

# ENVIRONMENTAL ASSESSMENT OF POLLUTION IN AN INDUSTRIAL ENVIRONMENT USING HEAVY METAL POLLUTION INDICES AND STABLE ISOTOPES, CASE STUDY OF THE INDUSTRIAL ZONE OF SIKKDA, NORTH-EAST ALGERIA

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**Abstract:**An environmental assessment study was conducted in the industrial area of Skikda in the Northeast of Algeria which involved physicochemical parameters, heavy metal concentrations, and stable isotopes of surface water, groundwater, and soil. The results revealed high concentrations of Cd, Ni, Fe, Cu, As, Cr, Pb, Co, and Mn in groundwater. The southern part exhibited the lowest heavy metal concentrations, while the industrial zone in the North contained the highest levels. Therefore, the industrial area showed significant pollution in groundwater by Cr, Pb, and As with respectively 0.5, 0.69, and 0.44 mg/l, surpassing the respective WHO (World Health Organization) standards of 0.05, 0.01, and 0.01 mg/l. Spatial analysis showed that the industrial area presents higher concentrations of As, Cr, Cd, Pb, Cu, Zn, Ni, and Fe which demonstrated similar trends in spatial distribution, their concentrations increasing within the industrial zone. However, the western part had no significant pollution sources except for a public landfill and SONATRACH industrial complex, high concentrations of Co and Mn in the south and the west parts were observed. Mean concentration in soils indicated that Cd is ranged between 35.32 to 95.12 ppm, for Fe between 145.1 and 702 ppm, As varies between 1.03 and 81.85 ppm, and Zn between 50 and 520.32 ppm and considered as dominant metals. However, Mn, Co and Cr were lower respectively with 1.97, 12.11 and 7.25 ppm. Cd and As were most influenced by the polluting companies, while Cr was mainly influenced by natural factors, such as pH and soil type. Based on the contamination degree index, the soil pollution levels of Cd, Pb, and As were classified as extremely contaminated. The statistical analysis indicated substantial anthropogenic contributions to groundwater contamination concentrated in the industrial area. The groundwater exhibits a range of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values, varying from 2.45 to -5.33‰ and 19.82 to -1.67‰ vs. the V-SMOW (Vienna-Standard Mean Ocean Water) standard, respectively. The mean isotopic composition is -2.50‰ for  $\delta^{18}\text{O}$ , -19.32‰ for  $\delta^2\text{H}$ , with a mean deuterium excess of 6.45. These values align with the Meteoric Water Line observed in the western Mediterranean region. It indicates a hydrological connection between recharge and groundwater which suggests a significant interaction between groundwater and surface water. Due to their proximity to the river and the shallow aquifer, the downstream area is more vulnerable to surface pollution. Furthermore, the young groundwater in the downstream can be attributed to the rapid recharge and replenishment of the aquifer caused by rainfall and quick infiltration and sustained by the shallow aquifer depth and sandy soil. Consequently, the rainwater and industrial wastes lead to faster pollutant infiltration. Anthropogenic sources, including industrial effluents from smelting, refining, manufacturing, steel and textile industries, electroplating, nickel-cadmium battery production, welding, PVC product and paint pigment manufacturing, were identified as major contributors to heavy metal pollution.

**Keywords:** Water pollution, multivariate statistics, stable isotopes, contamination index, Skikda, Algeria.

## 1. INTRODUCTION

Metal pollution has a negative impact on the

ecosystem due to its toxic, non-biodegradable, and properties it accumulates rapidly in the soil, water and sediment (Kumar et al., 2020), which can have

detrimental effects. Numerous natural processes, including rock weathering and the erosion of bedrock, along with anthropogenic endeavors such as mining, industrialization, and the production of pesticides, collectively play a role in the build-up of heavy metals within surface and subsurface water sources (Liu et al., 2022; Rezaei et al., 2019; Suvarapu & Baek 2017). Sediments and plants can serve as mutually reinforcing markers for contamination. Sediments typically represent the final repository of pollutants in both aquatic and terrestrial ecosystems, providing insight into the gradual accumulation of contaminants over time (Dhaouadi et al., 2023). Simply estimating the total amount of heavy metals present is insufficient for assessing their contamination and toxicity levels in the surrounding environment. Further research and analysis are necessary to accurately determine the extent of their presence and potential harm (Wagh et al., 2018).

