activities may play a role in the increase in radioactivity in the sediment. These variations in radioactivity levels reflect the complexity of the geology, tectonics, environmental processes and socio-economic activities of this North African area (Majerda Tuniso-Algerian transboundary basin). It is important to note that the radioactivity values mentioned are indicative and may vary depending on many factors, including local geological, geomorphological and climatic conditions; soil erosion; and human activities. In this context, the study area is climatologically under the influence of two types of air masses: (1) The first air mass has a Mediterranean origin, and the transport engine is the north/south direction wind; any radioactive activity (enrichment zone) in the southern European countries can be transported in this direction (to North Africa and the western part of the Middle East). (2) The second air mass is desert/Atlantic air mass, and the direction is south/north and west/east (to North Africa and to the western part of the Middle East). All industrial activities from uranium mines in Niger and other countries in Central Africa (Chad, Nigeria) will be transported by the wind ($100\text{--}150\text{ Km}\cdot\text{h}^{-1}$) and discharged in the study area (2000 Km) and in the rest of the MENA region countries, especially Saudi Arabia (3500 to 4500 Km). The radioactivity disintegration in air, soil and surface and/or groundwater in the study area can be expressed by the following equations:



Regional and global climate change has a key role in the balances and imbalances of ecological and environmental ecosystems. The conceptual mathematic model of the hydrodynamics of the surface water in these dams vs. the regional/global climate variation (dry/wet) (Figures 4 and 5) shows that the organic matter (OM) and the clay minerals have a good role in radioactivity adsorption, in the immobilization of radioactive isotopes and in cosmic radiation. Combined with the influence of the irregularity of the flooding stage due to the regional and global climate variability in North Africa, the increasing arid paleo-climate played a very important role in the decrease in radioactivity by reducing the supply of clay minerals (adsorption/release), radioactive materials and other minerals. This situation has also benefited primary paleo-productivity and anoxic conditions; their integrated effect could induce sapropelic organic matter accumulation (preservation and/or degradation). Therefore, the relationship between the OM content/clay minerals and the radioactivity is very complex. Rather than only assuming a positive correlation, its characteristics and formation mechanism need to be analyzed in a specific environment.

In the wet climate (Figure 4), rainstorms and/or sandstorms bring sediments rich in radioactive elements (e.g., clay, gypsum, organic matter, sandstone, salts), and rain showers recharge the dams and cause heterogeneity in the water column of the dams. This is why the level of radioactivity is high in the water column during wet periods. However, during the period of the dry climate (Figure 5), when rain showers and/or wind are almost null, the water column will be stratified (evaporation and density effects). The location where radioactive elements are deposited at the bottom part, their weight and the rate of radioactivity will be important in the basal parts of the dams. Moreover, during this period, shallow aquifers (alluvial and karstic) downstream of the dams will be recharged by infiltration (period of deep-water contamination).

It was noted that in all surface water samples from Ain Dalia and Sidi Salem dams (contaminated area) in this tectonized transboundary basin in North Africa, the concentrations of ${}^{238}\text{U}$ were higher than those of ${}^{232}\text{Th}$. ${}^{238}\text{U}$ incorporated with the upwelling of diapiric/metamorphic/sedimentary rocks together with limestone, dolomite, marl, salt,

gypsum and clay commonly found in Tebessa, Souk Ahras and Annaba mounts (in Algerian Atlas) and in El Kef and Jendouba mounts (in Tunisian Atlas) can explain these geochemical and radiological data in this report. The variability of the radioactivities can also be attributed to the oxidation–reduction conditions. Also, the fossil geothermal upwelling of the Northwestern Sahara Aquifer System (NWSAS) hydrothermal aquifers (40–45 Ky) through the major faults increases the dissolution of these radioactive minerals (the radioactivity disintegration increases with the temperature and the depth).

