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Assessment of potential contamination of groundwater in abandoned mining region of Ben Taieb, Northeastern Morocco using statistical studies

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Abstract---The objective of the study is to raise awareness of the effect of anthropogenic activity on groundwater in the urban area, water samples were collected from 12 wells in the area in April and September 2019. From these samples, pH and conductivity were determined using a pH meter/conductivity meter. From these samples, pH and conductivity were determined using a pH meter/conductivity meter, while heavy metal concentrations (Mn, Fe, Pb, Cu and AL) were determined by atomic analysis and ICP-MS. The study showed that groundwater in the study area is ($0.01\text{mg/l} < \text{Mn}^{2+} < 0.06 \text{ mg/l}$) and contains ($0.14\text{mg/l} < \text{Cu}^{2+} < 0.03 \text{ mg/l}$), ($0.02\text{mg/l} < \text{Fe}^{2+} < 0.4 \text{ mg/l}$), ($0.02\text{mg/l} < \text{Zn}^{2+} < 1.8\text{mg/l}$) and ($0.01\text{mg/l} < \text{AL}^{3+} < 0.05\text{mg/l}$). These concentrations are above the permissible limits recommended by the World Health Organization (0.05, 0.2, 0.3, 5 and 0.2 mg/l, respectively; $p > 0.05$). Bacteriological analyses show that the vast majority of the wells studied in the Ben Taib area harbour high densities of Faecal coliform (0 to more than 420 CFU/100ml) and Fecal Streptococci (0 to over 25 CFU/100ml). The presence of these high quantities of pathogens, which are indicators of pollution and bacteriological contamination by wastewater, could be due to anthropic activities.

Keywords---groundwater, ICP-MS, landfill, heavy metal contamination.

Introduction

Groundwater, which is located in permeable geological formations named aquifers, is a valuable renewable resource. In India, groundwater is a precious resource for agriculture and mining, and it is mostly utilized as drinking water (Pande et al. 2020; Sharma, Tripathi, and Chandra 2020). The study of environmental contamination by discharges containing heavy minerals (Baize 1997) have shown that the increase in concentrations of heavy metal contamination is mainly generated by anthropogenic activity. It is true that mining activity (Su 2014), through the processes of ore extraction, milling usually in the open air (dust) and discharge of liquid and solid tailings, necessarily leads

to the contamination of the surrounding environment by its tailings, dust and untreated water that is discharged into nature.(El-Fadeli et al. 2015; Falck 2015; Edraki et al. 2014; Candeias et al. 2018; Gueddari Hicham et al. 2021).

This article is the first to investigate the deterioration of water resources caused by the region's lithology, mining tailings, and, in particular, the discharge of wastewater caused mostly by the town of Ben Taib's autonomous sanitation. Microbiological testing was used to determine the influence of wastewater on groundwater quality and public health. Precipitation, which is a transit factor for pollutants from mining waste, is irregular in the study region(Van Lam, Van Hoan, and Duc Nhan 2019). The influx of wastewater from village activities, on the other hand, is constant and might be the primary source of contamination from the abandoned M'hajer mine.

Material and Methods

Study area

The Ben Taieb commune is located in the Driouch province's northwest region, at an altitude of 250 to 400 m. Several rivers flow through the area, such as the Oued Aghbal and the Oued Ouchane (Fig.1).The areas are located at the level of quaternary alluvium, within which at least three in which at least three levels of alluvial terraces can be identified: Late Quaternary, Amirian, Tensiftian-Presosoltanian, and Rhabian-Soltanian (Barathon, Delibrias, and Weisrock 1988). In the northern and north-western parts of the areas, there are lenses of calcareous Cretaceous calcareous shales. The north-eastern part of the area is marked by the presence of lenses of red silts dating from the Villafranchian period(Carlier 1973). Finally, to the west and north of the areas, there are scree and slope deposits.The slopes are low overall and moderate to the north of the areas, in contact with the gentle landforms. There does not appear to be a particularly dominant slope process.

