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Characterization of the Youssoufia-Morocco- Mine Fluoride-Contaminated Water and Their Detrimental Effects on Human Health

Moufti Ahmed

Abstract

In Youssoufia, the second phosphate mining center of our country (Morocco), the drinking water needs of the rural population are of underground origins. Indeed, most of Youssoufia's rural areas feed on traditional wells. The main purpose of this chapter is to evaluate the degree of contamination of mine water along the pumping canal by fluoride. Wells located near this channel were also analyzed to see the influence of the existence of black phosphate in this region on these wells. At the end of this analytical part, it is obvious to conclude that the dewatering waters of the black phosphate mines of Youssoufia, known as dewatering water along the canal, contain significant fluoride concentrations in the order of 3–4 mg/l on average and the waters of the wells located near this canal have fluoride concentrations higher than the standard recommended by the National Office of Drinking Water in Morocco and the World Health Organization which is 1.5 mg/l. Indeed, a number of residents residing in Youssoufia suffer from fluorosis.

Keywords: fluoride, characterization, Morocco, mine water, human health

1. Introduction

In Morocco, the establishment of a water resources management policy both quantitatively and qualitatively is not a whim of organization but a necessity for survival. In fact, the reserves of drinking water are not infinite, and many regions suffer either from the lack or the intolerable waste of this vital density.

In Youssoufia, the second phosphate mining center of our country, the drinking water needs of the rural population are of underground origins. Indeed, most rural areas of Youssoufia feed from traditional wells, the closest to each Douar. The drinking water supply is made from four holes of the BAHIRA water table located 24 km southeast of Youssoufia.

On the other hand, there is black phosphate mine water that is not waste water, in the common sense of the term, because it has never actually been used. These are the waters of a multitude of superimposed layers drowning the different layers of phosphates in the southern zone of the Gantour deposits, which requires

predigestion to allow the exploitation of these deposits. Currently, this predigestion is carried out essentially in the recipes 7 and 9 where the average flow reaches in 6–8000 m³/day, and at present, it exceeds 35,000 m³/day [1].

The main purpose of this chapter is to evaluate the degree of contamination of mine water along the pumping canal by fluoride. Wells located near this channel were also analyzed to see the influence of the existence of black phosphate in this region on these wells.

2. Choice of the zone

In Morocco, the phosphate areas have a geographical area extending from Khouribga, Oued Zem and Tadla to the northeast, Settat to the center, and Ben Guerir and Youssoufia to the west [2]. The choice of the Youssoufia zone is justified on the one hand by the fact that the latter contains significant concentrations of fluoride of the order of 3 mg/l on average in mine water [3–5], and on the other hand, that all the studies that have already been done on regions other than Youssoufia [6, 7].

3. Overview of the study area (Youssoufia)

3.1 Historical aspect

The city of Youssoufia was born in 1930 following the discovery of a phosphate deposit in the Gantour plateau by the French geologist Lois Gentil. Since then, the city took the name of the latter until 1960, when it was renamed Youssoufia by his majesty Mohamed V following the visit he made to this locality on the same date [8].

The development, extension and exploitation of the deposit, as well as the increasing demand for labor, have given the Youssoufia center considerable economic growth and accelerated urbanization.

3.2 Geographic location

The city of Youssoufia is located east of the city of Safi, at a distance of 80 km, north of the city of Marrakech, at a distance of 100 km and south of the city of Casablanca, at a distance of 220 km. It is part of the Doukkala-Abda region, Safi province (**Figure 1**). It is also part of the Gantour plateau, one of the four main deposits of the cherifian office of phosphates (OCP) group, limited to the north by the RAHMANA, to the east by the MOISSAT hills, to the south by the Bahira, and to the west by the TASSAOUT Wadi.

The city of Youssoufia is crossed by a railway that connects the phosphate deposits of Ben Guerir and Youssoufia with the port of SAFI. It is also served by: the Jamaat Shaim road to the northwest, the road to Chemaia on one side and Ben Guerir on the other, the road that joins the main road 12 to Marrakech to the south, and the new road to Sidi Bennour to the north.

Despite this important network of roads and railway lines, the city of Youssoufia remains a locality and on the fringe of the existing clean economic activities on the roads (e.g., Ben Guerir, Sidi Bennour,...) and this is because of the hand of OCP on the city as a single manager concerned with the development-only activities related to the mining sector.

3.3 The climate

The climate of the city of Youssoufia is semicontinental, arid in winter, the average rainfall is about 272 mm per year, and the average minimum temperatures vary between 13°C in January and 25.1°C in July. Highs above 30°C can be observed in the