^{40}K is a radiological and toxic element that is abundant in rocks and oceans/seas [21]. Its high rate in the surface water (dams and drainage networks) of the transboundary Majerda area may be due to the leaching of topsoil of nearby agricultural areas that employ inorganic potassium fertilizers to boost soil nutrients (orange, wheat, barley). When fertilizers are used on agricultural land (TSP, DAP), this isotope (^{40}K) can percolate by infiltration and be leached in significant proportions into nearby vulnerable water reservoirs (alluvial and/or karstified aquifers). The rational safety of drinking water is an important water quality parameter of concern [14]. Most countries base their rational risk regulation and guidelines for drinking water on the UNSCEAR reports [18] and WHO limits [24]. The ^{40}K and ^{238}U rates obtained in this present study were significantly higher than the UNSCEAR and WHO world average limits of 10.0 and 1.0 $\text{Bq}\cdot\text{L}^{-1}$, respectively, for drinking water. The rate of ^{232}Th is near the limit of 0.1 $\text{Bq}\cdot\text{L}^{-1}$. However, the values of the radioactivity in the sediment show severe contamination and can be very dangerous for human health. From the radiological point of view, the accumulation of ^{238}U , ^{232}Th and ^{40}K radionuclides due to the ingestion of water from the Majerda dams could present a low-dose radiological risk of longer-term effects on the health status of the Majerda population (the higher agriculture land in Tunisia and in North Africa, as it has been known for a long time until today: Matmour Carthage). In a comparison with other international studies (Table 3), it was found that the mean radioactivity concentrations of ^{40}K and ^{238}U were greater than those observed in water samples from Port Harcourt (Nigeria) [34]; Kuala Lumpur (Malaysia) [35], Ghana, Nigeria, Egypt, Makkah (Saudi Arabia) [36] and Gafsa (Tunisia) [16]. The ^{232}Th concentration is lower than that found in some of these locations, except for the value 0.12 $\text{Bq}\cdot\text{L}^{-1}$ from Saudi Arabian drinking water reservoirs [36].

Table 3. Comparison of specific activity of ^{238}U , ^{232}Th and ^{40}K (water and sediment) with other studies from different parts of the world (*: control water and sediment samples from non-polluted area—Tunisia and Algeria).

Region/Country	^{238}U , $\text{Bq}\cdot\text{kg}^{-1}$	^{232}Th , $\text{Bq}\cdot\text{kg}^{-1}$	^{40}K , $\text{Bq}\cdot\text{kg}^{-1}$	References
Sidi Salem dam (Water)/Tunisia	1.72	0.068	94.6	Present study
Sidi Salem dam (Sediment) /Tunisia	2.67	0.18	197.87	Present study
* Sidi El Barrak dam (Water)/Tunisia	0.82	0.032	67.98	Present study
* Sidi El Barrak dam (Sediment)/Tunisia	0.45	0.024	45.62	Present study
Aïn Dalia dam (Water)/Algeria	1.9	0.09	131.43	Present study
Aïn Dalia dam (Sediment)/Algeria	4.34	0.27	286.61	Present study
* Beni Haroun dam (Water)/Algeria	0.7	0.04	98.7	Present study
* Beni Haroun dam (Sediment)/Algeria	0.52	0.03	75.4	Present study
Gafsa Phos. Rock/Tunisia	702	75	90	[16]
Tunisia	-	29	32	[37]
Egypt	686	5.7	68.6	[21]
Morocco	-	20	10	[38]
Algeria	-	64	22	[39]
Saudi Arabia	-	17–39	242–2453	[36]
Germany	-	15	720	[38]
USA	-	49	200	[40]

Table 3. Cont.

Region/Country	^{238}U , Bq·kg ⁻¹	^{232}Th , Bq·kg ⁻¹	^{40}K , Bq·kg ⁻¹	References
India	-	65	2624	[39]
Jordan	-	2	8	[37]
Kuala Lumpur/Malaysia	-	1.2	35.1	[35]
Buruta/Nigeria	-	26.9	61	[34]
Oman	-	2.26	44.83	[41]
Kuwait	-	6	227	[42]
Iran	-	17.61	361.6	[43]
Turkey	-	9.0	157.7	[44]

The ^{238}U , ^{232}Th , and ^{40}K concentrations observed in this Tuniso-Algerian transboundary basin are also compared with those reported for other regions of the MENA region (North Africa and Middle East) and worldwide average values in Table 3. However, the mean value of the activity concentration of ^{238}U for the Tunisia zone was higher in the southern part of Tunisia (phosphate-U/petroleum mining basin) [16] but lower in the Majerda basin (study area) when compared to the average values reported for the Middle East regions (e.g., Saudi Arabia, Qatar, Bahrain, Emirate, Kuwait) and the worldwide average values; the overall mean value for the entire study region was similar to these reported values.

