Research Article

Actual and Predictive Transport Modeling of Fluoride Contamination of the Sfax-Agareb Coastal Aquifer in the Mediterranean Basin

Samira Melki 1, Amina Mabrouk El Asmi, 1 Mohamadou Ould Baba Sy, 2 and Moncef Gueddari 1

1 Laboratory of Geochemistry and Environmental Geology, Department of Geology, Faculty of Sciences of Tunis, University of Tunis El Manar, Tunis 2092, Tunisia
2 Sahara and Sahel Observatory, Tunis 1080, Tunisia

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

Received 1 November 2019; Revised 12 March 2020; Accepted 23 March 2020; Published 22 April 2020

Academic Editor: Maurizio Barbieri

Copyright © 2020 Samira Melki et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The Tunisian coast is suffering from several active or abandoned polluted sites, suspected to have released high concentrations of various contaminants infiltrating the environment and probably causing groundwater degradation. Within this scope, this study comes to assess and model the Sfax-Agareb aquifer contamination by fluoride released through phosphogypsum leachate percolation. For that, a spatial-temporal monitoring of fluoride contents was achieved for the period between October 2013 and October 2014. Observed data show that hazardous water contamination is occurring especially close to the phosphogypsum leachate collection basins. At this level, groundwater fluoride concentrations may reach up to 29 mg/L. Flow and transport modeling to evaluate fluoride contamination plume expansion in 2030 was achieved using MODFLOW and MT3DMS software packages based on a homogeneous and isotropic aquifer conceptual model. Flow and transport model calibrations were assessed by varying hydraulic conductivity, effective porosity, and dispersivity and then validated through observed data for two reference dates (October 2013 and October 2014). Based on the Tunisian NT 106-002 liquid discharge norms, fluoride contamination front was set at 3 mg/L. Numerical simulation shows that, in 2014, plume contamination by fluoride in the saturated zone extended over 250 m from the contamination source. In 2030, the spatial extent of this contamination will extend over a distance of 900 m towards the sea, following the aquifer flow direction. At the control piezometer, fluoride concentrations will increase from 29 mg/L in 2014 to 86 mg/L in 2030. This study, using numerical modeling, gives new insights for short- and medium-term prediction of eventual fluoride concentrations in the saturated zone of the Sfax-Agareb aquifer.

1. Introduction

Industrialization progress during the last century has led to a significant growth of industrial waste, of various toxic products, thrown in the natural environment, hence escalating the risk of its contamination [1, 2]. Solid byproducts from chemical industries are considered one of the most hazardous forms of pollution that society has created [3]. For that, controlled landfills were installed in developed and underdeveloped countries for its disposal as an alternative solution for this increasing pollution risk. Unfortunately, such resolutions, although delimiting areas of disposals and waste discharges, remain a major source of environmental hazards [4]. More particularly, leachate from certain solid waste disposal sites may contaminate groundwater resources in the immediate vicinity of discharges via diffusive transport, and/or by direct infiltration through landfill coating, and/or by some failure in the leachate collection system [5]. For that, the understanding and comprehension of contaminants nature, their origin, their mode, and their speed of propagation and diffusion are pillar steps in order to implement suitable solutions and to be able to preserve and protect water resources [6]. This most often requires an integrated approach to the problem, including the use of
properly planned and controlled analytical monitoring as well as mathematical modeling for groundwater contaminant transfer [7].

Contaminant migration, in saturated zones, was previously numerically modeled by Zheng and Wang [8]. The authors implanted a modular three-dimensional multispecies transport model to simulate advection. Later, Mondal and Singh [9] have proposed a solute transport model to evaluate contaminant migration in an industrial belt. Recently, De windt and Spycher [10] have assessed nuclear waste geological disposal through a reactive transport modeling. These simulations allow quantitative and qualitative estimation of contaminant migration as a function of space and time. Added to groundwater flow, contaminant aquifer transfer is also associated with several mechanisms, as, for example, the advection mechanism, hydrodynamic dispersion, adsorption-desorption, and/or degradation [11]. These mechanisms may influence contaminants diffusion, may slow their progression, and may help to degrade them or even their transformation into other substances [12, 13]. Such schematization via mathematical or numerical modeling allows obtaining key information in order to answer given questions, in particular those concerning the identification of pollution sources, the becoming of pollutants, water resource contamination risks, and the protection and depollution strategy to be implemented [14].

