Research Article

Inferred Industrial and Agricultural Activities Impact on Groundwater Quality of Skhira Coastal Phreatic Aquifer in Southeast of Tunisia (Mediterranean Region)

Samira Melki, Amina Mabrouk El Asmi, and Moncef Gueddari

Laboratory of Geochemistry and Environmental Geology, Department of Geology, Faculty of Sciences of Tunis, University of Tunis El Manar, 2092 Tunis, Tunisia

Correspondence should be addressed to Samira Melki; melkisamiralefi@hotmail.fr

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In Tunisia, it has been proven through various previously published studies that agricultural overexploitation and urban and industrial activities increase the risk of groundwater quality deterioration. The present study is a new research to be added to groundwater appraisal and comes to assess groundwater quality of the phreatic Skhira aquifer in relation to surrounding anthropic activities and also tries to evaluate potential risk threatenings of the local population. For that, 20 water well samples covering the phreatic aquifer were analyzed for physical and chemical parameters, major cations and anions, nutrient elements, fluorine, and some trace metal elements. Results show that the area close to the phosphogypsum storage site is the zone which is the most affected by industrial activity. This area corresponds to the upstream part of the aquifer, in terms of the trending flow, and records the highest conductivity values, high H$_2$PO$_4^-$, F$^-$, SO$_4^{2-}$, and Zn$^{2+}$ concentrations. Groundwater samples in this area are also characterized by a relatively low hydrogen potential (acid pH). High NO$_3^-$ are recorded especially upstream of the aquifer and are thought to be caused by high fertilizer use. Overall, most analyzed samples do not meet the World Health Organization norms and therefore are not suitable as drinking waters. In addition, well water use for irrigation represents a medium to high sodicity and alkanization risk. The current study sheds light on the increasing deterioration risk of the aquifer and is an awakening call for decision-makers to imply means for urgent solutions.

1. Introduction

Either worldwide or on a regional or a local scale, groundwater pollution is gaining momentum and is fastly wide spreading. The main causes are related to overexploitation, increase in urban and industrial activities and a more generalized irrigation [1]. Such pollution induced a hydraulic disequilibrium in terms of demand but also a remarkable increase in water cost. Several Mediterranean countries are already facing a situation of severe water quality degradation [2]. In Tunisia, a country with an arid climate, over most of its territory, exploitable water resources became progressively limited and unable to satisfy the increasing demand especially for agricultural use and industrial development [3]. This water crisis deepened with time and is unfortunately forecasted to worsen in the future. Tunisia depends heavily on waterfall and at the same time is subject to various natural and anthropic processes which are rendering the water crisis even worst. In fact, from the South, the Saharan dunes are in a continuous progression towards the North and forest areas are shrinking as a response to urban expansion. To this, we add an agriculture centered on continuous water irrigation, a low-citizen awareness of water importance and moderate use, and an alarming worldwide climate change which is foreseen. All these are combined factors making Tunisia subject to a tense water crisis which would become critical if practical solutions are not applied in the near future. In addition, current mobilized waters may face more shortage due to phreatic aquifer overexploitation, exploitation of nonrenewable underground deep aquifers, the siltation of dams, and overall pollution which may affect all these resources. On the other hand, groundwater resources of the Mediterranean
coastal plains in the southern bank of the basin (Middle East and North Africa) show a qualitative and quantitative deterioration worsening with time [4].

In Tunisia, water aquifers constitute an important part of water resources with a hydric potential representing 42% of total volume, estimated at 4840 million m³ [5]. However, seawater intrusion due to overexploitation, agricultural activity, and industrial discharges may lead to the degradation of groundwater quality and reduced opportunities for their use. The assessment of the availability and quality of these waters is becoming essential and crucial in the integrated management of water resources.

In the southeast of Tunisia, the Skhira region is marked by a high aridity with a deficiencic hydric balance. The economic activities in this region are diverse and have steadily increased over the last twenty years. Since 1980, the introduction of new hydraulic-agricultural practices in the Skhira area had greatly damaged the natural environment through the increasing of exploitation wells [6]. There are currently over 600 wells, the majority of which are abandoned or are transformed into deep boreholes [7]. Several previous studies have shown that irrigation in arid zones leads to, inescapably, major soil and groundwater degradation.

Industrial activities in the Skhira region are mainly focused on production of chemical fertilizers and phosphoric acid, by transformation of natural phosphates. This production generates, in addition to gaseous and particulate emissions into the atmosphere, a big quantity of liquid discharges and huge amounts of phosphogypsum which is stored on site [8, 9]. These discharges have an effect on the surrounding environment, especially soil, and on the quality of surface and underground waters [10]. The phreatic aquifer of Skhira provides an important water resource, widely exploited to satisfy the growing social and economic needs in the region. Thus, periodic monitoring of groundwater quality is essential. Within this context, this study is aimed at assessing the phreatic aquifer quality through specific parameters, in particular the physical-chemical measurements, major cations and anions, the nutrient elements, fluoride, and some trace metal elements. This will help to identify the various factors and phenomena that govern their spatial variation and to evaluate the groundwater suitability for human consumption and irrigation purposes.

