water

MDPI

Article

Assessment of Surface Water Quality Using the Water Quality Index (IWQ), Multivariate Statistical Analysis (MSA) and Geographic Information System (GIS) in Oued Laou Mediterranean Watershed, Morocco

Hamza El Azhari [1], El Khalil Cherif [2,*], Otmane Sarti [3], El Mustapha Azzirgue [1], Houria Dakak [4], Hasna Yachou [4], Joaquim C. G. Esteves da Silva [5,*] and Farida Salmoun [1]

1 Laboratory of Physical Chemistry of Materials, Natural Substances and Environment, Chemistry Department, Sciences, and Technology Faculty, Abdelmalek Essaâdi University, Tangier 90090, Morocco
2 Institute for Systems and Robotics, Instituto Superior Técnico, University of Lisbon, 1649-004 Lisbon, Portugal
3 Department of Chemical Engineering, University of Abdelmalek Essaadi, Tangier 90000, Morocco
4 Research Unit on Environment and Conservation of Natural Resources, Regional Center of Rabat, National Institute of Agricultural Research (INRA), P.O. Box 6356, Instituts, Rabat 10101, Morocco
5 Centro de Investigação em Química (CIQUP), Instituto de Ciências Moleculares (IMS), Departamento de Geociências, Ambiente e Ordenamento do Território, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
* Correspondence: c.elkhalil@uae.ac.ma (E.K.C.); jcsilva@fc.up.pt (J.C.G.E.d.S.)

Abstract: Surface water is used for a variety of purposes, including agriculture, drinking water, and other services. Therefore, its quality is crucial for irrigation, human welfare, and health. Thus, the main objective is to improve surface water quality assessment and geochemical analysis to evaluate anthropogenic activities' impact on surface water quality in the Oued Laou watershed, Northern Morocco. Thirteen surface water samples were characterized for 26 physicochemical and biological parameters. In this aspect, emerging techniques such as multivariate statistical approaches (MSA), water quality indices (WQI), irrigation water quality (IWQI), and Geographic Information System (GIS) were employed to identify the sources of surface water pollution, their suitability for consumption, and the distribution of surface water quality. The results showed that the major ion concentrations were reported in the following order: Ca^{2+}, Na^{+}, Mg^{2+}, and K^{+}; and HCO_3^{-} > CO_3^{2-} > Cl^{-} > SO_4^{2-} > NO_3^{-} > F^{-} > PO_4^{3-} > NO_2^{-}. It was also demonstrated that almost all parameters had concentrations lower than World Health Organization (WHO) limits, except for bicarbonate ions (HCO_3^{-}) and the biochemical oxygen demand for five days (BOD_5), which exceeded the WHO limits at 120 mg/L and 3 mg/L, respectively. Furthermore, the types of Ca^{2+}-HCO_3^{-} (Calcium-Bicarbonate) and Ca^{2+}-Mg^{2+}-HCO_3^{-} (Calcium-Magnesium-Bicarbonate) predominated in surface water. The Principal Component Analysis (PCA) indicates that the Oued Laou river was exposed to two forms of contamination, the first being attributed to anthropogenic activities such as agriculture, while the second reflects the water-sediment interaction. The Hierarchical Cluster Analysis (HCA), reflecting the mineralization in the study area, has classified the samples into four clusters. The Inverse Distance Weighting (IDW) of the WQI indicates that 7.69% and 38.46% of the surface water represent, respectively, excellent and good quality for drinking. At the same time, the IWQI revealed that 92.30% of the water surface is good for irrigation. As a result, the combination of WQIs, PCA, IWQI, and GIS techniques is effective in providing clear information for assessing the suitability of surface water for drinking and its controlling factors and can also support decision-making in susceptible locations such as the Oued Laou river in northern Morocco.

Keywords: Morocco; Oued Laou watershed; WQI; IWQI; surface water quality; hydro geochemistry; PDC; HCA; IDW

Citation: Azhari, H.E.; Cherif, E.K.; Sarti, O.; Azzirgue, E.M.; Dakak, H.; Yachou, H.; Esteves da Silva, J.C.G.; Salmoun, F. Assessment of Surface Water Quality Using the Water Quality Index (IWQ), Multivariate Statistical Analysis (MSA) and Geographic Information System (GIS) in Oued Laou Mediterranean Watershed, Morocco. *Water* **2023**, *15*, 130. https://doi.org/10.3390/w15010130

Academic Editor: William Frederick Ritter

Received: 28 November 2022
Revised: 23 December 2022
Accepted: 24 December 2022
Published: 29 December 2022

1. Introduction

Water supply is considered a fundamental requirement for human activity and socioeconomic development as well as an essential condition of the natural world and human life equilibrium, and it is essential for human well-being. The surface water consists of several sources such as streams, rivers, springs, ponds, lakes, and reservoirs that are formed by precipitation in the watershed and can enter and settle in streams, rivers, and lakes [1], where the rivers are considered the most often used sources of surface water in the world for domestic consumption, agriculture, and industry [2] due to their abundance and accessibility, which have led to rapid human population growth and progress near watercourses [3]. Therefore, rivers, particularly in developing nations, have suffered from significant environmental pressures associated with contamination from intensive agricultural pesticide runoff and effluent from manufacturing processes, sewage, and other urban waste sources, which are considered human effects [4,5]. In addition to natural causes such as air pollution deposition [6], climate change [7], water interaction with lithogenic structure [8], and geochemical factors [9].

Morocco, like many other nations (African countries, India, etc.), suffers from surface water pollution due to the semi-arid climate that pervades most of its areas, droughts, and human pollution [10]. As a result, a significant risk threatens humans' and animals' lives [11], where Surface water is considered as one of the most important sources of traditional agricultural usage in Morocco, where most farmers use surface water networks to irrigate their fields. The irrigated area in Morocco is estimated at 1.46 million ha, which is approximately 17% of the total agricultural area of the country [12], as well as for drinking by a considerable portion of the population in some rural regions (big atlas, medium, and small). However, excessive agricultural practices, geogenic pollution, and grown urbanization have placed contentious pressure on surface water resources and have led to potentially negative impacts on the physicochemical characteristics of water and water quality [13].

The Oued Laou plays a vital role in maintaining the socioeconomic development of the northern region of Morocco. As the primary source of water, it receives significant amounts of residential and agricultural waste, all of which degrade the river's water quality [14] and constitute serious hazards to the aquatic system in the Oued Laou River [15]. Therefore, identifying the gaps concerning the knowledge of water quality is an essential step in understanding the natural and anthropogenic factors affecting the sustainability of these resources., In Morocco, water quality monitoring and water resource management have been recognized as national obligations for attaining sustainability. Other research and studies must be supported to maintain adequate water resource management and long-term sustainability.

Therefore, monitoring river water quality is a practical approach to ensuring the effective management of water resources and environmental protection and determining surface waters' suitability for irrigation [16]. This traditional approach to water quality for drinking and irrigation is costly, time-consuming, and human resource intensive. In addition, many studies suggest using new tools for data preparation for modeling and prediction [17]. Present variations in river water quality simply and clearly, at certain times and locations, so they may be presented in an approachable way [18].

Water quality is evaluated using physical and chemical properties that indicate water characteristics and variables that impact water quality according to international standards [19]. Hence, physicochemical and bacteriological parameters such as Hydrogen Potential (pH), Temperature (T), Turbidity (Turb), Salinity (Sal), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand for 5 days (BOD_5), Phosphate (PO_4^{3-}), Nitrite (NO_2^-), Nitrate (NO_3^-), Ammonium (NH_4^+), Dissolved Oxygen (DO), conductivity (EC), and FC (fecal coliform) provide an initial understanding of water facies [20], different geochemical processes, and water categorization [21]. The Piper Diagram is an applicable and commonly used method for defining the main geochemical control processes driving the chemical composition of surface water [22]. Moreover, water quality indices (WQIs) are among the better approaches for explaining water quality [23] and have been developed by many authors since Horton's [24] work, as they convert original data from many water quality parameters into a single number to understand water quality [25,26] and assist strategic planning linked to water quality management programs through numerical index values [27], which is calculated using a mathematical process based on various water quality criteria [28].

The Irrigation Water Quality depends on its quantity and the type of salts in the water. The most important issues related to the deterioration of water quality are increased salinity, reduced permeability, and exposure to particularly toxic ions [16]. Therefore, assessments of the quality of irrigation usage are defined by its physicochemical parameters using imitative techniques such as the Wilcox Diagram [29]. This technique is applicable and commonly utilized to estimate water quality for irrigation purposes.

Therefore, the aforementioned techniques for assessing irrigation water quality and WQIs are used to evaluate water quality, which presents a useful understanding of the quality of water used for irrigation. The individual water quality index parameter is not appropriate for assessing the validation of water for irrigation because it can be restrictive and can often produce inadequate performance in the assessment [30]. Several studies have proposed a water quality index based on the weighted score of each variable [31]. WQIs that contain the Irrigation Water Quality (IWQ), Na%, SAR, PI, KI, and RSC can satisfy the requirements for effective monitoring and assessment of irrigation water suitability [32]. The main concept in the development of WQIs is to combine several variables into a single numerical value. The goal of the WQIs is to identify the waters in relation to their potential uses and chemical and physical characteristics and to control their allocations [26]. For this reason, the analytical parameters need to be weighted and aggregated. Therefore, WQIs are used to evaluate water quality in this study. Previous studies have used the WQI to determine surface water quality. For e.g., Gad et al. [21], reported that the DWQI values of the two Nile (Egypt) branches revealed that 53% of samples varied from excellent to good water, 43% of samples varied from poor to very poor water, and 4% of samples were unsuitable for drinking. Ferahtia et al. [33], mentioned that the WQI values of the studied Wadis were higher than 100, indicating that the El Hodna watershed (Algeria) waters are unfit for human consumption, irrigation, and aquatic life. Additionally, Elsayed et al. [31] found that several WQI values across two years revealed that 82% of samples represent a high class and the remaining 18% constitute a medium class of water quality for irrigation use with respect to the Irrigation Water Quality (IWQ) value, while the Sodium Percentage (Na%) values across two years indicated that 96% of samples fell into a healthy class and 4% fell into a permissible class for irrigation. In addition, the Sodium Absorption Ratio (SAR), Permeability Index (PI), Kelley Index (KI), and Residual Sodium Carbonate (RSC) values revealed that all surface water samples were appropriate for irrigation use in the Northern Nile Delta, Egypt.

Multivariate statistical approaches (MSA) have been commonly used to understand the mechanisms that affect surface water quality [34], in particular, correlation analysis (CA), factor analysis (FA), discriminant analysis (DA), and principal component analysis (PCA) [35]. Those tools have been extensively used to describe water quality [36].

Therefore, CA is a multivariate technique to classify the physicochemical parameters into classes according to the interrelation between the chemical constituencies of surface water resources [37] while the PCA is an extensively employed multivariate analytical approach that reduces a range of original variables, such as geochemical data, to a minimal figure of indices (i.e., principal components or factors) for interpreting variations between observed data that are not observable from the simple correlation analysis [38]. Thus, the CA and PCA are efficient methods for identifying common trends and anomalies of dispersion, reducing the initial dimension of datasets, and improving understanding of the geogenic and environmental origins of soluble ions and metals in water [39].

In various investigations, PCA has been utilized to identify anthropogenic and natural factors affecting surface water quality [40]. At the same time, hierarchical cluster analysis

(HCA) classifies the water samples based on their similar hydro chemical characteristics. This approach is most commonly utilized in earth sciences [41]. GIS can also help to alleviate some of these issues, particularly the combination of a water quality assessment method and a spatial analysis tool, such as the IDW technique, which can greatly improve the visualization of research results [42].

Understanding the processes that control surface water quality remains a complex challenge for researchers, given the large amount of data collected during a particular study. At the end of the twentieth century, a better understanding was obtained through the surface WQI [43], and the goal of it is to identify the waters in relation to their potential uses and physical-chemical characteristics and to control their allocations [44].

The objective of this exploratory study is to (1) assess the physicochemical and bacteriological properties of the Oued Laou watershed, (2) assess surface water quality using MST, WQIs, and GIS techniques; (3) discuss water suitability for drinking, health and safety compatibility of water for agriculture and consumption, and (4) evaluate various agricultural parameters such as Sodium Adsorption Rate (SAR), Permeability Index (PI), Magnesium Hazard (MH), Sodium Ratio (% Na), and Sodium Carbonate (SCR).

2. Materials and Methods

2.1. The Study Area

The Oued Laou watershed is a Mediterranean basin located between the provinces of Tetouan and Chefchaouen in northwest Morocco. It is located in the heart of the Rif chain (High Rif). It is a tiny basin with an area of 930 km^2, and a length of 154 km [45]. It is considered one of the key watershed and hydrological networks of northern Rif, carrying substantial volumes of water during the rainy season. Oued Talembote, Oued Ouarra, and Oued Maggo are the three most major wadis that feed Oued Laou (Figure 1).

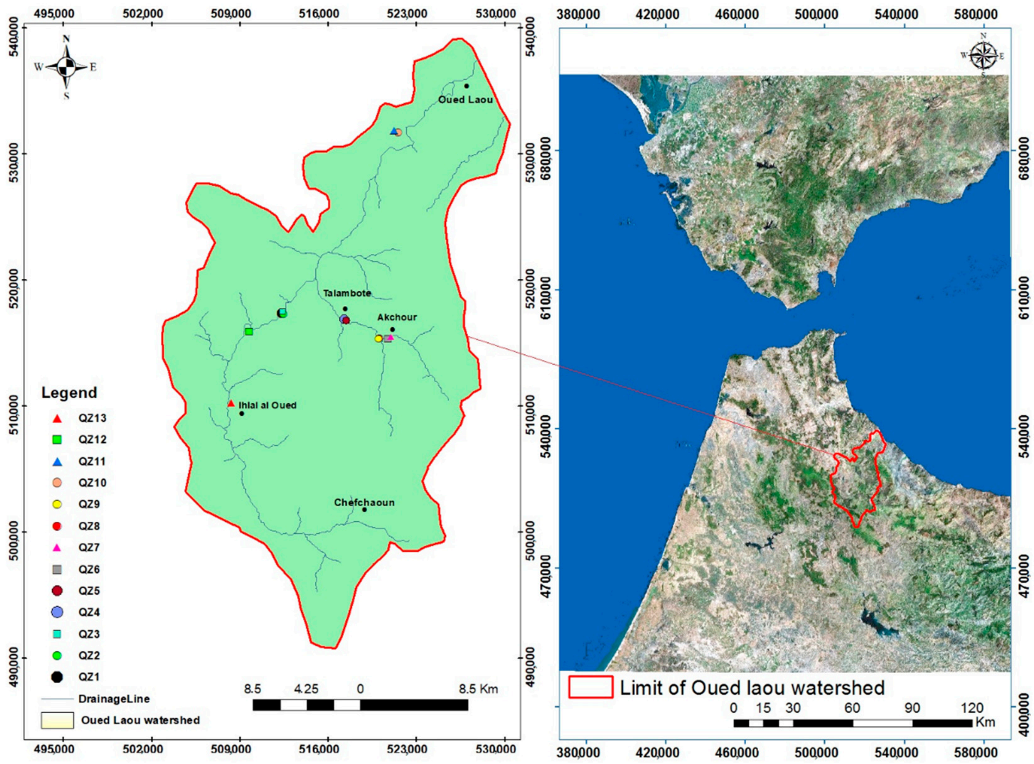


Figure 1. The study area of the Oued Laou watershed, northern Morocco, with the locations of 13 surface water sample points (QZ1, QZ2, QZ3, QZ4, QZ5, QZ6, QZ7, QZ8, QZ9 QZ10, QZ11, QZ12, QZ13).

The climate in this region varies from sub-humid Mediterranean in the mountains to semi-arid along the coastal edge. The annual average temperature is 18.6 °C, with 700 mm of annual average rainfall in humid, relatively cold winters and dry, warm summers. The majority of precipitation occurs between November and March [45]. The region's climatology is impacted by the relief's altitude and position regarding the sea. The region's diversified plant cover includes woods, meadows, scrub, and agriculture. Agriculture covers 30% of the region's land area, with just 5% being irrigated and 25% being non-irrigated [46].

In terms of hydrogeology, the geological formations of the study area are primarily made up of impermeable or low-permeability facies. Only the limestone chain, the plains, the alluvial valleys, and a few small, isolated basins benefit from rainwater infiltration. These elements limit the groundwater reservoirs of the area, with the exception of the following hydrogeological units: the limestone range, Rhiss-Neckor, Mar-til-Allila, and Oued Laou [47].

In addition, the Oued Laou watershed belongs to the Rif domain; the terrain is metamorphic and consists of gneiss, schists, limestone, and dolomites of primary and Permo-Triassic ages: The Sebtides and Ghomarides. a material that extends from the Strait of Gibraltar to the Jebha Accident and is composed mainly of limestone and dolomitic facies (Trias, Lias). In the east, the Beni Idder layer is made up of clayey-marly limestone and flyschs of sandy micaceous marl (Cretaceous and Tertiary), which extends from the Strait of Gibraltar to Chaouen (Figure 2). The mountains are the consequence of a relatively modern formation, and they are all excessively rocky, varying in altitude from 0 m to 2122 m above sea level [47].