Fluoride-contaminated groundwater has previously been reported in South African countries [15]. The presence of fluorides in groundwater depends on aquifer's geological, chemical, and physical characteristics [16], area tectonic setting, and its related anthropogenic activities [17]. Microfractures due to tectonic setting may even facilitate rapid infiltration of wastewater and leachate into permeable areas and facilitate the circulation of fluids. The main source of fluoride in groundwater is the dissolution of fluorinated minerals, particularly apatite and fluorspar [16]. Fluorides are also released into environment through various industrial activities. Their concentrations may reach more than 100 times the natural content of inorganic fluorides in surface and groundwater [18]. Industries producing and using phosphate fertilizers are among the largest emitters of fluoride [19–22].

In southeastern Tunisia, on the eastern coast of Sfax City, the phosphoric acid (H₃PO₄) plant produces enormous quantities of phosphogypsum (PG) [23]. The processed crude phosphates originate from the Gafsa area (Southern Tunisia) where sedimentary phosphates are exploited for decades in Tunisia. These phosphates are Lower Eocene in age (Ypresian) and have been thoroughly previously studied from geological, mineralogical, geochemical, structural, and economic point of view [23, 24]. The used mineral phosphate is the carbonate fluorapatite (CFA) with a common structural formula as follows: (Ca₄₋₅Mg₀.₁₃Na₀.₂₂)(PO₄)₂₋₅(CO₃)₀₋₄₋₅(OH)₀₋₇ₒ₋₅(F)ₒ₋₅. On the other hand, phosphate extraction from the Tunisian Mining Basin of Gafsa-Metlaoui and its associated processing activities in either Gafsa, Gabes, or Sfax have been proved to have an impact on the local landscape and the continental and/or marine ecosystem.

It is worth noting that the presence of fluorides in water resources at contents higher than 1.5 mg/L [25] generally induces the development of human pathologies such as dental or bone fluorosis. Very large quantities may even have been linked to cancer [26]. In addition, gaseous fluorides and dust have various toxic effects [27]. Furthermore, fluorides can accumulate in plants from phosphate byproducts leaching waters thrown into the environment and contaminating soils. Higher toxicity risks are observed depending on the acidity and alkalinity of the soils [28]. Additionally, plant enzymes exposed to fluorides at a content of around 20 mg/L are believed to be inhibited. Photosynthetic activity can also be affected as well as plant growth. Leaf necrosis has been observed at concentrations of F⁻ of around 500 mg/L [27].

In marine ecosystems, as the case of the Gulf of Gabes of Tunisia, aquatic organisms living in estuarine zones are found to be more sensitive to fluorides. A concentration of 0.5 mg/L can affect aquatic organisms in waters with low ionic strength [27]. Also, fluorides are found to act on the enzymatic activity of fish and on the metabolism of algae. Consequently, the chronic effects of fluorides can lead to the disturbance of metabolism and trophic transfers in fauna and flora in continental and/or marine ecosystems [29].

In the Sfax industrial unit, the carbonate fluorapatite is attacked by sulfuric acid [30]. Therefore, the release of certain impurities such as phosphorus and fluoride after the phosphate attack reaction is not without effect on the surrounding environment, in particular on soil and on water quality [31–33].

Within this context, particular attention is given to the effect of infiltration of acidic leached fluorides on the Sfax-Agareb groundwater quality. For that, the present study is a first attempt to model and predict, using the Visual MODFLOW Classic, eventual fluoride concentrations in the saturated zone of the Sfax-Agareb aquifer and the extent of the area affected by the element pollution on short and medium terms. The outcome of this modeling will help to define the adequate means to reduce and eventually remove undesirable effects.