2. Presentation of the Study Area

The study area is located in the south-east part of Tunisia, on the northern coast of the Gulf of Gabes, at 75 km south of the Sfax City and at 60 km north of the Gabes City (Figure 1). The study area is located between 34°20′ and 34°54′ north latitude and between 10°02′ and 10°42′ east longitude. Agriculture is the main economic activity in the Skhira region, reinforced by phosphate industry. The Skhira region is under the combined influence of a Saharan climate, hot and dry to the Southwest, and a Mediterranean climate, relatively wet and temperate to the North. It is characterized by scarce rains becoming reasonably abundant during the cold period between the months of November and April and totally drought between the months of May and October. The average annual precipitation is around 180 mm. The mean annual temperature is 23°C [11].

Geologically, the outcrops of the Skhira region consist mainly of sandy-clay sediments termed the Segui formation, rich in gypsum at the top with some thin silty sand levels [12]. This formation is Miocene-Pliocene to Early Quaternary in age (Figure 2(a)). The Skhira aquifer, the current case study, is constituted by sandy horizons either of upper Miocene-Pliocene sediments in the downstream part or of lower Pliocene-Villafranchien sediments in the upstream side (Figure 2(b)). In shallow areas, the aquifer is represented by permeable sandy and silty Quaternary sediments [13]. The Skhira aquifer is limited by the Bir Ali Ouedrane aquifer in the north, Sebkhat Naouel in the west, the Gabes-North aquifer in the south, and by the sea to the east (Figure 1). This aquifer is mainly recharged by meteoric waters. The piezometric level varies from 40 m in the upstream side to 10 m near the coast [14]. Groundwater flows in a north-west to southeast direction, with a hydraulic gradient of 5.15·10⁻⁵ [15].

3. Materials and Methods

3.1. Sampling. Chemical characterization and spatial variation monitorings of Skhira groundwater quality were performed in order to identify the polluting elements from phosphogypsum waste in the industrial area and from the overfertilization related to agricultural activities. A spatial monitoring of different parameters of groundwater evaluation was carried out in January 2014. Samples were taken from 20 wells, which cover most of the Skhira phreatic aquifer. We have to be precise that samples were selected only from wells still in use and only those equipped with a pumping system allowing water to be renewed. Abandoned wells were not included in this study as we believe that they do not represent the current status of the aquifer. For that, water sampling at different depths was performed using a submersible pump while respecting the sampling standards. We proceeded to water renewal by sufficient pumping, accompanied by pH, conductivity, and dissolved oxygen content control. Sampling was carried out when the values of these parameters are believed to have been stabilized. Temperature, pH, dissolved oxygen content, and conductivity were measured in situ using calibrated portable digital meters. Samples taken were acidified using a 0.1 NHNO₃ and kept at 4°C until final laboratory analyses [16].

3.2. Analytical Methods. All geochemical analyses were carried out at the Environment and Geochemistry Laboratory of the Faculty of Sciences of Tunis. Laboratory analyses concerned the nutrient elements (nitrates, nitrites, ammoniacal nitrogen, and orthophosphates), major elements (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, and HCO₃⁻), fluorne, and some trace elements (Zn²⁺, Al³⁺, Cu²⁺, and Fe³⁺). Anions and cations in solution were analyzed by the following ion chromatography technique: the aqueous sample is injected on an anion or cation column to separate the desired ions according to their concentrations and their sizes. For example, fluorides, chlorides,
bicarbonates, nitrates, nitrites, phosphates, and sulphates in solution are separated on an anionic column and quantified by means of a conductimetric detector positioned at the column outlet [17].

3.3. Chemical Methods. The evaluation of water quality of the Skhira aquifer was determined using different software (AquaChem 2014.2 and XLSTAT 2013 for Windows) and several methods such as geochemical methods combined with GIS. In order to calculate the thermodynamic equilibrium of the Skhira groundwater in relation to associated minerals in the reservoir rock and in the unsaturated zone sediments, we used the PHREEQC program which allows the determination of various coefficient activities on the basis of different established chemical laws (Debye-Huckel’s simple law, Debye-Huckel’s extended law, and Water and Debye-Huckel’s law). This program takes into account kinetic laws in some reactions and allows simulating certain phenomena at the water-sediment interface of the unsaturated zone [18].

3.4. Statistical Analysis. In this study, geostatistical modeling was applied to all gathered physical and chemical data on all studied wells of the Skhira aquifer. This modeling combines the SIG tool to geostatistical techniques. The interpolation of ordinary “Krigeag” shows a good prediction of the average error close to zero. After applying different variogram models for each groundwater quality parameter of the current study, the error was calculated using cross-validation and is listed in Table 1. The best found kriging parameters were selected from the cross-validation results. The groundwater quality prediction maps (Figures 3–5) show the concentration distribution from the cross-validation process. This geostatistical approach generated spatial previsions for nonsampled points through estimation of the lowest error [19].

Multivariate statistical analysis of the experimental data has been performed using XLSTAT. In this study, only the principal component analysis (PCA) and Pearson correlation matrix analysis were undertaken. The application of PCA offers a clearer understanding of groundwater quality and enables comparison of the different waters as well as
their geochemical correlations [20]. The combination of different established elements (samples and parameters) was used to assess the spatial variation of the groundwater chemical composition and to identify the most common pollution sources.

4. Results and Discussion

4.1. Groundwater Geochemical Characteristics. Results of the physical and chemical parameter analyses of 20 water samples collected from the Skhira aquifer are given in Table 2.
The Skhira aquifer temperatures are little variable with values ranging between 10.1 and 11.8°C. This little variation could be related to the thermic equilibrium between geological strata and infiltrated water.

