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Spatial Distribution, Health Risks and Heavy Metal Pollution Assessment of Surface Water Under Multiple Anthropogenic Stressors: Case Study in Middle Moulouya Watershed, Morocco

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Abstract

The worldwide issue of surface water contamination by heavy metals is a matter of great concern, as it has the potential to affect human health. This study intended to compute heavy metal contamination and human health risks in surface water using the following pollution indices: heavy metal pollution index (HPI), contamination index (CI), metal index (MI), ecological risk index (ERI), human health risk and statistical analysis. For this purpose, eleven water samples were gathered and analyzed by ICP-AES for trace metals such as Pb, As, Zn, Cd, Cu, and Ni. The results showed that heavy metal concentrations varied significantly throughout the study area, with Pb, As, and Cd levels exceeding the WHO limits for drinking purposes. Pollution indices indicated low to high water contamination, with HPI results ranging from 16.41 to 862.18 and from 12.76 to 774.03, above the critical value of 100, requiring serious interventions to reduce heavy metal pollution. MI results range from 0.90 to 20.92 and from 0.70 to 18.41 and CI values range from 0.34 to 20.38 and from 0.15 to 17.86 in the dry and wet periods, respectively, with different contamination levels observed throughout the study area; ERI showed low to considerable ecological risk. Nonetheless, the non-carcinogenic risk, THI < 1, indicates low health risks, while the carcinogenic risk for As and Cd was significantly higher than the negligible threshold of 10^{-6}, suggesting tolerable health risks. However, managing the contaminated area and minimizing the metal concentrations and predominant routes through which metals impact human health should be priorities for long-term development and to establish a favorable environment.

Keywords: ecological risk; heavy metal pollution; human health risk; middle Moulouya; surface water quality

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1. Introduction

Water is essential to life; it is a global concern to provide a safe, palatable, and easily accessible supply [1]. However, as towns and cities continue to grow, surface water contamination from human-derived sources, such as industrial discharge, inadequate wastewater systems, improper disposal of waste, trash from construction, and agricultural runoff, are increasing [2]. In addition, water body features are also influenced by other factors, such as biological processes, organic compounds, and elements leaching from adjacent soil, mineral weathering in the bedrock, and atmospheric deposition. Moreover, the hydrological elements that affect the amount of nutrients in the surface water include river and water discharge, level, and flow velocity [3]. Therefore, to prevent harmful impacts on human health, surface water must be safeguarded, and its quality must be regularly assessed.

The main causes of surface water degradation are diffuse and punctual pollution [4]; punctual sources are easy to manage because they typically have a clear origin [5]. However, dispersed sources are more challenging to control due to their unclear origin, such as metals that end up in lakes and rivers [6]. While mining, agriculture, and mineral processing with chemical and metallurgical operations are the primary anthropogenic activities, atmospheric movement and bedrock erosion are the natural origins of heavy metals [7]. As a result, there are three ways that surface water may become polluted: (i) by residues that are close to sources of pollution, (ii) by water runoff and/or wind after extraction, and (iii) by dissolution in mine sites [8].

In agricultural contexts, the excessive use of chemicals such as fertilizers, pesticides, and animal feed additives may make nearby surface water more likely to become contaminated with metals [9]. However, environmental pollutants such as heavy metals are the main cause of deteriorating surface water quality around the world [10]. Indeed, due to the accumulation of heavy metals in the biota, their toxicity, and their lack of environmental degradability, their pollution is a major problem [11]. In this regard, different studies have been conducted to evaluate heavy metal contamination in surface water, emphasizing recorded metal concentrations compared to maximum allowable thresholds such as the World Health Organization standards [1] (WHO 2011), and determining the contamination sources [12,13]. Furthermore, the level of heavy metal pollution in water samples has been measured using mathematical methods such as the metal index and the heavy metal pollution index [14]. In addition, the correlation matrix and multivariate techniques such as principal component analysis (PCA) were used to extract information from the recorded data and determine the linkages between parameters that impact water quality.

According to [15], abandoned mining sites in Morocco are a source of heavy metal pollution, especially where no environmental management program has been implemented to reduce the impact. This is the case of the Zaida mines, situated in high Moulouya, which ceased operations in 1986 after starting operations in 1972 [16]. Mining was conducted in quarries, and the cerussite ($PbCO_3$) ore was processed on-site using gravimetry and flotation. This technique produces approximately 12 Mt of abandoned tailings without rehabilitation [17]. These tailings are a major cause of pollution in rivers and adjacent soils [18,19]. Moreover, the severe contamination of the Moulouya River by these tailings has been confirmed by previous studies [20,21]. Furthermore, soil contamination is significantly higher north of the mine tailings, as prevailing winds disperse particles throughout the basin. The sediment assessment showed that Pb is the main contaminant, with concentrations exceeding 200 mg/kg, notably downstream of the tailings. However, significant heavy metal levels were also detected 14 km from the tailings alongside the Moulouya River, which is attributed to the distinctive hydrological transport patterns in the area [22]. These investigations have either measured the fluxes of trace metals from mining regions or evaluated the water and sediment pollution caused by mine tailings. Nevertheless, none of them have combined heavy metal pollution indices and their effects on human health and the potential spread of this pollution to the middle Moulouya region. Our investigation fills this gap in the literature. The objective of this research is therefore to evaluate the potential spread of heavy metals from abandoned mining sites in the upper Moulouya to the middle Moulouya, and to assess the effects of wastewater and agricultural activities on the surface water quality across the river system. This is accomplished using heavy metal pollution indices, human health risk assessments, and statistical techniques to determine the sources and risks of contamination. The findings of this study may provide valuable insights for managing a polluted area characterized by erratic precipitation and a semi-arid climate.

2. Materials and Methods

2.1. Study Area

The Moulouya basin is subdivided into three subbasins: the high, the middle and the lower Moulouya. The Middle Moulouya basin was the main focus in this investigation, situated in central eastern Morocco between 32°50′–33°50′ N and 4° W. This area has a surface of 16,800 km^2, with altitudes ranging from 534 m to 3321 m (Bounacere Montain), and is bordered by the High Plateau eastward, the folded Middle Atlas to the west, the High Atlas to the south and the Bouyacoubat threshold to the north. Three regions border the area: Fes-Meknes, Oriental and Draa-Tafilalt. The Moulouya River, which drains into the Mediterranean, crosses the studied area. Owing to its geographic location, the area is distinguished by semi-arid climate with cold dry winters and hot summers. The average annual precipitation in the area ranges from 160 to 300 mm, summer temperatures can reach up to 45 °C, while winter temperatures can drop as low as −2 °C. The rainfall in the basin is generally brief and intense, which increases erosion and leads to severe inundation [23]. The flow of the Moulouya River is characterized by high floods during the rainy periods and low water levels in the dry period [24]. The geographic coordinates of the research area location and gathered samples are presented in Figure 1.

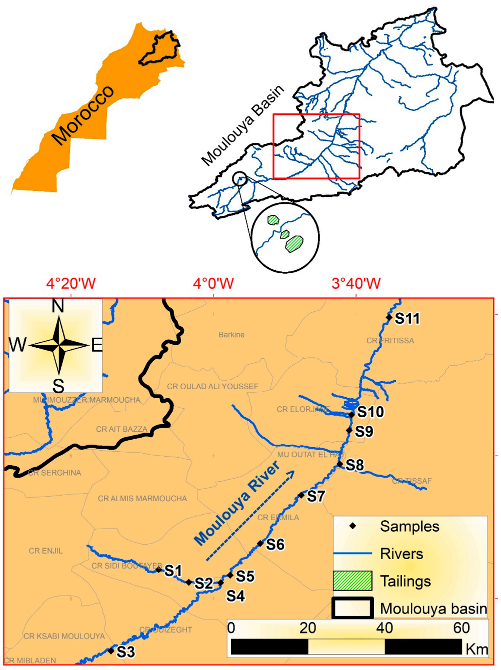


Figure 1. Studied area map showing surface water sampling station in the middle Moulouya basin (authors' own work).