2. Presentation of the Study Area

The study area is located on the coastal fringe of Sfax, in southeastern Tunisia, between latitudes 34° 43’ and 34° 40’ North and longitudes 10° 46’ and 10° 41’ East (Figure 1). It is located in the industrial zone devoted mainly to phosphate processing, which covers about 120 hectares [34]. The byproduct "PG" is stored on-site, occupying an area of about 50 hectares and reaching a height exceeding 50 m [34]. Liquid discharge from the phosphoric acid production unit constitutes the most important part of the overall factory waste and it is carried to the PG deposit where it undergoes a decantation that separates the solid phase from gypsum repulping waters [35]. Phosphogypsum deposit leaching, under the effect of rainwater, causes the transfer of pollutants to surrounding aquatic environments and to neighboring groundwater [36]. The leachates are collected in
basins, southwest of the phosphogypsum deposit, before being rejected into the sea (Figure 1).

The low-altitude study area is under the influence of a dry and hot Saharan climate of southwest of Tunisia and the relatively humid and temperate Mediterranean climate characterizing eastern and northern Tunisia. The average annual rainfall for the period between 2005 and 2015 is about 220 mm/year [37]. The average monthly rainfall varies between 47 mm in October, considered as the wettest month, and 1.2 mm in July, corresponding to the driest month [30]. The average annual evaporation is 1883 mm for the period between 2005 and 2015 [30] and the average monthly evaporation ranges from a 112 mm low in January to 243.5 mm high in July [37].

3. Geological and Hydrogeological Features of the Study Area

The outcropping geological formation of the study area (Figure 2(a)) consists mainly of sandy clays rich in gypsum and silty sands [39] of Miocene-Pliocene to Early Quaternary age [40]. The phosphate processing industry is built on relatively recent alluvium consisting mainly of sands, alluvia, and calcareous gyspatic crusts. The study area (Figure 2(b)) is part of the Sfax-Agareb phreatic aquifer which is constituted of Miocene-Pliocene-Quaternary sand-clay sediments of the Segui Formation [38, 41]. Underneath the phosphogypsum deposits, the sandy formation aquifer was encountered from 4 to 7 m [42]. The horizontal permeability of the aquifer was measured in situ by the Lefranç tests in the vicinity of boreholes. It ranges from 8 × 10^{-6} to 1 × 10^{-3} m/s [42]. The piezometric map, elaborated based on measurements made in five piezometers (Figure 3) during October 2013, shows water table levels fluctuating between 1.5 and 5 m depth and flowing according to a west-east direction. Water supply is provided mainly by meteoric water infiltrations. The recharge rate is estimated around 7.6 mm/year [43]. The hydraulic gradient of the Sfax-Agareb aquifer, captured by the five piezometers, increases upstream to downstream and ranges from 0.001 to 0.004, with an average of 0.002. Piezometric level monitoring, conducted between October 2013 and October 2014 (Figure 4), indicates an almost steady state with the exception of piezometer SP1 where a small increase was recorded in March 2014.

4. Materials, Methods, and Modeling Tools

4.1. Sampling and Geochemical Analyses. Groundwater sampling was conducted on a bimonthly basis in order to acquire representative data for fluoride content spatial and temporal distribution and to define the contamination source. Using a submerged pump, samples were collected during six campaigns between October 2013 and October 2014 from five piezometers implanted in the phosphate plant and complying with sampling standards. The pH and electrical conductivity (EC) were checked all through and measured in situ using calibrated portable digital meters [44]. The analysis of phosphogypsum (PG) leachates was carried out in October 2013 and in October 2014 from the collection basins, southwest of the phosphogypsum deposit. Water samples were stabilized by adding few drops of diluted HNO_3 and filtered to remove the suspended matter. They were subsequently analyzed by ionic liquid chromatography ISO 10304-1. The aqueous sample is injected into an anionic column to separate the desired ions according to
Recent and actual alluvium
Paralic Sebkhas
Middle and upper Pleistocene
Continental Pleistocene
Pliocene: Villafranchian
Maine Pliocene
Cross section
Piezometer
Study area

Figure 2: Continued.
Figure 2: Geological map of Sfax-Agareb region (a) and hydrogeological cross section along transect AA' (b) [38].

Figure 3: Piezometric map of Sfax-Agareb phreatic aquifer at the PG deposit during October 2013.
where $V_x$, $V_y$, and $V_z$ are the $x$, $y$, and $z$ components of the Darcy velocity, $K_x$, $K_y$, and $K_z$ are coefficient of permeability along the three main orthogonal directions, and $h$ is the hydraulic gradient.