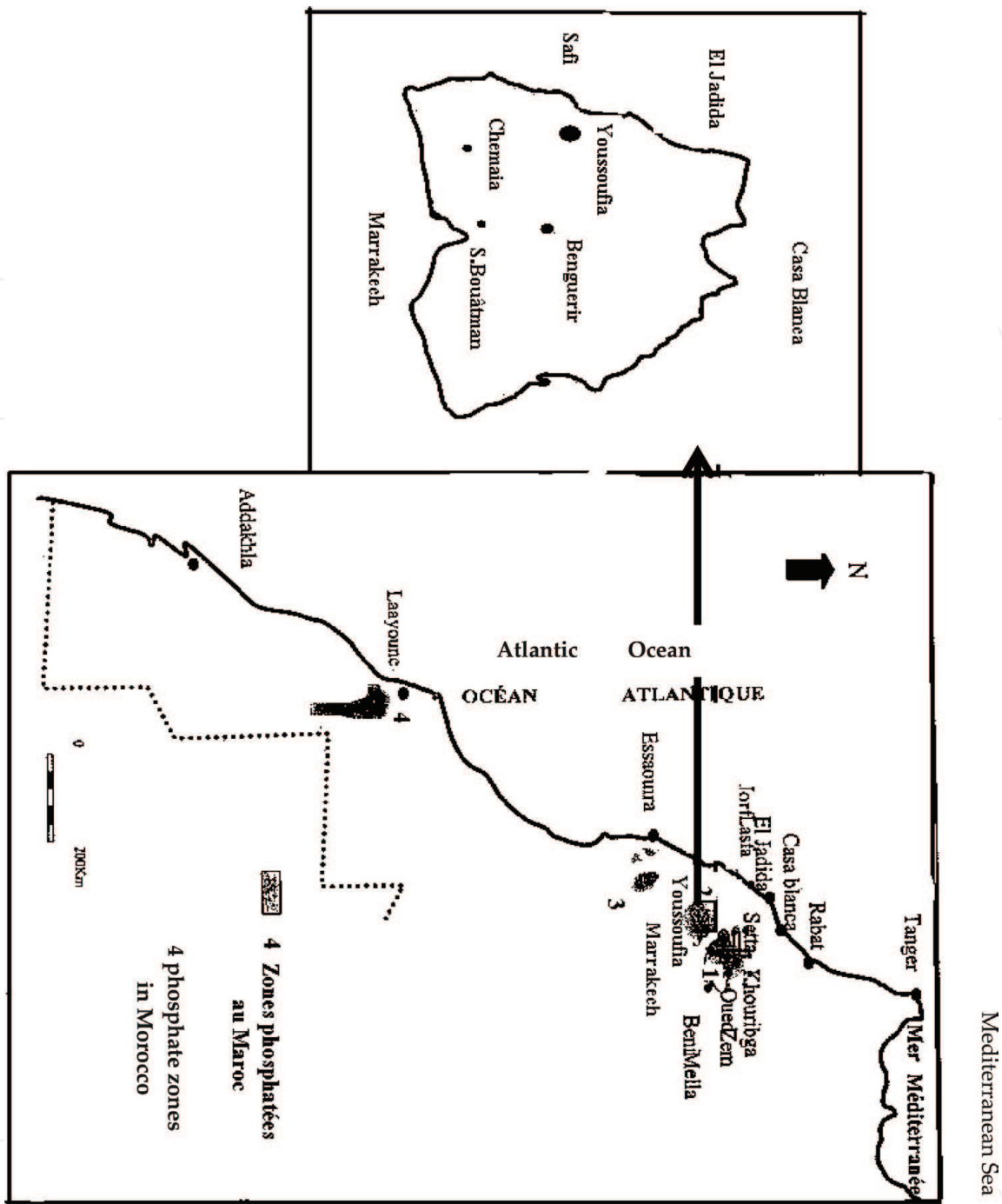


Figure 1.
Geographic location of Youssoufia.

region. The coldest months are December, January, and February when the minimum average is 8.6°C. The winds are relatively weak with predominance of the northern directions during the dry season and the northeast during the wet season [8, 9].

The monthly averages (**Table 1**) show that there is a rainfall accident in November, December, January, and February, which allows a medium or wet year for a crop life until March or April due to the water potential accumulated in the ground. Outside these periods, the existence of a vegetative life is linked to the supply of water by irrigation. The months of July and August are the driest [10, 11].

3.4 Mining potentials

In terms of phosphate, the region is full of a large amount of phosphate; it is the largest reserve of the country after Khouribga. Its reserves are estimated at 2 billion m³, which are located in the Gantour plateau [12].

Month	Jan.	Feb.	March	April	May	June	July	August	Sept.	Oct.	Nov.	Dec.	Ann.
Average monthly (mm)	39	34	39	22	17	2	0	0	10	25	40	44	272

Table 1.
Average monthly rainfall (Youssoufia station, period 1933–2000).

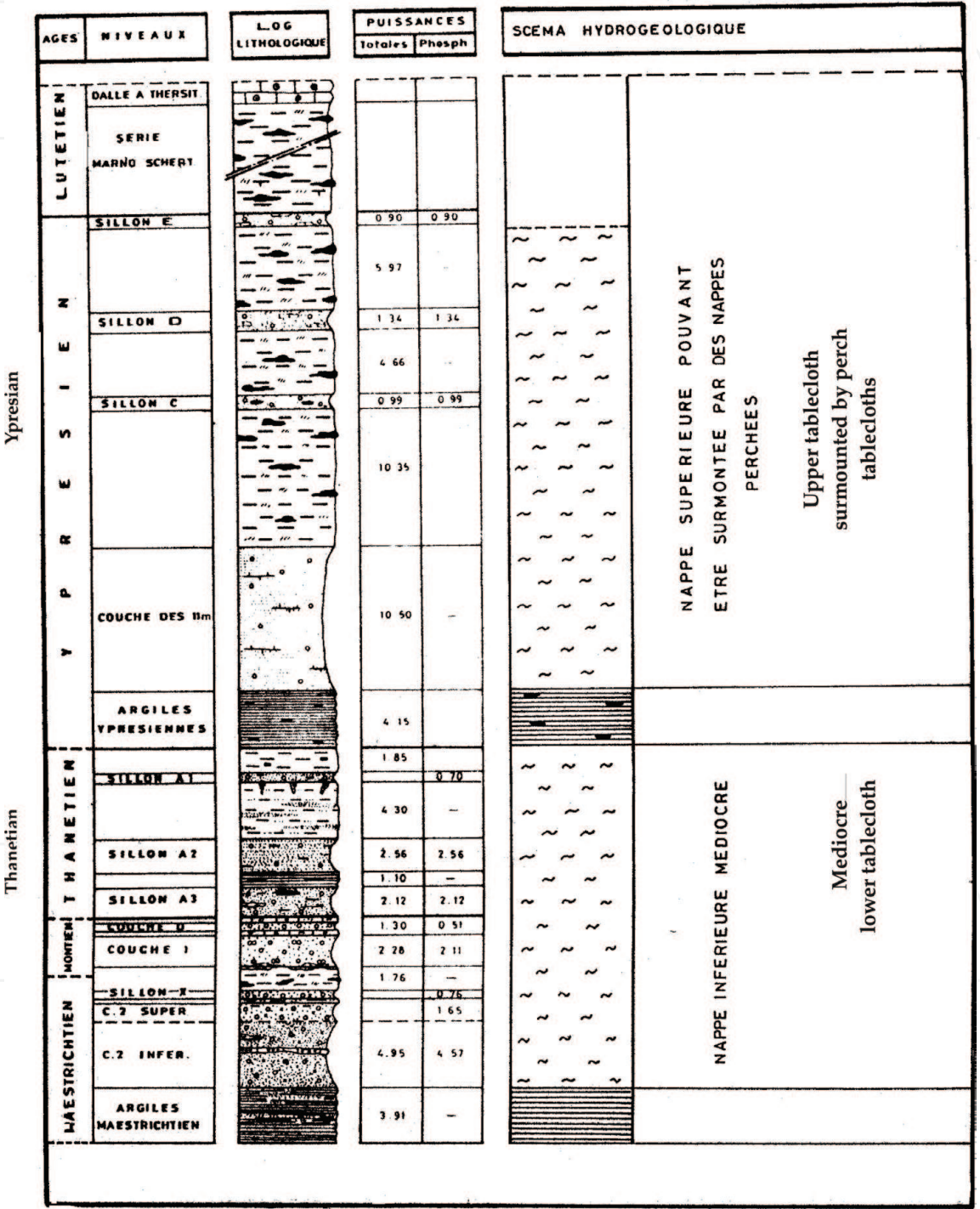


Figure 2.
Average lithological section of the Youssoufia black phosphate deposit.