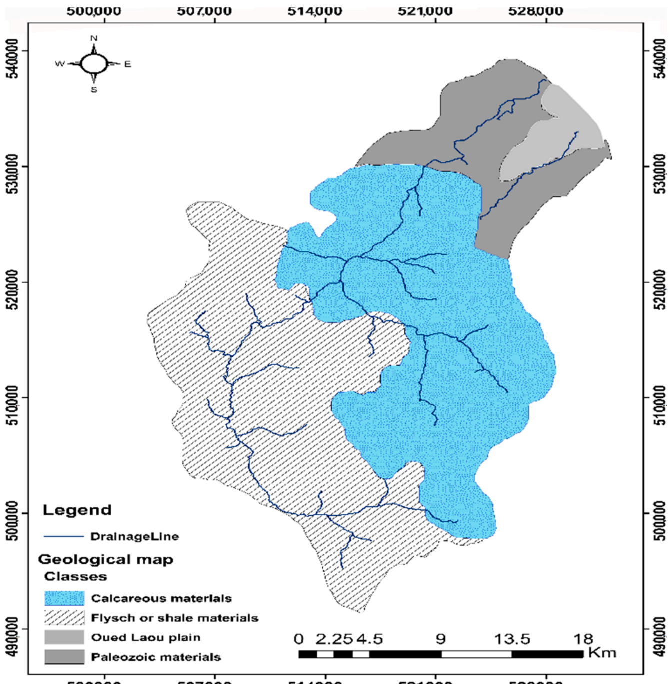


Figure 2. Geologic carte of the study area.

2.2. Sampling and Chemical Analysis

In this study, surface water samples were collected in June 2021 at 13 different locations (three samples were collected at each location) (Figure 1) for 26 physicochemical and bacteriological parameters. The sampling stations were chosen with uniform spacing and little variation. Based on the geographical conditions and accessibility of the Oued Laou area and according to the most known sites for human activities (tourism, urbanism, and agriculture) and geological significance (Figure 1).

Temperature and pH were measured in the field using a mercury thermometer and a pH meter, respectively (HANNA Hi 8519N; HANNA Instruments, Woonsocket, RI, USA). Dissolved oxygen (DO), electric conductivity (EC), and salinity (Sal) were measured immediately using oxygen meters CO411 (FLMETRON, Witosa, Poland), Thermo ORION 105 (USA), and EUTECH Instruments SAL6$^+$ (CAKTON, Bethesda, MD, USA), while turbidity (Tur) was measured by a turbidity meter model HACH 2100P (Hach, Lognes, France). All of these parameters were measured in situ and filtered immediately with a 45 µm filter.

In order to obtain high-quality homogenized samples at locations of strong water flow, the water samples were taken at a depth of 30 cm in 500 mL polyethylene bottles [48].

To prevent cross-contamination, the bottles were cleaned with distilled water before filling and washed with local sample waters three times. The sampling was carried out according to Standard Methods for the Examination of Water and Wastewater [49]. Transportation and storage were carried out at a temperature of 0 °C to 4 °C.

The total dissolved solids (TDS) and BOD_5 were analyzed using a HANNA HI 2550 multi-parameter (HANNA Instruments, USA) and a WTW Oxitop IS 6 inductive stirring system (USA). Chemical Oxygen Demand (COD), alkalinity (ATC), and total hardness (TH) were measured according to the following protocols: NF T.90.101; NF EN ISO 9963-1 (2/1996); and EDTA titration methods, respectively. The concentrations of Ca^{2+}, Mg^{2+}, carbonate, and bicarbonate were determined using the titrimetric technique. Na^+ and K^+ cations were estimated using a microprocessor flame photometer (graphical display) (LT 671, New Zealand). Chloride (Cl^-), fluoride (F^-), nitrate ($NO_3{}^-$), ammonium ($NH_4{}^+$), and sulfate ($SO_4{}^{2-}$) were measured using particular ion electrodes HANNA HI 4007, HANNA HI 4010, HANNA HI 4013, HACH ISENH4181, HANNA HI 4012 (HANNA Instruments, USA), respectively. Total coliforms (TC) and fecal coliforms (FC) were analyzed using the membrane filtration technique [50]. The chemical measurements were carried out in triplicate to guarantee the sample analysis's precision.

2.3. Multivariate Statistical Analysis

Using IBM SPSS Statistics 25, multivariate statistical analyses were conducted in this study on a dataset of 26 physical-chemical parameters from 13 stations, including: T, EC, pH, TDS, COD, BOD_5, Turb, Sal, Cl^-, $SO_4{}^{2-}$, $PO_4{}^{3-}$, $NO_3{}^-$, $NO_2{}^-$, $NH_4{}^+$, Ca^{2+}, Mg^{2+}, Na^+, K^+, $CaCO_3$, $CO_3{}^{2-}$, DO, TH, TAC, FC, TC, and $HCO_3{}^-$, which are used for PCA and HCA extraction. The PCA is defined as a statistical approach focused on the interdependencies of variables [51]. The degree of correlation between the values was assessed using Spearman's test.

The correlation coefficient of +1 indicates a perfect relationship between the variables; −1 means a perfect relationship. Still, the variables move in opposite directions; a value of zero means that there is no relationship between the variables. An r value between 0.5 and 0.7 is regarded as a moderate correlation, while a significance level of $p = 0.7$ is regarded as a high correlation and was produced by employing Kaiser normalization and an orthogonal rotation factor [52].

For HCA, Ward's method [53] using Euclidean distance was used as a similarity measure to perform clustering [51]. A similarity measure to perform cluster analysis (CA). Each cluster is based on a set of physicochemical parameters to find similarities between sampled locations. Based on the computed WQI value, water quality distribution maps were created using ArcGIS software (ver. 10.6).

2.4. Water Quality Index WQI

Through the water quality indexes, surface water quality assessments and adjustments to needs are reliable [54]. The WQI is a method used to categorize water sources into different classes based on the comparison of water quality parameters with international or national standards. In 1965, Horten became the first scientist to modify the WQI [24]. He selected the 10 most common parameters and included them in a mathematical equation to analyze the quality of drinking water. This concept is used to evaluate water quality. In many parts of the world so far, a lot of researchers have modified the approach based on the weighting of each water quality parameter [55]. Many scientists and experts have discussed the importance of WQI in providing an overview of water quality. This significance is demonstrated by incorporating all water quality measures into a single, easily comprehensible, and easily interpreted value [56].

In this study, we used WQI according to the classical method to estimate the influence of natural and anthropogenic factors on water quality, based on 14 key parameters of the surface water chemistry of Oued Laou, such as pH, EC, BOD_5, TH, Cl^-, $PO_4{}^{3-}$, FC, TDS, $SO_4{}^{2-}$, Ca^{2+}, Mg^{2+}, $NH_4{}^+$, $NO_3{}^-$, and $NO_2{}^-$ mentioned in Table 1. Using the criteria that the WHO recommends (2017) According to the potential influence on human health, each criterion is given a particular weight (Wi), ranging from 1 "the lowest impact on water quality" to 5 "the highest impact" (Table 1) [57].

Table 1. Relative weight assigned to physicochemical parameters.

Water Quality Parameters	WHO 2017	Weight Wi	Wr
EC	1000	4	0.074074074
pH	6.5–8.5	4	0.074074074
TH	500	3	0.055555556
Cl^-	250	3	0.055555556
$PO_4{}^{3-}$	5	3	0.055555556
$NO_2{}^-$	3	3	0.055555556
$NO_3{}^-$	50	5	0.092592593
$NH_4{}^+$	35	3	0.055555556
Ca^{2+}	75	2	0.037037037
Mg^{2+}	50	2	0.037037037
DO	5	5	0.092592593
$SO_4{}^{2-}$	250	4	0.074074074
TDS	1000	5	0.092592593
$HCO_3{}^-$	120	3	0.05555556
TC	100	3	0.05555556
BOD_5	3	2	0.03703704

The parameters with the highest weights of "5" have been associated with adverse health effects, such as $NO_3{}^-$ and TDS, whereas "4" will be given to pH, EC, FC, $SO_4{}^{2-}$, and TH. The parameters BOD_5, Mg^{2+}, Ca^{2+}, $NH_4{}^+$, $NO_2{}^-$, and Cl^- are given a minimum weight of "2" to "3" because of their lower or indirect influence in surface water [58]. The relative weight (Wi) for each parameter was determined using the following Equation (1) [59]:

$$\mathrm{Wi} = \frac{\mathrm{wi}}{\sum_{k=0}^{n} \mathrm{wi}} \quad (1)$$

Wi is the weight of parameter "i", and "n" represents the total number of parameters. The quality score was then determined by dividing the variable concentration by the parameter standard established by WHO 2017 [60], and multiplying the result by 100 using the Equation (2) [57]:

$$\mathrm{Qi} = \frac{\mathrm{Ci}}{\mathrm{Si}} \times 100 \quad (2)$$

Qi is the quality index, "Si" is the standard norm, and "Ci" is the concentration of the sample in mg/L. Because the pH criterion ranged from 6.5 to 8.5 [60], the rating scale was derived by the Equation (3) [58]:

$$\mathrm{Qi} = \frac{(\mathrm{CpH} - 8.5)}{(6.5 - 8.5)} \quad (3)$$

The following formula is used to determine the "SI" sub-index for each parameter [61].

$$SI = Wi \times Qi \quad (4)$$

"Qi" is the parameter value, while "Wi" is the relative weight. According to the following equation, the WQI score for each sample was determined as the sum of all sub-indices computed for all variables [61]:

$$WQI = \sum_{k=1}^{n} Wi \times Qi = \sum_{1}^{n} SI \quad (5)$$

The WQI scores for all surface water samples were then categorized into one of five water quality classes [62], as indicated in the figure (Table 2).

Table 2. Classification of water quality [56].

Ranking	WQI Value	Explanation
<50	Excellent water	Good for human health
50–100	Good water	Suitable for human consumption
100–200	Poor water	Water in poor condition
200–300	Very poor water	Needs special attention before use
>300	Unsuitable for drinking	Requires too much attention

2.5. Irrigation Water Quality IWQI

The amount of dissolved salts or other unwanted elements determines the appropriateness of irrigation water. The physical and chemical qualities of major river water parameters, such as T, pH, EC, TDS, hardness, sodium, potassium, calcium, magnesium, chloride, sulfuric acid, salts, nitrates, carbonates, bicarbonates, and other substances, are used in this evaluation to establish irrigation suitability [63]. The following section presents several calculations that might help in determining the appropriateness of irrigation water.

Salt risk related to calcium and magnesium concentrations is determined by the sodium adsorption ratio (SAR). Increased salt levels in water can have a negative impact on soil properties and decrease soil permeability [64]. The following Equation (6) is used to compute SAR [63]:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}} \quad (6)$$

Furthermore, understanding that excess calcium and magnesium have detrimental effects on the soil, the residual sodium carbonate (RSC) plays an essential part in the categorization of irrigation water, which is computed by the below Formula (7) [65].

$$RSC = \left[\left(HCO_3^{-} + CO_3^{-}\right) - \left(Ca^{2+} + Mg^{2+}\right)\right] \quad (7)$$

The percentage of sodium (%Na) and the risk of magnesium "MH" are often used to measure the appropriateness of water for agricultural applications. A higher soluble salt concentration in irrigation water lowers permeability. While the high concentration of Mg^{2+} ion in water has a detrimental impact on soil quality, making the soil alkaline, resulting in low crop production, is estimated using the following Equations (8) and (9) [16].

$$Na\% = \frac{\left(Na^{+} + K^{+}\right) * 100}{\left(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}\right)} \quad (8)$$

$$MH = \frac{\left(Mg^{2+} * 100\right)}{\left(Ca^{2+} + Mg^{2+}\right)} \quad (9)$$

The adequacy of irrigation water is also evaluated using the permeability index, or "PI". According to, excess Ca^{2+}, Mg^{2+}, and bicarbonate create soil permeability problems. The index is computed as follows [32]:

$$PI = \frac{\left(Na^{+} + \sqrt{HCO_3^{-}}\right) * 100}{\left(Ca^{2+} + Mg^{2+} + Na^{+}\right)} \tag{10}$$

The Kelly Index (KI) is used to determine irrigation water quality. Sodium is compared to calcium and magnesium. A KI > 1 indicates an excess of salt, whereas a KI < 2 indicates a shortfall in water and is computed using the following Formula (11) [64]:

$$\mathrm{KI} = \frac{\mathrm{Na}^{+}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}} \tag{11}$$

Salinity Potential (PS): Salt constantly dissolves in irrigation water, increasing salinity. The salinity of the river progressively increases year after year. It is a serious issue for downstream water consumers [66]. The term "potential salinity" refers to the quantity of salt that builds up in the soil as determined by the formula below [64].

$$\mathrm{PS} = \mathrm{Cl}^{-} + \frac{1}{2}\mathrm{SO_4}^{2-} \tag{12}$$

Residual sodium bicarbonate (RSBC) Because most natural waters lack substantial levels of carbonate ions and bicarbonate ions do not precipitate magnesium ions, the danger of alkalinity will be measured by an indicator known as residual carbonic acid. Sodium hydrogen: and computed using the Equation (13) [65].

$$\mathrm{RSBC} = \mathrm{HCO_3}^{-} - \mathrm{Ca}^{2+} \tag{13}$$

All ionic concentrations are measured in meq/L in all of these Equations (6)–(13).

The various irrigation water quality indicators discussed above have various repercussions and may influence choices. That's why the irrigation water quality indicator (IWQI), which was developed using Equations (2) and (5) and the variables EC, Na%, PI, SAR, RSBC, and MH, was developed to overcome this lack. These irrigation water quality requirements were weighted (Wi) based on how important they are for irrigation (Table 3).

Table 3. Weight of each parameter and the appropriate limit for irrigation [67].

Parameter	Reference	Unit	Suitable Limit for Irrigation	Unit Weight (Wn)
MH	Pawal (1972)	No unit	50	0.110
RSC	Eaton (1950)	meq/L	2.5	0.793
Na%	Wilcox (1955)	%	60	0.040
SAR	Richard (1954)	No unit	18	0.033
EC	Wilcox (1955)	µS/cm	2250	0.023
PI	Doneen (1964)	No unit	85	0.001

3. Results and Discussion

3.1. Hydro Chemical Characteristics of Surface Water

The findings of the statistical summaries of the physicochemical and biological properties of the investigated surface water samples indicate a wide variation in the different individual parameters listed in Table 4. The surface water temperatures ranged from 17.7 to 24.8 °C, with an average temperature of 20.78 °C (Figure 3). Most of the samples in the study area showed almost neutral to alkaline properties, with a pH ranging from 7.2 to 8.4, lower than the maximum value recommended by [60]. In general, the high pH values were due to the natural existence of carbonates and bicarbonates [68]. The EC value ranges between 301 and 524 µs/cm, with a mean value of 435 µS/cm. EC values of surface water were below the WHO limit of 1000 µs/cm (Figure 3). The TDS ranged from 180.6 to 314.4 mg/L (Table 4), and all samples were below the maximum permissible amount recommended by WHO (2017). All samples showed values above the WHO threshold for DO, set at 2 mg/L, indicating a higher degree of oxygenation in surface waters. The DO concentration varied from 6.83 to 10.22 mg/L (Table 4). The BOD_5 levels were higher than the 3 mg/L standard set by the WHO, ranging from 4.02 to 14.94 mg/L. The concentrations of COD vary from 31.31 to 59.81 mg/L, with the highest values observed at sites QZ12 and QZ13 (Table 4). The samples' turbidity readings vary from 0.12 to 9.33 NTU, and exceed the WHO's threshold is set at 5 NTU in some locations [60]. The results indicate that, in comparison to the river downstream, the upper portion of the river is narrower and has a faster flow. The turbidity levels exceeded the range prescribed by WHO at three locations QZ10, QZ12, and QZ13.

At locations QZ10, QZ12, and QZ13, he forms of nitrogen, such as NO_2^- and NH_4^+, exhibited significantly too low concentrations, with an average concentration of 0.03 mg/L and 0.68 mg/L, respectively, which were below the levels of 3 and 35 mg/L suggested by WHO for drinking water [60]. NO_3^- can originate from domestic wastewater, agricultural effluents such as fertilizers, and soil erosion [69]. Only two samples, QZ12 (12.42 mg/L) and QZ13 (19.9 mg/L) (Table 4), showed significant amounts but were still less than the 50 mg/L limit established by the (WHO, 2017) [60]. Similarly, fluoride (F^-) levels at 13 locations range between 0.21 and 1.01 mg/L (Figure 3), which fall within the acceptable range of 1.5 mg/L. Geogenic sources such as apatite, clay, and biotite, as well as extended interaction with the aquifer in an alkaline environment, are major contributors to the higher fluoride content in this area [70]. Water contamination by fluoride could cause diseases such as infant methemoglobin, thyroid disease, neural tube defects, abdominal pain, diarrhea, vomiting, hypertension, gastric cancer in adults, and infant blue baby syndrome if their concentrations exceed the allowable limits [71].

The concentrations of Ca^{2+} and Mg^{2+} ranged from 41.6 to 73.4 mg/L and 24.96 to 48.24 mg/L, respectively, with the highest values recorded at QZ11, QZ13, and QZ10 (Table 4). None of the samples surpassed the drinking water standard limit of Ca^{2+} and Mg^{2+} set at 75 and 50 mg/L [60], respectively. Disorders including Alzheimer's, diabetes, and cardiovascular diseases could be generated by high water hardness (over 300 mg/L) [72]. Calcium and magnesium are formed via the dissolution of carbonate minerals and ferromagnesian minerals in igneous and metamorphic rocks, and magnesium carbonate (dolomite) in sedimentary rocks [73].