2.2. Sampling

In June 2024 (dry period) and December 2024 (wet period), considering the numerous activities found in the research area, industrial, domestic and agricultural activities including mining extraction in High Moulouya and sewage from Missour and Outat El Haj cities, samples of water were gathered in pre-cleaned polyethylene bottles from 11 stations that were dispersed through the Middle Moulouya and were chosen for their accessibility and ability to accurately represent the freshwater properties in the river of Moulouya and its tributary Chouf Chreq, which serve as drinking and irrigation water. Moreover, sampling sites were carefully chosen at regular intervals, considering regional geographic characteristics and giving priority to regions connected to the many activities (domestic, tailings and agricultural) in the study area. The collected samples were preserved separately by adding a few drops of nitric acid solution (7M) and shipped immediately to the laboratory in an ice box at 4 °C.

2.3. Chemical and Physical Analysis

Three parameters of water quality and seven heavy metals were evaluated in the investigation, including pH, electrical conductivity (EC), and temperature (T in °C), which were measured in situ using a portable multi-parameter analyzer (Aquaread AQUALINK, Broadstairs, UK). The concentrations of heavy metals (Cu, As, Pb, Cd, Zn, Ni and Cr) were analyzed using an ICP-AES (Ultima Expert Horiba Jobin Yvon, Horiba Scientific, Palaiseau, France) after the digestion process, which involves heating the water samples to 95 °C with a mixture of nitric acid (HNO_3) and hydrochloric acid (HCl) (in a ratio of 1:3) to make the extractable metals available for analysis and filtering the samples before analysis. An ultrapure water sample was used for the blank test under the same conditions [20]. To determine the accuracy and preserve the quality of the extraction procedure, every experiment was triplicated, and if the relative standard deviation for each sample was less than 5%, the measurement was retained and the average was computed [25,26]. This sophisticated technique enables the precise measurement of heavy metals, enhancing the accuracy and reliability of analytical results, with a detection limit of 10^{-1} µg/L and controlled with ICP-Expert Sequential software. The instrument was calibrated with 0.1, 1.00, 10.00 and 25.00 mg/L concentrations using ICP multi-element standard solution VIII (Merck, Rahway, NJ, USA, 24 elements) and Na_2HPO_4 [20].

2.4. Evaluation of Surface Water Pollution

2.4.1. Contamination Index (CI)

The CI, which evaluates the heavy metal contamination levels, summarizes the aggregate impact of multiple quality issues harming water [27], and was computed using Equation (1):

$$\mathbf{CI} = \sum_{\mathbf{i}=1}^{\mathbf{n}} \mathbf{C_{fi}} \quad (1)$$

where $\mathbf{C_{fi}} = (\mathbf{C_{Ai}}/\mathbf{C_{Ni}}) - 1$

C_{fi} signifies the contamination factor, C_{Ai} is the analytical value and C_{Ni} denotes the parameter's highest allowable concentration, with reference (Table 1). Three groups were created from the resulting CI value, which indicates regions with different levels of contamination [28], as shown in Table 1.

Table 1. Classes of the CI.

CI Value	CI Class
<1	Low
1 < CI < 3	Medium
>3	High

2.4.2. Heavy Metal Pollution Index (HPI)

HPI is an effective method for assessing the combined impact of each heavy metal on water quality [29,30]. Each chosen parameter is allocated by weight (W_i) or by ranking to compute the heavy metal pollution index using Equation (2):

$$\mathbf{HPI} = \frac{\sum_{i=1}^{n} \mathbf{W_i Q_i}}{\sum_{i=1}^{n} \mathbf{W_i}} \tag{2}$$

where W_i is the unit weight of the i-th parameter, and the subindex Q_i is calculated using Equation (3):

$$\mathbf{Q_i} = \sum_{i=1}^{n} \frac{(\mathbf{M_i} - \mathbf{I_i})}{(\mathbf{S_i} - \mathbf{I_i})} \times 100 \tag{3}$$

M_i signifies the measured concentration of heavy metals, I_i signifies the ideal value and S_i is the ith parameter's standard values supplied by the WHO guidelines 2017, as illustrated in Table 2. The highest allowable concentration (MAC_i) of the chosen parameter is inversely correlated with the unit weightage (W_i), and three categories are used to classify water according to the HPI [31], as illustrated in Table 3.

Table 2. The WHO Standards 2017 of heavy metals.

Parameters	S_i (µg/L)	MAC_i (µg/L)
Pb	10	10
Zn	3000	3000
Cu	2000	2000
Cd	3	3
Ni	70	70
As	10	10
Cr	50	50

Table 3. Classes of the HPI.

HPI Value	HPI Class
<15	Low water pollution
15 < HPI < 30	Medium water pollution
>30	High water pollution

2.4.3. Heavy Metal Index (MI)

In accordance with [28], the heavy metal index (MI), which is computed according to Equation (4), provides a general quality assessment of water according to the concentration of heavy metals:

$$\mathbf{MI} = \sum_{i=1}^{n} \frac{\mathbf{Ci}}{\mathbf{MACi}} \tag{4}$$

where C_i and MAC_i are the i-th parameter's monitored concentration and the highest allowable concentration (MAC_i); six classifications were created from the overall results signifying water pollution [32], as presented in Table 4.

Table 4. Heavy metal index (MI) classification.

MI Value	MI Class
<0.3	Very pure
0.3 < MI < 1	Pure
1 < MI < 2	Slightly affected
2 < MI < 4	Moderately affected
4 < MI < 6	Strongly affected
>6	Seriously affected

2.4.4. Ecological Risk Index (ERI)

The ecological risk gives a quantitative evaluation of the possible ecological risk presented by heavy metals in water [33]. This approach aids in evaluating the effects of several metals by considering their relative toxicities and concentrations. By considering their toxic-response factor and pollution index, the heavy metal potential under analysis was practically assessed using equations as follows:

$$\mathbf{ERI} = \sum_{i=1}^{n} \mathbf{RI} = \sum_{i=1}^{n} \boldsymbol{T_i} * \mathbf{PI} \tag{5}$$

$$\mathbf{PI} = \frac{\boldsymbol{C_s}}{\boldsymbol{C_b}} \tag{6}$$

where the *i*-th heavy metal's pollution index is denoted by PI; C_s signifies the sample's concentration of heavy metal; "C_b" means relevant background values; RI is the ith heavy metal's potential ecological risk factor and the heavy metals' toxic-response factor T_i is provided as "As = 10; Cu, Pb and Ni = 5; Zn = 1; Cd = 30" [34]. There are four classes for ERI results [28], as illustrated in Table 5.

Table 5. Classes of the ERI.

ERI Value	ERI Class
<150	Low ecological risk
150 < ERI < 300	Moderate ecological risk
300 < ERI < 600	Considerable ecological risk
>600	Very high ecological risk

2.4.5. Human Health Risk Assessment

- Noncarcinogenic health risk assessment

The approach employed by United States Environmental Protection Agency (USEPA) [35] was used to compute the noncarcinogenic risk of drinking water polluted with heavy metals for both children and adults. The following formulas were used to assess the chronic daily intake mg/kg/day for children and adults:

$$\mathbf{CDI_{ingest}} = \left[\frac{\mathbf{Ci \times IngR \times CF \times EF \times ED}}{\mathbf{ABW \times AT}}\right] \tag{7}$$

$$\mathbf{CDI_{dermal}} = \left[\frac{\mathbf{Ci \times SA \times CF \times AF \times ABS \times EF \times ED}}{\mathbf{ABW \times AT}}\right] \tag{8}$$

where CDI is the metal's chronic daily intake (mg/kg/day) Ci denotes metal concentration (mg/L), ED denotes the exposure duration in years, and IngR represents the metal's daily ingestion (mg/day). EF represents the exposure frequency (days/years), ABW denotes the body weight in kg, AT denotes exposure time, ABS is the dermal permeability coefficient (cm/h), CF is the conversion factor, and SA is the exposed skin area (cm^2) [36].

$$\mathbf{HQ} = \frac{\mathbf{CDI}}{\mathbf{RfD}} \tag{9}$$

$$\mathbf{THI} = \sum\left(\mathbf{HQ_{ingestion}} + \mathbf{HQ_{dermal}}\right) \tag{10}$$

where HQ denotes hazard quotient, and THI denotes the Total Hazard Index, which is calculated by adding up the HQ for every metal. Based on USEPA (2005), THI > 1 suggests that exposure to metals is likely to have adverse health effects, whereas a value less than 1 indicates low health risk [31].