The individual mean values of ^{238}U , ^{232}Th and ^{40}K activity concentrations for each zone as well as the overall mean value were lower when compared to the average values reported for the Middle East and the world. It is interesting to observe that the ^{238}U activity is higher in the sediment when compared to the ^{232}Th concentration in the proposed uranium-mining region (cumulative impact).

In this work, the control samples were taken from dams' water far from polluted areas (Beni Haroun dam, Algeria, and Sidi El Barrak dam, Tunisia). The analyses show low values compared to the analyses of samples from contaminated dams (Ain Dalia dam, Algeria, and Sidi Salem, Tunisia).

High ^{238}U , ^{232}Th , and ^{40}K rates have been detected in surface water associated with diapirism/metamorphic/sedimentary rocks of the Algerian Atlas. These high concentrations are attributed to uranium minerals in granites and uranium minerals in pegmatites associated with these rock types of the Tuniso-Algerian Atlas and may also be the result of the combination of these regional rocks' origin with the atmospheric circulation (Mediterranean origin from the north and Atlantic/desertic origin from the south).

6.2. Risk Map of the Radioactivity Distribution in the Study Area

Through a combination of 12 parameters (altitude; tectonics/fracturation; slope; lithology; aquifer levels/thickness; radioactivity rates of ^{238}U , ^{232}Th and ^{40}K ; drainage network; surface/groundwater flow direction; rate/direction of rain and wind), using remote sensing, GIS and geochemistry analysis, we can establish a risk map (Figure 6). The most significant values of radioactivity are observed at Ain Dalia dam located near the diapirism outcrops (Algerian territory) and also at Sidi Salem dam (Tunisian territory) due to the cumulative effect and finally in the final outlet (Tunis Gulf of the Mediterranean Sea/Carthage Sea) with average values. The lowest values are observed in high altitudes in the study area. The drainage network with permanent surface water has an important role in the transportation of the radioactive sediment and also has a role in the dilution of this radioactivity from the source of radioactivity (diapirism sediment) to the Tunis Gulf (cumulative sediments).