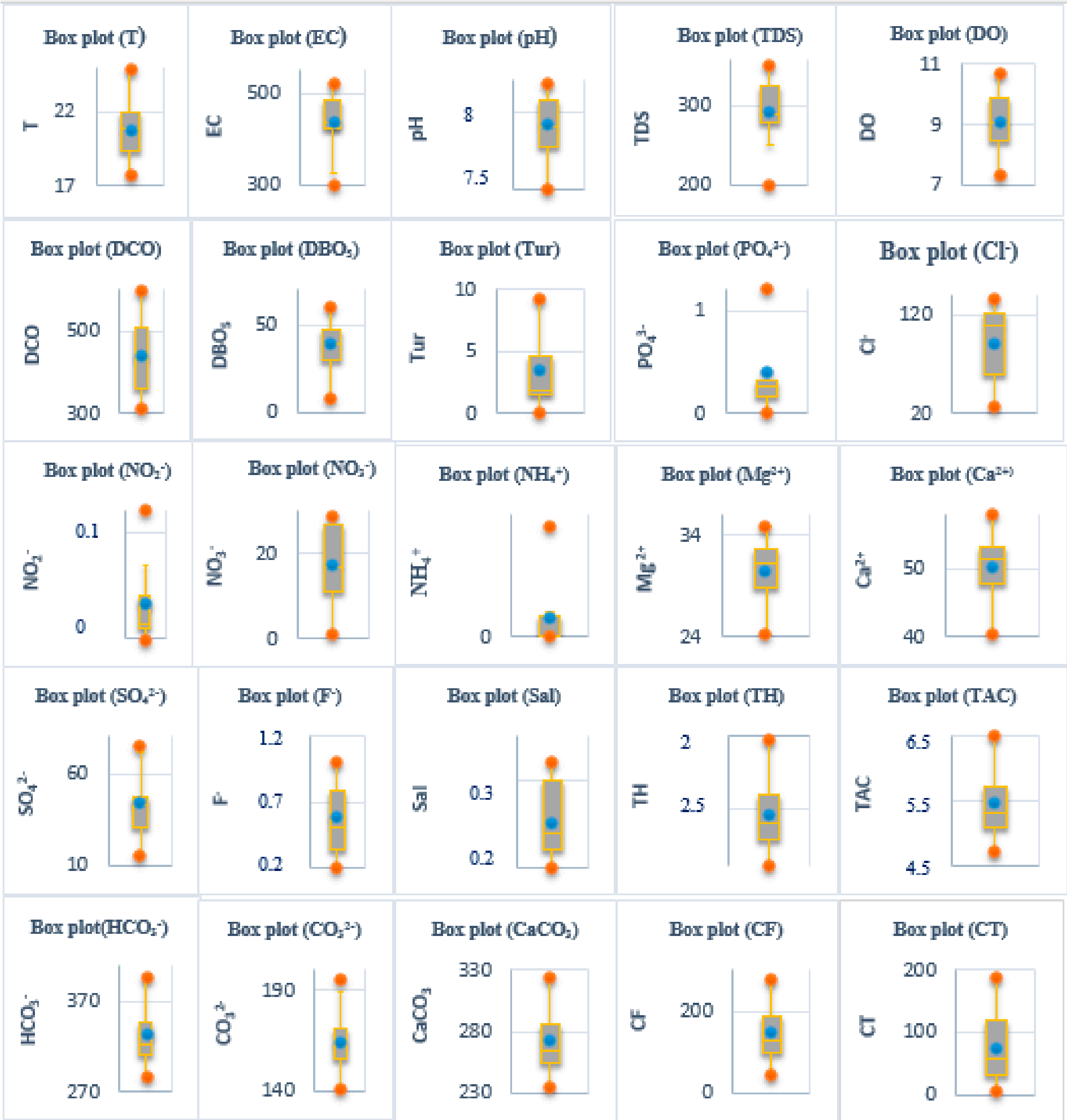


Figure 3. Score variability of the data.

Table 4. The physicochemical and bacteriological in situ measurement results at 13 sample points in the Oued Laou watershed.

Samples	T	EC	pH	TDS	DO	BOD_5	COD	Tur	SAL	TH	TAC	PO_4^{3-}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	$CaCO_3$	F^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	FC	TC
QZ1	21.4	399	7.74	239.4	8.59	11.23	32.2	1.51	0.3	2.9	5.3	0.14	49.6	0.01	10.92	28.65	323.3	159	265	0.31	0.91	26.67	0.34	58	34.8	117	32
QZ2	21.6	436	7.91	261.6	6.83	14.94	31.9	1.87	0.32	2.8	5.2	0.26	59.8	0.09	10.23	30.76	317.2	156	260	0.34	0.74	28.52	0.52	50	33.6	180	49
QZ3	24.8	328	8.07	196.8	7.21	12.32	44.6	0.06	0.2	2.08	4.9	0.01	27.3	0	0.9	15.13	298.9	147	245	0.21	0.001	9.27	0.7	41.6	25	147	24
QZ4	22.2	422	7.91	253.2	8.72	11.13	36	1.73	0.31	2.6	5	0.18	101	0.02	4.37	41.5	305	150	250	0.51	0	51.13	3.56	52	31.2	99	127
QZ5	21.9	445	7.78	267	9.64	10.87	36.5	1.89	0.31	2.63	5.4	0.33	79.4	0.07	7.75	40.9	329.4	162	270	0.43	0	57.71	3.92	52.6	31.6	123	134
QZ6	19.4	432	7.94	259.2	8.89	11.07	42.5	4.67	0.30	2.58	6.3	0.17	127	0.01	7.92	45.37	384.3	189	315	0.66	0	92.87	1.53	51.6	31	89	32
QZ7	19.1	487	7.97	292.2	8.31	11.03	46.9	3.54	0.33	2.44	6.5	0.32	121.3	0.01	8.21	43.12	396.5	195	325	0.29	0	89.76	1.43	48.8	29.3	126	79
QZ8	17.7	429	7.77	257.4	7.95	12.19	49.7	1.9	0.301	2.4	6	0.31	129.3	0.013	8.11	47.45	366	180	300	1.01	0	55.09	1.34	48	28.8	45	119
QZ9	18	488	7.5	292.8	8.05	12.05	50.7	1.12	0.331	2.39	5.7	0.27	98.38	0.011	6.94	45.34	347.7	171	285	0.94	0	51.67	1.65	47.8	28.7	187	84
QZ10	22.7	503	8.17	301.8	9.37	10.26	53.8	8.87	0.35	2.72	5.1	1.15	113	0.04	8.24	68.2	311.1	162	255	0.78	0	36.02	3.5	54.4	32.6	220	189
QZ11	20.1	301	7.86	180.6	7.66	4.21	31.1	0.09	0.19	3.67	4.7	0.01	24	0	0.5	19.2	286.7	141	235	0.34	0.001	8.45	0.59	73.4	48.2	78	6
QZ12	20.4	467	8.16	280.2	9.96	9.85	59.8	9.33	0.32	2.67	5.23	0.94	110	0.04	12.42	71.13	319	156.9	261.5	0.88	4.06	71.32	4.55	53.4	32	276	47
QZ13	20.9	524	8.11	314.4	10.22	8.89	56.2	9.02	0.36	2.79	5.71	1.2	136	0.12	19.9	74.8	348.31	171.3	285.5	0.76	3.2	82.13	5.23	55.8	33.5	227	58
Max	24.8	524	8.17	314.4	10.22	14.94	59.8	9.33	0.32	3.67	6.5	1.2	136	0.12	19.9	74.8	396.5	195	325	1.01	4.06	92.87	5.23	73.4	48.2	276	189
Min	17.7	301	7.5	180.6	6.83	4.21	31.1	0.06	0.2	2.08	4.7	0.01	24	0	0.5	15.13	286.7	141	235	0.21	0	8.45	0.34	41.6	25	45	6
MEAN	20.78	435	7.91	261.3	8.57	10.77	44	3.50	0.25	2.66	5.46	0.40	90.46	0.03	8.18	43.96	333.3	164.6	273.23	0.57	0.68	50.81	2.22	52.8	32.3	147	75
STDV	1.97	64.6	0.19	38.77	1.04	2.44	9.82	3.39	0.04	0.37	0.54	0.41	38.80	0.03	4.96	18.62	33.32	16.07	27.312	0.27	1.35	28.24	1.69	7.43	5.44	67	53

The concentrations of sodium and potassium were below the maximum allowable value of portability suggested by the WHO (2017), noting that the concentration of Na^+ and K^+ varies respectively between 8.45 and 92.87 mg/L and between 0.34 and 5.23 mg/L, the maximum values of Na^+ and K^+ recorded respectively in stations QZ6 and QZ13 (Figure 3). The alteration of silicate minerals is the main source of concentrations of Na^+ and K^+ [74]. These ions are not harmful at normal levels, but when they exceed the allowed limits, they can harm human health, such as hypertension, heart disease, or kidney problems.

The proportions of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) control alkalinity in water. Alkalinity uptake in the samples was below 200 mg/L, the levels allowed by WHO 2017. Furthermore, CO_3^{2-} and HCO_3^- concentrations ranged from 145 to 195 mg/L and 286.7 to 396.5 mg/L, respectively, with a notable maximum value in QZ7 (Table 4). The main causes of carbonate alteration are changes in calcite and dolomite rocks [75].

In QZ7, QZ6, QZ8, and QZ13, chloride levels ranged from 24 to 136 mg/L, which is lower than the 250 mg/L drinking water standard. Phosphate is a necessary nutrient for plant growth. Except for QZ13, all surface water samples had low phosphate PO_4^{3-} concentrations. QZ10 and QZ12 showed maximum values, ranging from 1.2, 1.15, and 0.94 mg/L, respectively, and did not exceed the standard value of 5 mg/L. The bacterial contamination indicators, such as coliforms, are one of the most crucial characteristics for assessing the water quality since they provide insight into the presence of fecal and, consequently, the possibility for pathogen contamination [76]. According to the data, a station close to QZ12 and QZ13 recorded high amounts of fecal coliform, measuring 276 and 227 CFU/100 mL, respectively (Table 4). These levels were not in compliance with the WHO standard. The other stations have shown low fecal coliform contamination of surface water, which could be attributed to animal or human feces and can induce gastroenteritis in patients. To be declared drinkable, no pathogens should be present per 100 mL of drinking water [77]. While total coliform (TC) concentrations were high at stations QZ5 and QZ10 (Table 4), the significant prevalence of total coliforms in the waterways indicates that the pollution is due to residential sewage (feces) [78]. Human activity and area geology are two major elements of river hydrology and water quality in general [75].

The variability of the data assessment was used to analyze the principal ions in the surface water samples. The concentrations of the sample's principal cations were sorted in the following order based on the analytical data: $Ca^{2+} > Na^+ > Mg^{2+} > K^+ > NH_4^+$. The higher Ca^{2+} concentrations indicate the presence of large amounts of limestone and other dissolved substances. While the relatively higher concentration of Na^+ and K^+ in the upper part of the Oued Laou valley could be related to chemical fertilizers or other anthropogenic activities.

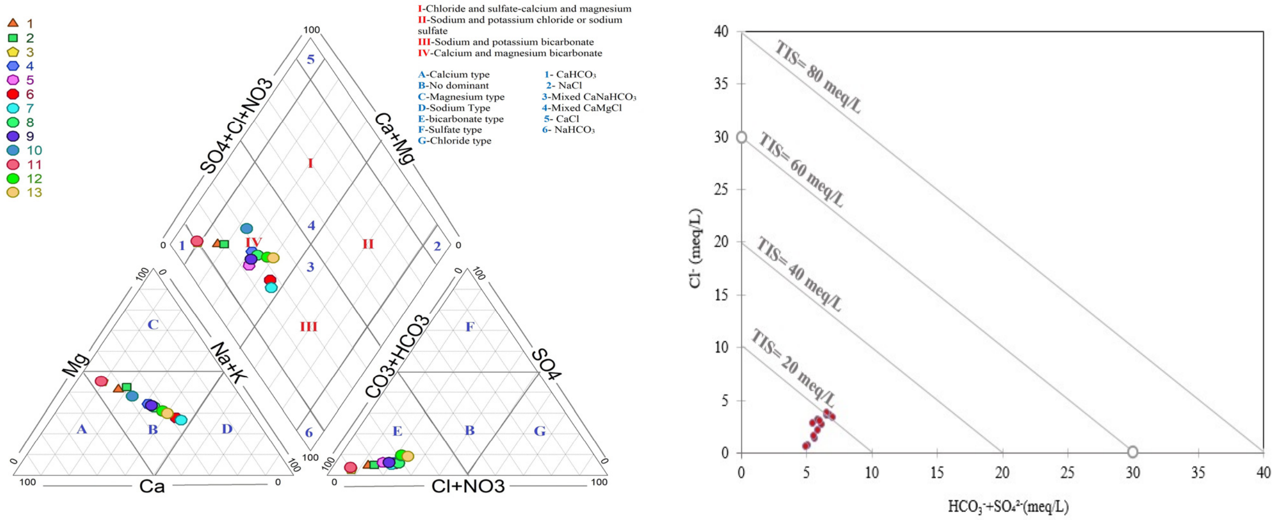
$HCO_3^- > CO_3^{2-} > Cl^- > SO_4^{2-} > NO_3^- > F^- > PO_4^{3-} > NO_2^-$ are the primary anions found in surface water samples, as shown in Figure 3, which depicts a change in the concentrations of Cl^-, SO_4^{2-}, HCO_3^-, and NO_3^-. The research area's increase in Cl^- levels can be attributed to Pliocene sediments. SO_4^{2-} levels may rise due to the depletion of sulfate minerals (such as gypsum), fertilizer inputs, and municipal waste.

HCO_3^- is formed when carbonic acid dissolves carbonate minerals and silicate minerals in the exploration area. However, some sample sites have detected changes in the order of the ions "$SO_4^{2-} > HCO_3^- > CO_3^{2-} > Cl^-$", especially in the samples QZ13, QZ12, and QZ10. At sites QZ11, QZ13, QZ5, and QZ4, the cation order is Ca^{2+}, Na^+, Mg^{2+}, and K^+. In general, the content of major ions changed in response to water-rock interaction. However, at some sites, anthropogenic pollutants predominate.

3.2. Hydro Chemical Evolution and Surface Water Types

To better understand the geochemical mechanisms that govern water quality, hydrochemical data were analyzed through imitative approaches, which were proposed by M. Piper in 1944 [79].

Based on analytical data from the most dominated parameters of the physicochemical analysis (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}), Piper's trilinear diagram was used to define the geochemical facies and surface water types in the Oued Laou watershed and their interaction with rocks (Figure 4a).



(**a**) (**b**)

Figure 4. Piper diagrams of the ionic composition of surface water samples from Oued Laou (**a**). Total ionic salinity (TIS) diagram (**b**).

Based on the cation plot, all samples fell in the center (Zone B), indicating no apparent dominance of any cation in the surface water. However, Na^+ and Ca^{2+} were found at significant concentrations in most sample sites, showing apparent carbonate alteration. On the other hand, the anion diagram revealed that all samples were found in Zone E, indicating HCO_3^- dominance and paralleling the weathering of the carbonate-dominated lithology. The chemical properties of the analyzed surface water samples revealed Ca^{2+}-HCO_3^- and Ca^{2+}-Mg^{2+}-HCO_3^- type water, which indicates that all the samples fall into the non-alkaline carbonate domain. In general, the alkaline earth metal content (Ca^{2+} + Mg^{2+}) outnumbers the alkali (Na^+ + K^+), and the weak acid level (CO_3^{2-} + SO_4^{2-}) outnumbers the strong acid level (CO_3^{2-} + HCO_3^-), which vary from 60% to 90% and 70% to 95%, respectively. However, bicarbonate is a by-product of the dissociation of carbonic acid from the solubility of atmospheric carbon dioxide and humic acids present in the soil or the weathering of silicates [80]. The observed chemical changes may be regulated by natural sources, such as rock-water interactions, anthropogenic sources, irrigation returns, and chemical fertilizers.

Total Ionic Salinity (TIS) analysis was performed to determine the salinity content of the water samples based on Cl^-, HCO_3^-, and SO_4^{2-} [81]. Figure 4b shows the comparable salinity, which ranges from 5 to 10.35 meq/L, knowing that the majority of samples (1, 2, 4, 5, 9, 10, and 12) have TIS between 5 and 9 meq/L, while samples 3 and 11 showed a TIS < 6 meq/L. It was noted that the highest TIS > 10 meq/L was observed in samples 6, 7, 8, and 13, which had the highest values of Cl^-, SO_4^{2-}, TDS, EC, PO_4^{3-}, and EC in all the samples.

3.3. Correlation Matrix

A correlation matrix serves to investigate the interactions between water quality indicators and the origin of water-soluble compounds in the Oued Laou watershed [82]. A Pearson correlation matrix was created using the actual values of the 26 variables chosen for statistical analysis (Table 5), including pH, EC, DO, BOD_5, COD, TDS, TH, TAC, Sal, Turb, Na^+, K^+, Ca^{2+}, Mg^{2+}, F^-, SO_4^{2-}, Cl^-, FC, TC, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, HCO_3^- and $CaCO_3$. The effects of various hydrological, geological, and human activities on water quality may result in high or low correlations between hydrochemical parameters [83].

Table 5. Pearson correlation matrix of water parameters.