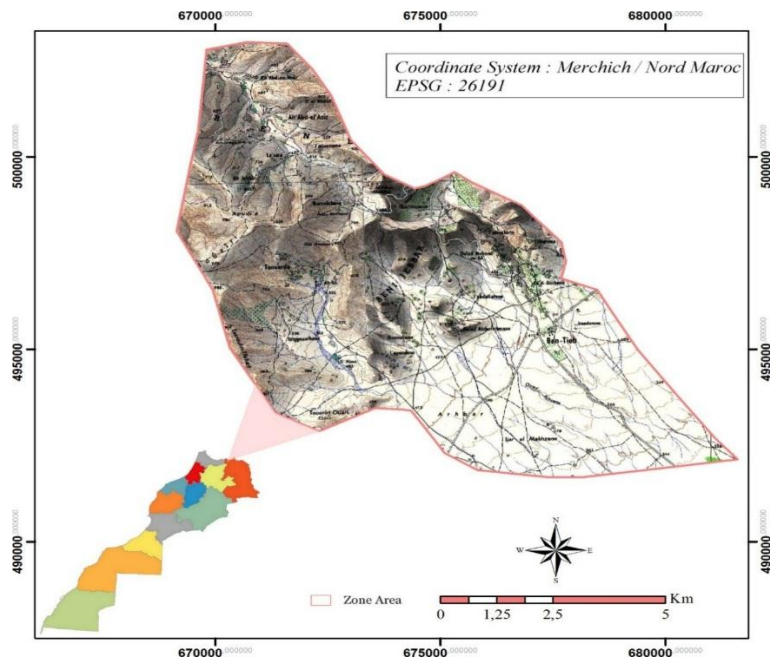


Figure 1. Location of the study area.

Bacteriological analyses

Total coliforms, faecal coliforms, and faecal streptococcus were the germs we were looking for in the waters of the eight sites studied. These measures are used to evaluate the quality of drinking water. The membrane filter method was used to search for bacteria in the water examined, and it conformed to "AFNOR" criteria. (Rodier, J, Bernard LEGUBE 2009). All water samples were promptly chilled to 4°C in a portable cooler and transported to the laboratory. The protocols used to conduct the chemical analysis of the main ions are as follows: (Yahya et al. 2017; Zouhri et al. 2019):

- Bacteriological analysis was carried out in the laboratory immediately in the following sample. The results are presented as the number of colonies per unit of volume. The investigation includes the following elements Total Coliforms (TC), Fecal Coliforms (FC), and Fecal Streptococci (FS) according to ISO 9308-1, ISO 9308-1 and ISO 7899-2 respectively;
- Enumeration of total coliform bacteria per 100 cm³, using membrane filtration (0.45 µm) and culture on Tergitol TTC 7 Agar 24 h at 37°C ;
- Faecal coliform bacteria count per 100 cm³, using membrane filtration (0.45 µm) and culture on Tergitol Agar TTC 7 Agar 24 h at 44°C;
- Enumeration of faecal streptococcal bacteria per 100 cm³, using membrane filtration (0.45 µm) and culture on Slanetz Bartley Agar 24-48 h at 37°C.

Physical and chemical analyses

For each sample, certain measurements were taken in situ to be able to quantitatively determine the parameters that change after sampling; such as temperature (T (°C)), hydrogen potential (pH), electrical conductivity (Cond

($\mu\text{S}/\text{cm}$), and dissolved oxygen (O₂d). We performed these measurements using a MULTI 350I portable multi-parameter meter. -The other parameters were measured in the laboratory according to the analysis methods recommended by (Rodier, J, Bernard LEGUBE 2009):

- The determinations are carried out by Flame Atomic Absorption Spectrometry (Varian Model 475-AA) is a method that essentially allows the determination of metals in solution, we used it as a method of identification and quantification of 4 metals (Zn, Mn, Fe, Cu).
- The determinations are carried out by mass spectrometry with inductively coupled plasma ICP-MS according to the ISO17294-2:2016 standard, used for the determination of trace elements (Hg, AL, Cd, Cr, Br, Ni, Pb).