The groundwater sample pH is overall neutral, with values ranging between 6.45 and 7.19. The lowest values are found within samples SK18 and SK19 which are under the direct influence of gypsum-rich infiltrated waters supplied from the industrial zones where phosphoric acid is processed (Figure 3(a)). These supplied phosphogypsum leachates have a low pH of 2.7 [21]. Water sample electrical conductivity (EC) values range from 2820 to 17200 μS/cm. The EC spatial repartition shows that the most charged waters with dissolved salt are those collected close to the phosphogypsum storage zone. A general increase in EC is observed following the water flow trends which are from south-west to south-east and from north-west to north-east (Figure 3(b)). This increase is related to the water-sediment interaction of the unsaturated zone and to gypsiatic water infiltration. The latter shows an electric conductivity of 19000 μS/cm [21]. However, we have to emphasize that based on [14, 22–24], salinity around the Skhira coast has increased with time from 1-4 mg/L to 2-10 mg/L between 1994 and 2013. This increase is intimately related to water overexploitation of the aquifer. Such increase suggests a marine intrusion, still to be thoroughly investigated in the future using isotopic signatures. The dissolved O2 contents range between 1.2 and 6.1 mg/L. The lowest value was recorded in the water sample collected from the SK18 piezometer, located near the gypsiatic water storage ponds. The magnitude of the spatial variation of these levels would be dependent on the thickness of the unsaturated zone, the recharge rate, temperatures acting on the solubility of oxygen, and the upstream-downstream mixing effect [25].

H2PO4- is found to be the dominant form of inorganic phosphorus dissolved in analyzed waters, with contents ranging between 1.23 and 33.67 mg/L. This is the most stable form of orthophosphate at pH values between 2.2 and 7.2 [26]. The richest water samples in H2PO4- are those collected from SK17 and SK18 piezometers, which are located close to the phosphogypsum dump of the Skhira industrial zone (Figure 4(a)). The low contents are recorded at the upstream side of the aquifer. The spatial variation of these levels is related to the infiltration of phosphogypsum leaching waters and to diffusion according to the flow direction of the aquifer.

Nitrogen is present in natural waters as a particulate dissolved organic form and as a dissolved inorganic form [27]. Dissolved inorganic nitrogen (DIN) analyses targeted nitrates (NO3-), nitrites (NO2-), and ammoniacal nitrogen (NH4+). In the Skhira aquifer, the DIN contents range between 5.79 and 130.7 mg/L for NO3-, from 0.01 to 0.08 mg/L for NO2-, and from 0.01 to 0.14 mg/L for NH4+. The highest NO3- contents are measured in piezometers located in the central and northwestern parts of the aquifer (Figure 4(b)). These zones correspond to irrigated perimeters overinseminated by nitrogen fertilizers. The most charged waters in NO3- and NH4+ are those collected from wells drilled in the industrial zone. We note a positive correlation between NO3- and O2 (Figure 6(a)) combined to a negative correlation between NO3- and O2 (Figure 6(b)) and also between NH4+ and O2 (Figure 6(c)). This implies that oxygen content variation is the driving mechanism of nitrogen distribution in the aquifer. In fact, the most nitrate-rich waters are found to be the most oxygenated, which explains the stability of NO3- ions and their predominance over other forms of dissolved inorganic nitrogen. The spatial distribution of nitrate levels would be monitored by physical-chemical parameters and environmental factors related to soils that control NH4+ nitrification of chemical fertilizers and/or soil organic matter degradation [28]. However, this distribution is also guided by the unsaturated zone thickness and lithology which ensures nitrate transfer to the saturated zone [29, 30].

The negative correlation between nitrogen (DIN) and orthophosphates (Figure 6(d)) suggests that these two elements do not share the same origin. The nitrogen origin of the Skhira aquifer waters would be mainly related to agricultural activity and the infiltration of organic matter-rich water, as is the case of the water sample collected from SK18 wells.

Figure 7 presents the major element contents with the following predominance order:

(i) Na+ > Ca2+ > Mg2+ > K+, for cation

(ii) Cl- > SO4- > HCO3-, for anion

The Cl- contents range between 18.44 and 100.19 meq/L and is the dominant anion for the Skhira aquifer. The Na+ contents range from 17.82 to 165 meq/L and is the dominant cation. The Ca2+ contents vary from 12.48 to 34 meq/L, Mg2+ contents are between 8.4 and 44.08 meq/L, and SO4- contents are between 15.62 and 142.66 meq/L, while HCO3-
Figure 3: Spatial distribution maps of pH (a) and electrical conductivity (b) in groundwaters of the Skhira aquifer. See mean error (ME) and root mean square error (RMSE) in Table 1.
Figure 4: Spatial distribution maps of orthophosphates (a) and nitrates (b) in groundwaters of the Skhira aquifer. See mean error (ME) and root mean square error (RMSE) in Table 1.
Figure 5: Spatial distribution maps of sulphate (a) and fluoride (b) in groundwaters of the Skhira aquifer. See mean error (ME) and root mean square error (RMSE) in Table 1.
| Samples | T (°C) | pH | CE (µS/cm) | O2 dissolved | Na | Cl | K | Ca | Mg | HCO3 | SO4 | NO3 | NO2 | NH4 | H2PO4 | F | Al | Fe | Zn | Cu |
|---------|-------|----|------------|--------------|----|----|---|----|----|------|-----|-----|----|-----|-------|---|----|----|----|----|
| SK1     | 11.2  | 7.17 | 2820       | 6.1          | 447| 654| 12| 256| 144| 101  | 750 | 90.1| 0.01| 0.02| 1.23  | 0.03| 0.12| 0.04| 0.04| <0.01 |
| SK2     | 10.1  | 7.17 | 2870       | 5.9          | 467| 672| 15| 264| 136| 104  | 766 | 83.7| 0.01| 0.05| 1.43  | 0.05| 0.05| 0.03| 0.04| <0.01 |
| SK3     | 11.4  | 7.19 | 3210       | 5.8          | 498| 698| 16| 291| 176| 113  | 900 | 96.7| 0.03| 0.03| 1.76  | 0.07| 0.12| 0.04| 0.15| <0.01 |
| SK4     | 11.1  | 7.15 | 3312       | 5.6          | 410| 759| 15| 378| 189| 120  | 920 | 86  | 0.01| 0.03| 1.98  | 0.05| 0.11| 0.02| 0.06| <0.01 |
| SK5     | 11    | 7.13 | 3356       | 5.7          | 454| 786| 24| 305| 197| 133  | 940 | 63.9| 0.02| 0.04| 2.63  | 0.04| 0.13| 0.05| 0.16| <0.01 |
| SK6     | 10.8  | 7.1  | 3450       | 5.7          | 659| 806| 14| 301| 101| 135  | 1075| 74.3| 0.01| 0.02| 2.8   | 0.04| 0.13| 0.04| 0.32| <0.01 |
| SK7     | 11.8  | 7.18 | 4506       | 6.7          | 763| 1033|16 | 354| 211| 124  | 1127| 130.7|0.01| 0.01| 4.9   | 0.08| 0.14| 0.14| 0.3 | <0.01 |
| SK8     | 11.4  | 7.01 | 4557       | 5.9          | 770| 1098|25 | 317| 258| 144  | 1232| 98.3 |0.01| 0.05| 2.7   | 0.06| 0.14| 0.03| 0.29| <0.01 |
| SK9     | 10.8  | 7.15 | 4789       | 5.4          | 794| 1101|17 | 378| 175| 147  | 1322| 76.8 |0.01| 0.07| 2.45  | 0.05| 0.14| 0.41| 0.3 | <0.01 |
| SK10    | 10.9  | 7.09 | 4980       | 5.4          | 803| 1243|14 | 454| 201| 154  | 1453| 63  | 0.02| 0.03| 2.78  | 0.07| 0.12| 0.06| 0.41| <0.01 |
| SK11    | 11.3  | 7.05 | 4988       | 5.3          | 898| 1283|24 | 472| 198| 156  | 1642| 55.6 |0.02| 0.02| 2.89  | 0.08| 0.12| 0.04| 0.29| <0.01 |
| SK12    | 11.7  | 7.19 | 5023       | 5.3          | 1033|1321|12 | 453| 211| 153  | 1759| 55  | 0.03| 0.02| 4.27  | 0.04| 0.07| 0.02| 0.28| <0.01 |
| SK13    | 11    | 7.11 | 5124       | 5.2          | 1024|1387|13 | 489| 212| 155  | 1899| 45  | 0.02| 0.04| 4.5   | 0.07| 0.13| 0.27| 0.36| <0.01 |
| SK14    | 10.8  | 7.12 | 5250       | 5.2          | 1107|1454|11 | 402| 190| 177  | 2027| 39.7 |0.01| 0.12| 4.2   | 1.1 | 0.12| 0.42| 0.37| <0.01 |
| SK15    | 11.2  | 7.16 | 6260       | 5.2          | 1601|1462|27 | 466| 225| 140  | 2265| 42.38|0.02| 0.02| 18.3  | 3.5 | 0.13| 0.02| 0.41| <0.01 |
| SK16    | 11.3  | 7.12 | 8300       | 5.1          | 1603|1545|43 | 404| 201| 260  | 2009| 31.21|0.01| 0.075| 16.3  | 3   | 0.15| 0.37| 0.31| <0.01 |
| SK17    | 10.7  | 7.06 | 8940       | 5.1          | 1933|1535|25 | 557| 245| 162  | 3110| 45.89|0.01| 0.1  | 33.67 | 1.9 | 0.15| 0.35| 0.47| <0.01 |
| SK18    | 11.8  | 6.45 | 17200      | 1.2          | 3795|3552|59 | 675| 529| 1690| 6848| 5.79 |0.08| 0.12| 21.67 | 10.3| 0.18| 0.78| 0.51| <0.01 |
| SK19    | 11.2  | 6.94 | 12840      | 4.5          | 1618|1730|24 | 619| 370| 165  | 2675| 25.64|0.02| 0.12| 16.5  | 5   | 0.14| 0.54| 0.37| <0.01 |
| SK20    | 11.2  | 7.03 | 9740       | 4.6          | 1827|1690|22 | 680| 355| 262  | 3584| 24.14|0.02| 0.14| 17.67 | 3.3 | 0.13| 0.65| 0.39| <0.01 |

*Units in mg/L except pH and EC (µS/cm).*
contents are between 1.65 and 27.7 meq/L. These elements form the bulk of the mineralization of the Skhira aquifer. As has already been shown through EC measurements, waters with the highest dissolved salts are those collected from wells located in the coastal zone and also north-east of the aquifer, in the industrial zone.