- Carcinogenic risk assessment

Human exposure to trace metals is a primary cause of cancer, and the equations employed by USEPA were used to compute the possible carcinogenic risk.

$$\mathbf{CR} = \mathbf{CDI} \times \mathbf{CSF} \tag{11}$$

$$\mathbf{LCR} = \sum \mathbf{CR}(\mathbf{dermal} + \mathbf{ingestion}) \tag{12}$$

where CSF signifies cancer slope factor in mg/kg/day, CR denotes cancer risk, and LCR is the lifetime risk. Moreover, LCR < 10^{-6} denotes negligible carcinogenic risk, showing minimal health risk. LCR between 10^{-6} and 10^{-4} indicates that the carcinogenic risk is significantly higher than the negligible threshold of 10^{-6}, which suggests that while there may be some level of risk, it is within a range deemed manageable. LCR > 10^{-4} indicates high risk and require serious interventions [37].

2.5. Statistical Analysis

The Kolmogorov–Smirnov test was performed to assess the normality and homogeneity of parameter distribution. Since there was no normal distribution in the experimental data, the non-parametric Spearman's correlation was used to examine the important relationships among the contaminants and determine their potential sources.

Multivariate statistical analyses, including the PCA, were extensively used to determine the potential sources of contamination. Principal component analysis is a dimensionality reduction technique commonly used to convert complex datasets into principal components (PCs), facilitating interpretation. To assess the suitability of the data for this analysis, the Kaiser–Meyer–Olkin (KMO) test and Bartlett's sphericity test were conducted on the parameter correlation matrix [38,39]. The factor loadings in this investigation exceeding 0.7 were deemed significant. Statistical analysis was elaborated using the dry period. The dataset was statistically analyzed using SPSS V26, XLSTAT 2016 and ArcGIS 10.7 for the maps.

3. Results and Discussions

Rivers are useful indicators of land use because their water chemistry reflects changes in the watershed [40]. Human activity and regional geology are significant factors influencing river water quality [41]. Consequently, rivers with lengthy flow paths exhibit distinct water quality classifications. Diffuse pollution has been identified in some studies as the primary cause of the declining water quality of rivers [42]. This study aims to identify the surface water quality of the Middle Moulouya basin. Water samples (n = 11 designated S1–S11) were collected from the Moulouya River and its tributary, Chouf Chreq, during June 2024 (dry period) and December 2024 (wet period). The physicochemical parameters and heavy metal concentrations of the samples are presented in Table 6, along with basic statistical summaries.

Table 6. Physicochemical parameters of water samples (n =11) during the dry and wet periods, expressed as minimum (Min), maximum (Max), average (Avg), and standard deviation (SD), compared with WHO (2017) drinking water quality standards.

	Dry Period (Samples n = 11)									Wet Period (Samples n = 11)									
Samples	**T °C**	**pH**	**Cond (µS/cm)**	**Pb (µg/L)**	**Cu (µg/L)**	**As (µg/L)**	**Zn (µg/L)**	**Cd (µg/L)**	**Ni (µg/L)**	**T °C**	**pH**	**Cond (µS/cm)**	**Pb (µg/L)**	**Cu (µg/L)**	**As (µg/L)**	**Zn (µg/L)**	**Cd (µg/L)**	**Ni (µg/L)**
S1	29.2	8.1	1522	12	2.2	0.00	2.8	0.00	0.1	20.1	7.9	1655	9	2.0	0.00	2.4	0.00	0.00
S2	28.4	7.9	1370	9	1.7	0.00	2.3	0.00	0.1	18.2	7.8	1466	7	1.6	0.00	1.9	0.00	0.00
S3	25.5	8.4	3150	52	46	43	24	34	4.4	15.6	8.2	3270	45	39	35	22.8	31	3.5
S4	27.3	8.1	2640	47	37	37	22.4	27	3.9	17.5	8.1	2850	42	33	32.6	19.3	24.4	3.10
S5	27.9	7.7	3390	54	41	40	17.3	32	3.3	15.1	7.3	3780	49	38	38.3	17	27	2.80
S6	28.1	7.5	3930	46	36	32	14.7	28	3.1	16.9	7.1	4120	38	31	27	13.9	25	2.63
S7	29.4	7.2	3520	35	32	27	12.9	22	2.9	14.1	7.6	3720	32.6	29.3	23.9	12.1	17.3	2.44
S8	28.7	7.4	3070	26	29	19	11	19	2.2	16.7	7.4	3210	21.5	26.7	17.4	10.3	14	2.09
S9	26.5	7.3	3690	29	33	24	9.6	21	1.8	15.5	7.5	3090	25	30	22.8	9.1	18.5	1.65
S10	25.1	7.5	2960	25.9	27	23.2	8.1	18	1.1	13.9	7.7	2670	22	24.5	20.5	7.7	14.1	0.77
S11	27.7	7.7	2540	23.1	24.8	17.7	7.66	16.3	0.8	13.4	7.3	2470	18	21.6	15.4	6.1	12.7	0.63
Min	25.1	7.2	1370	9.00	1.70	0.00	2.30	0.00	0.1	13.4	7.1	1466	7	1.6	0.00	1.2	0.00	0.00
Max	29.4	8.4	3930	54	46	43	24	34	4.4	20.1	8.2	3780	45	39	38.3	22.8	31	3.50
Avg	27.61	7.71	2889.27	32.63	28.15	23.9	12.07	19.75	2.15	16.09	7.63	2936.45	28.1	25.2	21.2	11.1	16.7	1.80
SD	1.41	0.46	827.06	15.49	14.31	14.41	7.13	11.30	1.50	2.03	0.41	838.83	14.26	12.64	12.66	6.68	10.16	1.25
WHO Standards (2017)	-	6.5–8.5	1000	10	2000	10	3000	3	70	-	6.5–8.5	1000	10	2000	10	3000	3	70

3.1. Physical and Chemical Parameters of Surface Water

The pH of water, which indicates its acidic or basic nature, is a key parameter for both potable and agricultural uses. It influences the water hardness, alkalinity and solubility of metals [43]. The pH results of the river water ranged from 7.1 to 8.2 in the wet period with an average value of 7.63 and 7.2 to 8.4 with an average of 7.71 in the dry period, indicating that the water in this river section is slightly neutral to alkaline. This basicity may be primarily caused by the limestone and marino-dolomitic lithology of the areas that the Moulouya River and its tributary traverse, which are rich in carbonates and provide natural buffering capacity. The temperature values ranged from 25.1 to 29.4 °C in the dry period and 13.4 to 20.1 °C in the wet period, revealing that the lowest value was assessed for samples S10, while the highest value was observed for samples S7. Additionally, this is certainly impacted by the seasonal variation, given that the samples were gathered in dry and wet periods. However, if there is organic matter existing in the research area, the temperature can accelerate its degradation, producing complex acidic substances [44].

The electrical conductivity (EC) is an important parameter for assessing water quality and directly correlates with the total dissolved solid concentration in water. However, the EC results fall into a range of 1370–3930 µs/cm during the dry period and 1466–3780 µs/cm in the wet period, which are typically high at the Moulouya River and moderate at the Chouf chreq tributary. The principal cause of the conductivity fluctuation may be the Moulouya River's bicarbonate waters, which drain limestone and dolomite from the upper basin. However, abandoned mining tailings, situated near water resources, are heavily mineralized [24], which could lead to greater conductivity of water.

3.2. Heavy Metals of Surface Water

Heavy metals can be found in groundwater and surface water. Their sources are linked to either natural or human-caused processes [45]. Cu, As, Zn, Pb, Cd, Cr and Ni analyses were executed by ICP-AES, and only the Cu, Pb, Cd, Zn, As and Ni concentrations exceeded their detection limits.

The mean concentrations of the analyzed metals in each period adhere to the decreasing order of Pb > As > Cd > Zn > Cu > Ni. Moreover, Pb, As and Cd were identified as the major pollutants in the studied area, and the result indicates that sample S3 had the greatest Pb concentration, while the minimum concentration found at sample S2, almost 81.81% of the sample (S3–S11 and S1), surpassed the 10 µg/L WHO standard, possibly due to the wastewater inputs from Missour and Outat El Haj cities and drain mine tailings from high Moulouya. Moreover, the analyzed metals show moderate mobility, which indicates that the current study is consistent with previous study that showed that Moulouya River is a medium of heavy metal transport [19]. In accordance with Bouzekri et al., 2020 [20], the Pb concentration reached up to 268 µg/L in the high Moulouya River section near the abandoned Pb mine Zaida, while Pb inputs from agricultural leaching and roads are most likely the cause of the Pb contamination in other stations [46]. Additionally, the results of spatial distribution show that the upper value is situated in the south of the study area, receiving pollution from high Moulouya and domestic wastewater from nearby urban centers, as shown in Figure 2a.