Discussion

Microbiological quality of analysed waters

Ben Taieb's aquifers are more contaminated with faecal coliforms and faecal streptococci (Fig.1). The existence of extremely high levels of pathogenic germs, which are indicators of wastewater pollution and microbiological contamination, clearly indicates the negative impact of human activities and insufficient waste management on the quality of groundwater utilized in the region. The measurement of total coliforms provides information on a well's potential sensitivity to surface contamination. Thus, it is possible to hypothesize that the contamination rate is particularly high during wet seasons, but the total coliform rate is high during dry periods. Observations show that a high EC/SF ratio (>4) can be considered as a good indication of man-made pollution (Yahya et al. 2017; Singh 2017; G Hicham et al. 2021).

- Coliforms in total (TC): TC was detected in almost all of the tested wells and springs. Their amounts varied between wells and water springs and were affected by the sample time, whether wet or dry. During the dry period, we found that the rate of TC rose. TC values vary from 475 to 2000 CFU/100 mL in June during the monsoon season of 2019, and from 420 to 1150 CFU/100 mL in November during the dry period of the same year (Fig.A;C-2).
Faecal coliforms (FC):FC is an indication of faecal pollution and can be found in virtually all wells and springs that have been sampled. Their rates were higher during the dry period, and their amounts were often lower when compared to the TC. During the rainy season, FC levels varied from 0 to 420 CFU/100 mL in June, whereas during the dry season, FC values ranged from 0 to 310 CFU/100 mL in November (Fig.B;C-2).
- Faecal streptococci (FS): FS are indicators of faecal contamination and are present in almost all wells and water springs, but generally with smaller rates than FC. In the wet period, FS values ranged between zero to 25 CFU/100 mL. In the dry period, the FS values varied between zero to 15 CFU/100 mL in November (Fig.D;C-2).

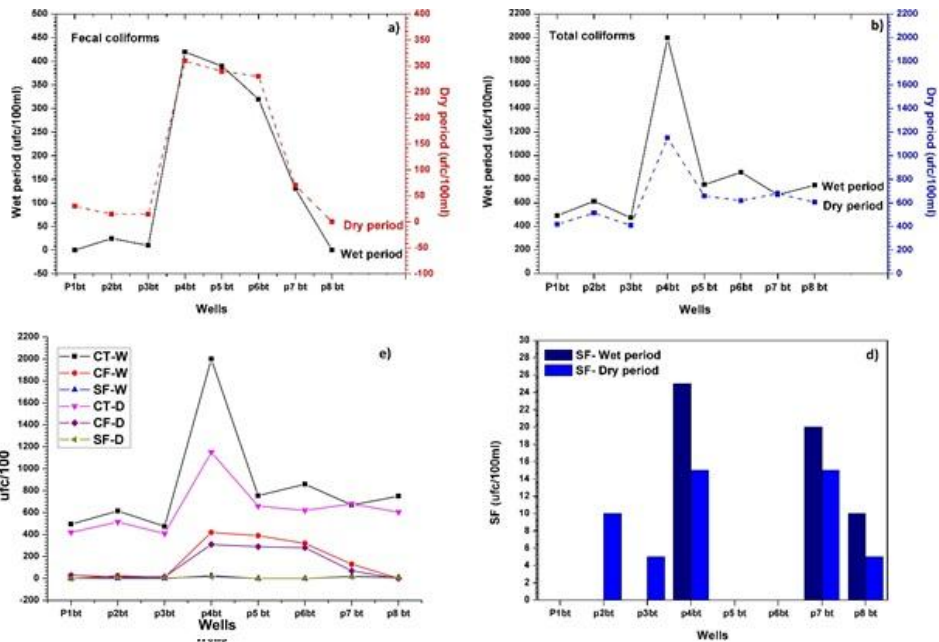


Figure 2. Graphic variation of Bacteria in the Ben Taieb water table (Wet period): A-fecal Coliforms, B-Total Coliforms, C-Comparison of all bacteria, D-Fecal Streptococci

Physicochemical quality of analysed waters

The results of the studies of the twelve water samples are given in graphs that illustrate the spatial distribution of the various elements investigated. While cadmium and mercury are nearly absent in all samples, a similar result was found for the Nekor basin (Ghalit et al. 2017), the other elements are present in various amounts (Table.1).