The high sulphate contents recorded downstream (Figure 5(a)), north-east of the aquifer, and near the

Figure 6: Bivariate plot of O$_2$ dissolved versus NO$_3^-$ (a), NH$_4^+$ (b), and NO$_2^-$ (c). Bivariate plot of H$_2$PO$_4^-$ versus DIN (NO$_3^- +$NH$_4^+$+NO$_2^-$) (d).

Figure 7: Box plot of major elements of the Skhira aquifer.
Table 3: Saturation indices (SI) of CaCO₃, CaSO₄·2H₂O, and CaF₂ in the Skhira phreatic aquifer.

| Samples   | SK1 | SK2 | SK3 | SK4 | SK5 | SK6 | SK7 | SK8 | SK9 | SK10 | SK11 | SK12 | SK13 | SK14 | SK15 | SK16 | SK17 | SK18 | SK19 | SK20 |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Is calcite| -0.38 | -0.37 | -0.28 | -0.19 | -0.26 | -0.31 | -0.2 | -0.38 | -0.16 | -0.14 | -0.17 | -0.13 | -0.16 | -0.17 | -0.01 | -0.09 | 0.14 | 0.03 | 0.05 |
| Is gypsum | -0.6 | -0.58 | -0.52 | -0.42 | -0.49 | -0.43 | -0.41 | -0.44 | -0.32 | -0.24 | -0.2 | -0.15 | -0.2 | -0.4 | -0.23 | 0 | 0.17 | -0.02 | 0.1 |
| Is fluoride| -0.85 | -3.24 | -2.98 | -3.17 | -3.46 | -3.42 | -2.85 | -3.18 | -3.21 | -2.88 | -2.77 | -3.41 | -2.89 | -0.58 | 0.43 | 0.26 | -0.07 | 1.2 | 0.78 | 0.42 |
phosphogypsum dump could have an atmospheric origin in relation to the emission of sulfur gases, SO₂, and H₂S [31].

In our study, we tested the saturation state with respect to calcite and gypsum. The considered dissolution reactions and the solubility product constant values (T = 25°C and P = 1 atm) are as follows [32]:

\[
\text{Calcite} : \text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{Ca}^{++} + \text{HCO}_3^- \quad \log K = 1.71.
\]

\[
\text{Gypsum} : \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \leftrightarrow \text{Ca}^{++} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad \log K = -4.61.
\]

The water saturation indices of the study area with respect to calcite vary from -0.38 to 0.14 (Table 3). Their variations according to pH show that slightly acidic waters are supersaturated with respect to CaCO₃ (Figure 8(a)), which confirms the influence of pH on the solubility of this mineral [32].

The saturation indices for gypsum vary from -0.6 to 0.17 (Table 3). Water saturation in regard to gypsum near the industrial zone (SK17, SK18, and SK20; Figure 8(b)) is mainly related to phosphogypsum acid leachate percolation, which favors the solubility of the mineral during infiltration through the unsaturated zone sediments. These results show that the dissolution of gypsum and calcite in the north-east part of the aquifer, normally accelerated in most acidic waters, has led to the increase in calcium and sulphate concentrations in these waters, exceeding the solubility thresholds of the two minerals [32]. In the rest of the aquifer and under natural recharge conditions, gypsum and calcite undersaturation states may reflect that the dissolution of these two minerals locally controls the total water saline load.

The main source of fluoride in groundwater is the dissolution of fluoride-rich minerals, particularly apatite and fluorine [33]. The groundwater fluoride contents are governed by various factors like temperature, pH, salinity, the amount of fluoride in the host rock, the presence or absence of complexes or colloids, and the solubility of fluorinated minerals [34]. In addition, the F⁻ anion is not included in adsorption processes or ionic exchanges (as these two mechanisms are only relevant for cations). This leaves only the precipitation-dissolution mechanism as the controlling factor for F⁻ contents. In the Skhira aquifer, the fluorine contents vary between 0.03 and 10.3 mg/L. The highest contents are measured in water samples collected from piezometers located around the phosphogypsum dump, in particular that of Sk18 (Figure 5(b)) where gypsatic waters are held and are heavily charged in F⁻ with concentrations reaching even 3500 mg/L [21]. Saturation states of fluorite (CaF₂) levels were tested, taking into account the following dissolution equation (T = 25°C and P = 1 atm) [33]:

\[
\text{Fluorite} : \text{CaF}_2 \leftrightarrow \text{Ca}^{++} + 2\text{F}^- \quad \log K = -10.96.
\]

The saturation indices for fluorite vary from -3.46 to 1.2 (Table 3). Based on water saturation index calculations, it is

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**Figure 8:** Saturation indexes of CaSO₄·2H₂O (SI) versus pH (a). Saturation indexes of CaCO₃ (SI) versus pH (b). Saturation indexes of CaF₂ (SI) versus pH (c).
Table 4: Pearson correlation matrix of water quality variables of the Skhira phreatic aquifer.