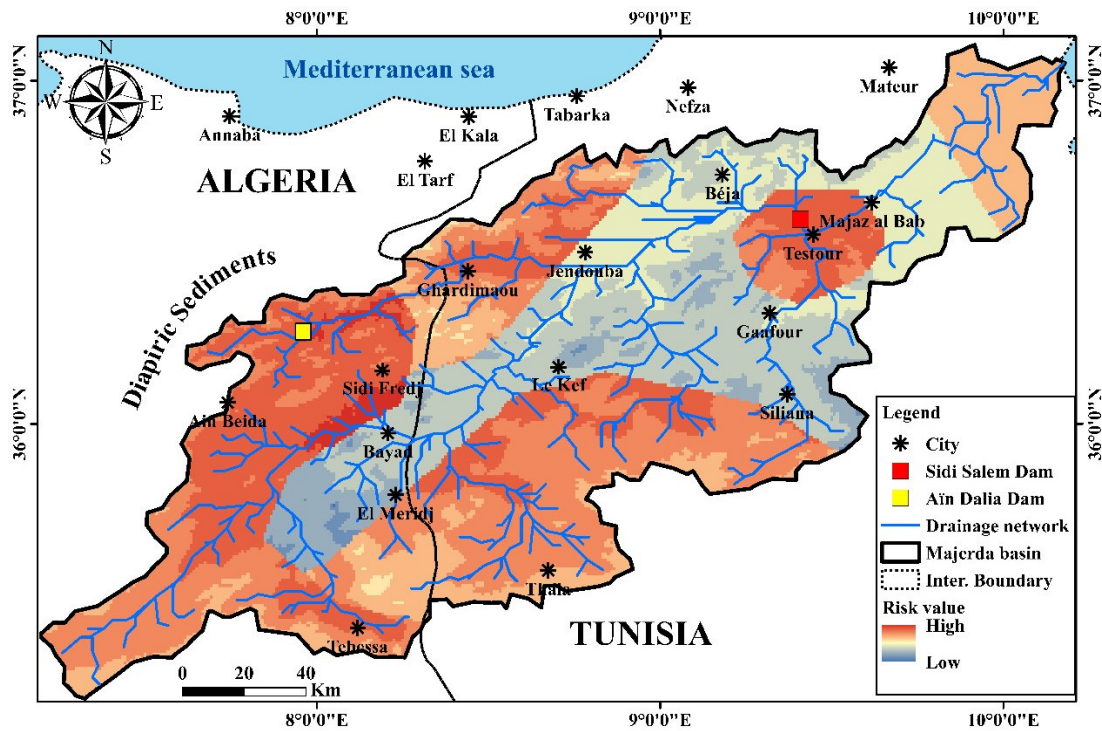


Figure 6. Risk map of the spatial distribution of radioactivity in the study area with the drainage network.

The highest levels of radioactivity are observed at the level of the diapirism rocks which constitute the source and the origin of the contamination in the Algerian territory (Transboundary Algero-Tunisian Atlas). The outlet of the watershed (Tunis Gulf) is marked by very high levels of radioactivity. This is essentially due to the cumulative effect. The lowest values are observed at high altitudes, generally in carbonates, whose radioactivity rate is low (Figure 7).

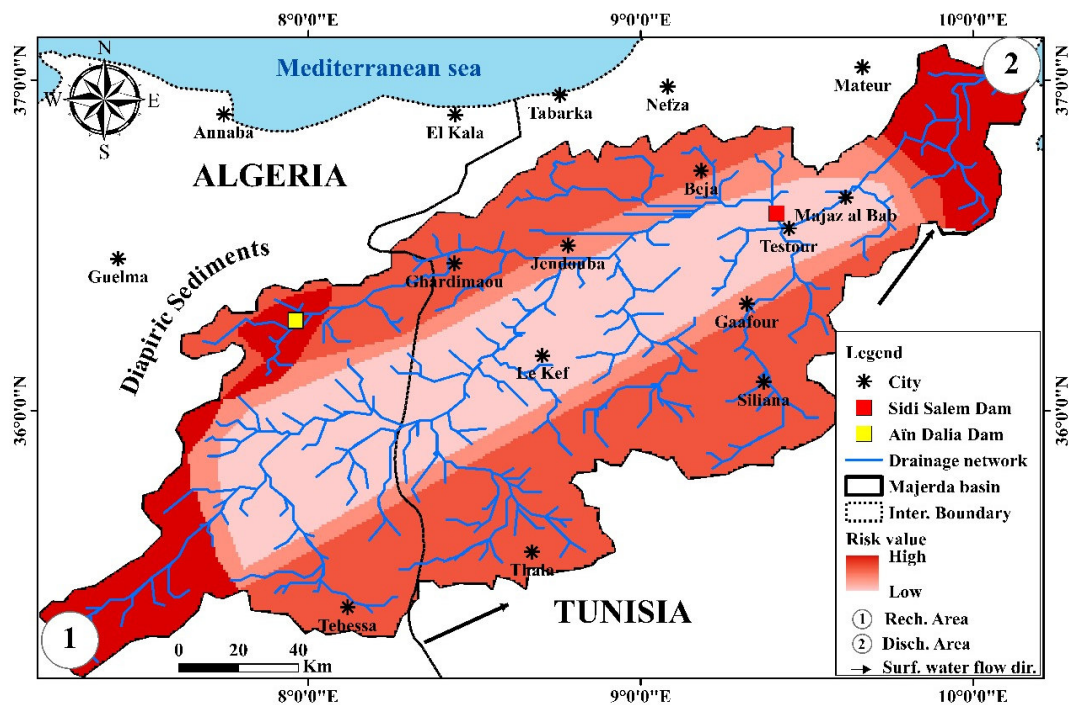


Figure 7. Health risk map of the radioactivity impact in the study area.