Variables	**EC**	**pH**	**TDS**	**DO**	**COD**	**BDO_5**	**Turb**	**$PO_4{}^{3-}$**	**Cl^-**	**$NO_2{}^-$**	**$NO_3{}^-$**	**$NH_4{}^+$**	**Ca^{2+}**	**Mg^{2+}**	**$SO_4{}^{2-}$**	**F^-**	**SAL**	**TH**	**TAC**	**$HCO_3{}^-$**	**$CO_3{}^{2-}$**	**Ca CO_3**	**FC**	**TC**	**Na^+**	**K^+**
EC	**1**																									
pH	0.135	**1**																								
TDS	**1.000**	0.135	**1**																							
DO	0.596	0.363	0.596	**1**																						
COD	0.635	0.412	0.635	0.523	**1**																					
BDO_5	**0.782**	0.383	**0.782**	**0.811**	0.601	**1**																				
Turb	0.693	**0.690**	0.693	**0.770**	**0.741**	**0.744**	**1**																			
$PO_4{}^{3-}$	**0.738**	0.590	**0.738**	**0.733**	**0.749**	**0.775**	**0.937**	**1**																		
Cl^-	**0.823**	0.177	**0.823**	0.587	**0.671**	0.670	0.647	0.588	**1**																	
$NO_2{}^-$	0.535	0.303	0.535	0.412	0.171	0.553	0.492	0.615	0.266	**1**																
$NO_3{}^-$	**0.748**	0.242	**0.748**	**0.617**	0.467	**0.749**	**0.703**	**0.722**	0.587	**0.741**	**1**															
$NH_4{}^+$	0.360	0.471	0.360	0.571	0.523	0.615	0.692	0.652	0.262	0.529	**0.728**	**1**														
Ca^{2+}	−0.311	−0.004	−0.311	0.155	−0.344	−0.255	0.036	0.032	−0.290	0.005	−0.046	0.116	**1**													
Mg^{2+}	−0.388	−0.023	−0.388	−0.021	−0.434	−0.382	−0.062	−0.055	−0.391	0.029	−0.115	0.065	**0.975**	**1**												
$SO_4{}^{2-}$	**0.846**	0.418	**0.846**	**0.802**	**0.799**	**0.833**	**0.917**	**0.918**	**0.825**	0.500	**0.737**	0.612	−0.061	−0.175	**1**											
F^-	0.564	−0.065	0.564	0.429	**0.720**	0.434	0.508	0.545	0.704	0.124	0.396	0.317	−0.130	−0.207	**0.735**	**1**										
SAL	0.283	0.029	0.283	0.273	−0.041	0.339	0.337	0.351	−0.040	**0.669**	0.688	0.669	0.211	0.232	0.278	0.073	**1**									
TH	−0.310	−0.006	−0.310	0.043	−0.427	−0.298	0.004	0.008	−0.343	0.106	−0.019	0.119	**0.975**	**0.992**	−0.109	−0.187	0.323	**1**								
TAC	0.529	−0.164	0.529	0.163	0.325	0.213	0.173	0.054	0.710	−0.022	0.373	−0.058	−0.370	−0.420	0.307	0.289	−0.160	−0.403	**1**							
$HCO_3{}^-$	0.529	−0.164	0.529	0.163	0.325	0.213	0.173	0.054	0.710	−0.022	0.373	−0.058	−0.370	−0.420	0.307	0.289	−0.160	−0.403	**1.000**	**1**						
$CO_3{}^{2-}$	0.588	−0.104	0.588	0.202	0.378	0.249	0.250	0.140	**0.751**	−0.015	0.381	−0.083	−0.368	−0.426	0.373	0.330	−0.186	−0.404	**0.988**	**0.988**	**1**					
$CaCO_3$	0.529	−0.164	0.529	0.163	0.325	0.213	0.173	0.054	0.710	−0.022	0.373	−0.058	−0.370	−0.420	0.307	0.289	−0.160	−0.403	**1.000**	**1.000**	**0.988**	**1**				
FC	0.554	0.482	0.554	0.444	0.615	0.568	**0.714**	**0.757**	0.191	0.525	0.544	**0.712**	−0.126	−0.142	0.621	0.285	0.539	−0.093	−0.182	−0.182	−0.135	−0.182	**1**			
TC	0.534	0.027	0.534	0.338	0.268	0.493	0.260	0.409	0.477	0.162	0.061	−0.266	−0.244	−0.311	0.458	0.394	−0.265	−0.278	0.064	0.064	0.165	0.064	0.068	**1**		
Na^+	**0.703**	0.137	0.703	0.594	0.499	0.578	0.534	0.383	**0.870**	0.242	0.567	0.316	−0.246	−0.342	0.649	0.420	0.040	−0.300	**0.817**	**0.817**	**0.809**	**0.817**	0.138	0.157	**1**	
K^+	0.619	0.450	0.619	**0.877**	0.579	**0.841**	**0.741**	**0.784**	0.573	0.583	0.548	0.586	0.004	−0.114	0.819	0.464	0.231	−0.064	−0.013	−0.013	0.022	−0.013	0.563	0.459	0.500	**1**

Note: The significant correlations (alpha = 0.05) are in boldface.

According to the Pearson correlation matrix analysis in Table 5, the high significant correlation coefficient (r = 1) between EC and TDS indicates that the conductivity of water depends on TDS. EC and TDS had positive correlations with PO_4^{3-}, Cl^-, NO_3^-, SO_4^{2-}, and Na^+, which provide information on the main parameters controlling the salinity and mineralization of Oued Laou surface water.

A high correlation (r > 0.9) was observed between Ca^{2+}, Mg^{2+}, and TH, indicating that water hardness is defined as the combined concentration of calcium and magnesium ions in water samples.

The sampled surface water was high in sodium, bicarbonate, chloride, and sulfate. The strong correlation (r > 0.8) between sulfate and chloride is due to several factors, such as natural and human activities. There was also a significant positive correlation (r > 0.741) between the main cation Na^+ and the bicarbonates (Cl^-, HCO_3^-, CO_3^{2-}, $CaCO_3$), as well as between (Cl^- vs. SO_4^{2-}) and (Na^+ vs. SO_4^{2-}). This significant association gives information on the chemical weathering and leaching of salts in surface waters and suggests that salt dissolution in the surface water is the main source of Na^+ and Cl^-.

The strong relationship between NH_4^+ and NO_3^- (r > 0.7) could explain the low NH_4^+ concentrations in surface waters. As previously stated, there is a significant relationship between DO and NO_3^-, implying that oxygen levels control the nitrification process in the river. While the high correlation between SO_4^{2-} and (Cl^-, K^+) may be due to a long history of evaporation and seasonal impacts [84]. Other significant correlations were also found (r > 0.735) between F^- and SO_4^{2-}, due to the dissolution of fluorite and some silicate minerals, such as mica (the principal source of F^- in surface water) [85]. The association between NO_3^- and PO_4^{3-} in water samples may indicates anthropogenic contamination, primarily from agricultural and/or domestic wastes [86].

The presence of ammonium in the water is an indicator of possible microbiological contamination. Turbid water provides information about the suspension or dissolution of organic and inorganic particles in water. The significant positive correlation between ammonium and turbidity with FC (r = 0.712) could inform the parameters controlling the organic contamination of the Oued Laou river caused by wastewater discharge from human activities and the application of agricultural fertilizers. Therefore, a low dissolved oxygen environment will lead to an increase in fecal coliforms [87]. Additionally, high turbidity allows the fixation of microorganisms on suspended particles. Consequently, the bacteriological quality of turbid waters is questionable [88].

The significant relationship between COD and Cl^--SO_4^{2-}-PO_4^{3-} (r > 0.7) suggests that COD concentration may influence the occurrence of Cl^- and SO_4^{2-} in the Oued Laou river.

3.4. Principal Component Analysis

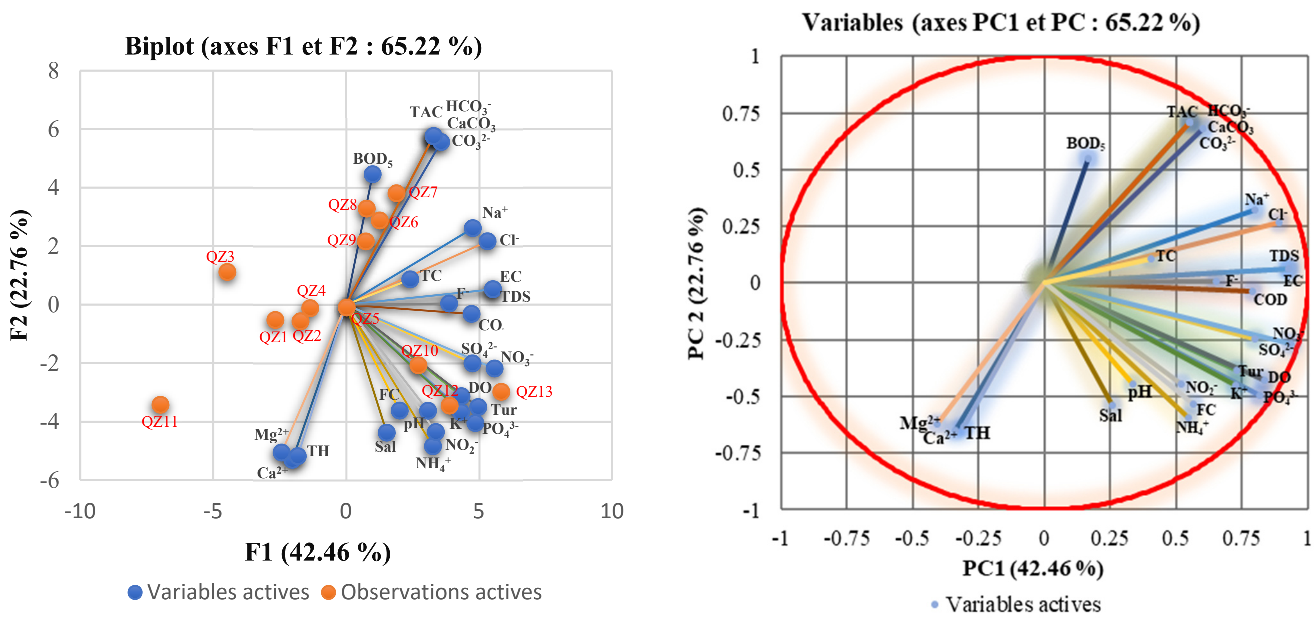
The PCA loading for 26 parameters allows the extraction of five principal components, explaining 89.73 percent of the overall variance of the data (Table 6).

Table 6. Rotated factor loadings of principal components on physicochemical and biological parameters.

Parameters	Components				
	PC1	PC2	PC3	PC4	PC5
EC	0.858	0.004	0.002	0.004	0.076
pH	0.114	0.198	0.042	0.033	0.306
TDS	0.858	0.004	0.002	0.004	0.076
DO	0.530	0.148	0.033	0.044	0.000
BOD_5	0.028	0.300	0.391	0.182	0.037
COD	0.626	0.002	0.035	0.085	0.110
Tur	0.696	0.185	0.000	0.013	0.041
Sal	0.066	0.289	0.000	0.552	0.035
TH	0.115	0.425	0.396	0.002	0.030
TAC	0.305	0.500	0.159	0.021	0.009
PO_4^{3-}	0.665	0.247	0.009	0.019	0.000
Cl^-	0.796	0.071	0.035	0.037	0.005
NO_2^-	0.267	0.199	0.014	0.197	0.085
NO_3^-	0.637	0.061	0.014	0.219	0.004
SO_4^{2-}	0.877	0.072	0.001	0.032	0.002
HCO_3^-	0.305	0.500	0.159	0.021	0.009
CO_3^{2-}	0.359	0.466	0.138	0.004	0.004
$CaCO_3$	0.305	0.500	0.159	0.021	0.009
F^-	0.422	0.000	0.001	0.088	0.029
NH_4^+	0.301	0.354	0.000	0.108	0.125
Na^+	0.639	0.103	0.124	0.002	0.016
K^+	0.526	0.205	0.010	0.068	0.008
Ca^{2+}	0.093	0.405	0.468	0.011	0.014
Mg^{2+}	0.166	0.385	0.399	0.000	0.016
FC	0.321	0.286	0.164	0.030	0.023
TC	0.164	0.011	0.077	0.300	0.373
Eigenvalue	11.039	5.918	2.833	2.097	1.444
Variability (%)	42.459	22.761	10.896	8.064	5.555
Cumulative	42.459	65.220	76.116	84.180	89.735

The F1-F2 duo accounts for more than 65.22% of the data (Figure 5). Based on these percentages, the processes governing the chemical development of the region's waters are essentially contained in these five components.

The first component (PC1) accounts for 42.45% of the total variation, with large positive loadings of EC, TDS, Cl^-, and SO_4^{2-} and moderate loadings of K^+, COD, PO_4^{3-}, NO_3^-, Na^+, Tur, and DO. This component indicates that EC in the surface water is influenced by the amounts of TDS, SO_4^{2-}, NO_3^-, and Na^+. These are the primary ions regulating surface water mineralization at the research site due to the significant positive charge of EC, NO_3^-, and the medium charge of Na^+. Taking everything into account, the most abundant elements in surface water are Na^+, Cl^-, HCO_3^-, and TDS. This is explained by the presence of clays and limestones across the research region.



(**a**) (**b**)

Figure 5. Classification of water quality based on the principal component analysis (**a**,**b**).

DO and COD are used to assess the amount of pollution in surface waters by lowering organic and inorganic components [83]. Because all other forms of inorganic nitrogen have been oxidized, resulting in an increase in NH_4^+ and FC, which are routinely used to determine the level of fecal contamination, the significant positive loading of DO for this component could indicate a fluctuation of nitrates in surface waters. The considerable positive presence of NO_3^- and PO_4^{3-} is mostly associated with the use of chemical or biological fertilizers and wastewater. Although SO_4^{2-} is primarily derived from soluble inorganic nitrogen and inorganic salts, it is affected by agricultural activities (sulfate fertilizers) and bacterial oxidation of sulfur compounds [16]. While the moderate NO_2^- charge in the study area of natural aquifers is linked to anthropogenic factors based on the denitrification process [89], because of its limited solubility, the ion fluorine is frequently inactive in pH-neutral surface waters and is absorbed by other materials that replace clay. However, in an alkaline environment, hydroxyl (OH) groups are easily exchanged into F-, and interaction with water in dry climates would be the primary cause of the fluoride concentration increase. This suggests that fluoride-added water is often excessively alkaline and soft [90]. QZ1, QZ3, QZ11, and QZ13 had the greatest effect on the PC1 score (>0.5), whereas QZ10 and QZ12 had a modest effect.

With moderate positive loadings of HCO_3^-, CO_3^{2-}, $CaCO_3$, and alkalinity, the second component (PC2) explains 22.76 percent of the overall variance. The presence of TAC and HCO_3^- in this component suggests that surface water alkalinity is related to bicarbonate ions, which are the result of a natural disintegration process of the calcareous sedimentary rocks that dominate the Oued Laou catchment basin. The sources of pollution on this axis include both natural and anthropogenic (domestic, industrial, and agricultural).

The fact that CO_3^{2-} has a moderate loading on the PC2 factor indicates that it is formed through weathering, carbonate dissolution, gypsum dissolution, and bacterial decomposition of organic pollution, among other processes [91]. Stations QZ6, QZ7, and QZ8 also had the greatest impact on the PC2 score.

PC3 accounts for 10.89% of total variability and is distinguished by significant positive Mg^{2+}, Ca^{2+}, and BOD_5 loading. This component's substantial Ca^{2+} loading may explain why Ca^{2+} predominates over Mg^{2+} in surface water samples, and it may also suggest that Ca^{2+} has a comparable source to nitrate in surface water. This component is generally associated with anthropogenic contamination induced by agricultural operations in the study region. The presence of Mg^{2+} ions in the research area suggests that they were formed as a result of interactions between the dolomitic limestone and water, which explains the increase in Mg^{2+}.

The fourth component (PC4) indicates that 8.06% of the total variance was mostly caused by salinity with a moderate load, which was caused by lithology or highly dry climate features that naturally cause substantial evapotranspiration and concentrate the soil solution [92]. Stations QZ2 and QZ4 accounted for the majority of PC4 scores.

The PC5 has a moderately positive pH and TC load, accounting for 5.55 percent of the overall variability. This demonstrates how the pH variation in the research region serves as a gauge for the concentration of key ions in surface water. The pH being close to neutral might encourage the development of bacteria in surface water, especially total coliforms. This high TC load may result from a spillover phenomenon whereby all human and animal waste is discharged into the river water. Similar observations have been made by Zegmout [93].

The positive loads of factors 1 and 2 are greater than those of factors 3, 4, and 5. This demonstrates that they are the result of rock-water interaction. PCA results show that dissolved inorganic nitrogen (NH_4^+, NO_3^-, and NO_2^-) significantly contributes to PC1 and PC5, and that human activities may have a considerable impact on the amounts of dissolved inorganic nitrogen in surface waters.

3.5. Hierarchical Cluster Analysis

The sample stations are geographically categorized using the Euclidean distance and ward linkage approach as a measure of similarity or dissimilarity [94]. Hierarchical cluster analysis (HCA) was employed in this study to corroborate the results of PCA [95]. The HCA findings for the physicochemical parameters indicated four types of clustering (Figure 6).

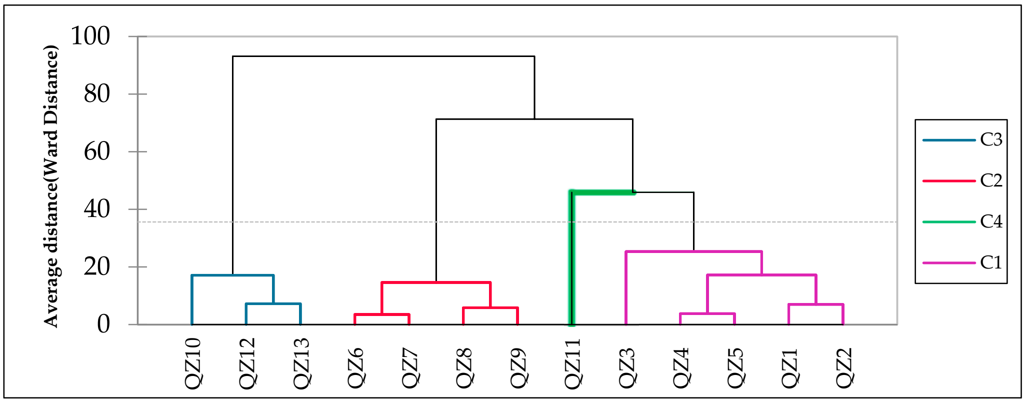


Figure 6. Dendrogram of water surface samples based on physicochemical parameters (Ward method).

Cluster 1 is divided into two sub-clusters. The first covers QZ1-QZ2 and QZ4-QZ5, whereas the second just includes QZ3. It represents the northwestern and southern regions of the Oued Laou basin, which is composed of limestone and shale. This zone's water quality examination revealed considerable amounts of Cl^-, NO_3^-, SO_4^{2-}, TC, and Na^+. It represents the greatest concentrations of these chemicals in the research area. Except for QZ3, the placement of QZ1-QZ2 and QZ4-QZ5 in this group is owing to the high concentration of Ca^{2+}, which is presumably connected to the dissolution of the bicarbonate rocks. Only QZ3 was classified as the cleanest sample in Group 1 since all physicochemical and biological characteristics were present in low quantities and no WHO limits were exceeded.