The flow equation (or diffusivity):

$$\frac{\partial}{\partial x} \left( K_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_{yy} \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_{zz} \frac{\partial h}{\partial z} \right) - S \frac{\partial h}{\partial t}$$

$$+ \sum_{i=1}^{r} W_i \delta(x-x_i)\delta(y-y_i)\delta(z-z_i) = 0,$$

where $S$ is specific storage, $r$ is the source number (wells), and $W_i$ is the volumetric flux rate per unit volume.

The dispersion (or transport) equation [46]:

$$\frac{\partial}{\partial x} \left[ D_{xx} \frac{\partial C}{\partial x} + D_{xy} \frac{\partial C}{\partial y} + D_{xz} \frac{\partial C}{\partial z} \right]$$

$$+ \frac{\partial}{\partial y} \left[ D_{yx} \frac{\partial C}{\partial x} + D_{yy} \frac{\partial C}{\partial y} + D_{yz} \frac{\partial C}{\partial z} \right]$$

$$+ \frac{\partial}{\partial z} \left[ D_{zx} \frac{\partial C}{\partial x} + D_{zy} \frac{\partial C}{\partial y} + D_{zz} \frac{\partial C}{\partial z} \right]$$

$$- \left[ V_x \frac{\partial C}{\partial x} + V_y \frac{\partial C}{\partial y} + V_z \frac{\partial C}{\partial z} \right]$$

$$+ Q(C^w - C) - n_r \left[ 1 + E(C) \right] \frac{\partial C}{\partial t} = 0,$$

where $C$ is the pollutant concentration. $E(C)$ is a function representing the chemical adsorption properties, $C^w$ is the concentration of the pumped fluid, and $D_{xx}$, $D_{yy}$, $D_{zz}$, $D_{xy}$, $D_{yz}$, and $D_{xz}$ are components of the hydrodynamic dispersion tensor [46].

5. Results and Discussion

5.1. Fluoride Contamination Assessment. At the catchment basins, southwest of the PG deposit, the analyzed leachates are found heavily charged with fluoride displaying 1905 mg/L in October 2013 and 2100 mg/L in October 2014. Such contents exceed the national norm of 3 mg/L set for fluoride in effluents representing treated or not treated wastewater discharge, directly or indirectly thrown into the receiving environment [50]. The leachates display very low pH (1.3) and show the highest EC values (Table 1).

Analyzed groundwater conductivities vary between 8810 and 34900 $\mu$S/cm, being the lowest in the upstream part of the study area and the highest in the southeastern part of the aquifer at piezometer SP4 (Figure 5(a)). A significant increase is observed, following the groundwater flow direction (west-east), related to water-sediment interaction of the...
unsaturated zone, and/or salty water intrusion, and/or PG leachate infiltration [35].

The analyzed water pH is acid to near neutral, with values ranging from 5.18 to 7.6. The lowest pH concerns the downstream part at piezometer SP1, which is under the direct influence of PG leachate infiltrations, while the highest pH characterizes the upstream part (SP3). A slight increase in pH is recorded during the water table recharge period (January and March) due to a mixing effect caused by infiltrated rainwater (Figure 5(b)).

At the industrial zone, the fluoride Sfax-Agareb groundwater contents vary between 0.5 and 29 mg/L throughout both sampling periods. The highest contents are measured in waters sampled from piezometers located around the PG leachate collection basins, in particular piezometer SP4 (Figure 5(c)). Moreover, for the same piezometer, the fluoride content variation, over time, is known to decrease during the recharge period of the aquifer compared to the rest of the year.

### 5.2. Conceptual Model Construction

The choice of the conceptual model is conditioned not only to seek a high degree of precision, but also by the quantity and quality of the available data [51].