In 2000, the United States Environmental Protection Agency (USEPA) [45] published the final regulations on radionuclides in drinkable water. In these regulations, the objectives of maximum contaminant levels (MCLGs) and maximum contaminant levels (MCLs) are given, along with the monitoring, reporting and public notification requirements for radionuclides. These rules only apply to community water systems. MCLGs (non-enforceable health targets) are zero for all radionuclides, according to a cancer risk model without a threshold for ionizing radiation products (Table 4) [45].

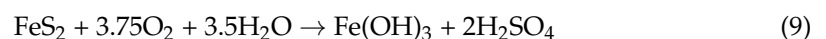
Table 4. US Environmental Protection Agency maximum contaminant levels for radionuclides in drinking water (other than radon) [45].

Contaminant	Maximum Contaminant Levels
Uranium	30 microg·L ⁻¹
Combined ²²⁶ Rn and ²²⁸ Ra	5 pCi/L (0.185 Bq·L ⁻¹)
Gross alpha (excluding Rn and U but including ²²⁶ Ra)	15 pCi/L (0.555 Bq·L ⁻¹)
Beta particle and photon radioactivity	40 mrem/y (0.04 mSv·y ⁻¹)

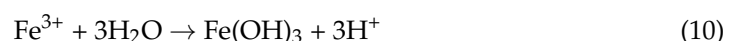
6.3. Spatial Distribution of the Potentially Toxic Elements (PTEs)

The implication of drinking contaminated water may be in retarding certain biological and/or physiological processes. The anthropogenic activities (mining extraction) along the transboundary Majerda River which feeds the two reservoirs (Aïn Dalia and Sidi Salem dams) are the principal cause of the increase in the Pb and Ni levels in the water samples. Runoff from mines, dumps and agricultural practices visibly present along the road and around the riverbank is a plausible source of PTEs. Fertilizers and other agrochemical applications are a major contributing factor to the ubiquity of Pb in surface water bodies [22]. Lead is mainly used in the manufacture of lead batteries; it remains in landfills near rivers and streams and can serve as a source of lead pollution [46,47].

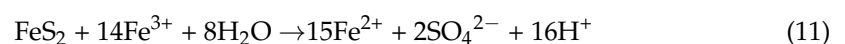
The enrichment of the Pb concentration in surface water from dams or through a cumulative effect can cause serious health issues such as poor memory, social disturbances and reduced cognitive ability [48]. Zn, Ni and Fe are very abundant elements in the environmental ecosystem (diapiric, meta-magmatic and metamorphic rocks) in the study area [49]. The cultivation of cropland is the main occupation of the inhabitants of the study area; therefore, a high concentration of elements in nearby streams and rivers is expected when the use of nitrogen fertilizers is common [50]. According to Hamed et al. [16,51], Cd is also present in a polluting form in apatite fertilizers. The sediment affected by sulfate minerals increased in acidity, in many cases reaching values below pH = 3.5 due to the acidity of the water (pH ≈ 5.2) and the pyrite sludge which, given its heterogeneity, ranged between 3.8 < pH < 5 [16]. The acidification of soils was aggravated by the oxidation of the sludge at the surface and even continued after sludge removal tasks. The oxidation of sulfides involves oxidation, hydrolysis and hydration processes, as summarized by Stumm and Morgan [52] in Equation (9).



This reaction starts with the release of Fe²⁺, which is converted into Fe³⁺ under oxidizing conditions. When soil pH is above 4, then Fe³⁺ precipitates as iron hydroxide and the pH becomes more acidic (Equation (10)).



However, when soil pH remains under 4, Fe³⁺ can oxidize pyrite. This reaction is faster and can generate more acidity (Equation (11)).



The concentration of these elements in sediment samples is almost 20 times that in water (Table 5); this is explained by the cumulative effect and by the presence of organic matter and fine clay sediments which are fixators of these PTEs. In the polluted area, these elements can provoke many serious human illnesses.

Table 5. Specific activity concentrations of ^{238}U , ^{232}Th , ^{40}K ($\text{Bq}\cdot\text{Kg}^{-1}$) and the PTEs (Fe, Pb, Zn, Ni, Cu, Cr, Cd) ($\text{mg}\cdot\text{Kg}^{-1}$) in dams' surface water and sediments.