Cluster 2 has two sub-clusters (QZ6-QZ7) and (QZ8-QZ9), which represent the central and northwest regions of the Oued Laou basin near Akchour. Analyses of the water quality in this location reveal increased levels of PO_4^{3-}, Cl^-, SO_4^{2-}, and TC. Cluster 2 has similar qualities to Cluster 1, but they are more apparent.

Cluster 3 is made up of QZ10, QZ12, and QZ13. These three sites had greater EC, pH, Sal, FC, and Na^+ levels than the other samples. However, the amounts of PO_4^{3-}, NO_3^-, SO_4^{2-}, and NH_4^+ were greater in cluster 3 than in clusters 1 and 2, indicating that high levels of phosphates in surface water are produced by human pollution, notably detergent-containing residential wastewater [96]. Furthermore, the average salinity in cluster 3 was lower than in clusters 1 and 2, and the Ca^{2+} concentration was greater in cluster 3 than in clusters 1 and 2.

Cluster 4 contained a single sample (QZ11) found in the northwestern portion of Oued Laou near the urban center. This sample contains the lowest quantities of nitrates, indicating that the area is not influenced by agricultural operations or anthropogenic contamination. Given the highest Ca^{2+} and Mg^{2+} concentrations, the load of Mg^{2+} ions indicate that they can be derived from rock-water interaction processes. In general, the clustering results are based on the rate of surface water mineralization, which resulted in four classes in the following order of mineralization: Cluster 1 > Cluster 4 > Cluster 2 > Cluster 3.

3.6. Water Quality Index

The suitability of surface water sources was assessed using the Water Quality Index method, which leads to a friendly interpretation of water quality by assembling different parameters into a single number. The WQI was calculated using the concentration of 15 parameters as per their relative significance in the overall quality of water for drinking, domestic, and irrigation purposes (Table 1) and Figure 7 and their permissible limits for water according to the International Regulations (WHO 2017). The surface water quality index divides water bodies into four groups based on pollution levels [22]. This approach also provides a more accurate assessment of drinking water quality [97].

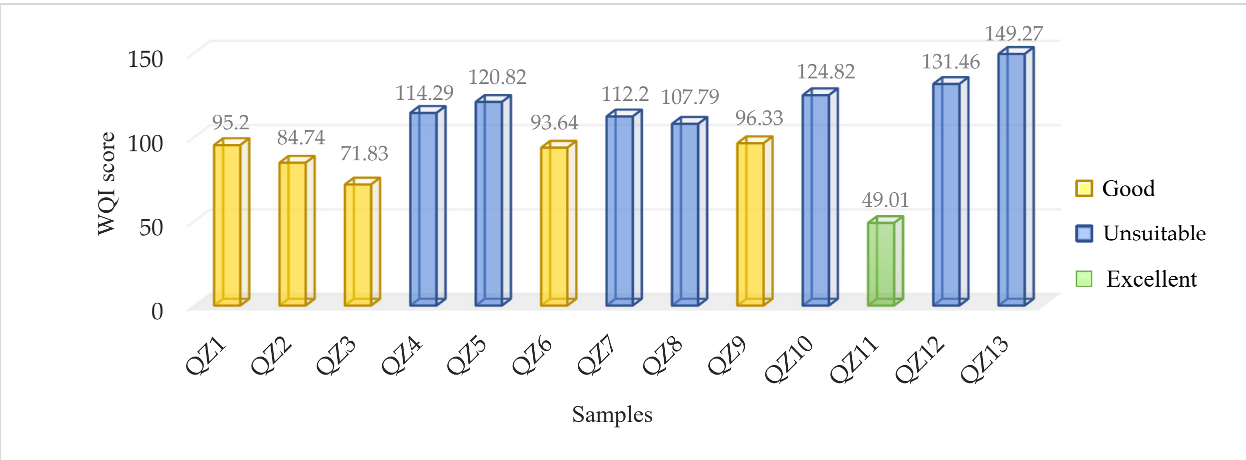


Figure 7. WQI results in the study area.

The results of the calculated WQI, as displayed in Figure 7, suggest that the WQI ranged from 49.01 to 149.27, indicating that the overall water quality of the studied rivers was graded into three categories: "excellent-green", "good-yellow", and "bad-blue". According to this classification, except for one sampling site taken from the Oued Laou River that was within the limits of class 1 (excellent quality) with a relatively stable contribution of pH to the WQI, all the WQI values were more than 50.

Whereas 38.46 percent belong to class 2 (good quality), and 53.48 percent fall into the poor-quality category.

Sample QZ11 contained water of excellent quality, scoring 49.01, and is thus classified as excellent for rural consumption. While QZ1, QZ2, QZ3, QZ4, QZ6, and QZ9 were rated as good drinking water, ranging from 50 to 100. In contrast, the samples QZ5, QZ7, QZ8, QZ10, QZ12, and QZ13 were classified as poor water types with a value greater than 100, which can be attributed to their contact with anthropogenic activities.

The highest value, 149.27, was recorded at QZ13 because it was related to high nitrate, calcium, and phosphate levels and, secondarily, to organic and oxidizable materials exceeding requirements in some places. The WQI assessment indicated that the eastern and southern areas of the study area were unfit for drinking (Figure 7). Previous studies that used the WQI to determine surface water quality discovered similar results. For example, Sudhakaran et al. [98] reported and interpreted that the WQI values of the water in the Netravati River range from 33.21 to 298.66, indicating that the water quality ranges from excellent to very poor. While Hou et al. [99] indicated that WQI values ranged from 17.8 to 77.8 in five reservoirs, which indicated "good" to "very poor" water quality in the reservoirs. No significant differences in WQIs were found between the mountain and Yellow River (China) reservoirs. As is the case for Taloor et al. [100], a record that, according to the Water Quality Index (WQI), 45% of samples fall into the excellent category, and 50% of spring samples fall into good categories for drinking purposes for the Basantar watershed of the Jammu Himalaya (Kashmir, India).

3.7. Hierarchical Cluster Analysis and WQIs

We examined the categorization of the two criteria using the surface water quality index, whose findings show that the WQI is divided into three appropriate groups, and the HCA findings (Figure 8). This comparison allows us to evaluate the similarity between the two methods. The samples with the most comparable WQI values were found to be categorized into the same cluster and subsequently into sub-clusters. When cluster 2 (QZ6, QZ7, QZ8, and QZ9) is compared to cluster 3 (QZ10, QZ12, and QZ13), it is clear that the classification is based on WQI results. where QZ13 had the highest value (149.29), followed by QZ12 (131.46), and QZ10 (124.82) was assigned to cluster 3. while the sub-clusters (QZ7 and QZ8) of cluster 2 were grouped into different sub-clusters. They are, however, all in the same category (blue). classified as "poor water quality".

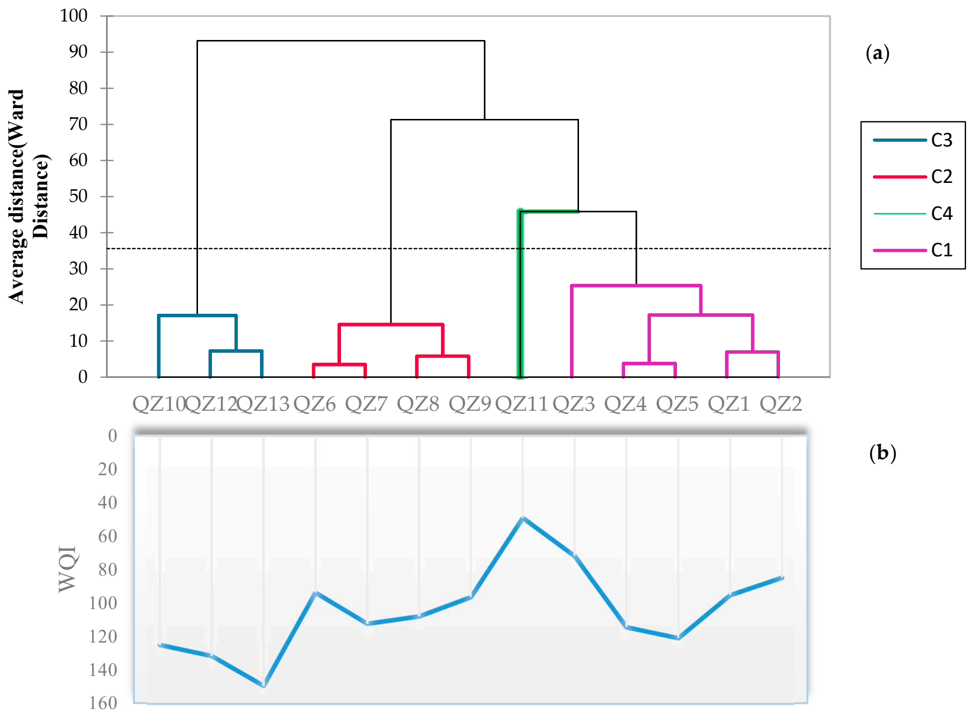


Figure 8. Schematic comparison and combination between HCA (**a**) and WQI (**b**) classification.

On the contrary, the sample QZ11, which has the lowest WQI value (49.01), was placed alone in Cluster 4, which is distinguished by "good water quality" (green). as is the case with Cluster 1, which contains QZ1, QZ2, QZ4, QZ5, and QZ3, which have slightly different WQI scores of (95.2), (84.74), (114.29), (120.82), and (71.83), respectively. In this case, HCA could group QZ4 and QZ5 into the same sub-cluster, different from the QZ1, QZ2, and QZ3 "good quality water" group (yellow), due to the almost identical WQI values with slight differences. It was also noted that the good water quality zones QZ3 and QZ11 are close to each other.

The HCA, on the other hand, can identify and segregate them into two groups since it establishes additional categories. Despite this, both approaches produce comparable findings, and combining them can lead to a more accurate surface water quality evaluation and interpretation.

3.8. Irrigation Water Quality Assessment

The surface water suitability for irrigation purposes is calculated to determine the influence of minerals and salts in surface waters on plants and soil, which may affect plant growth by chemically lowering water intake via osmotic pressure changes or metabolic responses such as those caused by hazardous chemicals. The same is true for soil structure, permeability, and aeration. The IWQI purpose is calculated (Table 7), according to the cumulative effect of the nine hazard groups: EC, Na%, SAR, RSC, RSBC, PI, KI, PS, and MH [98].

Table 7. Water quality parameters for irrigation in Oued Laou surface water samples.

Sample	SAR	RSC	Na%	MH	PI	RSBC	KI	PS	EC
QZ1	0.68	4.8	16.76	50	33.20	2.4	0.19	2.13	399
QZ2	0.76	5.1	19.12	52.83	34.98	2.7	0.23	2.45	436
QZ3	0.27	5.64	9.18	50	48.40	2.82	0.09	1.25	328
QZ4	1.37	4.8	30.80	50	30.05	2.4	0.42	3.31	422
QZ5	1.54	5.54	33.16	50	29.84	2.77	0.47	2.69	445
QZ6	2.51	7.44	44.13	50	27.61	3.72	0.78	3.90	432
QZ7	2.49	8.12	44.66	50	29.35	4.06	0.79	3.71	487
QZ8	1.54	7.2	33.60	50	34.21	3.6	0.49	0.72	429
QZ9	1.45	6.62	32.37	50	34.09	3.31	0.46	3.28	488
QZ10	0.94	5.06	23.33	50	32.04	2.38	0.28	3.93	503
QZ11	0.18	1.71	4.73	52.27	26.90	1.03	0.05	1.69	301
QZ12	1.89	5.12	37.59	50	27.08	2.56	0.58	3.88	467
QZ13	2.13	5.84	39.90	50	26.12	2.92	0.65	4.73	524
Min	0.18	1.71	4.738	50	26.12	1.03	0.04	0.72	301
Max	2.51	8.12	44.66	52.83	48.40	4.06	0.79	4.73	524
Average	1.37	5.61	28.41	50.39	31.84	2.82	0.42	2.90	435.46

Notes: SAR sodium absorption ratio, RSC residual sodium carbonate, Na% percent sodium, MH magnesium hazard, IP permeability index, RSBC, residual sodium bicarbonate, PS potential salinity; KI Kelley index.

The electrical conductivity levels reflected by salinity damage are essential considerations in evaluating the suitability of water used for irrigation because of their effect on the osmotic pressure of the soil solution and the ability of plants to absorb water via their roots [101]. According to Wilcox (1955), C1 surface water (low salinity risk) can be used to irrigate most crops and soils. In the case of moderate leaching, secondary water C2 (moderate salinity risk) can be used for irrigation. Water with relatively high salinity (class C3) may be suitable for salt-tolerant plants but not for normal watering, especially in soils with limited drainage. Water with high salinity (C4) cannot be used in soils with limited (Table 8) [102].

Based on the results of the samples studied in our study area, it was determined that all the samples were classified as moderately brackish, ranging from values below 750 µS/cm, consistent with Richards' value, which indicates good to acceptable irrigation water quality according to the EC value (Table 7).

The salt concentration, or "alkali danger", which is expressed in the SAR, is a crucial factor for assessing the suitability of surface water for irrigation. Sodium Adsorption Rate (SAR) affects the soil, so irrigation water with high salt levels is of special concern and symbolizes the sodium danger because salt affects the soil. SAR also takes water from plants and decreases soil permeability [103].

This activity is particularly sensitive to finely structured soils, particularly those with high clay content. Some modifications may be required to achieve a stage with a high SAR. Ca^{2+} and Mg^{2+}, when present in sufficient amounts in the soil, help balance the effects of Na^{+} and maintain healthy soil properties [104]. SAR is used to categorize surface waters into four groups. Excellent (SAR < 10), Good (10 < SAR <18), Suspicious (18 < SAR < 26), and Unsuitable (SAR > 26). Water sample SAR varied from 0.18 to 2.51, with an average of 1.37 (Table 7). As a result, according to a USSL diagram [105], the categorization of irrigation water quality is in the form of EC against SAR values. EC is used as the salinity risk index, and SAR gives the sodium risk for irrigation water.

According to the Richards classification [105], the plot revealed that about 15.35% of the surface water samples fell into the C2-S1 category. In comparison, approximately 84.62% of the samples fell into the C3-S1 category, which shows that the surface waters in the investigated area have a medium salinity and low sodium content (Figure 9). According to the US Salinity Laboratory classification [106], the surface waters in the study area are within a low salinity field (<2250 µa/cm); thus, the water is highly appropriate for irrigation.

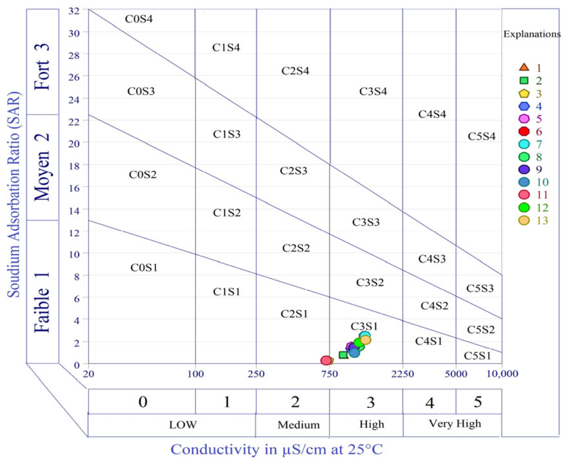


Figure 9. USSL diagram for assessing irrigation water quality.

Similar results were found by Elsayed et al. [31], SAR revealed that most surface water samples fell into the C2-S1 category and a few samples fell into the C3-S1 category, which shows that the surface waters in the Nile River are suitable for irrigation. While Pivić et al. [102] found a different result for SAR, whose values varied between 0.01 and 10.34 meq/L. The obtained SAR values showed that all tested irrigation water samples, except one, were of excellent quality, and one sample was of good quality in the Republic of Serbia.

The sodium percentage (Na%) is also used to assess the risk of sodium in soil and particle clogging. An excess of sodium with carbonate ions will help turn the soil into alkaline soil; in contrast, sodium mixed with chloride ions will accelerate the formation of saline soil, which ultimately worsens the infiltration capacity of the soil and reduces plant growth [95]. According to the classification of Wilcox (1955) [29], surface waters are divided into five types (Table 8).

Table 7 shows that the Na% in the water samples for irrigation in the study area ranged from 4.73 to 44.66%, with an average of 28.41%. Therefore, the Wilcox plot [29] related to the percentage of sodium and total concentration displayed in Figures 10 and 11d reveals that 30.76% of the water samples are in good condition. In comparison, 69.24% are classified as "excellent to permitted" with excessive content.

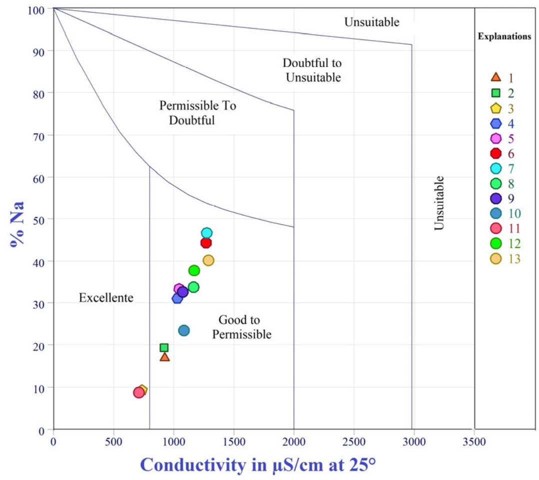


Figure 10. Wilcox 1955 diagram for irrigation water quality.

Similar results were found by Amrani et al. [107] in the region of Timahdite-Almis Guigou, Middle Atlas, Morocco. The water contained less than 60 percent sodium, which is considered healthy and was recommended for irrigation [16]. The high concentration of Na^{+} in irrigation water tends to be absorbed by clay particles, displacing Mg^{2+} and Ca^{2+} ions. The exchange of soluble Na^{+} for Ca^{2+} and Mg^{2+} in the soil reduces permeability and ultimately leads to poor internal drainage. The restriction of air and water circulation during wet conditions affects soil hardness after drying [108].