| Variables | T (°C) | pH | EC | O₂ | Na | Cl | K | Ca | Mg | HCO₃ | SO₄ | NO₃ | NO₂ | NH₄ | H₂PO₄ | F | Al | Fe | Zn |
|-----------|--------|----|----|----|----|----|---|----|----|------|-----|-----|-----|-----|-------|--|----|----|----|
| T°C       | 1      | 0.3448 | -0.2821 | 0.3502 | 0.4080 | 0.3888 | 0.2748 | 0.4795 | 0.3992 | 0.3418 | -0.0142 | 0.5064 | -0.0976 | 0.0988 | 0.3494 | 0.4027 | 0.1394 | 0.2339 |
| pH        | 1      | -0.7796 | 0.8479 | -0.7591 | -0.8097 | -0.7664 | -0.5462 | -0.8120 | -0.8756 | -0.7994 | 0.4963 | -0.7304 | -0.5314 | -0.3805 | -0.8257 | -0.6325 | -0.6563 | -0.4568 |
| CE        | 1      | -0.8847 | 0.9412 | 0.9293 | 0.7763 | 0.8600 | 0.9259 | 0.7627 | 0.9332 | -0.7574 | 0.6726 | 0.7391 | 0.7654 | 0.9451 | 0.5974 | 0.8518 | 0.6886 |
| O₂        | 1      | -0.9138 | -0.9429 | -0.7757 | -0.7448 | -0.8569 | -0.9169 | -0.9445 | 0.7765 | 0.7797 | 0.7765 | 0.7869 | 0.7663 | 0.7397 | 0.7663 | 0.7397 | 0.7663 | 0.7397 |
| Na        | 1      | 0.9694 | 0.8191 | 0.8144 | 0.8719 | 0.8404 | 0.9822 | -0.7565 | 0.7355 | 0.6561 | 0.7937 | 0.9400 | 0.5921 | 0.7910 | 0.7367 |
| Cl        | 1      | 0.7911 | 0.8118 | 0.8950 | 0.8804 | 0.9718 | -0.7494 | 0.7946 | 0.6268 | 0.6491 | 0.9164 | 0.5742 | 0.7873 | 0.7403 |
| K         | 1      | 0.4933 | 0.7222 | 0.7998 | 0.7665 | -0.5573 | 0.6597 | 0.4191 | 0.6068 | 0.8376 | 0.6343 | 0.5586 | 0.4502 |
| Ca        | 1      | 0.8257 | 0.5216 | 0.8390 | -0.7900 | 0.5231 | 0.6795 | 0.7293 | 0.7321 | 0.4329 | 0.7656 | 0.7563 |
| Mg        | 1      | 0.7866 | 0.9052 | -0.6217 | 0.7538 | 0.6721 | 0.6137 | 0.8894 | 0.5483 | 0.7700 | 0.5879 |
| HCO₃      | 1      | 0.8721 | -0.5042 | 0.8999 | 0.4324 | 0.4061 | 0.8448 | 0.5001 | 0.6209 | 0.4372 |
| SO₄       | 1      | -0.7516 | 0.7864 | 0.6853 | 0.7283 | 0.9238 | 0.5993 | 0.8114 | 0.7054 |
| NO₃       | 1      | -0.4840 | -0.6834 | -0.6368 | -0.7192 | -0.3187 | -0.6955 | -0.6246 |
| NO₂       | 1      | 0.2728 | 0.2972 | 0.7513 | 0.3292 | 0.4579 | 0.3828 |
| NH₄       | 1      | 0.6081 | 0.6419 | 0.3867 | 0.9012 | 0.4966 |
| H₂PO₄     | 1      | 0.6968 | 0.5216 | 0.6157 | 0.6625 |
| F         | 1      | 0.5649 | 0.7649 | 0.5731 |
| Al        | 1      | 0.5732 | 0.6085 |
| Fe        | 1      | 0.6062 |
| Zn        | 1      | 1      |
found that samples selected from the industrial zone are the only waters saturated to oversaturated with respect to fluorine. Away from the phosphogypsum storage zone, water samples are found undersaturated with respect to fluorine, in response to mixing with infiltration meteoric waters, and the greater distance from fluorine supply by the phosphogypsum dump. We note that waters saturated with respect to fluorine are also found saturated with respect to calcite and gypsum indicating a spatial dependency related to the phosphogypsum storage zone. Away from this zone, waters become undersaturated in fluorine, calcite, and gypsum. Furthermore, the most acid waters are found saturated with respect to fluorine [35] (Figure 8(c)).

The aluminum contents range between 0.05 and 0.18 mg/L. The highest aluminum concentrations are recorded in the water sample collected from the SK18 piezometer, described above as having the lowest pH value and therefore favorable to the solubility of the element [35]. The iron contents in the analyzed waters range between 0.02 and 0.78 mg/L. The highest concentrations are also recorded at the SK18 piezometer, where the salinity is peaking and the pH is the lowest. Zinc speciation in water depends on many factors such as pH, the amount of dissolved material, and redox potential. A low pH is necessary to maintain the zinc in solution [36]. Zinc concentrations in analyzed water samples vary between 0.04 and 0.51 mg/L. The highest value characterizes the water sampled near the gypsum collection basins, where zinc contents reach up to 4 mg/L [21]. All analyzed Skhira phreatic aquifer water samples show copper concentrations below detection limit which is around 0.01 mg/L. The absence of trace elements or their presence at very low concentrations in the analyzed groundwater samples compared to those detected in the gyspatic waters can be explained by the sequestering function of soils overlying the unsaturated zone [37].