Table 1
Descriptive statistics of metal elements Variable

Variable (mg/l)	Mean	Minimum	Maximum	WHO Standard (Edition 2011)
Lead	0.0015	0.001	0.0025	0.01
Magnesium	0.034	0.01	0.06	0.05
Nickel	0.018	0.002	0.05	0.02
Copper	0.072	0.03	0.14	0.2
Zinc	0.4	0.02	1.8	5
Chromium	0.02	0.0005	0.054	0.05
Iron	0.146	0.02	0.4	0.3
Aluminum	0.026	0.01	0.05	0.2
Brome	0.035	0.02	0.05	-

The research revealed that the various metal concentrations of Zn, Cu, Cd, Pb, Ni, Br, and Al in the abandoned mine wells are within the WHO recommended limits, excluding iron, which has a concentration range of 0.110 - 0.4 mg/l, which exceeds the WHO permissible value of 0.3 mg/l, indicating that all three wells are contaminated (Fig.3). The majority of the samples examined had manganese concentrations below 0.05 mg/L (Fig.3), which corresponds to the WHO standard (Edition 2011). Except for one sampling point, the manganese levels in the wells were around 0.05 mg/L. This is considered above the recommended standards.

Groundwater, which is considered the purest form of drinking water as compared to surface water (Offodile 2014), has a higher concentration of iron than water from the abandoned mine, which would be expected to have higher values due to the mining activity that has occurred in the area(Luzati et al. 2016). This high concentration of iron in groundwater can be attributed to the leaching of common fractures generated by geology and lead-zinc mineralization (Leach et al. 2001; Velasco et al. 2003), with which iron was commonly associated. The leaked metal slowly percolates through the earth's strata, reaching and polluting the groundwater(Zhang et al. 2020).

In addition, iron, which occurs naturally in the earth's crust, is adsorbed. In the earth's crust it is adsorbed to oxide minerals; adsorbed to clay mineral surfaces(Truche et al. 2018); associated with sulphide minerals or organic carbon and these clay minerals are ubiquitous in the study area(D. Liu et al. 2019; Zhang et al. 2020).The mineralization was determined to be an iron oxide (Fe₂O₃) containing 35% iron in M'hajer (Table.2), a deposit that had been recognized since the Spanish colonization's inception. The tests conducted by the Spanish organization (Usit Color) have resulted in the following Mineralization conclusions: iron oxyde (Hematite and Oligiste)(Knouz et al. 2016). Natural dissolution or desorption of iron from these source materials can introduce iron into groundwaterthe iron and manganese content of groundwater in Ben taib is affected by several major factors, particularly Fe- and Mn-based chemicals and organic matter deposited all through the Holocene(Lenstra et al. 2020; Zawierucha, Kozłowski, and Malina 2016; W. Liu et al. 2021). During the field study, it was discovered that once colourless groundwater is collected from the wells, it will become red or yellow after a brief period of contact with air. This implies that the groundwater is depleted (Carretero and Kruse 2015).A microbially driven redox mechanism mediated by organic matter can result in Fe, Mn mobilisation in groundwater (Neidhardt et al. 2014;Hem 1985). Under these conditions, iron and manganese from soiland aquifers will be discharged into groundwater(Palmucci, Rusi, and Di Curzio 2016).

Table 2

Levels of chemical components of Hematite mineral in M'hajer Mine(Knouz et al. 2016)