The study of environmental contamination caused by urban and various researchers have extensively discussed industrial wastewater containing heavy metals. (Rahman et al., 2020; Samia et al., 2013) have attributed the increase in heavy metal pollution primarily to human activities. Conversely, the continuous monitoring and assessment of groundwater and surface water face significant challenges due to pollution, over exploitation, and the degradation of heavy metals (HMs). HMs are prevalent environmental pollutants due to their toxic properties, persistence, and tendency to accumulate in living organisms (Ugwanga & Kgabi 2021).

Groundwater contains HMs in colloidal, particulate, and dissolved forms, with potential natural sources being weathered rocks and leaching of volcanic remnants. Anthropogenic sources of HM contamination include improper solid waste disposal, as well as the discharge of domestic and industrial effluents. The contamination of soil with heavy metals from industrial activities is on the rise. Heavy metals in soil exhibit high mobility, toxicity, and resistance to degradation, making them easily absorbed by crops during growth. As a result, heavy metals have a pronounced impact on both crop productivity and the caliber of crops, concurrently posing threats to human well-being along the food chain, (Saleem et al., 2015; Singh & Kumar 2017).

Industries located in close proximity contribute to higher levels of pollution from sewage, exhaust emissions, and waste discharged into the surrounding soil, which eventually reaches rivers and the atmosphere. Therefore, hydro-chemical assessment plays a crucial role in evaluating groundwater quality when used for irrigation purposes (Dinesh Kumar et al., 2014).

Several studies have been conducted to investigate the condition of groundwater and surface water, as well as the sources of pollution influenced by both natural and human-induced processes (Mehdi et al., 2011; Mohamadi et al., 2021; Rezaei et al., 2019). Groundwater metals studies commonly utilize pollution indices as an approach to assess water quality. Pollution indices are valuable tools for water quality professionals, environmental managers, and decision makers as they condense the various parameters into a single numerical value. When studying heavy metals, pollutants are typically monitored by comparing their concentrations with the recommended allowable levels set by water standards. By determining the pollutant concentrations, different pollution indices can be developed. Several water quality indices and their corresponding methodologies have been introduced for the purpose of evaluating water quality. In the context of assessing groundwater pollution in Skikda city, specifically concerning nine significant heavy metals (As, Cr, Cu, Fe, Mn, Ni, Pb, Co and Zn) a series of heavy metal pollution indices, namely HPI (Heavy Metal Pollution Index), HEI (Heavy Metal Evaluation Index), Cdeg (Degree of Contamination), and m-HPI (Modified Heavy Metal Pollution Index), were employed. This evaluation was conducted based on research conducted by Chaturvedi et al., (2018), Prasad & Mondal (2008) and Rajkumar et al., (2019).

The objective of this research is to: i) Identify the local distribution of major heavy metals and assess the various types of HPI applications in water and soil and sediment in order to gain a global perspective; ii) use statistical tools such as the application of linear correlation and multivariate statistical analysis utilized in order to categorize and analyze groundwater, surface water, and soil and aiming to identify the key factors that influence their chemical composition; iii) use the isotopic methods particularly suitable and often effective to elucidate the hydrological cycle and its impact on the pollutant dispersion in the studied area, it was carried out from the data values of stable water isotopes ( $^{18}\text{O}$  and  $^2\text{H}$ ) taken in the dry period of the year 2022; iv) to achieve the assessment of the impact of industry activities on the environment mainly the heavy metal pollution in groundwater, surface water, soil and sediments.

### **1.1. Area description**

Skikda, situated in the northeastern of Algeria, falls within the small Kabylie region. positioned on the Tellian fringe, it is bordered by the Mediterranean Sea to the north, by Constantine and Guelma to the south, by the petite Kabylie of Jijel to the west, and by the Edough massif to the east (Figure 1). The area

comprises rugged mountains and flat plains, with altitudes ranging from 300m to 1000m above the sea level (Vila 1980).

A sub-humid and humid climate, with the highest temperatures occurring in July (reaching 35°C) and the lowest in January (around 8°C) characterized the studied region. The annual average temperature stands at 23°C, and the yearly precipitation amounts to 746.9mm. Groundwater plays a vital role as a water resource for irrigation, drinking water, and industrial purposes. However, in recent years, climate change, reduced precipitation, and excessive groundwater extraction have contributed to a significant decline in the local piezometric levels.

The socio-economic context revolves around three primary activities: industry, agriculture, and fishing. Industrial operations are agglomerated in four zones: the industrial zone, the port zone, the small zone, and the urban fabric. Conversely, agricultural activity has considerably reduced following the establishment of the industrial zone and subsequent urban expansion. Consequently, the population has increased, reaching 890,000 inhabitants as of 2020 (Directorate for Budgetary Programming and Monitoring, 2020).