	^{238}U	^{232}Th	^{40}K	Fe	Pb	Zn	Ni	Cu	Cr	Cd
Dalw ²	1.90	0.09	131.43	5.430	0.0980	0.087	0.024	0.063	0.015	0.025
Dals ³	4.34	0.27	287.61	201.9	5.88	5.046	0.216	0.441	0.06	0.20
Dtnw ⁴	1.72	0.068	94.6	9.700	0.065	0.061	0.018	0.043	BDL ¹	0.130
Dtns ⁵	2.67	0.18	197.87	136.7	3.41	3.22	0.182	0.213	BDL ¹	0.15
WHO limits	1.0	0.1	10.0		0.01		0.07	2.00	0.05	0.003

¹ BDL: below detection limit. ² Dalw: Algerian dam water. ³ Dals: Algerian dam sediment. ⁴ Dtnw: Tunisian dam water. ⁵ Dtns: Tunisian dam sediment.

6.4. Relationship between Radioactive Elements and PTEs

In this part, we use the Pearson's correlation matrix and principal component analysis (PCA) methods to reveal the relations between variables and relations between samples.

6.4.1. Pearson's Correlation Matrix

The correlation coefficients between the variables are presented in Table 6. ^{238}U , ^{232}Th , ^{40}K , Pb, Zn and Cu have a significantly high correlation between 0.95 and 0.99, indicating that the radioactive elements have a good genetic relationship with the PTEs. However, Cr and Cd have a medium correlation (0.46–0.57), and the rest of the chemical elements have a correlation between 0.58 and 0.88.

Table 6. Correlation matrix between the radioactive elements (^{238}U , ^{232}Th and ^{40}K) and the PTEs.

	U	Th	K	Fe	Pb	Zn	Ni	Cu	Cr	Cd
U	1.000									
Th	0.980	1.000								
K	0.982	0.996	1.000							
Fe	0.943	0.985	0.965	1.000						
Pb	0.969	0.995	0.981	0.996	1.000					
Zn	0.954	0.990	0.974	0.999	0.998	1.000				
Ni	0.889	0.959	0.938	0.989	0.973	0.985	1.000			
Cu	0.994	0.995	0.991	0.974	0.991	0.982	0.935	1.000		
Cr	0.880	0.781	0.816	0.672	0.737	0.698	0.574	0.822	1.000	
Cd	0.748	0.751	0.692	0.821	0.810	0.810	0.781	0.775	0.463	1.000

6.4.2. Principal Component Analysis (PCA)

The PCA showed three principal groups: Group 1 (^{238}U , ^{232}Th , ^{40}K , Pb, Zn, Fe, Ni and Cu) shows a good correlation between the radioactive elements and the PTEs, Group 2 (Cd) indicates an inversion relative to Groups 1 and 3, and Group 3 (Cr) indicates an inversion relative to Group 2 and is not correlated with Group 1 (Figure 8).