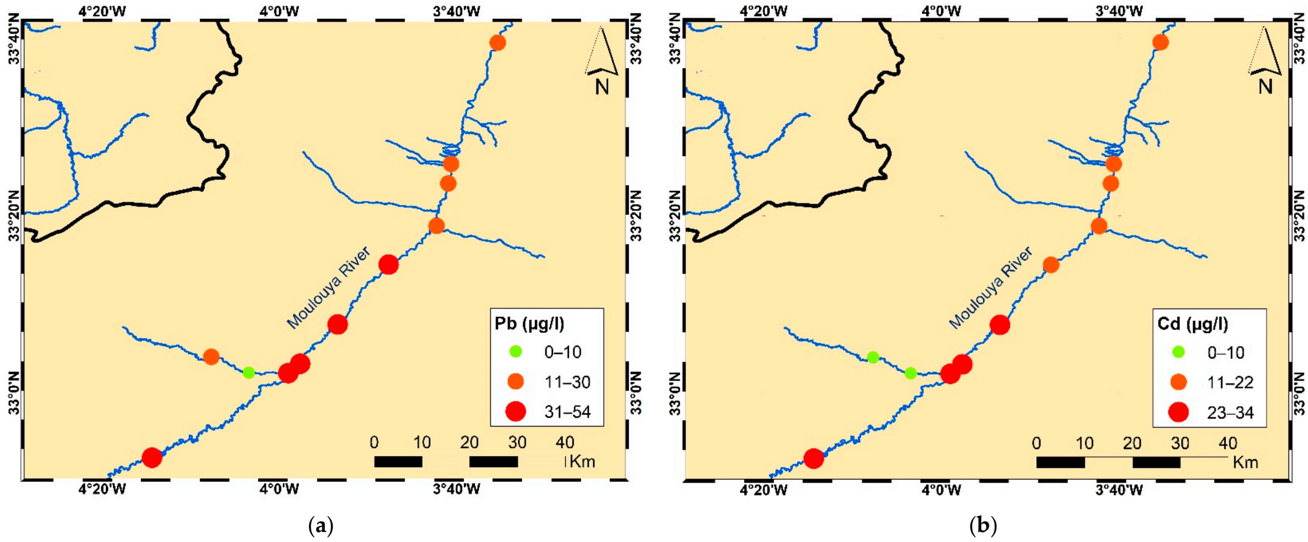


Figure 2. Spatial distribution maps of (**a**) Pb and (**b**) Cd during dry period(authors' own work).

The principal source of cadmium (Cd) is geogenic (like minerals) that include magnesium and calcium ions. However, Cd is frequently used in human activities including battery manufacturing, the use of phosphate fertilizer and pesticide applications [47]. On the other hand, an intensive agricultural operation that uses fertilizers is carried out alongside the Moulouya River, which may be a source of Cd contamination in the studied area. Additionally, a similar study shows that the occurrence of leaching and runoff is a major cadmium input into the river [46]. The greatest Cd concentration was noted at sample S5, and the minimum value was observed at sample S1, proving that the contamination levels varied spatially (Figure 2b). All samples except S1 and S2 surpassed the 3 µg/L WHO standard.

Naturally occurring in many environmental compartments, arsenic (As) is greatly affected by natural and human-induced practices, including mining, the use of pesticides, and agricultural practices that use additives containing arsenic [48]. In this study, over 80% of the samples exceeded the 10 µg/L WHO standard, with sample S3 containing the highest As concentration, while the samples S1 and S2 had the lowest concentration, which indicates high contamination in the Moulouya River and low contamination at the Chouf Chreq tributary. These findings may be directly related to the effect of the residues situated adjacent to the Moulouya River. In accordance with El Hachimi et al., 2013 [24], very high amounts of heavy metal are found in mining wastes in high Moulouya, whose As is found to be 192 mg/kg. Another study has indicated that wind transport is the primary element influencing the movement of fine particles from mine residues to the nearby soils in arid areas [49]. Tailings are easily eroded and usually contain significant metal concentrations. Furthermore, these metals can be dispersed as particle-bound and/or aqueous solutions [17]. Moreover, agricultural practices may be another source of As. The As contamination in the soils of apple orchards in the high Moulouya could confirm this, is derived from pesticides reaching the aquatic ecosystem by leaching [50,51] or by erosion [52]. The spatial distribution indicates a difference in the contamination levels across the study area (Figure 3a). There are health risks associated with this spatial distribution, given that prolonged exposure to high As concentrations through potable water may result in serious health risks, such as skin lesions, developmental impacts, and even cancer [53].

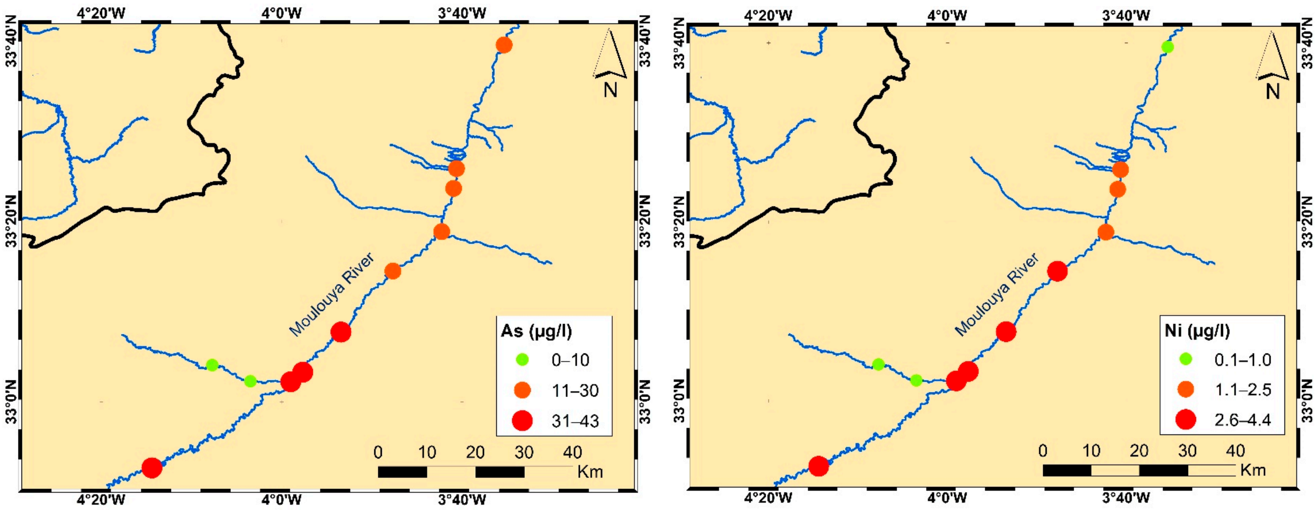
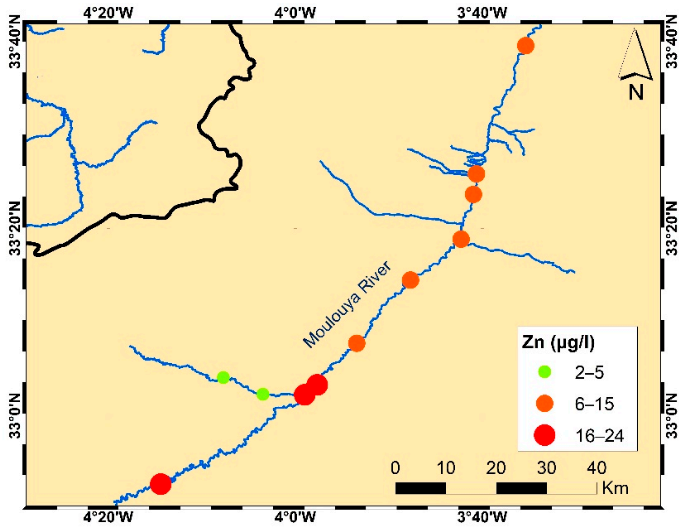


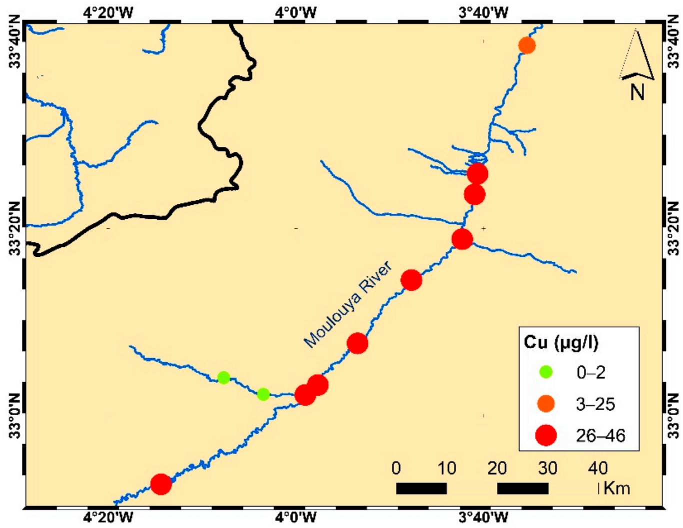
Figure 3. Spatial distribution maps of (**a**) As and (**b**) Ni during dry period (authors' own work).