Phosphate mining is carried out in two areas, clear phosphate and black phosphate. There is a drying unit with a capacity of 60 million tons per year and a black phosphate calcination unit. The O.C.P for some years directs its exploitations on

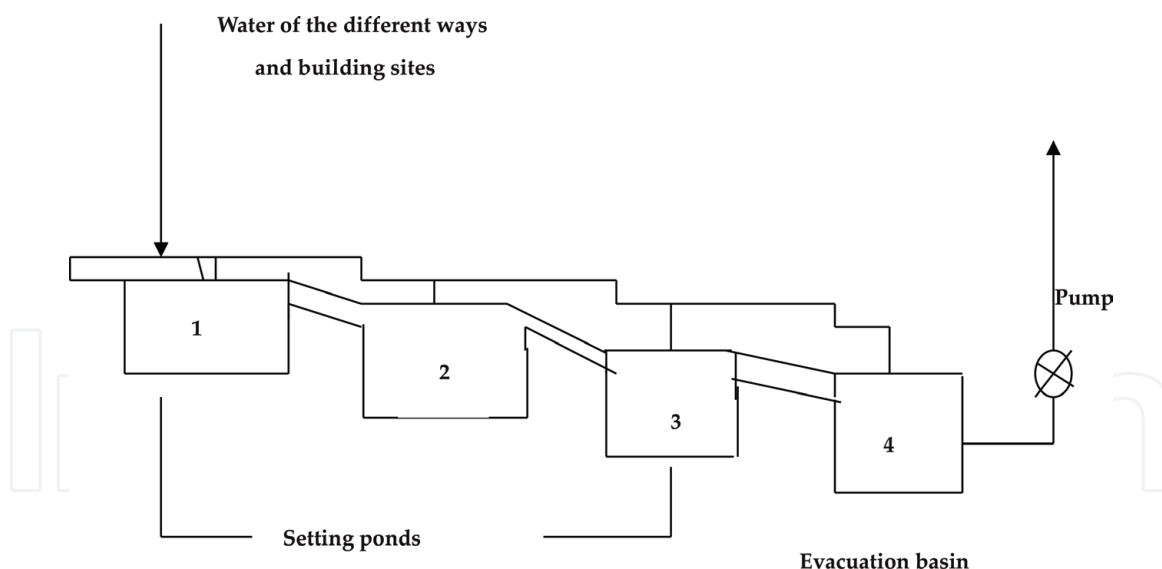


Figure 3.
 Mine stations “Exhaure” and design of shallow basins.

Ben Guerir where they are in open sky, when with the city of Youssoufia, they are executed in great depth. This has practically caused a stagnation of the depth since 1970, and a very significant regression since 1984.

3.5 Overview of the hydrogeology of the Youssoufia flood zone

The sedimentary basin is in the form of a subsidence basin, it is a tectonized and folded primary substratum during the New Caledonian tectonic phases and a cover ranging from quaternary to quaternary affected by attenuated tectonic replicas of the tectonic Alpine phase. Currently in the zone of Youssoufia, it is the layer 1 that is in exploitation. It also exploits the layer 0 when the interlayer layer 1-layer 0 is absent or friable. As it moves south, light phosphate is exploited in recipes 5 and 6 (discovery), where it exploits in addition to layer 1 and layer 0, groove X (see **Figure 2**; [10]). The lithological section of this deposit (**Figure 3**) shows that the black phosphate of Youssoufia is located at an average depth of more than 150 m, up to 180 m. The phosphate layer is located below the aquifer, which results in particularly delicate mining problems, which had to be controlled. The exploitation of this deposit is done underground [11].

Layer 1 (Montien): it is a loose sandy phosphate whose power is of the order of 2–2.5 m. The base of this layer is usually in the form of a phosphate limestone. This layer is also surmounted by a cardinal spacer. This spacer separates layer 1 from layer 0.

The layer 0 (Montien): it is a loose sandy phosphate less rich in view than the layer 1. The X groove is encountered in the Maastrichtian, which is characterized by an alternation of phosphate levels and sterile levels with predominantly marly levels. The phosphate levels are in the form of phosphated sands called from bottom to top: layer 6, 5, 4, 3, 2, and the groove X. The layers 0 and 1 are in the Montien, Sillon X in the Maastrichtian.

4. Dewatering water (Exhaure water)

Underground mining at Youssoufia began in 1930 with the extraction of the clear, dry phosphate that runs along the northern limit of the deposit, whose work has bypassed the area drowned in its northern and western parts.

Element	P ₂ O ₅	CaO	CO ₂	SiO ₂	Al ₂ O ₃	F ⁻
Percentage	32.5	52	3.7	3.9	0.36	3.9

Table 2.
Average composition of black phosphate.

In fact, this zone is characterized on one hand by the existence of organic matter giving the phosphates their blackish color and acting on its content, which necessitates their calcination before delivery [11], and on the other hand by the presence of water in extraction sites from groundwater that have been discovered since 1960 by the exploitation of recipe 7 and then by recipes 8 and 9. This water called “mine water” is pumped to the outside of the mine to allow the exploitation of these deposits [13]. The observation in recent years of the tonnage dewatering discharge relationship predicts a flow of more than 35,000 m³/day from the year 2000. The average composition of black phosphate is shown in **Table 2** [11].

Extraction of black phosphate in the submerged area of Youssoufia occurs between two underground aquifers. In this zone, there are two types of devices for precleaning the upper water table: surface precleaning (caving and tracing) and spot precleaning (wells and predigestion soundings) [10].

4.1 Exhaure “mine water”

The water that impedes the smooth progress of phosphate extraction in the underground workings of the flooded Youssoufia zone comes from:

- lightning strikes;
- tracing;
- operating wells; and
- precleaning drains.

To ensure the smooth running of extraction, a dewatering infrastructure was set up for the evacuation of these waters to the day. The scheme adopted for evacuation consists of three phases [10]:

First phase: it concerns the collection of water from the various roads and sites by essentially pneumatic pumps installed in the cuvettes. The water will be evacuated to the nearest settling stations (to the headway).

Second phase: the water collected during the first phase is collected in the secondary basins. These waters are discharged in a 50/60 pipe where 80/90 is connected directly to the pipe 6", which is different in the main dewatering station. Typically, these pumps supply intermediate basins, and the main station consists of a succession of settling ponds (**Figures 3 and 4**).

Third phase: this is the main phase of dewatering; all the water from the sector collected in the settling ponds is repressed by electric pumps (GFP, Rotos, Guinard, and Deplechin). This water is discharged to the day through wells in 6 “pipes to be conveyed by gravity in 10” pipes, which reject them away from the farms to avoid any recycling of water. The position of the dewatering stations that force the inflow of water toward the day depends on the hydrogeology of the zone and the dynamics of exploitation [10] (**Figure 4**).