4.2. Statistical Study. Table 4 includes all correlation coefficients between all studied variables. A very good positive correlation is noted between electrical conductivity and major elements. These elements constitute the main mineralization
of the Skhira aquifer. In addition, the predominance of dissolved inorganic nitrogen depends heavily on dissolved oxygen contents. For that, NO$_3$ is found in oxygenated waters whereas NH$_4^+$ and NO$_2$ are associated with oxygen-poor waters. We note also that calcium bears a geochemical behavior similar to sulphates and fluoride which indicates that the element is associated with SO$_4$ and F$^-$. The negative correlations between metallic trace elements and pH show that increasing the water’s pH induces lowers trace metallic contents and their rather association to the particular phase.

Taking into consideration all the gathered geochemical results of the Skhira phreatic aquifer, a statistical analysis through principal component analysis (PCA) was carried out. The results show that the explanation percentages are distributed unequally according to several axes (Table 5). The first two axes represent 79.6% of the total variance with 68.1% for the F1 axis and 11.5% for the F2 axis. The main plane is generated by axes F1 and F2 because they contain the maximum of information. We note that conductivity and Na$^+$, Cl$^-$, SO$_4^{2-}$, and Ca$^{2+}$ concentrations and, to a lesser extent, Mg$^{2+}$ and HCO$_3^-$ contents do present a fairly good correlation (Figure 9). They are well distributed on either side of axis F1, forming a single group. These variables form the bulk of the Skhira phreatic aquifer mineralization. The F2 axis can be assimilated to pH, dissolved O$_2$, and nitrates, a result which is consistent with the stability conditions of nitrate (Eh and pH). In the F1-F2 axes, the data projection helps distinguish three clusterings: the first group (I) is composed of the least dissolved salt-rich waters and corresponds to the upstream side of the study area; the second group (II) is composed by the most mineralized waters within the downstream area of the study zone, probably influenced by marine intrusion; and the third group (III) is composed of waters overcharged with very high contents in major elements and fluorine and cauterizing the north-east area of the study zone.

### 4.3. Quality Assessment of Skhira Aquifer Waters for Potability and Irrigation

The evaluation of the potential uses of the Skhira aquifer waters for human consumption was based on the comparison of the obtained chemical results with the Tunisian (NT.09.14) Norms and the

| Parameters | WHO (2011) | NT.09.14 (2012) | Number of samples exceeding the recommended value WHO | % of samples exceeding the recommended value WHO | NT.09.14 | % of samples exceeding the recommended value NT.09.14 |
|------------|------------|-----------------|-----------------------------------------------|-----------------------------------------------|----------|-----------------------------------------------|
| T$^\circ$C | —          | 25              | —                                             | 0                                             | —        | 0                                             |
| pH         | 6.5 to 8.5 | 6.5 to 8.5      | 1                                             | 1                                             | 5        | 5                                             |
| EC (μS/cm) | 1500       | 1500            | 20                                            | 20                                            | 100      | 100                                           |
| Na (mg/L)  | 200        | —               | 20                                            | —                                             | 100      | —                                             |
| Cl (mg/L)  | 250        | 600             | 20                                            | 20                                            | 100      | 100                                           |
| K (mg/L)   | 30         | —               | 2                                             | —                                             | 10       | —                                             |
| Ca (mg/L)  | 200        | 300             | 20                                            | 20                                            | 100      | 100                                           |
| Mg (mg/L)  | 150        | 150             | 20                                            | 20                                            | 100      | 100                                           |
| HCO$_3^-$ (mg/L) | 380    | —               | 1                                             | —                                             | 5        | —                                             |
| SO$_4$ (mg/L) | 250    | 600             | 20                                            | 20                                            | 100      | 100                                           |
| NO$_3$ (mg/L) | 45      | 45              | 13                                            | 13                                            | 65       | 65                                           |
| NO$_2$ (mg/L) | 3       | 3               | 0                                             | 0                                             | 0        | 0                                             |
| F (mg/L)   | 1.5        | 1.7             | 6                                             | 6                                             | 30       | 30                                           |
| Al (mg/L)  | 0.2        | 0.2             | 0                                             | 0                                             | 0        | 0                                             |
| Zn (mg/L)  | 3          | 3               | 0                                             | 0                                             | 0        | 0                                             |

| Type of water | EC (μS/cm) | Number of samples | % of samples |
|---------------|------------|-------------------|--------------|
| Non-saline water | <700       | 0                 | 0            |
| Slightly saline | 700-3000   | 2                 | 10           |
| Medium saline  | 3000-6000  | 12                | 60           |
| Highly saline  | >6000      | 5                 | 25           |
| Very saline    | >14000     | 1                 | 5            |
| Brine          | >42000     | 0                 | 0            |

| %Na | Class | Number of samples | % of samples |
|-----|-------|-------------------|--------------|
| 0-20 | Excellent | 0                 | 0            |
| 20-40 | Good    | 0                 | 0            |
| 40-60 | Permissible | 16               | 80           |
| 60-80 | Doubtful | 4                 | 20           |
| >80 | Unsuitable | 0                 | 0            |
International Standards of Potability Norms set by the World Health Organization (WHO). This assessment reveals that most analyzed water samples do not meet both standard norms and can be considered not suitable for drinking especially at the downstream side of the aquifer (Table 6). These waters cannot be used for human consumption without special treatment.