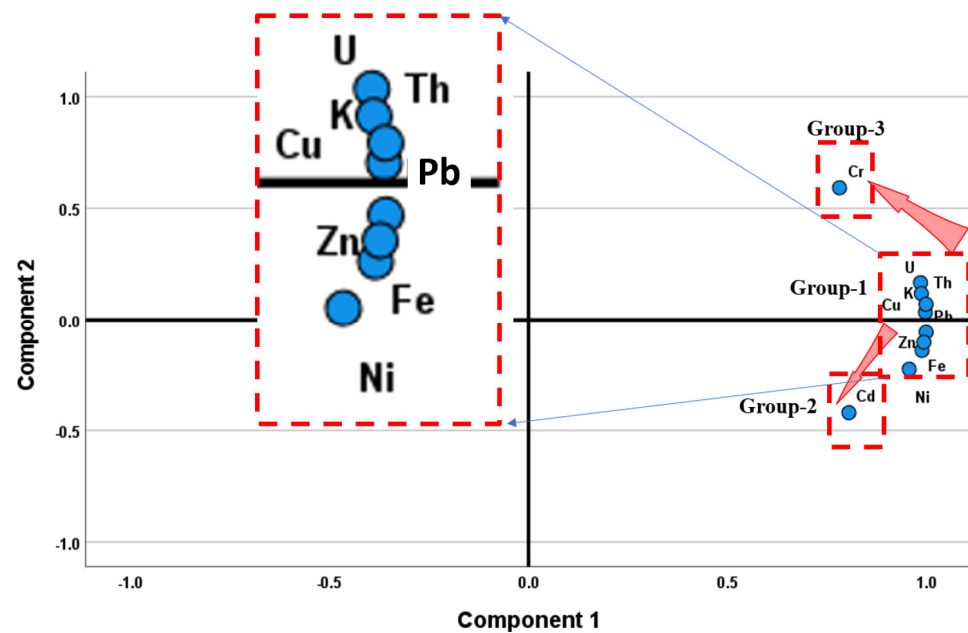


Figure 8. Projection of variables in PCA.

7. Conclusions and Recommendations

The radioisotopes of ^{238}U , ^{232}Th and their decay descendants (^{235}U , ^{231}Th , ^{230}Th , ^{234}U , ^{227}Th) as well as the single non-series ^{40}K are transported to water by leaching and by infiltration through the infiltration zone. The activity concentration of ^{40}K was higher than that of ^{238}U and ^{232}Th for the water and sediment samples. The activity concentrations follow the order $^{40}\text{K} > ^{238}\text{U} > ^{232}\text{Th}$. Potentially toxic elements (Fe, Pb, Zn, Ni, Cr, Cu and Cd) and associated health risks in surface water and sediment of dams have been investigated in this present study. The concentrations of Fe, Pb, Zn, Ni, Cr, Cu and Cd in surface water range from 5.430 to 9.700 $\text{mg}\cdot\text{L}^{-1}$, 0.022 to 0.168, 0.018 to 0.142, 0.065 to 0.366, BDL to 0.0351, BDL to 0.071 and BDL to 0.048 $\text{mg}\cdot\text{L}^{-1}$, respectively. In the sediments, the concentrations of Fe, Pb, Zn, Cu, Ni, Cd and Cr are of the order of 136.7, 3.41, 3.22, 0.213, 0.182, 0.15 $\text{mg}\cdot\text{L}^{-1}$ and BDL, respectively.

This specific study will serve as a reference and national index for carrying out any environmental health monitoring in the transboundary basin of North Africa (Tunisian–Algerian zone), in the Southern Mediterranean Basin and in other similar areas. The derived results will be transposable to other areas to verify any geochemical levels of surface and underground water resources (drinking water from dams, hill lakes and shallow aquifers). They will also provide future guidelines for providing safe drinking water sources to the community in the study area and may be transferable to similar locations in the MENA region (North Africa and the Middle East). This typical study showed that radioactivity in water gives clear information about radiation exposure from different sources. Likewise, it showed that different types of health epidemics and ecotoxicological effects of radioactive elements due to the ingestion of radium and radon from drinking water are equal to the total number of lung cancers due to the inhalation of these radionuclides. Long-term exposure to PTEs and other chemical contaminants, even at low levels, could have a harmful effect on the ecosystem and environment, especially including the impact of water quality on human health (under 17 years: the growing age of children). Most PTEs exist in the environment and occur naturally. Some PTEs are emitted into the environment from anthropogenic sources. The exposure of the human body to these toxic elements is either environmental, because the element already exists in nature, or through foreign sources.

Substances including radioactive elements and PTEs can cause negative effects on the environment and human health. Excessive levels of PTEs (Fe, Pb, Zn, Ni, Cr, Cu and Cd) can cause significant damage to every organ of the body and can result in neurological defects,

carcinogenicity, osteoporosis, etc. It is time to become aware of the control of transboundary water resources and to make master plans for quality and quantity control. To control the relationship between natural radiation and anthropogenic activities, and considering the fact that human senses cannot detect low radiation, international collaborations are essential to stop this type of quality degradation, especially of surface waters, which are in direct contact with the atmospheric column, ecosystem and human health. A global view on an international scale is crucial to fully understand the regional climatic situation in relation to regional socio-economic development.

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Conflicts of Interest: The present paper is an original work; it is the first in the study area, and all the authors declare that they have no conflicts of interest. The authors jointly carried out this research study, and they confirm that they are not associated with or involved in any profitable organization or company that has any financial interest.

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