The spatial distribution maps show that heavy metals such as Zn, Cu and Ni vary from upstream to downstream of the studied area, while all water samples contain concentrations under the WHO limit for Ni (Figure 3b), Zn (Figure 4a), and Cu (Figure 4b). Moreover, the levels of all the heavy metals studied are higher in the dry period than in the wet period, possibly owing to the dilution phenomenon. Additionally, the seasonal variation indicates that the overall heavy metal concentrations increase because of a decrease in precipitation during the dry period, which decreased river flow and, as a result, increased the concentration of contaminants in the surface water. This result agrees with previous research showing this seasonal variation using organic IQE global quality index [54] and pollution index [55]. These studies show that the water quality improves due to seasonal variation.

However, the Moulouya River contains the highest Pb, As and Cd concentrations compared to some other rivers across Morocco and worldwide, as shown in Table 7, indicating that this river's water is unsafe for drinking. This may be due to the impact of nearby tailings. Similar findings from the area around the Zaida mine show that the contamination is widely distributed toward the tailings' eastern, northeastern, and southwest sectors [22]. Another study has indicated that wind transport is the primary element influencing the movement of fine particles from mine residues to the nearby soils in arid areas [56]. Also, this water quality degradation may be due to pollutants from intense agricultural activities along the Moulouya river and the organic load of urban discharges from small city streams caused by the malfunction of the wastewater treatment plant, which are most likely the result of shoddy installation or maintenance. Additionally, a quantity of domestic wastewater that drains into the Moulouya River without any treatment from the Missour town has been observed even where there is a wastewater treatment plant. These findings are in line with earlier findings from statistical and physicochemical investigations [57] and those using water quality index IQE [54] and the SEQ-Eau global quality index [55], which indicates that the locations that are close to urban centers are the most polluted because of the wastewater.



(**a**)



(**b**)

Figure 4. Spatial distribution maps of (**a**) Zn and (**b**) Cu during dry period(authors' own work).

Table 7. Comparative study of heavy metal pollution in study area with some other rivers.

References	Dominant Activities	Maximum Concentrations (µg/L)					
		As	Pb	Ni	Zn	Cu	Cd
Current study	Agricultural, industrial, domestic discharges	43	54	4.4	24	46	34
Sebou River Morocco [58]	Industrial, agricultural, domestic activities	10.20	13.32	70.30	3100	2300	3.2
Serou River Morocco [59]	Industrial, agricultural runoff, domestic	-	24	23	28	104	18
Oued Beht Morocco [49]	Mining activities	3.6	2.4		6	5	0.2
Oued Fez Morocco [60]	Industrial, domestic	6	18	139	1.6	72	85
Tafna River Algeria [61]	Industrial, domestic wastewater	-	2.71	-	6.71	3	3.99
Sava River Serbia [62]	Industrial, agricultural, domestic wastewater	-	6.05	-	61.6	22.8	1.35
Mala Welna River Poland [63]	Industrial, sewage	-	40	15	115	89	3

While the diminished concentration of all pollutants observed at samples S10 and S11 may be due to the self-purification phenomenon of the river, to the urban communes' remoteness, and to the phenomenon of dilution, according to El Hamidi et al., 2022 [55], because urban areas are far away from the river's self-purification phenomenon and dilution, the water quality downstream of each contaminated location has improved. Moreover, similar findings with a rise in the pollution degree of surface water close to towns and a subsequent water quality improvement due to the river's self-purification phenomenon were obtained in the Oued Laou along the Atlantic coast's Tahaddart basin and the Mediterranean coast; they indicate good water quality except stations near urban centers, where there is untreated wastewater discharge and intense agricultural use of pesticide [64], and the water quality degradation in several Moroccan aquatic environments along the Oued Boufekrane that crosses the Meknes city is caused by this man-made source connected to agriculture and residential and industrial discharges [65]. Also, there is contamination in the Fez city rivers [66] and in the Niger Delta region [67].

3.3. Multivariate Statistical Analysis

3.3.1. Correlation Matrix Analysis

Correlation analysis was used in water quality studies and provided important information about how many factors interact and affect the chemical makeup of water [68]. Given that the analyzed datasets did not follow a normal distribution, as confirmed by the Kolmogorov–Smirnov (K-S) test, a non-parametric Spearman correlation analysis was applied to assess the relationships between variables (Table 8). The results revealed very strong positive correlations among all examined metals ($r > 0.9$; $p < 0.01$), indicating potential common sources and/or similar behavior during transport from the pollution source, as demonstrated in our previous work [69].

Table 8. Spearman's correlation analysis among the studied variables.

Variables	Cu	Zn	Pb	Cd	Ni	As	T °C	pH	Cond (µs/cm)
Cu	1								
Zn	0.964	1							
Pb	0.982	0.964	1						
Cd	0.970	0.943	0.989	1					
Ni	0.961	0.998	0.961	0.945	1				
As	0.980	0.961	0.980	0.973	0.963	1			
T °C	−0.391	−0.282	−0.282	−0.264	−0.292	−0.401	1		
pH	0.101	0.128	0.050	−0.002	0.122	0.099	−0.233	1	
Cond (µs/cm)	0.664	0.582	0.664	0.724	0.579	0.642	−0.091	−0.581	1

Strong positive correlations among the investigated metals indicate a shared origin and mutual dependence. Moreover, Pb indicates a significant positive correlation with As ($r = 0.980$), suggesting that these metals share the same source, which may be due to the mining tailings. The Cd indicates a high positive correlation with As ($r = 0.973$), and Cu with Zn ($r = 0.964$), suggesting that similar sources may cause these metals, whereas the widespread use of fertilizer and pesticides in nearby agricultural fields could be the cause [20]. Moreover, positive correlations were observed between EC and Cu, Pb, Zn, Ni, As, and Cd, highlighting its role in controlling water chemistry [31]. Overall, a high and significant correlation was found among the examined heavy metals, as evidenced by the predominance of strongly positive correlation coefficients ($p = 0.001$). These outcomes highlight the relevance and necessity of applying principal component analysis (PCA) in this study [70].

3.3.2. Principal Component Analysis (PCA)

The PCA is among the statistical analyses commonly used in environmental studies, particularly for classifying water samples according to their potential pollution [71]. In this investigation, the high Kaiser–Meyer–Olkin (KMO) value of 0.86, along with a significant result from Bartlett's sphericity test ($p < 0.001$), confirmed the suitability of the dataset for PCA application. The factor loadings, along with the cumulative percentage and variance explained by each factor, are presented in Table 9. The first two PCs accounted for 88.58% of the overall variance (71.36% for F1 and 17.22% for F2), with eigenvalues exceeding 1 (6.42 for F1 and 1.55 for F2). The first component explains 71.78% of the total cumulative variance and is strongly dominated by all measured heavy metals (each loading between ~0.93 and ~0.995) together with conductivity (loading ~0.796), indicating a common underlying gradient controlling the metal concentrations and ionic strength in the river system. This clustering suggests that metal mobilization, dissolution of metal-bearing minerals, and increased ionic strength (high conductivity) operate together as key processes, and when considered in the light of elevated metal loads in the basin and known human activities, this strongly reflects that anthropogenic inputs are likely the principal cause behind the elevated concentrations of these metals in the analyzed water. In contrast, temperature (T °C) and pH decouple from this main gradient; temperature loads negatively on F1 (~−0.425) and highly on F3 (~0.846), while pH loads negligibly on F1 (~0.016) but very highly on F2 (~0.985). These behaviors imply that the processes governing temperature and pH variation differ from those driving the metal-ion mobilization and conductivity. For instance, temperature may reflect seasonal variation, discharge regime, or surface water mixing rather than metal-bearing mineral weathering or anthropogenic metal input, and pH may be buffered by lithological conditions, atmospheric exchange, or catchment alkalinity, thus showing little co-variation with the metal conductivity factor. This interpretation aligns with multivariate studies in freshwater systems, which link high loadings of metals and ionic strength to anthropogenic sources (industrial, agricultural, and urban runoff), while pH and temperature often represent orthogonal environmental gradients [72].