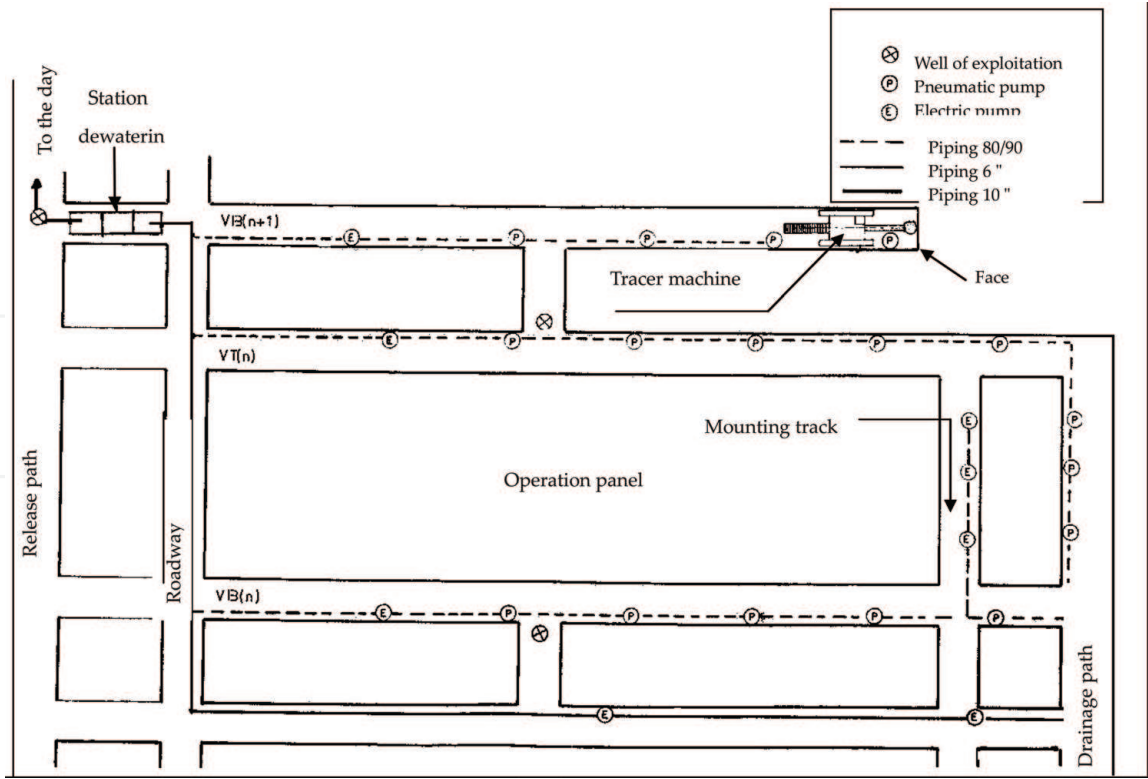


Figure 4.
Operating method.

5. Exhaure and quality

5.1 Characterization techniques for Yousoufia mine water

All the water samples are kept at 4°C in plastic bottles (Year 2001/2002) and analyzed in the laboratory “Water and Environment,” at the Faculty of Sciences of El Jadida within 24 h according to the standard French methods (AFNOR) [14, 15]. At each sampling, the temperature, TDS, conductivity, and pH were measured in situ in the field using an HACH conductivity meter, modeled 44,600 and a WTW pH meter, modeled 522 with a combined electrode. Turbidity is measured using a turbidimeter.

In this study, fluoride was assayed by potentiometric method using TISAB solution, a fluoride ion-specific electrode and a reference electrode (Ag/AgCl). It has the advantage of being simple, of rapid response and of being amenable to serial dosages [14, 16]. The apparatus used is a JENCO model 6209 type pH-ionometer equipped with a fluoride-specific electrode.

5.1.1 Nature and methods of taking samples

Samples were taken along the mine-water channel from recipe 9 “unit 9” (Douar OULED ABADE) from stations S1 to S5 and recipes (unit)7 and 8 (station S6) and the mixture of the three recipes located at neighborhood of SIDI AHMED and extend to El BIAR (stations S7, S8, and S9). Samples from wells near the dewatering water channel were also taken (**Figure 5**).

5.1.2 Results of characterization of mine water

Yousoufia mine water from black phosphates corresponds to natural ground-water characterized by a more or less variable chemical composition. **Table 3**

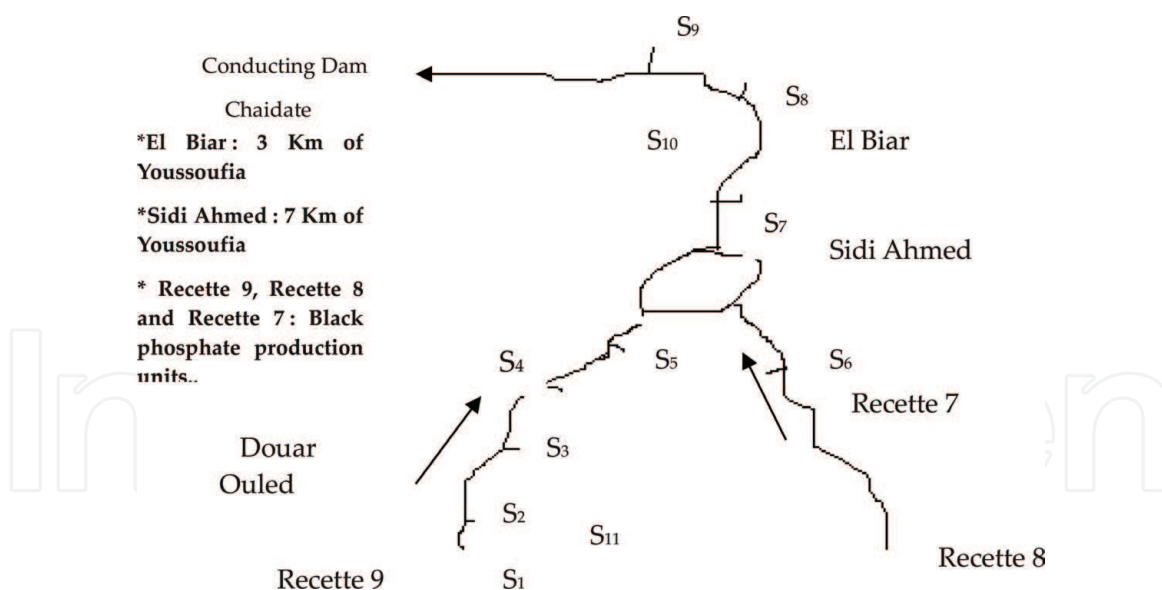


Figure 5.
Dewatering water sampling stations. S10 et S11 : Welles.

summarizes the results of physicochemical analyzes carried out along the canal. It is noted that these waters have electrical conductivities ranging from 1.2 to 1.4 ms/cm at 25°C and pH from 7.67 to 8.22, so we can conclude that these groundwater (mine water) are slightly alkaline.

5.1.2.1 Evolution of the fluoride content for the different stations

Table 4 presents fluoride standards for drinking water as a function of average annual temperature obtained from daytime daily maximums [17].

According to **Table 4**, the world Health Organization (WHO) standard for water with an average temperature of 21.66–27.77°C (average temperature of mine water) is set at 0.8 mg/l. Examination of the results obtained shows that the Youssoufia mine water along the canal has high levels of F^- of the order of 3.5 mg/l on average, thus much higher than the norms published by the WHO. It can be added that these important levels decrease along the canal, moving away from the recipe 9 (station 1) to the mixture of the three recipes 7, 8, and 9 (station 9) located near the village of Charige, the content of F^- decreases from 4.06 to 2.36 mg/l (**Figure 6**). The same results were found by Falgata [1].

This abnormal fluoride content is due to the fact that leaching of the black phosphate from this region contains from 3 to 4% of fluoride [18]. This was well verified in the study conducted by ARAFAN [19] on the monitoring of the release of fluoride ions by black phosphates, which shows that they release between 3 and 3.5 mg/l of fluoride for a stirring time greater than 100 up to 300 h for the different masses used (**Figure 7**). This quantity of fluorides released by black phosphate is greater than that released by white phosphate [20–22].