Chemical components	Levels %
Fe	36.46
Zr	0.0178
Sr	0.0061
Pb	0.0393

As	0.0086
Zn	0.0143
W	0.0072
Co	0.2838
Mn	0.0758
Mo	0.0011

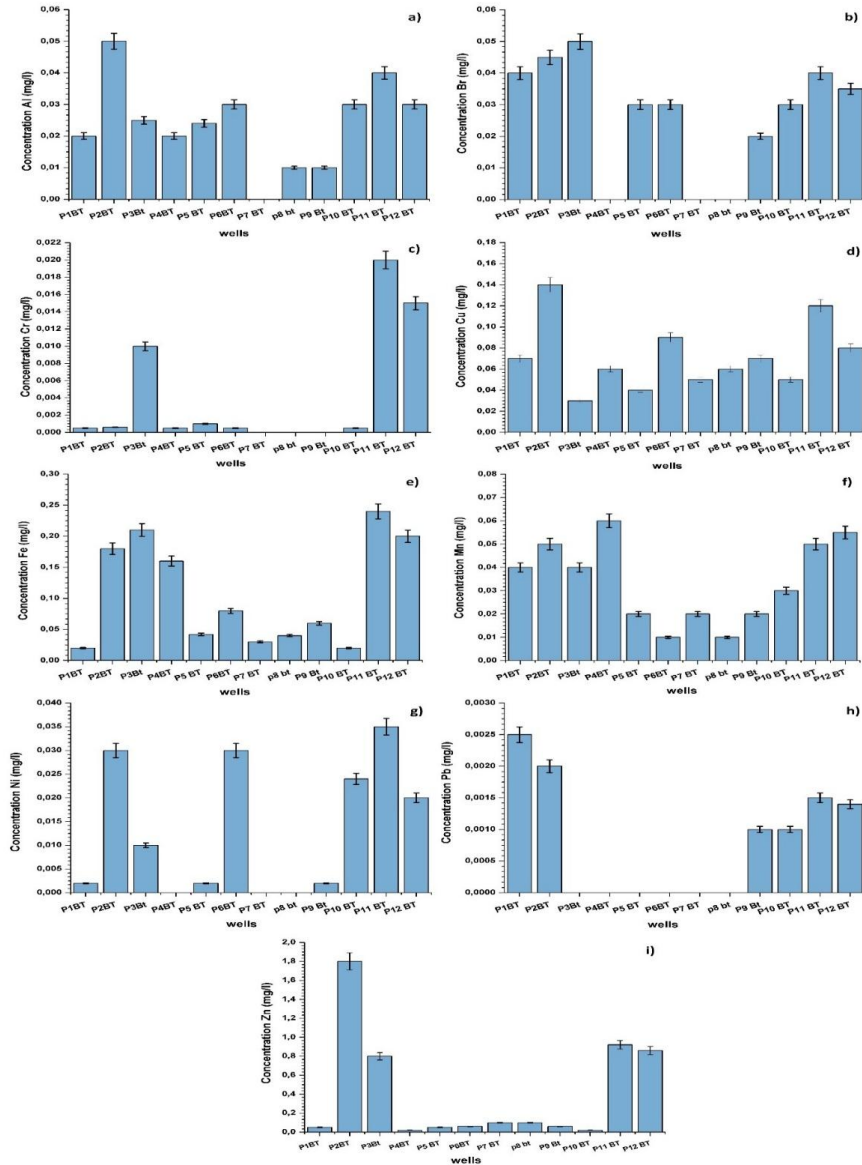



Figure 3. Graphic variation of the distribution of chemical parameters in Ben Taieb aquifer during the high-water period: A-Aluminum, B-Brome, C-Chromium, D-Copper, E-Iron, F-Manganese, G-Nickel, H-Lead, I-Zinc

Statistical studies

The physicochemical data are analyzed statistically employing Principal Component Analysis (PCA) on a table of 13 variables (Pb, Cu, Al, Fe, Zn, Cr, Cd, and Ni Electrical conductivity (Cond), PH, O2d, and T) and 42 people (wells and sources). The correlation matrix (table 1) of the various parameters investigated indicated a tight link between TDS and electrical conductivity on one side, and zinc with chromium, copper, and aluminium on the other. The correlation coefficients show this link. The major linkages are most likely due to the elements' shared origins. In our research, we used a statistical technique known as multivariate Principal Component Analysis (PCA). This is a quantitative and impartial approach for classifying groundwatersamples based on their geochemical characteristics.

Table 3
Correlation between variables and factors

	ZN	CU	CR	PB	AL	FE	Mn	Br	NI
ZN	1	0.68	0.48	-0.2	0.3	0.74	0.56	0.59	0.59
CU	0.68	1	0.27		0.42	0.45	0.35	0.33	0.7
CR	0.48	0.27	1	-0.17	0.63	0.77	0.51	0.45	0.48
PB	-0.2		-0.17	1		-0.33	0.11	0.23	-0.25
AL	0.3	0.42	0.63		1	0.51	0.43	0.59	0.8
FE	0.74	0.45	0.77	-0.33	0.51	1	0.73	0.44	0.5
Mn	0.56	0.35	0.51	0.11	0.43	0.73	1	0.34	0.26
Br	0.59	0.33	0.45	0.23	0.59	0.44	0.34	1	0.59
NI	0.59	0.7	0.48	-0.25	0.8	0.5	0.26	0.59	1