The construction of the groundwater flow and transport conceptual model was based on field data, hydrogeological and geotechnical interpretation outcomes, and bimonthly fluoride measurement results for the year 2013-2014. The following assumptions were made during the construction of the flow and transport model in the saturated zone of the Sfax-Agareb aquifer:

(i) Flow modeling in a steady state
(ii) Flow occurring towards the sea, deduced from the interpretation of the piezometric maps carried out for the year 2013-2014
(iii) The migration of contamination is horizontal, according to groundwater flow direction
(iv) The selected contaminant is fluoride (F⁻) because of its high content recorded throughout the monitoring period
(v) Only contaminant dispersion is considered, the adsorption being assumed to be negligible
(vi) The initial concentration of the pollutant element introduced into the model outside the “source zones” is 0 mg/L
(vii) The fluoride levels in the "source zone" of contamination are based on those measured in phosphogypsum leachates in October 2013 and October 2014

### 5.3. Flow Conceptual Model

Based on the geotechnical characterization report of Sfax [42], the following lithological succession is recognized from top to bottom:

(i) 1 to 2 m thick filling layer with a hydraulic conductivity (K) varying from 1.10⁻⁷ to 1.10⁻³ m/s
(ii) 2 to 3 m of sandy clays and phosphogypsum mix (K = 1 x 10⁻⁶ m/s)
(iii) 10 to 14 m of slightly gravelly sand layer, relatively permeable with a hydraulic conductivity ranging from 8 x 10⁻⁶ to 1 x 10⁻³ m/s
(iv) Very low permeability limy clays (K = 1 x 10⁻⁹ m/s).

The aquifer is considered unconfined and corresponds to a single layer of fine sand, 10 to 14 m in thickness, and displaying a hydraulic conductivity ranging between 8 x 10⁻⁶ and 1 x 10⁻³ m/s based on the Lefranc tests. The model is therefore a monolayer free aquifer set on a very low permeability clay substratum (Figure 6).

### 5.4. Transport Conceptual Model

A solute transport model was developed to study the long-term spatial and temporal evolution of fluoride contents, from October 2014 to October 2030. Changes in short-term concentrations between October 2013 and October 2014, associated with small fluctuations in piezometric levels and lack of pumping in the area, must therefore be replicated [52]. The flow model can therefore be assumed permanent and modeled under stationary conditions, using average conditions for this period.

Based on the bimonthly monitoring of Sfax-Agareb groundwater quality for the period between October 2013 and October 2014, abnormal high concentrations of F⁻, reaching 29 mg/L at piezometer SP4, were recorded. These high contents would have a fluoride contamination source located southwest of the phosphogypsum deposit, upstream of hydraulic piezometer SP4 where the PG leachate collection basins are placed.

### 5.5. Grid, Boundary Conditions, and Calibration of the Flow Model

The study area was discretized into “cells” of 50 m sided (Figure 7). Geometrical and hydrodynamic parameters
Figure 5: Distribution of EC (a), pH (b), and fluoride concentration (c) in Sfax-Agareb groundwater around the PG deposit.

Figure 6: Conceptual model of Sfax-Agareb phreatic aquifer at the PG deposit.
necessary for the simulation are attributed to each cell. Boundary conditions can be defined as either (i) conditions with imposed potentials, (ii) conditions with imposed flow, or (iii) conditions with imposed drain \[53, 54\].

In a constant regime, we impose potential values as boundary conditions. The translation of these conditions into the MODFLOW code is represented by a table (IBOUND) which allows to ensure if a particular cell is active, inactive, or with a fixed load. When a natural limit, such as the sea or a river, does not exist, a potential line resulting from measurements at the edges of the model domain can be used as a condition of imposed potential. Two boundary conditions of constant head type were applied at the flow model fringes, the first representing the sea and the second corresponding to the upstream side of the industrial site. The sea level is taken at elevation 0 m and the upstream hydraulic load at 5 m, calculated via the hydraulic gradient. The bottom is defined as an impermeable boundary because the exchange between the sand aquifer and the clay substratum is minimal and can be ignored. In the case of an unconfined aquifer, an important boundary condition is imposed on the surface of the model. This condition is represented by meteoric water recharge.

In the Sfax industrial zone, the calibration was carried out trying to reproduce as closely as possible the behaviour of the real hydrogeological system and obtain similar piezometric levels as measured in October 2013. This was achieved by varying horizontal hydraulic conductivity values of sand. We then compared the simulated piezometric levels to those measured at a given moment.

For this calibration step, the normalized RMS represents the average normalized square errors. This is the standard deviation that exists between these two sets of data. This calibration step is very important to minimize the normalized RMS to the lowest possible value [55]. The normalized RMS is at 39.27% before calibration, which indicates the large difference between the calculated hydraulic heads and those measured in 2013. After numerous calibrations by varying the horizontal hydraulic conductivity of sand, the normalized RMS value was reduced to 10.13% (Figure 8).