5.1.2.2 Orthophosphates and magnesium

From station 1 (S1) to station 9 (S9), the contents of orthophosphates (**Figure 8**) and those of magnesium (**Figure 9**) decrease along the dewatering channel, except that in the case of (Mg^{2+}), there is a slight increase in the station 6 (S6) and this is because the mine water of recipes 7 and 8 (station 6) are more concentrated in Mg^{2+} .

Moreover, we can note that the contents of (PO_4^{3-}) and (Mg^{2+}) do not exceed the standards published by WHO [23].

Stations/parameter	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
pH	7.67	7.73	7.87	7.93	7.99	7.86	7.83	8.10	8.20	7.89	7.92
T (°C)	25.4	25.3	25.3	25.5	25.4	25	25	24.9	24.9	25.3	25.1
E.C (ms/cm)	1.21	1.23	1.25	1.31	1.32	1.34	1.25	1.28	1.25	1.26	1.36
TDS (g/l)	0.58	0.58	0.61	0.63	0.58	0.58	0.57	0.68	0.65	0.44	0.75
Turbidity	120	120	122	122	122	0	14	0	1	46	0
Cl ⁻ (mg/l)	110.9	120.01	150.1	150.2	200	180	200	220	230	150.1	170
Hardness (mg/l)	135.70	174.85	160.3	158.80	160.4	157.11	154.96	154.96	156.08	140.90	162
Ca ²⁺ (mg/l)	48.49	80.19	94.39	98.02	100.7	84.17	94.18	96	100.1	72.14	84.2
Mg ²⁺ (mg/l)	87.21	82.66	65.64	60.78	55.37	72.94	60.78	58.07	55.92	68.76	77.8
Nitrate (mg/l)	28	8	14	16	8	28	20	6	4	18	6
Nitrite (mg/l)	0.23	0.011	0.15	0.105	0.064	0	0.01	0	0	0.044	0
AT	0	0	0	0	0	0	0	0	0	0	0
CAT (méq/l)	4.4	4.6	4.8	4.6	4.8	4.3	4.6	5.2	5.4	5.4	6.2
PO ₄ ³⁻ (mg/l)	0.5	0.44	0.38	0.31	0.22	0.2	0.21	0.13	0.03	0.12	0
Oxydabilité (mg/l)	2.8	2.2	1.4	2.2	2	1.4	2.2	2	1.6	1.4	1.6
Fluoride (mg/l)	4.06	3.82	3.4	3.35	3.26	2.76	3.04	2.89	2.36	1.51	1.63

Table 3.
The average of physicochemical parameters of Yousoufia mine water (year 2001/2002).

Average annual temperature (°C) of water from daytime maximums daily	Optimal levels of fluorides (ppm)	Maximum allowable levels of fluorides (ppm)	Limit levels of fluorides (ppm)
10	1	1.074	1.640
10.55	0.956	1.024	1.548
11.11	0.916	0.979	1.465
11.67	0.880	0.940	1.393
12.22	0.849	0.905	1.329
12.78	0.821	0.873	1.270
13.33	0.796	0.844	1.218
13.89	0.773	0.819	1.170
14.45	0.752	0.795	1.127
15	0.733	0.774	1.088
15.55	0.714	0.752	1.048
16.11	0.698	0.734	1.015
16.67	0.682	0.716	0.983
17.22	0.667	0.700	0.953
17.78	0.654	0.685	0.925
18.33	0.640	0.670	0.897
18.89	0.629	0.657	0.874
19.45	0.618	0.644	0.850
20	0.6	0.632	0.828
20.55	0.597	0.621	0.807
21.11	0.587	0.610	/
21.66 to 27.77			0.800
28.33 to 32.22			0.700

Table 4.
The fluoride level standards of drinking water at different temperatures.

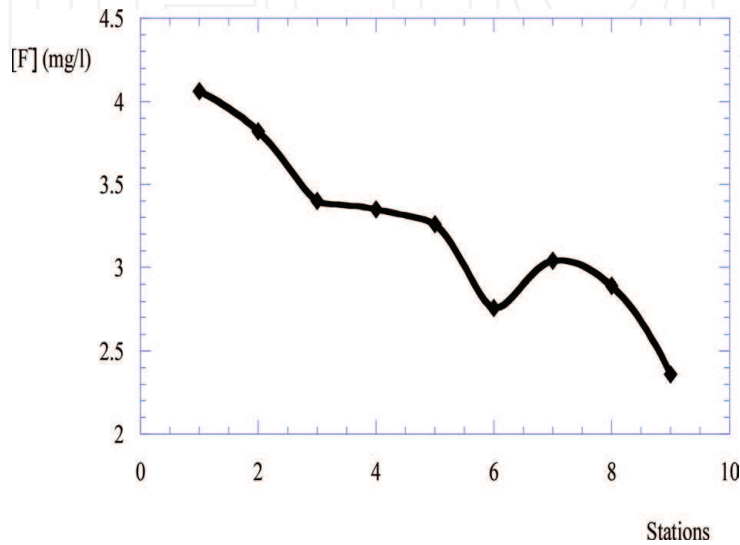


Figure 6.
Evolution of fluorides concentration along the mine water channel.

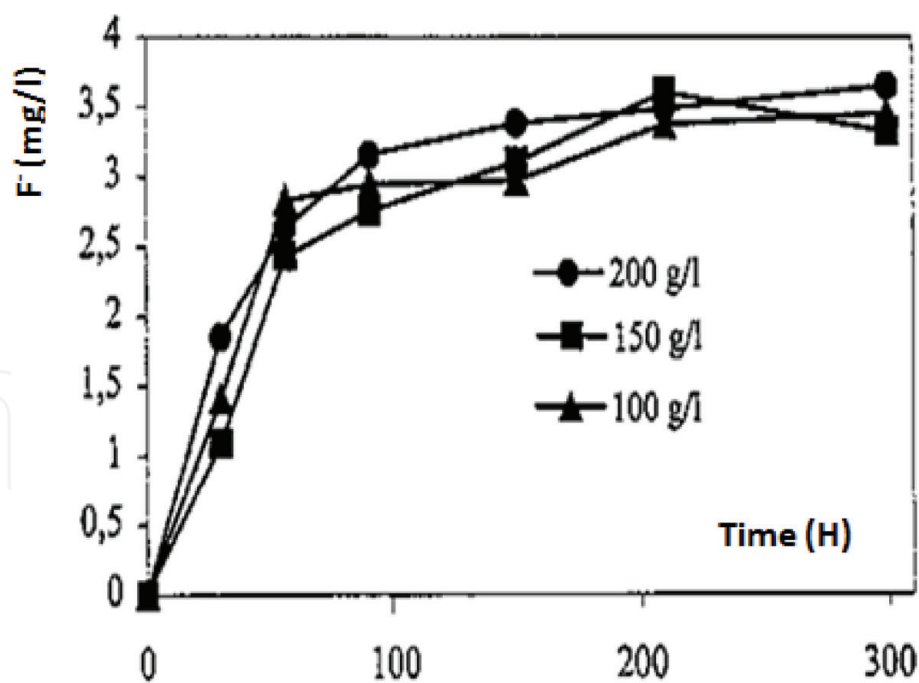


Figure 7.
Releasing fluorides as a function of time to different masses of black phosphate.