Table 9. Factors loadings of the examined parameters in the studied area.

	F1	F2	F3	F4	F5	F6
Cu	**0.984**	−0.104	−0.075	0.019	−0.023	0.119
Zn	**0.936**	0.279	0.165	0.127	−0.032	0.007
Pb	**0.969**	0.087	0.155	−0.147	−0.003	−0.089
Cd	**0.988**	−0.092	0.004	−0.101	−0.056	0.043
Ni	**0.947**	0.113	0.244	0.158	0.038	−0.053
As	**0.995**	0.041	−0.016	−0.044	−0.069	−0.019
T °C	−0.425	−0.319	**0.846**	−0.035	0.003	0.035
pH	0.016	**0.985**	0.112	−0.069	0.105	0.044
Cond (µs/cm)	**0.796**	−0.566	−0.115	−0.018	0.180	0.006
Eigenvalues	6.42	1.55	0.80	0.14	0.06	6.42
Variability (%)	71.36	17.22	8.92	1.52	0.62	0.22
Cumulative (%)	71.36	88.58	97.50	99.02	99.64	99.86

PCA loadings > 0.7 are shown in bold.

As shown in Figure 5, the biplot of the first two principal components (F1 vs. F2) captures approximately 88.6% of the total variance in the dataset, indicating that these axes provide a strong two-dimensional summary of the multivariate structure. The heavy-metal variables (Cu, Zn, Pb, Cd, Ni, As), plotted with long arrows pointing strongly toward the positive direction of F1, reinforce that F1 is primarily driven by elevated metal concentrations and high ionic strength (as reflected by the conductivity arrow also directed strongly towards F1). In contrast, the pH arrow points almost exclusively along the positive F2 axis, while the temperature arrow projects into the negative F1/negative F2 quadrant; this spatial separation indicates that the pH and temperature vary independently of the major metal conductivity gradient. The tight clustering of the sampling site points toward the heavy metal/conductivity direction, suggesting that most sites share a common condition of metal and ionic strength enrichment, which is likely linked to anthropogenic contamination, as previously argued. Meanwhile, sites lying farther toward the pH or temperature directions may reflect hydrological or lithological controls rather than metal contamination processes. In effect, the biplot visually confirms that two distinct processes govern the surface water quality: (1) a dominant contamination axis of metals and conductivity linked to anthropogenic input, and (2) secondary environmental gradients (temperature regime, pH buffering) less directly connected to the metal sources. These visual insights reinforce the interpretation of the component-loadings table and highlight how the multivariate structure elucidates the mechanistic drivers in the Moulouya River system.

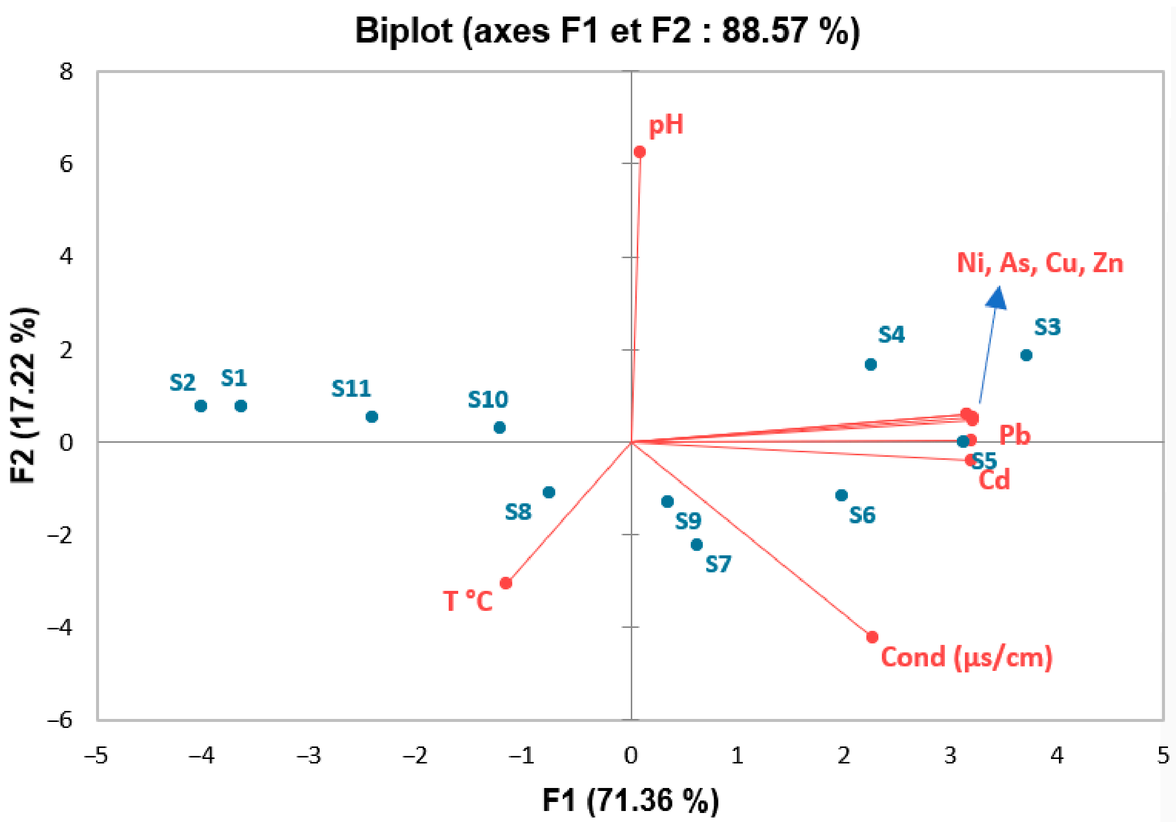


Figure 5. Biplots for principal component analysis reflecting the relationship between the examined samples and variables.

3.4. Pollution Evaluation Using HM Pollution Indices

3.4.1. Heavy Metal Pollution Index

The finding exhibits that HPI values vary from 16.41 to 862.18 with a mean of 503.37 in the dry period (Table 10), and from 12.76 to 774.03 with a mean of 428.78 for the wet period (Table 11). These results show the different levels of surface water contamination in the various zones of the studied area.

Table 10. Water quality classes using MI, HPI, CI and ERI results in dry period.

Samples	MI	Class	HPI	Class	CI	Class	ERI	Class
S1	1.20	Slightly affected	21.88	Medium water pollution	0.65	Low	6.01	Low ecological risk
S2	0.90	Pure	16.41	Medium water pollution	0.34	Low	4.51	Low ecological risk
S3	20.92	Seriously affected	862.18	High water pollution	20.38	High	409.44	Considerable ecological risk
S4	17.48	Seriously affected	700.29	High water pollution	16.93	High	330.88	Considerable ecological risk
S5	20.14	Seriously affected	819.81	High water pollution	19.59	High	387.34	Considerable ecological risk
S6	17.20	Seriously affected	709.59	High water pollution	16.65	High	335.31	Considerable ecological risk
S7	13.59	Seriously affected	558.85	High water pollution	13.05	High	264.79	Moderate ecological risk
S8	10.88	Seriously affected	467.05	High water pollution	10.33	High	222.23	Moderate ecological risk
S9	12.34	Seriously affected	522.14	High water pollution	11.79	High	248.71	Moderate ecological risk
S10	10.94	Seriously affected	454.23	High water pollution	10.39	High	216.29	Moderate ecological risk
S11	9.53	Seriously affected	404.63	High water pollution	8.99	High	192.37	Moderate ecological risk

Table 11. Water quality classes using MI, HPI, CI, and ERI results in wet period.