The established calibration shows a good consistency between the simulated flow and the natural flow of the aquifer since the majority of control points introduced into the flow model are within the 95% confidence interval (Figure 8).

Furthermore, the examination of the calculated piezometric map confirms the west-east flow direction (Figure 9). Flow parameters and calibrated values are shown in Table 2.

5.6. Numerical Fluoride Transport Model Calibration. Once calibrated, the flow model can be used to calibrate the transport model. A migration or transport model is composed of a "source zone" (Figure 7) and a "plume" of contamination that migrates along the direction of the aquifer flow in relation to the source zone.

To locate the plume, average concentrations of contaminant in each piezometer waters were considered for the six sampling campaigns. The contaminated zone was delimited in relation to concentration gradients between the upstream side, at piezometer SP3, and the downstream side. Results, herein reported, were compared to the Tunisian norms related to liquid discharges (NT 106-002). Subsequently, each panache was linked to a potential source of contamination.

Refinement of cells near the source zone and the control piezometers (Figure 7) as well as the sand dispersivity have been first adjusted in order to obtain the previously observed concentration (October 2014). The dispersivity values used for the transport model fit were selected from the literature for a medium of a similar nature.

Using available location and source history data, calculations of contaminant migration velocity and hydraulic conductivity applicable to saturated permeable horizons were performed as follows:

\[ K = V \frac{ne}{i}, \]

where \( K \) is the hydraulic conductivity, \( i \) is the hydraulic gradient, \( ne \) is the effective porosity, and \( V \) is the migration speed, which is given by

\[ V = \frac{S}{t}, \]

where \( S \) is the migration distance, i.e., the distance between the source and the contaminated piezometer, and \( t \) is simulation time.

From (5) and (6), we obtain the calculated hydraulic conductivity:

\[ K = \frac{S \ ne}{t \ i}. \]

During the transport model calibration, the hydraulic conductivity was adjusted to allow migration between the source and the control piezometer. Fluoride contamination was introduced into the model, assuming a constant and continuous source of contamination located to the south-west of the phosphogypsum deposit. In this case, the boundary condition is of constant concentration type.

The fluoride-related source of contamination was activated in the model during the period between October 2013 and October 2014 (365 days). The forecast simulation of contamination was of 6205 days (16 years). The transport model calibration aimed to adjust the \( F^- \) concentrations to approach \( F^- \) contents measured in 2014, at the control piezometer (SP4).

The calibration results indicate a very good agreement between the fluoride measured concentrations and those simulated. A low deviation between measured and simulated values of the order of 0.14 mg/L is recorded at the control piezometer SP4 (Figure 10).

The preliminary transport parameters and the calibrated values are shown in Table 3.

5.7. Forecast Simulations. Numerical simulation has allowed to delineate the aquifer fluoride contamination expansion and to highlight the most polluted sites. The simplified scenario considered for this study consisted of a linear
increase of fluoride from 17 mg/L in 2013 to 29 mg/L in 2014 and a prediction for the year 2030.

In the saturated zone of the Sfax-Agareb aquifer, at the phosphogypsum storage site and according to the two time references (October 2013 and October 2014), predictive simulations were established to evaluate fluoride contamination plume extension up to 2030. Based on the Tunisian norms of liquid discharges (NT 106-002), the fluoride contamination fronts were set at 3 mg/l.

The water quality of the Sfax-Agareb aquifer, near the phosphogypsum discharge, is deteriorating significantly and continuously. The model foresees extensions of the contaminated plume over 250 m in 2014 (Figure 11(a)) away from the source area. It forecasts an extension over 900 m in 2030 (Figure 11(b)). The contamination plume will bear an ellipsoid shape. The variation of concentrations calculated as a function of time (Figure 10) predicts fluoride content increase from 29 mg/L in 2014 to 86 mg/L in 2030. However, and taking into consideration the various assumptions mentioned in previous sections, we consider that this expansion is a worst scenario as retardation may occur with time and through sorption and through element complexation. These processes were not considered in the modeling.