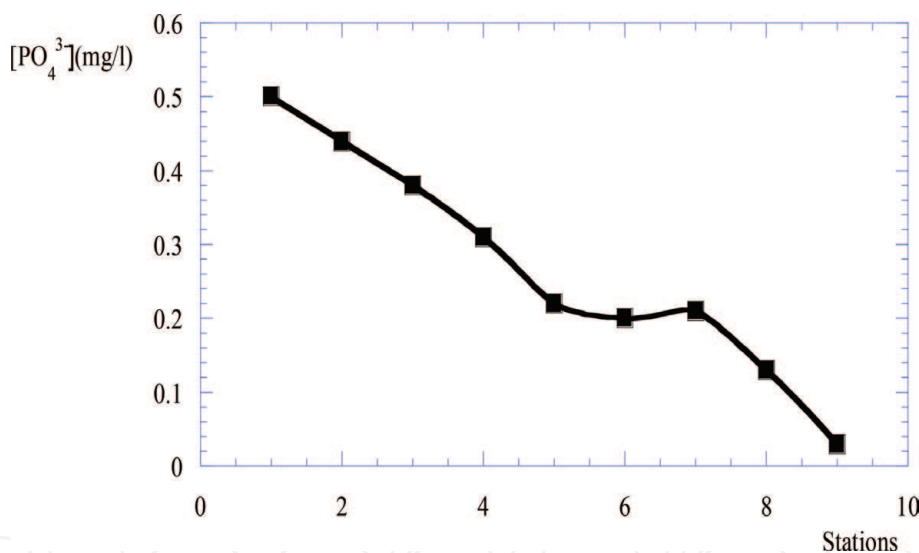


Figure 8.
Evolution of orthophosphates along the canal.

5.1.2.2.1 Relationship between the evolution of concentration of fluorides, magnesium, and orthophosphates concentration

A correlation is made between fluoride (F^-) and orthophosphate (PO_4^{3-}) contents (**Figure 10**) and between fluoride (F^-) and magnesium (Mg^{2+}) (**Figure 11**). The results showed that these three elements decrease in the same way since the correlations is linear. So, they undergo the same phenomenon along the channel, and this can be explained by the precipitation of $Mg_{5-x}Ca_x(PO_4)_3F, OH$, which is insoluble in water.

5.1.2.3 Calcium

For calcium, the acceptable limit set by WHO is 75 mg/l. In the study area, mine waters have significant calcium contents, that continue to increase away from station 9 (S9), from station 2 (S2), toward the mixture of the three recipes R7, R8 and

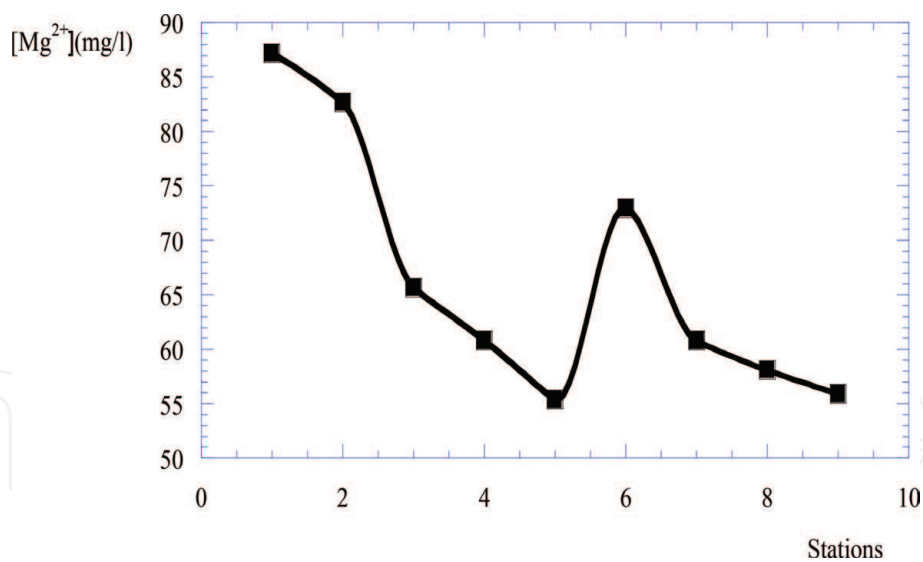


Figure 9.
Evolution of magnesium along the canal.

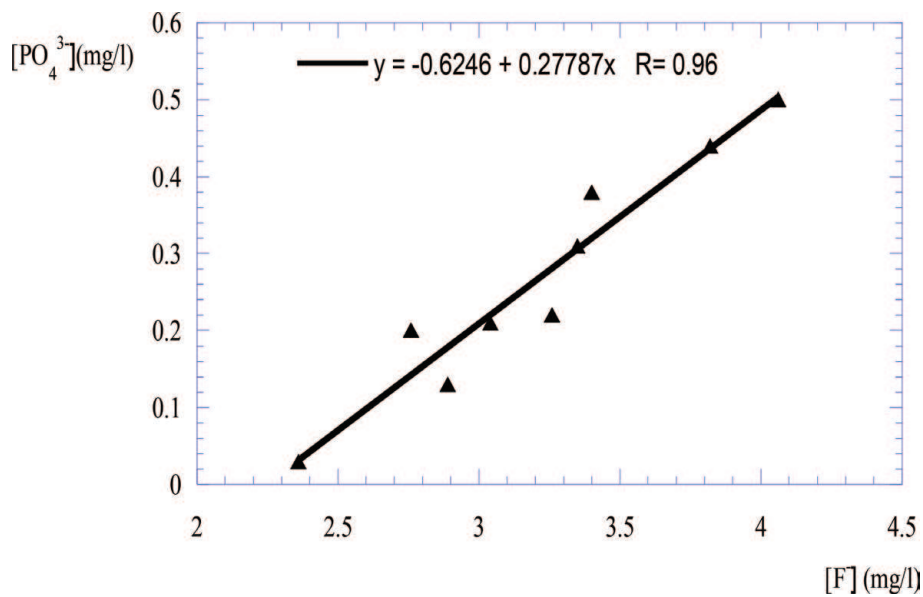


Figure 10.
Relationship between the evolution of concentration of fluorides and orthophosphates.