Samples	MI	Class	HPI	Class	CI	Class	ERI	Class
S1	0.90	Pure	16.41	Medium water pollution	0.35	Low	4.52	Low ecological risk
S2	0.70	Pure	12.76	Low water pollution	0.15	Low	3.50	Low ecological risk
S3	18.41	Seriously affected	774.03	High water pollution	17.86	High	367.85	Considerable ecological risk
S4	15.66	Seriously affected	630.46	High water pollution	15.11	High	297.91	Moderate ecological risk
S5	17.79	Seriously affected	706.27	High water pollution	17.25	High	333.10	Considerable ecological risk
S6	14.89	Seriously affected	625.09	High water pollution	14.34	High	296.27	Moderate ecological risk
S7	11.47	Seriously affected	453.59	High water pollution	10.92	High	213.45	Moderate ecological risk
S8	8.60	Seriously affected	354.63	High water pollution	8.05	High	168.36	Moderate ecological risk
S9	10.98	Seriously affected	462.01	High water pollution	10.43	High	220.49	Moderate ecological risk
S10	8.97	Seriously affected	363.17	High water pollution	8.42	High	172.62	Moderate ecological risk
S11	7.59	Seriously affected	318.22	High water pollution	7.05	High	151.50	Moderate ecological risk

According to the HPI results, the predominant category in the wet and dry period with 81.81% of samples is considered as "high water pollution" with HPI values recorded at 862.18 above the critical value of 100 and higher than similar studies in the Sebou River [58], where they revealed an HPI value of 109.39. This substantial amount suggests a serious pollution issue in the examined samples, with the water regarded as unfit for drinking, indicating severe heavy metal pollution in the studied area, which requires serious attention to metal pollution. While both anthropogenic activities, such as fertilizer use, mining practices and agricultural runoff, domestic wastewater from urban centers and natural mechanisms like minerals leaching from the soil, may be responsible for the medium and high pollution levels, the highest HPI was found in Sample S3, while the minimum value was found in sample S2.

3.4.2. Contamination Index (CI)

The result shows that CI ranged from 0.34 to 20.38 with a mean of 11.74 in the dry period (Table 10) and from 0.15 to 17.86 with a mean of 9.99 in the wet period (Table 11), demonstrating the significant variation in pollution levels across the study area. Furthermore, samples S1 and S2 represent a small subset, indicating lower contamination levels at these locations than the rest of the research region. However, over 81% of the samples were classified within the group of 'High contamination' (CI > 3). Moreover, the highest CI was recorded at sample S3 with a CI value of 20.38 in the dry period, highlighting the serious pollution problems that are probably caused by extensive human activities such as agricultural runoff along the Moulouya River, abandoned mining and domestic wastewater, which require serious attention for metal pollution. The lowest CI concentration was observed at sample S2 with a CI value of 0.15 in the wet period, suggesting that this place seems less impacted by heavy metal pollution, possibly as a result of less demanding domestic, industrial or agricultural practices.

3.4.3. Heavy Metal Index (MI)

The results obtained of MI vary from 0.90 to 20.92 with a mean of 12.28 in the dry period (Table 10), and range from 0.70 to 18.41 with a mean of 10.54 in the wet period (Table 11), whereas the MI states that 81.8% of the samples fall within "Seriously affected" because MI levels surpass 6. However, this category highlights serious contamination issues, specifically at sample S3, which had the greatest MI value of 20.92. These findings indicate that the combined effects of industrial and agricultural practices, including runoff from farmed areas and the release of untreated wastewater, are the main sources of contamination.

3.4.4. Ecological Risk Index (ERI)

The ecological risk index is a crucial indicator used to evaluate the possible ecological hazard caused by heavy metals in water [73]. In this study, the ERI results varied from 4.51 to 409.44 with a mean of 237.98 in the dry period (Table 10) and from 4.52 to 367.85 with a mean of 202.69 in the wet period (Table 11). Moreover, the surface water in this river section is divided into three different categories using ERI: 'Moderate ecological risk', 'Considerable ecological risk', and 'Low ecological risk'. Specifically, 18.18% of the samples were classified as 'Low ecological risk' because the ERI results were still below 150. Meanwhile, 45.45% fall within 'Moderate ecological risk', and over 36% are classed as 'Considerate ecological risk'. Furthermore, the highest value of 409.44 was found for sample S3, indicating a region with a significant concentration of heavy metals, while the lowest value was found in sample S2.

3.4.5. Human Health Risk Assessment

The noncarcinogenic risk of adults and children caused by heavy metals in both ways is mentioned in Table 12. The maximum, mean and minimum concentrations of HMs were used to sum up an overall concerning human health risk range in the studied area.

Table 12. Noncarcinogenic risk for children and adults using both exposure routes.

Metals	Levels	Conce (mg/L)	Children				Adults			
			Oral Ingestion		Dermal Exposure		Oral Ingestion		Dermal Exposure	
			CDI	HQ	CDI	HQ	CDI	HQ	CDI	HQ
Pb	Min	0.009	2.88×10^{-7}	8.22×10^{-5}	3.22×10^{-10}	6.14×10^{-7}	1.23×10^{-8}	3.52×10^{-6}	5.01×10^{-11}	9.53×10^{-8}
	Mean	0.033	1.05×10^{-6}	3.01×10^{-4}	1.18×10^{-9}	2.25×10^{-6}	4.52×10^{-8}	1.29×10^{-5}	1.84×10^{-10}	3.50×10^{-7}
	Max	0.054	1.73×10^{-6}	4.93×10^{-4}	1.93×10^{-9}	3.68×10^{-6}	7.40×10^{-8}	2.11×10^{-5}	3.00×10^{-10}	5.72×10^{-7}
Cu	Min	0.0017	5.43×10^{-8}	1.36×10^{-6}	6.09×10^{-11}	1.52×10^{-9}	2.33×10^{-9}	5.82×10^{-8}	9.45×10^{-12}	2.36×10^{-10}
	Mean	0.0280	8.95×10^{-7}	2.24×10^{-5}	1.00×10^{-9}	2.51×10^{-8}	3.84×10^{-8}	9.59×10^{-7}	1.56×10^{-10}	3.89×10^{-9}
	Max	0.0460	1.47×10^{-6}	3.68×10^{-5}	1.65×10^{-9}	4.12×10^{-8}	6.30×10^{-8}	1.58×10^{-6}	2.56×10^{-10}	6.40×10^{-9}
Zn	Min	0.000	7.35×10^{-8}	2.45×10^{-7}	8.23×10^{-11}	2.74×10^{-10}	3.15×10^{-9}	1.05×10^{-8}	1.28×10^{-11}	4.26×10^{-11}
	Mean	0.012	3.84×10^{-7}	1.28×10^{-6}	4.30×10^{-10}	1.43×10^{-9}	1.64×10^{-8}	5.48×10^{-8}	6.67×10^{-11}	2.22×10^{-10}
	Max	0.024	7.67×10^{-7}	2.56×10^{-6}	8.59×10^{-10}	2.86×10^{-9}	3.29×10^{-8}	1.10×10^{-7}	1.33×10^{-10}	4.45×10^{-10}
Ni	Min	0.0001	3.20×10^{-9}	1.60×10^{-7}	3.58×10^{-12}	1.74×10^{-10}	1.37×10^{-10}	6.85×10^{-9}	5.56×10^{-13}	2.70×10^{-11}
	Mean	0.0022	7.03×10^{-8}	3.52×10^{-6}	7.88×10^{-11}	3.82×10^{-9}	3.01×10^{-9}	1.51×10^{-7}	1.22×10^{-11}	5.94×10^{-10}
	Max	0.0044	1.41×10^{-7}	7.03×10^{-6}	1.58×10^{-10}	7.65×10^{-9}	6.03×10^{-9}	3.01×10^{-7}	2.45×10^{-11}	1.19×10^{-9}
Cd	Min	0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Mean	0.019	6.07×10^{-7}	1.21×10^{-3}	6.80×10^{-10}	1.36×10^{-6}	2.60×10^{-8}	7.44×10^{-6}	1.06×10^{-10}	2.11×10^{-7}
	Max	0.034	1.09×10^{-6}	2.17×10^{-3}	1.22×10^{-9}	2.43×10^{-6}	4.66×10^{-8}	1.33×10^{-5}	1.89×10^{-10}	3.78×10^{-7}
As	Min	0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Mean	0.024	7.67×10^{-7}	2.56×10^{-3}	8.59×10^{-10}	1.23×10^{-9}	3.29×10^{-8}	9.39×10^{-6}	1.33×10^{-10}	1.91×10^{-10}
	Max	0.034	1.09×10^{-6}	3.62×10^{-3}	1.22×10^{-9}	1.74×10^{-9}	4.66×10^{-8}	1.33×10^{-5}	1.89×10^{-10}	2.70×10^{-10}
HI for min. values				8.40×10^{-5}		6.16×10^{-7}		3.60×10^{-6}		9.56×10^{-8}
HI for max. values				4.10×10^{-3}		3.64×10^{-6}		3.09×10^{-5}		5.66×10^{-7}
HI for mean. Values				6.34×10^{-3}		6.17×10^{-6}		4.97×10^{-5}		9.59×10^{-7}