Water with large quantities of these ions tends to precipitate as calcium carbonate or magnesium carbonate from soil solutions, increasing the salt content and, therefore, the danger of alkalinity. Excessive bicarbonate and carbonate concentrations other than calcium and magnesium are alluded to as residual sodium carbonate (RSC) [109].

RSC is a valuable tool for examining the applicability of irrigation water. It is divided into three levels, according to the Eaton 1950 classification (Table 8) [110]. The RSC values of the 13 samples in our investigation varied from 1.71 to 8.12 meq/L, with an average value of 5.61 meq/L (Table 7). According to this result, 92.31% of the water samples had a value higher than 2.25 meq/L, which falls under the "unsuitable for irrigation" category based on the classification of Knowing that 7.69% (QZ11) of the water samples showed a marginally suitable category for irrigation, the water samples with positive RSC infer that the cumulative concentration of $CO_3{}^{2-}$ and $HCO_3{}^{-}$ is higher than the combined concentrations of Ca^{2+} and Mg^{2+}, which would indicate the presence of residual carbonate [102], which causes a decrease in soil fertilization. The exact variations in RSC values were shown by the IDW interpolation map (Figure 11g).

The residual sodium bicarbonate index (RSBC) has been proposed by Gupta et al. [111] to express the risk of alkalinity. Generally, a bicarbonate concentration above 10.0 meq/L affects plant growth in several ways. while RSBC values less than 5 meq/L were considered satisfactory [111]. In this study, RSBC values ranged from 1.03 to 4.06 meq/L (Table 7), with an average of 2.82 meq/L, which shows that all samples had RSBC values much lower than the acceptable level and may be used safely for irrigation.

Potential salinity (PS), which is the concentration of Cl^{-} plus half the concentration of $SO4^{2-}$, is used as one of the classifications for assessing the suitability of water for irrigation [112]. In the examined irrigation water samples, the potential salinity of water samples from the river Oued Laou ranged from 0.72 meq/L to 4.37 meq/L, with an average of 2.90 meq/L (Table 7). This means that 46.15% of the samples (QZ1, QZ2, QZ3, QZ5, QZ8, and QZ11) are excellent. while 53.85% of the samples are classified as good (Table 8). These variations in potential salinity levels might be attributed to the presence of chlorides in agricultural and wastewater discharges.

The RSBC and PS analytical data are shown geospatially on the IDW maps (Figure 11e,f).

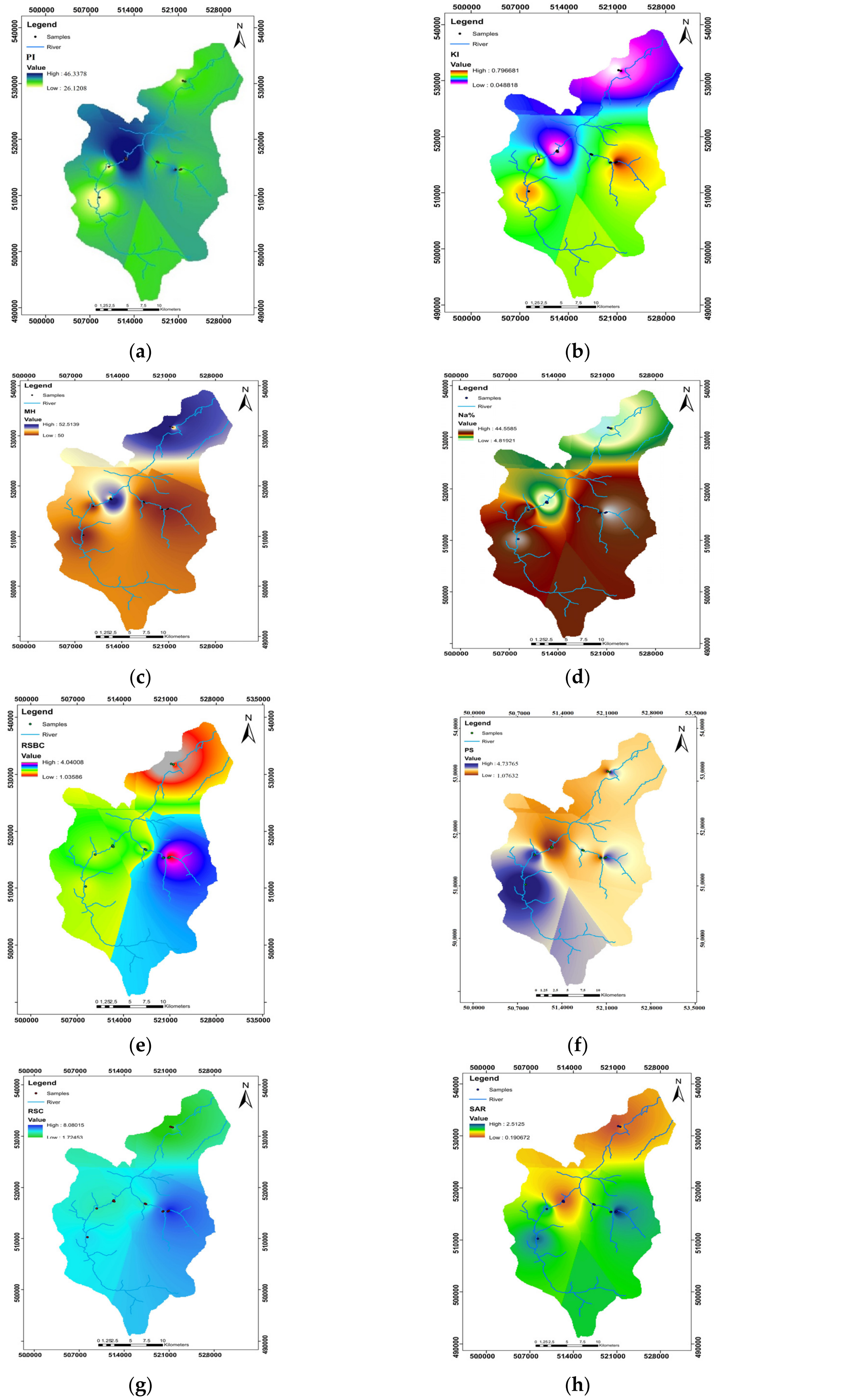


Figure 11. Spatial distribution map of surface water for (**a**) IP, (**b**) KI, (**c**) MH, (**d**) Na%, (**e**) PS, (**f**) RSBC, (**g**) RSC, and (**h**) SAR.

The use of water with high quantities of salt, calcium, magnesium, and bicarbonate alters soil permeability over time [104]. The Permeability Index (PI), developed by Doneen et al. [112], can better reflect the effects of irrigation. Based on the parameters employed, water can be divided into three classes: excellent, good, and poor (Table 8). Class I (>75%) and Class II (25–75%), respectively, are deemed suitable and moderate for irrigation, whereas Class III (25%) is deemed unsuitable [113]. The computed permeability index for water samples in the Oued Laou watershed spans from 26.12% to 48.40%, with an average of 31.48%. The analytical results are projected geospatially onto the IDW map (Figure 11a), revealing that all samples are dispersed in class II. This means that surface water is suitable for irrigation, and long-term irrigation will not affect soil permeability.

Paliwal et al. [114] developed the Magnesium Danger Index (MH) to assess the magnesium in irrigation water.Ca^{2+} and Mg^{2+}, in general, keep the water balanced, although they behave differently in physiological systems. The high Mg^{2+} content is usually due to the presence of replaceable Na^{+} in the irrigated soil, which negatively affects soil quality and causes it to become alkaline due to the adsorption of large amounts of water between magnesium and clay particles, reducing the soil's ability to infiltrate and crop production [115].

The MH values in our study varied from 50 to 52.83%, indicating that only 15.38% of the water samples (QZ3, QZ11) had a value of more than 50, which might have a detrimental influence on agricultural output and soil alkalinity. However, most of the tested samples (84.63%) had MH values greater than 50 and were appropriate for irrigation. The IDW variants of MH values are depicted in Figure 11c.

The Kelley index (KI) [116] was used in the research region to assess irrigation water quality. The levels of Na^{+}, Ca^{2+}, and Mg^{2+} in water are used to calculate the value of KI. A KI value >1 indicates that excess salt is hazardous for irrigation, but a KI value less than one indicates that water is good for irrigation [59]. The observed KI values in our study varied from 0.04 to 0.79 meq/L, with a mean of 0.42 meq/L (Table 7). According to Kelly's analysis (Table 8), the surface water at 13 locations was deemed enough for irrigation, and long-term irrigation will not negatively impact soil permeability potentially resulting from insufficient cation exchange, which results in a minor Na^{+} surplus [117]. The IDW differences in KI values are seen in Figure 11b.

The irrigation water quality indicator is based on the ideal limits of nine indices: CE, Na%, PI, PS, KI, SAR, RSC, RSBC, and MH (Table 7). The calculated IWQI ranges from 28.52 to 79.76, with an average value of 58.45 displayed in the graph (Table 7). demonstrating that the surface water quality at this location is outstanding or acceptable and suitable for irrigation. According to the results, one of the thirteen water samples was exceptional, while the other twelve were good. The samples with the highest IWQI values are QZ7, QZ6, QZ8, and QZ13, which mostly belong to the hydrochemical types Ca^{2+}-Mg^{2+}-HCO_3^{-}, which are close to Ca^{2+}-Na^{+}-HCO_3^{-} (Figure 4), indicating that Na^{+} is the dominant factor affecting irrigation water quality in this area.

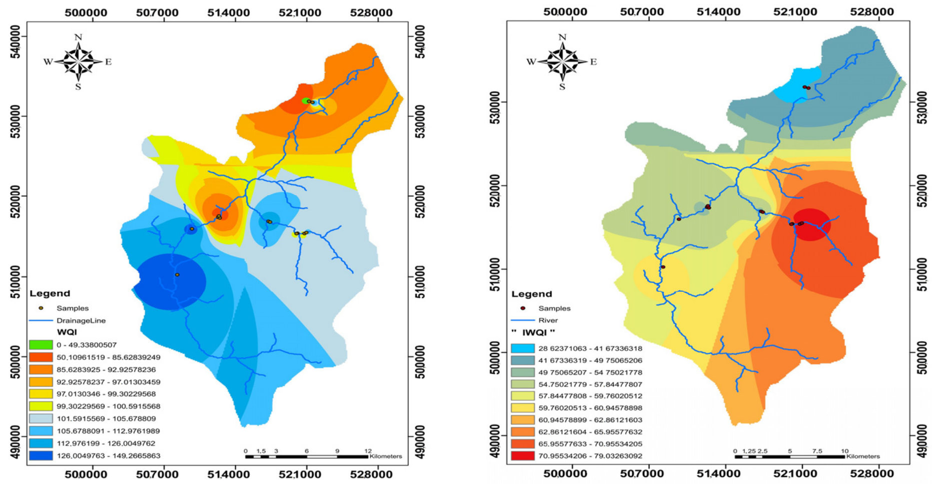
Table 8. Classification of waters based on salinity hazard EC and SAR values and sodium hazard classes based on USSL classification [118].

Index Classification	Range	Reference	Range (No. of Samples)	Remark on Quality	Water Type	Salinity Hazard Class
Salinity hazard EC (µS/cm)	100–250		-	Excellent	Low salinity water	C1
	250–750		301–524 (13 samples)	Good	Medium salinity	C2
	750–2250	[29]	-	Doubtful	High salinity water	C3
	>2500		-	Unsuitable	Very high salinity	C4
SAR	<10	[105]	0.18–2.51 (13 samples)	Excellent	Low sodium water	S1
	10–18		–	Good	Medium Sodium	S2
	19–26		–	Doubtful	High sodium water	S3
	>26		–	Unsuitable	Very high Sodium	S4 And S5
Sodium (%)	<20	[29]	4.73–9.18 (4 samples)	Excellent	–	–
	20–40		23.33–39.90 (7 samples)	Good	–	–
	40–60		44.13–44.66 (2 samples)	Permissible	–	–
	60–80		Nil	Doubtful	–	–
	>80		Nil	Unsuitable	–	–
RSC	<1.25	[110]	Nil	Safe/Good	–	–
	1.25–2.5		1.71 (1 sample)	Marginal/Doubtful	–	–
	>2.5		4.8–8.12 (12 Samples)	Unsuitable	–	–
RSBC	<0	[118]	Nil		Non-alkaline	–
	0		Nil		Normal	–
	0–2.5		1.03–2.4 (4 Samples)	Satisfactory	Low alkalinity	
	2.5–5		2.56–4.06 (9 Samples)		Medium alkalinity	
	5–10		Nil	Marginal	High alkalinity	
	>10		Nil		Very high alkalinity	
PS	<3	[112]	0.72–2.69 (6 samples)	Excellent	–	–
	3–5		3.28–4.73 (7 samples)	Good	–	–
	>5		Nil	Unsuitable	–	–
PI	>75%	[112]	Nil	Good		
	25–75%		26.12–48.40 (13 samples)	Suitable		
	<25%		Nil	Unsuitable		
KI	<1	[116]	0.04–0.79 (13 samples)	Suitable	–	–
	>1		Nil	Unsuitable	–	–
MH	<50	[114]	50 (11 samples)	suitability for irrigation	–	–
	>50		50–52 (2 samples)	Unsuitable for irrigation	–	–

3.9. Spatial Division

To show the regional distribution of water quality at each site, the geospatial distribution maps of WQI and IWQI were created using the inverse interpolation technique (IDW) to produce a database of surface water quality for consumption and irrigation water in the study area (Figure 12a,b). As a result, these maps have been proven beneficial and can be used to assess surface water quality and determine the best locations with the fewest dangerous pollutants [60].

According to Figure 12a, the water quality indices indicate that 7.69% of surface water samples were considered excellent for human consumption because of low local anthropogenic or agricultural activities, which are situated in the northwestern region (QZ11). In comparison, 38.46% of the samples were considered good quality in the central and western areas, especially the QZ1, QZ2, QZ3, QZ6, and QZ9 samples. However, because the zone is adjacent to anthropogenic activity, the water quality deteriorates with time because it is near irrigated fields, whereas 53.84 percent of the samples are considered poor quality in the central and southern parts of the zone study due to the influx of tourists as well as local residents.



(**a**) (**b**)

Figure 12. Spatial distribution of WQI (**a**) and IWQI (**b**) in the Oued Laou river.

According to Table 9, the good water quality samples for irrigation are situated in the same area as the IWQ. The eastern and southern sections, as well as the center part, are dominated by high-quality water. The research region has a sub-humid climate with substantial winter precipitation, resulting in low evaporation as the primary factor affecting surface water chemistry. Anthropogenic inputs significantly influence the central area, particularly through the discharge of untreated wastewater. In numerous places, little trenches containing untreated sewage may be seen, through which effluent is leached into the river.

Table 9. Classification of surface water samples based on IWQI.

Samples	IWQI	Usage Restriction
QZ1	50.75	Good
QZ2	56.34	Good
QZ3	56.78	Good
QZ4	51.83	Good
QZ5	57.91	Good
QZ6	73.87	Good
QZ7	79.35	Good
QZ8	71.09	Good
QZ9	66.46	Good
QZ10	51.02	Good
QZ11	28.52	Excellent
QZ12	54.96	Good
QZ13	60.92	Good

These operations have contaminated sample numbers QZ4, QZ5, QZ7, and QZ8. Before the area's tourism operations, the water was utilized for drinking, but it is now solely used for residential and agricultural purposes. During the rainy season, effluents are dumped into natural drains and precipitation, damaging surface water supplies.

The southern portion is the most impacted by agricultural runoff and human activity due to the prevalence of agricultural land and wastewater from the cities of Chefchaouen and Dchar Akarat. As sample number QZ13 in Dchar Akarat is characterized by increased concentrations of nitrates, potassium, and chloride, which are likely contributed by sources of rock nature or domestic wastewater, there is a need to control the discharge of anthropogenic effluents affecting surface water quality in this area.

4. Conclusions

This study aims to assess and identify the sources of surface water pollution in the Oued Laou watershed in northern Morocco using hydrochemical methods, WQI and IWQI, multivariate statistics, and GIS. To this end, 26 physicochemical and bacteriological parameters were analyzed, and an assessment of the surface water adequacy of irrigation was carried out. The results showed that the major ion concentrations were reported in the following order: Ca^{2+}, Na^+, Mg^{2+}, and K^+; and $HCO_3^- > CO_3^{2-} > Cl^- > SO_4^{2-} > NO_3^- > F^- > PO_4^{3-} > NO_2^-$. The Piper diagram projection revealed that the dominant water type is Ca^{2+}-Mg^{2+}-HCO_3^-. The WQI results in the study area resulted in the classification of surface water into three groups: (QZ11) excellent water, (QZ1, QZ2, QZ3, QZ6, and QZ9 good water), and (QZ4, QZ5, QZ7, QZ8, QZ10, QZ12, and QZ13 poor water). The water suitability for irrigation based on SAR, % Na, RSC, PI, MH, PS, and Kelly Ratio showed that the surface water was appropriate for agricultural purposes, except for RSC, which indicated that 23.07% of samples were categorized as "good/safe", and for MH, which revealed that 84.61% of samples were categorized as suitable. Those parameters led to the determination of irrigation water quality (IWQI), indicating that the majority of samples (92.31%) had "good quality" while 7.69% of the samples were categorized as "excellent quality". Coupled approaches have proven effective and robust in assessing surface water quality in the Oued Laou watershed. This will help decision makers in monitoring and managing water resources in northern Morocco. The results of this study may be relevant to areas with similar characteristics in Morocco and elsewhere. In perspective, other analyses such as heavy metals and other bacteriological analyses are necessary to develop a control approach in order to limit the negative impacts of surface water pollution in the context of sustainable development and the preservation of water resources.