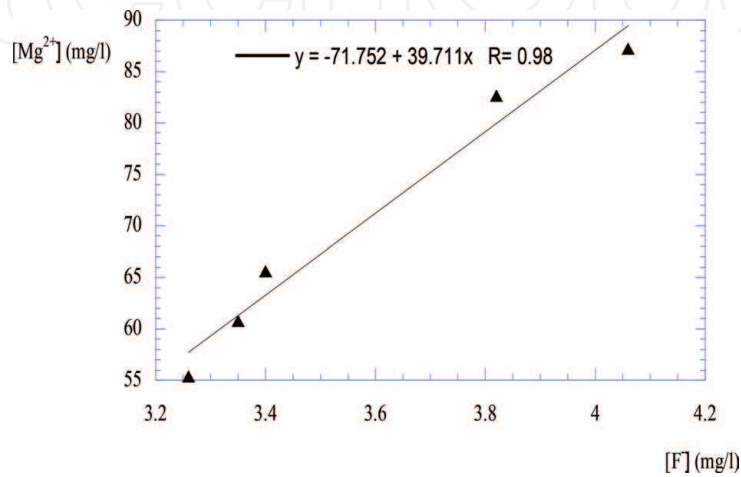


Figure 11.
Relationship between the evolution of concentration of fluoride and magnesium.

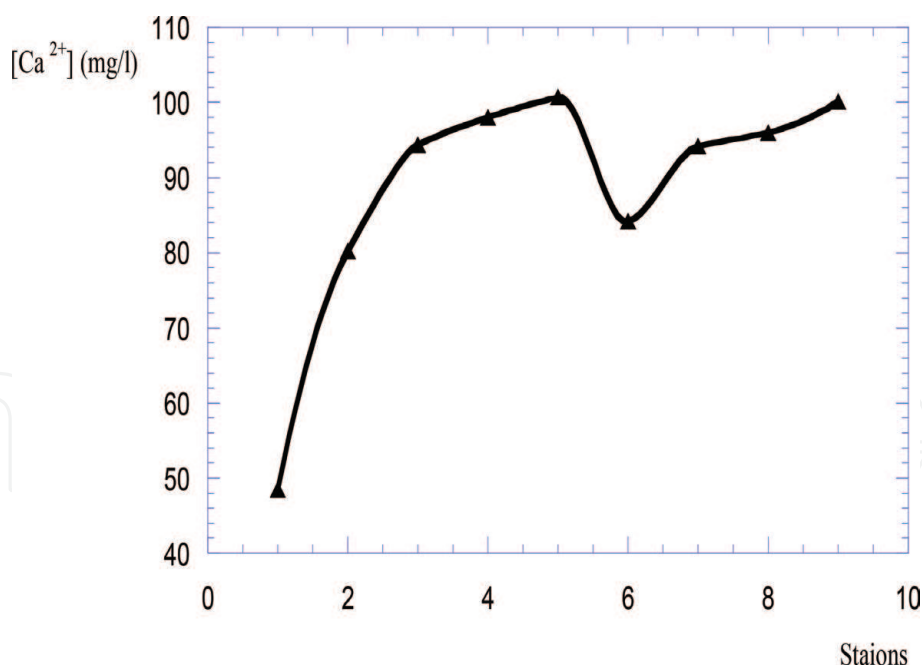


Figure 12.
 Evolution of calcium levels along the canal.

R9 (**Figure 12**). These levels are higher than the standard published by WHO. The low value of Calcium in station 6 (S6) is due to the fact that the dewatering water of recipe 7 (R7) is not very well concentrated in this element.

5.1.3 Impact of the phosphatic layer on the groundwater

In order to study the impact of the phosphatic layers on the water table, we sampled two wells (stations 10 and 11) located near the dewatering channel.

To better interpret the results, we have drawn figures that represent the concentration of the element considered in stations 5, 6, and 7 and we compared them with that of stations 10 and 11 to better make a comparison between dewatering water of recipe 9 before mixing (station 5), water of recette 7 and 8 (station 6), the mixture of the three recipes “recette” (station 7), and the well waters (stations 10 and 11). The results are as follows.

The results of the physicochemical analyzes carried out on the water of the well in question showed that these waters are contaminated by several elements, which influences their conductivity (CE) and the hardness (TH) (**Figures 13 and 14**). We can therefore conclude that the phosphatic layer influences the wells (S10 and S11), since the black phosphatic minewater has concentrations with a much higher hardness ($135 < [\text{TH}] < 175 \text{ mg/l}$), this is due may be leaching phosphatic soils. The same remark is noted for conductivity.

5.1.3.1 Fluoride concentration

Figure 15 shows that the well waters (S10 and S11) are contaminated with fluoride; the concentration of fluoride concentration $[\text{F}^- (\text{S}_{10}) = 1.51$ and $[\text{F}^- (\text{S}_{11}) = 1.63]$ is greater than the limit set by the WHO of 1.5 mg/l, which is in good agreement with previous results obtained by Mr. Mountadar and his collaborators [20] in a study of Khouribga well waters have shown that these waters are contaminated with fluoride $[(\text{F}^-) > 1.5 \text{ mg/l}]$, and also by Hassani et al. [19], who showed that the well waters in the vicinity of the Youssoufia calcination units have fluoride

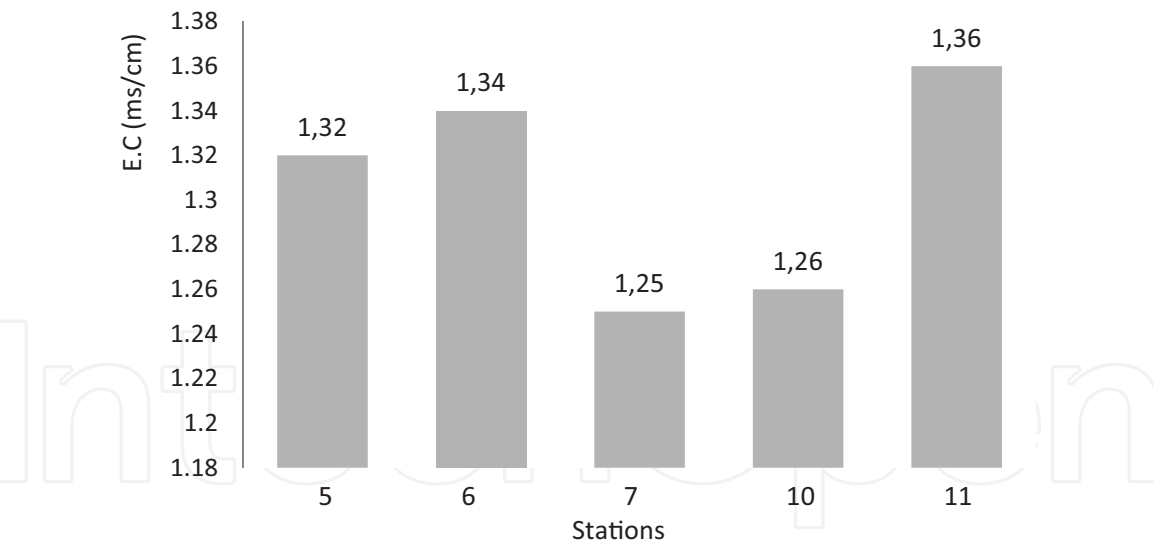


Figure 13.
Comparison between the conductivity of the waters along the canal and that of neighboring wells.