6. Conclusion

In the current study, a bimonthly spatial-temporal monitoring of fluoride contents in the Sfax-Agareb aquifer waters was achieved for one year (October 2013-2014). Results outline contamination induced by the surrounding industrial activities, especially phosphate treatment, but it is most alarming around the southwestern part of phosphogypsum deposit close to the PG leachate collection basins and where fluoride contents may reach up to 29 mg/L. Such contents largely surpass the Tunisian norms for drinking waters and irrigation water maximum fluoride permissible concentrations.

This characterization was further scrutinized through “Visual MODFLOW” modeling of the solute flow and transport in the Sfax-Agareb aquifer. The concept model was based on a single layer in a steady-state flow regime. Two temporal references (October 2013 and October 2014), for which measured data were available, have been used.
Figure 9: Predicted piezometric map of Sfax-Agareb phreatic aquifer at the PG deposit during October 2013.

Table 2: Calibrated flow model parameters in a steady-state of the Sfax-Agareb groundwaters during October 2013.

<table>
<thead>
<tr>
<th>Flow parameters</th>
<th>Units</th>
<th>Before calibration</th>
<th>After calibration</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity of sand (Kx)</td>
<td>m/s</td>
<td>$8 \times 10^{-6}$ at $1.1 \times 10^{-3}$</td>
<td>$2 \times 10^{-4}$</td>
<td>Data founded by GCT [42] during the geotechnical investigations in the study area</td>
</tr>
<tr>
<td>Hydraulic conductivity of sand (Ky)</td>
<td>m/s</td>
<td>$2 \times 10^{-4}$</td>
<td>$2 \times 10^{-4}$</td>
<td>Data founded by GCT [42]</td>
</tr>
<tr>
<td>Hydraulic conductivity of sand (Kz)</td>
<td>m/s</td>
<td>$2 \times 10^{-5}$</td>
<td>$2 \times 10^{-5}$</td>
<td>Data founded by GCT [42]</td>
</tr>
<tr>
<td>Refill (effective infiltration)</td>
<td>mm/an</td>
<td>7.6</td>
<td>10</td>
<td>Values founded by Trabelsi [43]</td>
</tr>
<tr>
<td>Effective porosity of sand</td>
<td></td>
<td>0.25 at 0.35</td>
<td>0.25</td>
<td>Values founded by Banton and Bangoy [56]</td>
</tr>
<tr>
<td>Total porosity of sand</td>
<td></td>
<td>0.3 at 0.4</td>
<td>0.3</td>
<td>Values founded by Banton and Bangoy [56]</td>
</tr>
</tbody>
</table>

Figure 10: Predicted fluoride concentration between 2014 and 2030 years in Sfax-Agareb phreatic aquifer at the PG deposit.
Calibration of flow model and transport model was achieved by varying hydraulic conductivity and the dispersivity of sand. The model was calibrated and validated, and predictive simulations were established to assess the extent of the fluoride plume within a simplified framework of a homogeneous and isotropic aquifer. The 16-year predictive simulation (up to 2030), based on a fixed 3 mg/L concentration front, shows that the spatial expansion of groundwater fluoride contamination spreads towards the sea with an ellipsoid-shaped plume spreading over a distance of 900 m. Fluoride contents are predicted to increase up to 86 mg/L at the control piezometer in 2030. The quantitative contamination expansion prevision is most distressing and urgent means of remediation have to be implemented. In this context, it is recommended to act upstream and improve the production process to include neutralization of phosphogypsum [34]. It is also recommended to set up means for wastewater recovery and recycling. Hydrogeological isolation by geomembranes and containment of phosphogypsum stocks can be also a good measurement to prevent aquifer pollution [57]. It is also necessary to take preventive measures beforehand and create protected and suitable sites for future phosphogypsum storage.

Already stocked phosphogypsum can be used as a substitute for natural gypsum in the manufacturing of cement [58] and/or the manufacturing of ceramics and plaster.
This will reduce the huge stock of phosphogypsum left to induce water pollution in the area.

**Data Availability**

All data used to support the findings of this study are included within the article and will be, in case the article will be accepted, accessible to readers.

**Disclosure**

Amina Mabrouk El Asmi, Mohamadou Ould Baba Sy, and Moncef Gueddari are coauthors.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

**References**