The factorial plane (1x2) projection of the variables reveals that 51.86 per cent of the total variance is represented (Fig.4). T, Electrical conductivity Pb, Cu, Al, Fe, Zn, Cr, Cd, and Ni are grouped in the positive pole while PH is grouped in the negative pole on the factor 1 axis, which accounts for 51.86 per cent of the total variation (Table 3, Fig.4). As a result, the factor 1 axis may be thought of as an axis that characterizes groundwater mineralization in the research region. The

analysis of individual projections on the factorial plane F1 reveals that the measurement points may be split into two groups:

- Group 1: Factor I accounts for 12.8 per cent of the variation and is governed by Mn, Fe, Cr, Zn. linked to minerals (FeCr₂O₄, PbCrO₄, FeS₂ and Fe₂O₃). These locations are on the positive side of axis 1.
- Group 2 comprises of the three individuals: - Factor II is responsible for 51.86 per cent of the variance; it has been shown that the most mineralized sites are AL, Cu, Br, and Ni linked to minerals (Al₂MgO₄ and Al₂O₃). Besides that, correlation explains pollution indices for agricultural and domestic activities. These locations are on the axis's negative side.

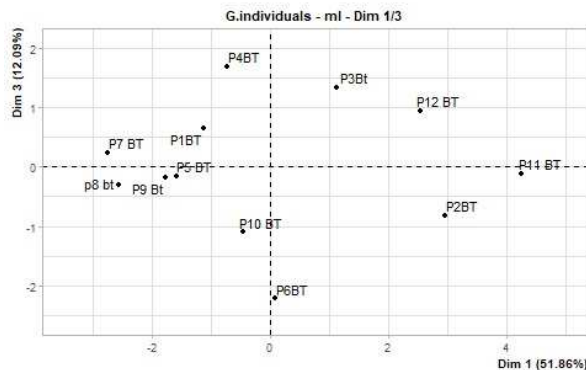
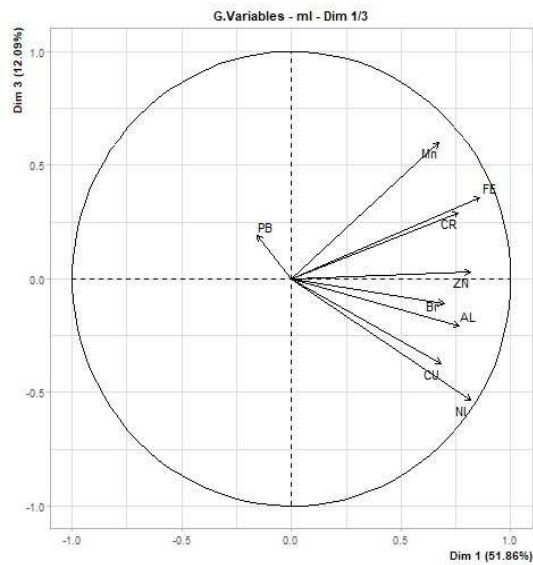


Figure 4. Main components analysis circle

Conclusion

The results of the physicochemical and bacteriological tests led us to the assumption that the contamination of the well water analyzed is widespread. In reality, the water under investigation contains characteristics that make it unfit for human consumption. This is mostly due to the following factors: This is mostly related to electrical conductivity, hardness, nitrates, nitrites, ammonium, trace metals (Fe, Mn, and Al), total germs, and total coliforms. Animal faeces and livestock effluents are the sources of pollution at the microbiological level. In terms of faecal coliforms and faecal streptococci, it appears that contamination is consistent. It is thus strongly advised that polluted wells be cleaned as soon as possible to protect groundwater, particularly at depth, from probable contamination spread. When compared to the literature measuring groundwater quality on a national and continental scale, it was discovered that the water from the wells in the Ben Taib region did not significantly surpass Moroccan or worldwide criteria. Certain precautions must, however, be taken to restrict the sources of contamination. In the future, not only will it be required to analyze the health concerns connected with the amount of pollution in these waters.

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