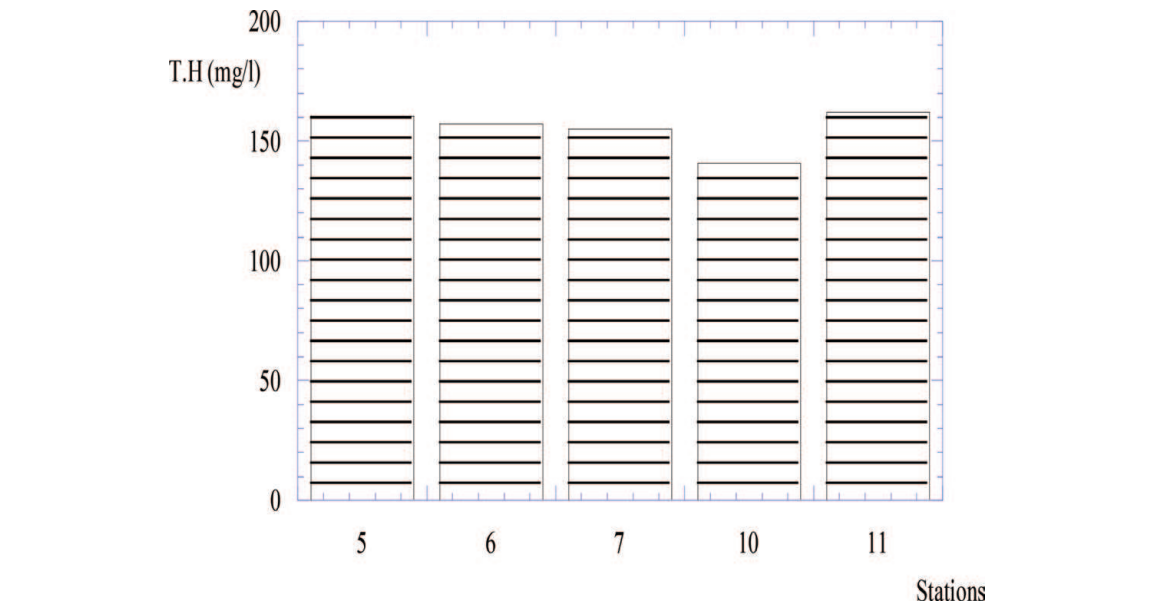


Figure 14.
Evolution of hardness in the study area.

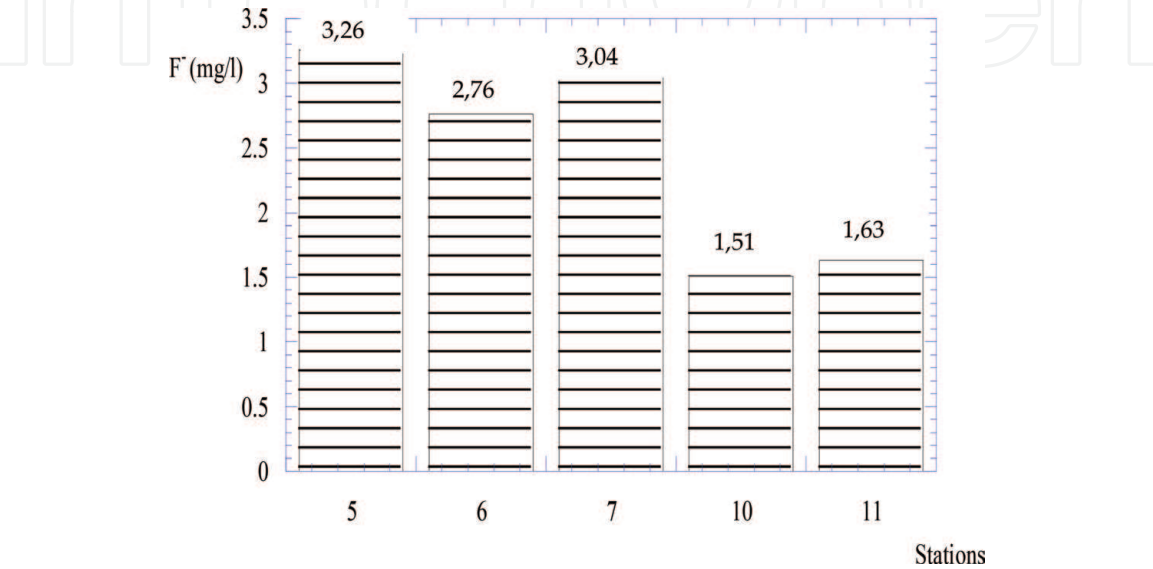


Figure 15.
Comparison between fluoride levels in mine water and neighboring wells.

concentrations between 1.5 and 2.8 mg/l. The consumption of such fluoride-laden water has negative health effects: dental fluorosis and skeletal disorders [3].

For the other elements, it can be said that they are comparable to those obtained for Youssoufia mine water and they do not exceed the standards set by the World Health Organization (WHO).

6. Conclusion

At the end of this analytical part, it is obvious to conclude that:

- Youssoufia mine water contains high concentrations of fluorides of the order of 3–4 mg/l on average; this is due to the fact that the black phosphate of Youssoufia contains 3–4% of F^- . This abnormal fluoride content is due to the fact that leaching of the black phosphate from this region contains 3–4% of F^- [3]. This was well verified in the study conducted by Garmes [2] on the monitoring of the release of fluoride ions by black phosphates, which shows that they release between 3 and 3.5 mg/l of F^- for a stirring time greater than 100 h up to 300 h for the different masses used. This quantity of fluorides released by black phosphate is greater than that released by white phosphate [20].
- The ions (F^-), (Mg^{2+}), and (PO_4^{3--}) are eliminated in the same way along the dewatering channel. This is probably due to the precipitation of magnesium orthophosphates.
- The waters of the wells near the canal are contaminated by fluoride ($F^- \rightarrow 1.5$ mg/l), and the same result was observed by Hassani and his collaborators [24] in a study made on wells located in the vicinity of the Youssoufia calcination units, which showed that these wells have F^- concentrations of between 1.5 and 2.8 mg/l. Indeed, a number of residents reside in Youssoufia suffer from fluorosis. Therefore, there is a permanent risk for the population using the groundwater near the phosphate mining plants in Youssoufia. In addition, Fandi [3] noted during a study (questionnaire) carried out on the inhabitants of the city of Youssoufia that:
 1. Caries is the most common dental disease and is more prevalent in urban than in rural areas, meaning that the diet consumed in cities can also affect the condition of the teeth.
 2. With regard to the state of the teeth, people from rural areas seem to be the most affected; in fact 36% of these subjects have a form of hyperplastic tooth compared to 9.67% of urban people, 45.33 and 49.33% of rural people, respectively, have yellow and rusty pigmentation against 40.32 and 38.71%, respectively, for urban people.
 3. For bone disorders, they are present in 61.3% in urban areas while this figure reaches 77.33% in rural areas.

We, therefore, note the main health problem resulting from the possibility of using mine water as drinking water where irrigation resides in the clinical manifestation of mottled enamel called “Darmous” in Morocco and “Disease of the factories.” In France [3, 8], this causes psychological problems for thousands of people residing in the phosphate zones.

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