For the adults' and children's groups, the HQ for water ingestion was greater than dermal contact, which is in line with previous research that found the ingestion route had the greatest detrimental impact on health among the exposure routes [69,74]. The HI was below the permissible value of 1, indicating that the health risks due to metal exposure by different routes remained low for those residing close to the research area. The highest computed total hazard index (THI) was 4.10×10^{-3} for children and 3.15×10^{-3} for adults, which is in line with the previous studies [69,75], which confirmed that children are more susceptible to pollutants than adults because of their sensitivity and weak immune system [75].

The carcinogenic risk was computed for heavy metals, including As, Pb, and Cd, using their CSF accessible and USEPA standards, as mentioned in Table 13. The computed carcinogenic risk for children and adults was within the range of 10^{-4} to 10^{-6} (Table 13), indicating that these metals' cumulative carcinogenic risk is significantly higher than the negligible threshold of 10^{-6}, and suggesting that while there may be some levels of risk, it is within a range deemed manageable [31]. These findings indicate that the heavy metals studied in the water may cause tolerable carcinogenic risk to the local population and highlight the need for effective interventions to safeguard human health. Moreover, our study is consistent with a similar study [76], which observed tolerable carcinogenic risk in the Karasu River exposed to domestic, industrial wastewater discharges, agricultural and mining practices.

Table 13. Carcinogenic risk for children and adults using both exposure routes.

Metals	Levels	Conce (mg/L)	Children			Adults		
			Oral Ingestion	Dermal Exposure	LCR	Oral Ingestion	Dermal Exposure	LCR
Pb (mg/L)	Min	0.0090	2.45×10^{-9}	2.74×10^{-12}	2.45×10^{-9}	1.05×10^{-10}	4.25×10^{-13}	1.05×10^{-10}
	Mean	0.0330	8.97×10^{-9}	1.00×10^{-11}	8.98×10^{-9}	3.84×10^{-10}	1.56×10^{-12}	3.86×10^{-10}
	Max	0.0540	1.47×10^{-8}	1.64×10^{-11}	1.47×10^{-8}	6.29×10^{-10}	2.55×10^{-12}	6.31×10^{-10}
As (mg/L)	Min	0.0000	0.00	0.00	0.00	0.00	0.00	0.00
	Mean	0.0240	1.15×10^{-6}	1.29×10^{-9}	1.15×10^{-6}	4.93×10^{-8}	2.00×10^{-10}	4.95×10^{-8}
	Max	0.0340	1.63×10^{-6}	1.83×10^{-9}	1.63×10^{-6}	6.99×10^{-8}	2.84×10^{-10}	7.01×10^{-8}
Cd (mg/L)	Min	0.0000	0.00	0.00	0.00	0.00	0.00	0.00
	Mean	0.0190	2.31×10^{-7}	2.58×10^{-10}	2.31×10^{-7}	9.89×10^{-9}	4.02×10^{-11}	9.93×10^{-9}
	Max	0.0340	4.13×10^{-7}	4.63×10^{-10}	4.13×10^{-7}	1.77×10^{-8}	7.19×10^{-11}	1.78×10^{-8}
Cumulative carcinogenic risk for min. values			2.45×10^{-9}	2.74×10^{-12}	2.45×10^{-9}	1.05×10^{-10}	4.25×10^{-13}	1.05×10^{-10}
Cumulative carcinogenic risk for mean values			1.39×10^{-6}	1.56×10^{-9}	1.39×10^{-6}	5.96×10^{-8}	2.42×10^{-10}	5.98×10^{-8}
Cumulative carcinogenic risk for max. values			2.06×10^{-6}	2.30×10^{-9}	2.06×10^{-6}	8.82×10^{-8}	3.58×10^{-10}	8.85×10^{-8}

For instance, the residents close to the research area were not likely exposed to both carcinogenic and non-carcinogenic risks because of metal exposure. The human activities that are close to the study region should receive serious interventions as they may cause metals to build up in the soil and water.

Future proposal solution:

The results of this study clearly demonstrate that the surface waters of the Middle Moulouya Basin are contaminated with high levels of lead (Pb), arsenic (As), and cadmium (Cd), exceeding the permissible limits set by the WHO for potable water. Consequently, it is critical to urgently implement effective and rational management strategies for protecting public health and achieving sustainable water management. Thus, it is imperative to mandate a multi-tiered intervention approach that includes advanced water treatment methods such as membrane filtration and adsorption [77]. From this point of view, adsorption is the most common technique used as a cost-effective heavy metal removal technology due to its simplicity, capability to remove heavy metals even at trace amounts, and low energy requirement. For future work, our team plans to assess the performance characteristics of the amorphous, high-purity (99.99%) nano-silica with a high surface area (381.0582 m^2/g) extracted from a local and abundant natural resource (Moroccan oil shale) as an efficient green adsorbent for the removal of Pb, As, Cd, and Zn from the Middle Moulouya basin. Additionally, this nanomaterial aligns with the principles of the circular economy, promoting the conversion of national industrial byproducts into a high-value resource intended for water purification [78]. Complementing this advanced technique, a hotspot-based management strategy should be applied by primarily targeting geographical areas that register the highest human impact index (HPI), metal index (MI), and contamination index (CI) values. Simultaneously, agricultural runoff, mining drainage, and industrial waste streams should be strictly controlled. A final necessary step is necessary for tracking the major changes in water quality in the Middle Moulouya Basin caused by the pronounced dry and wet climatic seasons.

Taken together, these strategies will make the water of this basin useful and increase environmental stability, ensuring agreement with national goals for a circular economy and sustainable development.

4. Conclusions

The objective of this investigation was to evaluate the water quality of the river in the middle Moulouya River basin, an area known for various anthropogenic activities, such as the intensification of agriculture along the river, industrialization, and abandoned mines in the upper river. To achieve this objective, 11 water samples were collected at different points in the study area during two distinct periods. To analyze these samples, different pollution indices, health risk analyses, statistical analyses, and GIS techniques were used. The results showed a significant difference in the concentration of heavy metals in the studied area, with the upstream area presenting the highest concentrations, originating from the upper Moulouya River region, characterized by old abandoned mines and intense agricultural activity. Pollution levels range from low to high, with most samples showing high contamination. MI results show water quality ranging from pure to severely affected. Additionally, HPI indices during the dry and rainy seasons indicate a degree of water contamination ranging from low to high, with most samples classified as "High water pollution". The CI results indicated that the water samples in this section of the river are classified as "High contamination", and the ERI showed low to considerable ecological risk. Additionally, statistical analyses (Correlation matrix and PCA) revealed strong correlations between the metals, indicating pollution from both anthropogenic and natural sources, which requires immediate action. Nonetheless, the carcinogenic and non-carcinogenic risks remain within tolerable limits for the health of the residents. Nevertheless, in the case of prolonged exposure without interventions that guarantee the safety of human health, the effects can be very serious.

This investigation indicates that the surface water in this region has been impacted by various anthropogenic activities: agricultural practices, tailings, and domestic wastewater, which significantly contribute to the contamination of this aquatic ecosystem. The fact that this river crosses many urban centers requires strict laws regulating the use of chemical fertilizers, mining activities, and sustainable agricultural activities, to reduce the leaching of heavy metals into surface waters.

For decision-makers and concerned parties, the data from this study is essential for developing strategies for effective surface water management strategies and reducing pollution. Nonetheless, to overcome the limitations of this study, we suggest that future studies expand the number of sampling sites, include other pollutants such as pesticides, and develop innovative remediation approaches to minimize heavy metal concentrations in water.

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