Author Contributions: Conceptualization, E.K.C., H.E.A. and E.M.A.; methodology, E.K.C., E.M.A., and H.E.A.; software, E.K.C. and H.E.A.; validation E.K.C., E.M.A., O.S., E.M.A., J.C.G.E.d.S. and H.E.A.; formal analysis, E.K.C., H.E.A., O.S., H.D., H.Y., E.M.A. and F.S.; writing—original draft preparation, E.K.C., E.M.A., J.C.G.E.d.S. and H.E.A.; writing—review and editing, E.K.C.,H.E.A., O.S., E.M.A., H.D., H.Y., J.C.G.E.d.S. and H.E.A.; visualization, E.K.C., H.E.A. and E.M.A.; supervision, E.K.C. and F.S.; funding acquisition, J.C.G.E.d.S. and E.K.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank all those who collaborated in this work on the field sampling, laboratory analysis, and writing manuscript teams. Joaquim C G Esteves da Silva would like to mention the R&D Units CIQUP (UIDB/000081/2020) and the Associated Laboratory IMS (LA/P/0056/2020). El Khalil Cherif was supported by FCT with the LARSyS—FCT Project UIDB/50009/2020 and by the FCT project VOAMAIS (PTDC/EEI-AUT/31172/2017, 02/SAICT/2017/31172).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Shil, S.; Singh, U.K.; Mehta, P. Water quality assessment of a tropical river using water quality index (WQI), multivariate statistical techniques and GIS. *Appl. Water Sci.* **2019**, *9*, 168. [CrossRef]
2. Khan, M.Y.A.; Gani, K.M.; Chakrapani, G.J. Assessment of surface water quality and its spatial variation. A case study of Ramganga River, Ganga Basin, India. *Arab. J. Geosci.* **2016**, *9*, 28. [CrossRef]
3. Gupta, S.; Gupta, S.K. A critical review on water quality index tool: Genesis, evolution and future directions. *Ecol. Inform.* **2021**, *63*, 101299. [CrossRef]

4. Kareem, S.L.; Jaber, W.S.; Al-Maliki, L.A.; Al-Husseiny, R.A.; Al-Mamoori, S.K.; Alansari, N. Water quality assessment and phosphorus effect using water quality indices: Euphrates River-Iraq as a case study. *Groundw. Sustain. Dev.* **2021**, *14*, 100630. [CrossRef]
5. Devi, P.; Singh, P.; Kansal, S.K. *Inorganic Pollutants in Water*; Elsevier: Amsterdam, The Netherlands, 2020; ISBN 978-0-12-818965-8.
6. Uddin, G.; Nash, S.; Olbert, A.I. A review of water quality index models and their use for assessing surface water quality. *Ecol. Indic.* **2020**, *122*, 107218. [CrossRef]
7. Wu, Z.; Lai, X.; Li, K. Water quality assessment of rivers in Lake Chaohu Basin (China) using water quality index. *Ecol. Indic.* **2020**, *121*, 107021. [CrossRef]
8. Jahin, H.; Abuzaid, A.S.; Abdellatif, A.D. Using multivariate analysis to develop irrigation water quality index for surface water in Kafr El-Sheikh Governorate, Egypt. *Environ. Technol. Innov.* **2020**, *17*, 100532. [CrossRef]
9. Gaur, N.; Sarkar, A.; Dutta, D.; Gogoi, B.J.; Dubey, R.; Dwivedi, S.K. Evaluation of water quality index and geochemical characteristics of surfacewater from Tawang India. *Sci. Rep.* **2022**, *12*, 11698. [CrossRef]
10. Soumaila, K.I.; Mustapha, N.; Mohamed, C. Assessment of Surface Water Quality using Indices and Geographic Information System in the Sebou River Basin, Morocco. *Eur. Sci. J.* **2021**, *17*, 249. [CrossRef]
11. Barakat, A.; El Baghdadi, M.; Rais, J.; Aghezzaf, B.; Slassi, M. Assessment of spatial and seasonal water quality variation of Oum Er Rbia River (Morocco) using multivariate statistical techniques. *Int. Soil Water Conserv. Res.* **2016**, *4*, 284–292. [CrossRef]
12. Molle, F.; Tanouti, O. Squaring the circle: Agricultural intensification vs. water conservation in Morocco. *Agric. Water Manag.* **2017**, *192*, 170–179. [CrossRef]
13. Obiri-Nyarko, F.; Asugre, S.J.; Asare, S.V.; Duah, A.A.; Karikari, A.Y.; Kwiatkowska-Malina, J.; Malina, G. Hydrogeochemical Studies to Assess the Suitability of Groundwater for Drinking and Irrigation Purposes: The Upper East Region of Ghana Case Study. *Agriculture* **2022**, *12*, 1973. [CrossRef]
14. Himi, M.; Stitou, J.; Rivero, L.; Salhi, A.; Tapias, J.; Casas, A. Geophysical Surveys for Delineating Salt Water Intrusion and Fresh Water Resources in the Oued Laou Coastal Aquifer. In Proceedings of the Near Surface 2010—16th EAGE European Meeting of Environmental and Engineering Geophysics, Zurich, Switzerland, 6–8 September 2010; European Association of Geoscientists & Engineers: Bunnik, The Netherlands, 2010. [CrossRef]
15. Nouayti, N.; Cherif, E.K.; Algarra, M.; Pola, M.L.; Fernández, S.; Nouayti, A.; da Silva, J.C.G.E.; Driss, K.; Samlani, N.; Mohamed, H.; et al. Determination of Physicochemical Water Quality of the Ghis-Nekor Aquifer (Al Hoceima, Morocco) Using Hydrochemistry, Multiple Isotopic Tracers, and the Geographical Information System (GIS). *Water* **2022**, *14*, 606. [CrossRef]
16. Alsubih, M.; Mallick, J.; Islam, A.R.M.T.; Almesfer, M.K.; Ben Kahla, N.; Talukdar, S.; Ahmed, M. Assessing Surface Water Quality for Irrigation Purposes in Some Dams of Asir Region, Saudi Arabia Using Multi-Statistical Modeling Approaches. *Water* **2022**, *14*, 1439. [CrossRef]
17. El Bilali, A.; Taleb, A. Prediction of irrigation water quality parameters using machine learning models in a semi-arid environment. *J. Saudi Soc. Agric. Sci.* **2020**, *19*, 439–451. [CrossRef]
18. Sutadian, A.D.; Muttil, N.; Yilmaz, A.G.; Perera, B.J.C. Development of river water quality indices—A review. *Environ. Monit. Assess.* **2016**, *188*, 58. [CrossRef]
19. Kikuda, R.; Gomes, R.P.; Gama, A.R.; Silva, J.A.D.P.; Dos Santos, A.P.; Alves, K.R.; Arruda, P.N.; Scalize, P.S.; Vieira, J.D.G.; Carneiro, L.C.; et al. Evaluation of Water Quality of Buritis Lake. *Water* **2022**, *14*, 1414. [CrossRef]
20. Banda, T.D.; Kumarasamy, M.V. Development of Water Quality Indices (WQIs): A Review. *Pol. J. Environ. Stud.* **2020**, *29*, 2011–2021. [CrossRef]
21. Gad, M.; Saleh, A.H.; Hussein, H.; Farouk, M.; Elsayed, S. Appraisal of Surface Water Quality of Nile River Using Water Quality Indices, Spectral Signature and Multivariate Modeling. *Water* **2022**, *14*, 1131. [CrossRef]
22. Chen, D.; Elhadj, A.; Xu, H.; Xu, X.; Qiao, Z. A Study on the Relationship between Land Use Change and Water Quality of the Mitidja Watershed in Algeria Based on GIS and RS. *Sustainability* **2020**, *12*, 3510. [CrossRef]
23. Kumar, A.; Matta, G.; Bhatnagar, S. A coherent approach of Water Quality Indices and Multivariate Statistical Models to estimate the water quality and pollution source apportionment of River Ganga System in Himalayan region, Uttarakhand, India. *Environ. Sci. Pollut. Res.* **2021**, *28*, 42837–42852. [CrossRef] [PubMed]
24. Horton, R.K. An Index Number System for Rating Water Quality. *J. Walter Poll. Cont. Fed.* **1965**, *37*, 300–306.
25. Brown, R. *Psycholinguistics: Selected Papers by Roger Brown*; Free Press: New York, NY, USA, 1970; 392p.
26. Akhtar, N.; Ishak, M.; Ahmad, M.; Umar, K.; Yusuff, M.M.; Anees, M.; Qadir, A.; Almanasir, Y.A. Modification of the Water Quality Index (WQI) Process for Simple Calculation Using the Multi-Criteria Decision-Making (MCDM) Method: A Review. *Water* **2021**, *13*, 905. [CrossRef]
27. Asadollah, S.B.H.S.; Sharafati, A.; Motta, D.; Yaseen, Z.M. River water quality index prediction and uncertainty analysis: A comparative study of machine learning models. *J. Environ. Chem. Eng.* **2021**, *9*, 104599. [CrossRef]
28. Xu, J.; Bai, Y.; You, H.; Wang, X.; Ma, Z.; Zhang, H. Water quality assessment and the influence of landscape metrics at multiple scales in Poyang Lake basin. *Ecol. Indic.* **2022**, *141*, 109096. [CrossRef]
29. Wilcox, L.V. *Classification and Use of Irrigation Waters*; U.S. Department of Agriculture: Washington, DC, USA, 1955.
30. Singh, G.; Rishi, M.S.; Arora, N.K. Integrated GIS-based modelling approach for irrigation water quality suitability zonation in parts of Satluj River Basin, Bist Doab region, North India. *SN Appl. Sci.* **2019**, *1*, 1438. [CrossRef]

31. Elsayed, S.; Hussein, H.; Moghanm, F.S.; Khedher, K.M.; Eid, E.M.; Gad, M. Application of Irrigation Water Quality Indices and Multivariate Statistical Techniques for Surface Water Quality Assessments in the Northern Nile Delta, Egypt. *Water* **2020**, *12*, 3300. [CrossRef]
32. Samtio, M.S.; Hakro, A.A.A.D.; Jahangir, T.M.; Mastoi, A.S.; Lanjwani, M.F.; Rajper, R.H.; Lashari, R.A.; Agheem, M.H.; Noonari, M.W. Impact of rock-water interaction on hydrogeochemical characteristics of groundwater: Using multivariate statistical, water quality index and irrigation indices of chachro sub-district, thar desert, sindh, Pakistan. *Groundw. Sustain. Dev.* **2023**, *20*, 100878. [CrossRef]
33. Ferahtia, A.; Mohammed Tahar, H.; Fateh, M.; Bensaci, E. Surface water quality assessment in semi-arid region (El Hodna watershed, Algeria) based on water quality index (WQI). *Stud. Univ. Babeș-Bolyai Chem.* **2021**, *66*, 127–142. [CrossRef]
34. Yang, F.; Liu, S.; Jia, C.; Gao, M.; Chang, W.; Wang, Y. Hydrochemical characteristics and functions of groundwater in southern Laizhou Bay based on the multivariate statistical analysis approach. *Estuar. Coast. Shelf Sci.* **2020**, *250*, 107153. [CrossRef]
35. Liu, J.; Zhang, D.; Tang, Q.; Xu, H.; Huang, S.; Shang, D.; Liu, R. Water quality assessment and source identification of the Shuangji River (China) using multivariate statistical methods. *PLoS ONE* **2021**, *16*, e0245525. [CrossRef] [PubMed]
36. Abdulsalam, A.; Ramli, M.F.; Jamil, N.R.; Ashaari, Z.H.; Umar, D.A. Hydrochemical characteristics and identification of groundwater pollution sources in tropical savanna. *Environ. Sci. Pollut. Res.* **2022**, *29*, 37384–37398. [CrossRef] [PubMed]
37. Abuzaid, A.S.; Abdel-Salam, M.A.; Ahmad, A.F.; Fathy, H.A.; Fadl, M.E.; Scopa, A. Effect of Marginal-Quality Irrigation on Accumulation of some Heavy Metals (Mn, Pb, and Zn) in TypicTorripsamment Soils and Food Crops. *Sustainability* **2022**, *14*, 1067. [CrossRef]
38. Arifullah; Changsheng, H.; Akram, W.; Rashid, A.; Ullah, Z.; Shah, M.; Alrefaei, A.F.; Kamel, M.; Aleya, L.; Abdel-Daim, M.M. Quality Assessment of Groundwater Based on Geochemical Modelling and Water Quality Index (WQI). *Water* **2022**, *14*, 3888. [CrossRef]
39. Tharmar, E.; Abraham, M.; Prakash, R.; Sundaram, A.; Flores, E.S.; Canales, C.; Alam, M.A. Hydrogeochemistry and Water Quality Assessment in the Thamirabarani River Stretch by Applying GIS and PCA Techniques. *Sustainability* **2022**, *14*, 16368. [CrossRef]
40. Akoto, O.; Adopler, A.; Tepkor, H.E.; Opoku, F. A comprehensive evaluation of surface water quality and potential health risk assessments of Sisa river, Kumasi. *Groundw. Sustain. Dev.* **2021**, *15*, 100654. [CrossRef]
41. Ghesquière, O.; Walter, J.; Chesnaux, R.; Rouleau, A. Scenarios of groundwater chemical evolution in a region of the Canadian Shield based on multivariate statistical analysis. *J. Hydrol. Reg. Stud.* **2015**, *4*, 246–266. [CrossRef]
42. Khouni, I.; Louhichi, G.; Ghrabi, A. Use of GIS based Inverse Distance Weighted interpolation to assess surface water quality: Case of Wadi El Bey, Tunisia. *Environ. Technol. Innov.* **2021**, *24*, 101892. [CrossRef]
43. Ben Brahim, F.; Boughariou, E.; Bouri, S. Multicriteria-analysis of deep groundwater quality using WQI and fuzzy logic tool in GIS: A case study of Kebilli region, SW Tunisia. *J. Afr. Earth Sci.* **2021**, *180*, 104224. [CrossRef]
44. Ma, X.; Wang, L.; Yang, H.; Li, N.; Gong, C. Spatiotemporal Analysis of Water Quality Using Multivariate Statistical Techniques and the Water Quality Identification Index for the Qinhuai River Basin, East China. *Water* **2020**, *12*, 2764. [CrossRef]
45. Amellah, O.; el Morabiti, K. Assessment of soil erosion risk severity using GIS, remote sensing and RUSLE model in Oued Laou Basin (north Morocco). *Soil Sci. Annu.* **2021**, *72*, 142530. [CrossRef]
46. Bayed, A.; Ater, M. *Du Bassin Versant Vers La Mer: Analyse Multidisciplinaire Pour Une Gestion Durable*; Institut Scientifique, Université Mohammed V de Rabat: Rabat, Morocco, 2008; ISBN 978-9954-20-660-7.
47. Aqnouy, M.; El Messari, J.E.S.; Ismail, H.; Bouadila, A.; Moreno Navarro, J.G.; Loubna, B.; Mansour, M.R.A. Assessment of the SWAT Model and the Parameters Affecting the Flow Simulation in the Watershed of Oued Laou (Northern Morocco). *J. Ecol. Eng.* **2019**, *20*, 104–113. [CrossRef]
48. Tiwari, K.; Goyal, R.; Sarkar, A. GIS-Based Spatial Distribution of Groundwater Quality and Regional Suitability Evaluation for Drinking Water. *Environ. Process.* **2017**, *4*, 645–662. [CrossRef]
49. Kaiser, H.F. The varimax criterion for analytic rotation in factor analysis. *Psychometrika* **1958**, *23*, 187–200. [CrossRef]
50. Oladipo, J.O.; Akinwumiju, A.S.; Aboyeji, O.; Adelodun, A.A. Comparison between fuzzy logic and water quality index methods: A case of water quality assessment in Ikare community, Southwestern Nigeria. *Environ. Chall.* **2021**, *3*, 100038. [CrossRef]
51. Backhaus, K.; Erichson, B.; Gensler, S.; Weiber, R.; Weiber, T. Cluster Analysis. In *Multivariate Analysis: An Application-Oriented Introduction*; Backhaus, K., Erichson, B., Gensler, S., Weiber, R., Weiber, T., Eds.; Springer Fachmedien: Wiesbaden, Germany, 2021; pp. 451–530. ISBN 978-3-658-32589-3.
52. Costa, D.D.A.; de Azevedo, J.P.S.; dos Santos, M.A.; Assumpção, R.D.S.F.V. Water quality assessment based on multivariate statistics and water quality index of a strategic river in the Brazilian Atlantic Forest. *Sci. Rep.* **2020**, *10*, 22038. [CrossRef]
53. Ward, J.H., Jr. Hierarchical Grouping to Optimize an Objective Function. *J. Am. Stat. Assoc.* **1963**, *58*, 236–244. [CrossRef]
54. Chakravarty, T.; Gupta, S. Assessment of water quality of a hilly river of south Assam, north east India using water quality index and multivariate statistical analysis. *Environ. Chall.* **2021**, *5*, 100392. [CrossRef]
55. Jehan, S.; Ullah, I.; Khan, S.; Muhammad, S.; Khattak, S.A.; Khan, T. Evaluation of the Swat River, Northern Pakistan, water quality using multivariate statistical techniques and water quality index (WQI) model. *Environ. Sci. Pollut. Res.* **2020**, *27*, 38545–38558. [CrossRef]