The main parameters used to assess water quality intended for irrigation are electrical conductivity, sodium content expressed in percent, and residual alkalinity [38]. The saline load of irrigation water, assessed through conductivity, conditions the osmotic pressure which, when too high, renders water absorption by the plants difficult [38]. As shown in (Table 7), around 60% of water samples have a medium salinity.

The mobility of sodic clays is usually increased when sodium concentrations are increased rendering soils harder and more coherent. This leads to soil permeability decrease and therefore a decrease in water mobility, hence becoming less available to plants' roots. The effect of sodium, carried by irrigation waters on soils, is estimated via the percentage of sodium.

\%
Na can be calculated using the following formula [39]:

\[
\%Na = 100 \times \frac{(Na + K)}{(Ca + Mg + Na + K)},
\]

where contents are expressed in meq/L.

\%
Na in the Skhira aquifer ranges between 45 and 68% (Table 8). Most groundwater samples with 40 to 60% Na are permissible for irrigation purposes. However, the SK 15, SK16, SK17, and SK18 piezometers, located in the industrial area, are doubtful for irrigation. Wilcox used the percentage of Na content (%) as a function of the electrical conductivity (EC) to evaluate the suitability of water for irrigation. The projection of the different analyzed samples on the diagram allows the distinction of two water groups (Figure 10):
(1) Group I: low-quality waters, which are moderately mineralized. They occur in the center and west parts of the aquifer.

(2) Group II: it includes highly mineralized waters with an extremely high risk of salinization and the highest percentage of sodium content. This group characterizes waters sampled from piezometers located in the downstream part of the aquifer.

Alkalinity measures the ability of water to neutralize acids. The neutralizing power of water is mainly related to the presence of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ ions. As a result, alkalinity can be expressed as follows [40]:

$$\text{Alc (meq/L)} = 2\text{Ca}^{2+} + 2\text{Mg}^{2+} + (\text{K}^+ + \text{Na}^+) - 2\text{SO}_4^{2-} - (\text{Cl}^-)$$

After the precipitation of alkaline-earth carbonates, the residual sodium carbonate (RSC) has the following expression [40]:

$$\text{Alc}_{\text{RSC}}(\text{meq/L}) = 2\text{Ca}^{2+} + 2\text{Mg}^{2+} - 2\text{Ca}^{2+} - 2\text{SO}_4^{2-}$$

If the residual alkalinity is positive, a risk of alkalinization may affect irrigated soils. If it is negative, after the precipitation of alkaline-earth carbonates, the soil water would follow a neutral saline pathway [41]. The residual alkalinity of the Skhira aquifer waters is negative (Table 9), removing the risk of soil degradation by alkalinization in case these waters would be used for irrigation.

5. Conclusion

Water quality monitoring shows that the influence of industrial activities, especially phosphate treatment, concerns mainly the downstream part north-east of the aquifer where the water is acidic and highly charged in $\text{SO}_4^{2-}$, $\text{H}_2\text{PO}_4^-$, and $\text{F}^-$. The waters sampled in the upstream portion are only influenced by the natural conditions of supply and the water-sediment interaction of the unsaturated zone.

The spatial distribution of nitrates would be controlled, in addition to the excessive use of nitrogen fertilizers, by physical and chemical factors.

Comparison of the analyzed water’s chemical results with national and international standards indicates that the majority of these waters do not meet the potability criteria. However, and for irrigation purposes, the majority of analyzed samples present a medium sodicity and alkalinization. Their use for irrigation requires a good drainage and a reasonable organic matter addition.

Based on the outcome of this study, we recommend that urgent remedial solutions have to be given to the area close to the phosphogypsum dump which seems to be the major cause of the current aquifer water degradation. An impermeable barrier has to be foreseen to stop highly charged water infiltration from this site to the aquifer. Furthermore, the use of the Skhira groundwater for drinking has to be preceded by proper treatment. The same water can be used for irrigation with a special care given to minimize the alkalinization and sodicity.

Data Availability

We have to emphasize that all data (physical and chemical parameters, major cations and anions, nutrient elements, fluorine, and some trace metal elements) used to support the findings of this study are included within the article and will be accessible to readers.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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| Samples | Alkalinity (meq/L) | RSC (meq/L) |
|---------|--------------------|-------------|
| SK1     | 19.64              | -47.94      |
| SK2     | 18.88              | -47.36      |
| SK3     | 23.31              | -56.58      |
| SK4     | 27.77              | -67.33      |
| SK5     | 22.35              | -61.15      |
| SK6     | 8.42               | -44.72      |
| SK7     | 28.05              | -68.53      |
| SK8     | 26.51              | -72.34      |
| SK9     | 15.78              | -64.56      |
| SK10    | 18.57              | -76.38      |
| SK11    | 15.25              | -77.64      |
| SK12    | 15.13              | -77.96      |
| SK13    | 10.84              | -81.69      |
| SK14    | 5.19               | -68.97      |
| SK15    | 18.78              | -81.80      |
| SK16    | 17.41              | -69.64      |
| SK17    | 8.33               | -93.88      |
| SK18    | 63.35              | -127.96     |
| SK19    | 34.27              | -120.86     |
| SK20    | 10.16              | -122.87     |

Table 9: Alkalinity and residual sodium carbonate (RSC) of selected groundwater samples.
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