56. Azzirgue, E.M.; Cherif, E.K.; Tchakoucht, T.A.; El Azhari, H.; Salmoun, F. Testing Groundwater Quality in Jouamaa Hakama Region (North of Morocco) Using Water Quality Indices (WQIs) and Fuzzy Logic Method: An Exploratory Study. *Water* **2022**, *14*, 3028. [CrossRef]
57. Kulisz, M.; Kujawska, J.; Przysucha, B.; Cel, W. Forecasting Water Quality Index in Groundwater Using Artificial Neural Network. *Energies* **2021**, *14*, 5875. [CrossRef]
58. Rupias, O.J.B.; Pereira, S.Y.; de Abreu, A.E.S. Hydrogeochemistry and groundwater quality assessment using the water quality index and heavy-metal pollution index in the alluvial plain of Atibaia river- Campinas/SP, Brazil. *Groundw. Sustain. Dev.* **2021**, *15*, 100661. [CrossRef]
59. Masoud, M.; El Osta, M.; Alqarawy, A.; Elsayed, S.; Gad, M. Evaluation of groundwater quality for agricultural under different conditions using water quality indices, partial least squares regression models, and GIS approaches. *Appl. Water Sci.* **2022**, *12*, 244. [CrossRef]
60. World Health Organization. *Guidelines for Drinking-Water Quality: Fourth Edition Incorporating First Addendum*; World Health Organization: Geneva, Switzerland, 2017; ISBN 978-92-4-154995-0.
61. Chucuya, S.; Vera, A.; Pino-Vargas, E.; Steenken, A.; Mahlknecht, J.; Montalván, I. Hydrogeochemical Characterization and Identification of Factors Influencing Groundwater Quality in Coastal Aquifers, Case: La Yarada, Tacna, Peru. *Int. J. Environ. Res. Public Health* **2022**, *19*, 2815. [CrossRef] [PubMed]
62. Kachroud, M.; Trolard, F.; Kefi, M.; Jebari, S.; Bourrié, G. Water Quality Indices: Challenges and Application Limits in the Literature. *Water* **2019**, *11*, 361. [CrossRef]
63. Mukherjee, I.; Singh, U.K.; Chakma, S. Evaluation of groundwater quality for irrigation water supply using multi-criteria decision-making techniques and GIS in an agroeconomic tract of Lower Ganga basin, India. *J. Environ. Manag.* **2022**, *309*, 114691. [CrossRef]
64. Batarseh, M.; Imreizeeq, E.; Tilev, S.; Al Alaween, M.; Suleiman, W.; Al Remeithi, A.M.; Al Tamimi, M.K.; Al Alawneh, M. Assessment of groundwater quality for irrigation in the arid regions using irrigation water quality index (IWQI) and GIS-Zoning maps: Case study from Abu Dhabi Emirate, UAE. *Groundw. Sustain. Dev.* **2021**, *14*, 100611. [CrossRef]
65. Mahammad, S.; Hoque, M.M.; Islam, A.; Majumder, A. Chapter 16—Assessment of Groundwater Quality for Irrigation Purposes: A Case Study of Hooghly District, West Bengal, India. In *Case Studies in Geospatial Applications to Groundwater Resources*; Shit, P., Bhunia, G., Adhikary, P., Eds.; Elsevier: Amsterdam, The Netherlands, 2023; pp. 289–314. ISBN 978-0-323-99963-2.
66. Basha, U.I.; Rajasekhar, M.; Ghosh, S.; Das, P.; Suresh, U. Spatial assessment of groundwater quality using CCME-WQI and hydrochemical indices: A case study from Talupula Mandal, Ananthapuramu district, South India. *Appl. Water Sci.* **2022**, *12*, 168. [CrossRef]
67. Elemile, O.; Ibitogbe, E.; Okikiola, B.; Ejigboye, P. Groundwater quality using indices for domestic and irrigation purposes in Akure, Nigeria. *Results Eng.* **2022**, *13*, 100347. [CrossRef]
68. Rahman, M.M.; Haque, T.; Mahmud, A.; Amin, A.; Hossain, S.; Hasan, Y.; Shaibur, M.R.; Hossain, S.; Hossain, A.; Bai, L. Drinking water quality assessment based on index values incorporating WHO guidelines and Bangladesh standards. *Phys. Chem. Earth Parts A/B/C* **2022**, *129*, 103353. [CrossRef]
69. Marghade, D.; Malpe, D.B.; Rao, N.S. Applications of geochemical and multivariate statistical approaches for the evaluation of groundwater quality and human health risks in a semi-arid region of eastern Maharashtra, India. *Environ. Geochem. Health* **2021**, *43*, 683–703. [CrossRef] [PubMed]
70. Ansari, J.A.; Umar, R. Evaluation of hydrogeochemical characteristics and groundwater quality in the quaternary aquifers of Unnao District, Uttar Pradesh, India. *Hydroresearch* **2019**, *1*, 36–47. [CrossRef]
71. Bao, Z.; Hu, Q.; Qi, W.; Tang, Y.; Wang, W.; Wan, P.; Chao, J.; Yang, X.J. Nitrate reduction in water by aluminum alloys particles. *J. Environ. Manag.* **2017**, *196*, 666–673. [CrossRef] [PubMed]
72. Sengupta, P. Potential Health Impacts of Hard Water. *Int. J. Prev. Med.* **2013**, *4*, 866–875.
73. Listyani, T.; A Prabowo, I. Groundwater in Bener area, its quality and contribution for agriculture. *IOP Conf. Ser.: Earth Environ. Sci.* **2022**, *985*, 012028. [CrossRef]
74. Dimri, D.; Daverey, A.; Kumar, A.; Sharma, A. Monitoring water quality of River Ganga using multivariate techniques and WQI (Water Quality Index) in Western Himalayan region of Uttarakhand, India. *Environ. Nanotechnol. Monit. Manag.* **2020**, *15*, 100375. [CrossRef]
75. Makubura, R.; Meddage, D.P.P.; Azamathulla, H.M.; Pandey, M.; Rathnayake, U. A Simplified Mathematical Formulation for Water Quality Index (WQI): A Case Study in the Kelani River Basin, Sri Lanka. *Fluids* **2022**, *7*, 147. [CrossRef]
76. Talat, R.A.; Al-Assaf, A.Y.; Al-Saffawi, A.Y.T. Valuation of water quality for drinking and domestic purposes using WQI: Acase study for groundwater of Al-Gameaa and Al-Zeraee qaurters in Mosul city/Iraq. *J. Phys. Conf. Ser.* **2019**, *1294*, 072011. [CrossRef]
77. Kambire, O.; Yao, K.M.; Eblin, S.G.; Tokpa, D.A.R.; Koffi-Nevry, R. Microbiological and physico-chemical characterisation of well water in the town of Korhogo, Côte d'Ivoire. *Int. J. Biol. Chem. Sci.* **2021**, *15*, 1264–1275. [CrossRef]
78. Zlatković, S.; Medić, O.; Predojević, D.; Nikolić, I.; Subakov-Simić, G.; Onjia, A.; Berić, T.; Stanković, S. Spatio-Temporal Dynamics in Physico-Chemical Properties, Phytoplankton and Bacterial Diversity as an Indication of the Bovan Reservoir Water Quality. *Water* **2022**, *14*, 391. [CrossRef]
79. Piper, A.M. A graphic procedure in the geochemical interpretation of water-analyses. *Eos Trans. Am. Geophys. Union* **1944**, *25*, 914–928. [CrossRef]

80. Ye, X.; Zhou, Y.; Lu, Y.; Du, X. Hydrochemical Evolution and Quality Assessment of Groundwater in the Sanjiang Plain, China. *Water* **2022**, *14*, 1265. [CrossRef]
81. Apollaro, C.; Di Curzio, D.; Fuoco, I.; Buccianti, A.; Dinelli, E.; Vespasiano, G.; Castrignanò, A.; Rusi, S.; Barca, D.; Figoli, A.; et al. A multivariate non-parametric approach for estimating probability of exceeding the local natural background level of arsenic in the aquifers of Calabria region (Southern Italy). *Sci. Total. Environ.* **2022**, *806*, 150345. [CrossRef] [PubMed]
82. Kothari, V.; Vij, S.; Sharma, S.; Gupta, N. Correlation of various water quality parameters and water quality index of districts of Uttarakhand. *Environ. Sustain. Indic.* **2021**, *9*, 100093. [CrossRef]
83. Nong, X.; Shao, D.; Xiao, Y.; Zhong, H. Spatio-Temporal Characterization Analysis and Water Quality Assessment of the South-to-North Water Diversion Project of China. *Int. J. Environ. Res. Public Health* **2019**, *16*, 2227. [CrossRef]
84. Rajendran, T.; Sabarathinam, C.; Kamaraj, P.; Prasanna, M.V.; Mathivanan, M.; Ghai, M.; Singh, D.K.; Ramanathan A.L. Irrigation Water Quality Assessment Using Water Quality Index and GIS Technique in Pondicherry Region, South India. *Int. J. Civ. Environ. Agric. Eng.* **2021**, *3*, 36–50. [CrossRef]
85. Fuoco, I.; Marini, L.; De Rosa, R.; Figoli, A.; Gabriele, B.; Apollaro, C. Use of reaction path modelling to investigate the evolution of water chemistry in shallow to deep crystalline aquifers with a special focus on fluoride. *Sci. Total. Environ.* **2022**, *830*, 154566. [CrossRef]
86. Abbas, H.; Abuzaid, A.S.; Jahin, H.; Kasem, D. Assessing the quality of untraditional water sources for irrigation purposes in Al-Qalubiya Governorate, Egypt. *Egypt. J. Soil Sci.* **2020**, *60*, 157–166. [CrossRef]
87. Avigliano, E.; Schenone, N.F. Human health risk assessment and environmental distribution of trace elements, glyphosate, fecal coliform and total coliform in Atlantic Rainforest mountain rivers (South America). *Microchem. J.* **2015**, *122*, 149–158. [CrossRef]
88. Adamou, H.; Ibrahim, B.; Salack, S.; Adamou, R.; Sanfo, S.; Liersch, S. Physico-chemical and bacteriological quality of groundwater in a rural area of Western Niger: A case study of Bonkoukou. *J. Water Health* **2020**, *18*, 77–90. [CrossRef]
89. Viaroli, P.; Nizzoli, D.; Pinardi, M.; Rossetti, G.; Bartoli, M. Factors Affecting Dissolved Silica Concentrations, and DSi and DIN Stoichiometry in a Human Impacted Watershed (Po River, Italy). *Silicon* **2013**, *5*, 101–114. [CrossRef]
90. Reddy, B.M.; Sunitha, V.; Prasad, M.; Reddy, Y.S.; Reddy, M.R. Evaluation of groundwater suitability for domestic and agricultural utility in semi-arid region of Anantapur, Andhra Pradesh State, South India. *Groundw. Sustain. Dev.* **2019**, *9*, 100262. [CrossRef]
91. Chadli, K.; Boufala, M. Assessment of water quality using Moroccan WQI and multivariate statistics in the Sebou watershed (Morocco). *Arab. J. Geosci.* **2021**, *14*, 27. [CrossRef]
92. Mohamadi, A.; Demdoum, A.; Bouaicha, F.; Menani, M.R. Evaluation of the quality of groundwater for its appropriateness for irrigation purposes using Water Quality Index (WQI), Mchira-Teleghma aquifer case study, northeastern Algeria. *Sustain. Water Resour. Manag.* **2021**, *7*, 97. [CrossRef]
93. Zegmout, M.; Basraoui, Y.; Meziane, M.; Chahlaoui, A.; Demnati, S.; Chafi, A. *Pollution Bacteriologique de la Zone Cotiere Saidia Moulouya (Region Orientale du Maroc)*; Université Mohammed Premier: Oujda, Morocco, 2011.
94. Das, C.R.; Das, S.; Panda, S. Groundwater quality monitoring by correlation, regression and hierarchical clustering analyses using WQI and PAST tools. *Groundw. Sustain. Dev.* **2021**, *16*, 100708. [CrossRef]
95. Varol, M.; Gündüz, K.; Sünbül, M.R. Pollution status, potential sources and health risk assessment of arsenic and trace metals in agricultural soils: A case study in Malatya province, Turkey. *Environ. Res.* **2021**, *202*, 111806. [CrossRef]
96. Khatri, N.; Tyagi, S. Influences of natural and anthropogenic factors on surface and groundwater quality in rural and urban areas. *Front. Life Sci.* **2015**, *8*, 23–39. [CrossRef]
97. Hong, T.T.K.; Giao, N.T. Analysis of Surface Water Quality in Upstream Province of Vietnamese Mekong Delta Using Multivariate Statistics. *Water* **2022**, *14*, 1975. [CrossRef]
98. Sudhakaran, S.; Mahadevan, H.; Arun, V.; Krishnakumar, A.P.; Krishnan, K.A. A multivariate statistical approach in assessing the quality of potable and irrigation water environs of the Netravati River basin (India). *Groundw. Sustain. Dev.* **2020**, *11*, 100462. [CrossRef]
99. Hou, W.; Sun, S.; Wang, M.; Li, X.; Zhang, N.; Xin, X.; Sun, L.; Li, W.; Jia, R. Assessing water quality of five typical reservoirs in lower reaches of Yellow River, China: Using a water quality index method. *Ecol. Indic.* **2016**, *61*, 309–316. [CrossRef]
100. Taloor, A.K.; Pir, R.A.; Adimalla, N.; Ali, S.; Manhas, D.S.; Roy, S.; Singh, A.K. Spring water quality and discharge assessment in the Basantar watershed of Jammu Himalaya using geographic information system (GIS) and water quality Index (WQI). *Groundw. Sustain. Dev.* **2020**, *10*, 100364. [CrossRef]
101. Kadri, A.; Baouia, K.; Kateb, S.; Al-Ansari, N.; Kouadri, S.; Najm, H.M.; Mashaan, N.S.; Eldirderi, M.M.A.; Khedher, K.M. Assessment of Groundwater Suitability for Agricultural Purposes: A Case Study of South Oued Righ Region, Algeria. *Sustainability* **2022**, *14*, 8858. [CrossRef]
102. Pivić, R.; Maksimović, J.; Dinić, Z.; Jaramaz, D.; Majstorović, H.; Vidojević, D.; Stanojković-Sebić, A. Hydrochemical Assessment of Water Used for Agricultural Soil Irrigation in the Water Area of the Three Morava Rivers in the Republic of Serbia. *Agronomy* **2022**, *12*, 1177. [CrossRef]
103. El-Rawy, M.; Ismail, E.; Abdalla, O. Assessment of groundwater quality using GIS, hydrogeochemsitry, and factor statistical analysis in Qena governorate, Egypt. *Desalination Water Treat.* **2019**, *162*, 14–29. [CrossRef]
104. El-Amier, Y.A.; Kotb, W.K.; Bonanomi, G.; Fakhry, H.; Marraiki, N.A.; Abd-ElGawad, A.M. Hydrochemical Assessment of the Irrigation Water Quality of the El-Salam Canal, Egypt. *Water* **2021**, *13*, 2428. [CrossRef]
105. Richards, L. Diagnosis and improvement of saline and alkali soils. *Soil Sci.* **1954**, *78*, 154. [CrossRef]

106. McGeorge, W.T. Diagnosis and Improvement of Saline and Alkaline Soils. *Soil Sci. Soc. Am. J.* **1954**, *18*, 348. [CrossRef]
107. Amrani, S.; Hinaje, S.; El Fartati, M.; Gharmane, Y.; Yaagoub, D. Assessment of Groundwater Quality for Drinking and Irri-gation in the Timahdite–Almis Guigou Area (Middle Atlas, Morocco). *Appl. Water Sci.* **2022**, *12*, 82. [CrossRef]
108. Tahmasebi, P.; Mahmudy-Gharaie, M.H.; Ghassemzadeh, F.; Karouyeh, A.K. Assessment of groundwater suitability for irrigation in a gold mine surrounding area, NE Iran. *Environ. Earth Sci.* **2018**, *77*, 766. [CrossRef]
109. Khanoranga; Khalid, S. An assessment of groundwater quality for irrigation and drinking purposes around brick kilns in three districts of Balochistan province, Pakistan, through water quality index and multivariate statistical approaches. *J. Geochem. Explor.* **2018**, *197*, 14–26. [CrossRef]
110. Eaton, F.M. Significance of carbonates in irrigation waters. *Soil Sci.* **1950**, *69*, 123–134. [CrossRef]
111. Mukonazwothe, M.; Munyai, L.F.; Mutoti, M.I. Groundwater quality evaluation for domestic and irrigation purposes for the Nwanedi Agricultural Community, Limpopo Province, South Africa. *Heliyon* **2022**, *8*, E09203. [CrossRef]
112. Doneen, L. *Notes on Water Quality in Agriculture*; Department of Water Sciences and Engineering, University of California: Davis, CA, USA, 1964.
113. Sharma, D.A.; Rishi, M.S.; Keesari, T. Evaluation of Groundwater Quality and Suitability for Irrigation and Drinking Purposes in Southwest Punjab, India Using Hydrochemical Approach. *Appl. Water Sci.* **2017**, *7*, 3137–3150. [CrossRef]
114. Paliwal, K.V.; Indian Agricultural Research Inst., N.D.W.T.C. *Irrigation with Saline Water*; New Delhi (India) IARI, Water Technology Centre: New Delhi, India, 1972.
115. Ghazaryan, K.; Movsesyan, H.; Gevorgyan, A.; Minkina, T.; Sushkova, S.; Rajput, V.; Mandzhieva, S. Comparative hydrochemical assessment of groundwater quality from different aquifers for irrigation purposes using IWQI: A case-study from Masis province in Armenia. *Groundw. Sustain. Dev.* **2020**, *11*, 100459. [CrossRef]
116. Kelley, W.P. Use of saline irrigation water. *Soil Sci.* **1963**, *95*, 385–391. [CrossRef]
117. Gao, L.; Wang, Z.; Shan, J.; Chen, J.; Tang, C.; Yi, M.; Zhao, X. Distribution characteristics and sources of trace metals in sediment cores from a trans-boundary watercourse: An example from the Shima River, Pearl River Delta. *Ecotoxicol. Environ. Saf.* **2016**, *134*, 186–195. [CrossRef]
118. Gupta, S.K.; Gupta, I.C. *Management of Saline Soils and Waters*; Oxford & IBH Publishing, Co.: New Delhi, India, 1987.