## 1.2. Geological and hydrogeological setting

Studies conducted (Durand-Delga 1969; Raoult 1974; Vila 1980; Wildi 1983) have identified various

terrains in Skikda, located in the northern hill area of Algeria. These terrains encompass a wide range of geological diversity, including sedimentary, metamorphic, and magmatic formations. Skikda is part of the Kabylia primary massifs and displays both simple and complex petro-structural features. The rugged mountain ranges in the Northeast are identified as the result of tectonic movements that occurred during the tertiary period, indicating significant tectonic activity in the region. The western part of Skikda, known as petite Kabylie, is characterized by allosteric formations resting on Cenozoic formations. Regarding lithology, three main sets of rocks have been identified in the area.

These include the sedimentary Numidian and Oligo-Miocene-Kabyle sandstone complex, mica schists, and a pelitic ensemble with minor metamorphism. Metamorphic rocks such as schists, mica schists, paragneiss, and orthogneiss are also present. The geological context indicates that metamorphic rocks, including gneiss and metapelite, are located in the northeast and northwest of the study area (Safia region). The central part of the region mainly consists of sedimentary rocks, such as sand, silt, and gravel (Marre, 1992), (Figure 2).

Locally near Skikda city, two types of terrains have been identified. The first type is a superficial terrain from the Quaternary and Tertiary periods,

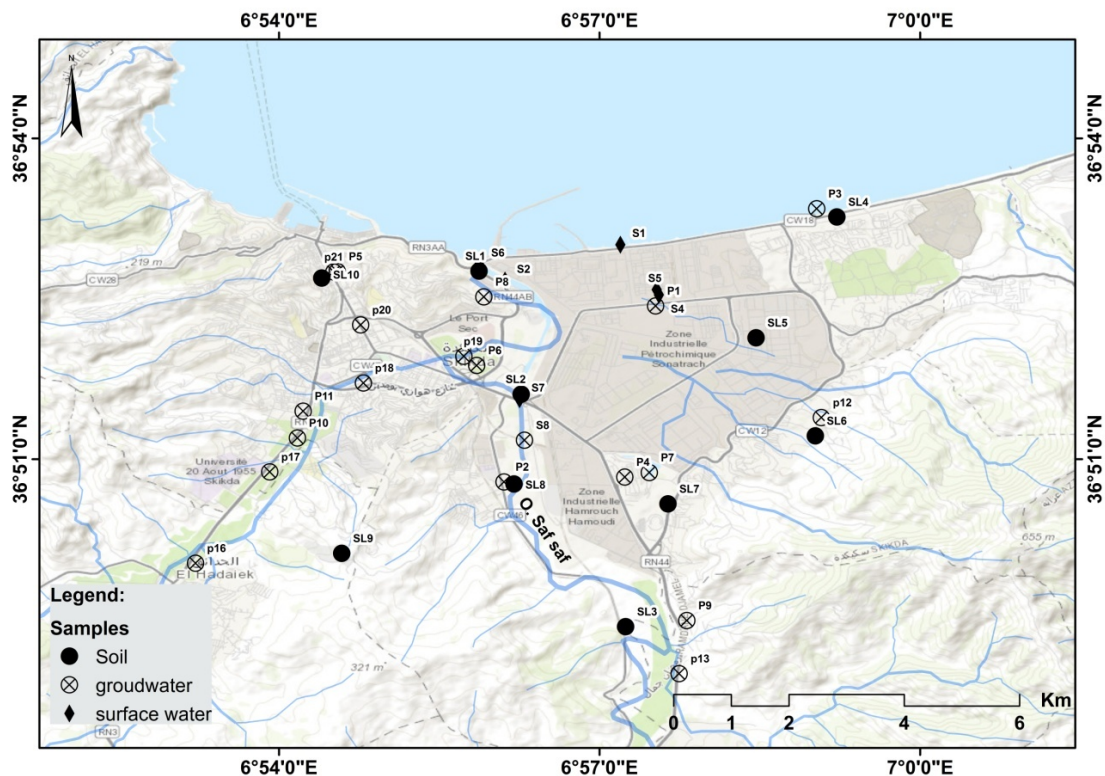


Figure1. Location map of the study area illustrating the distribution of samples, (P:groundwater samples, S: surface water samples , SL:soil samples)

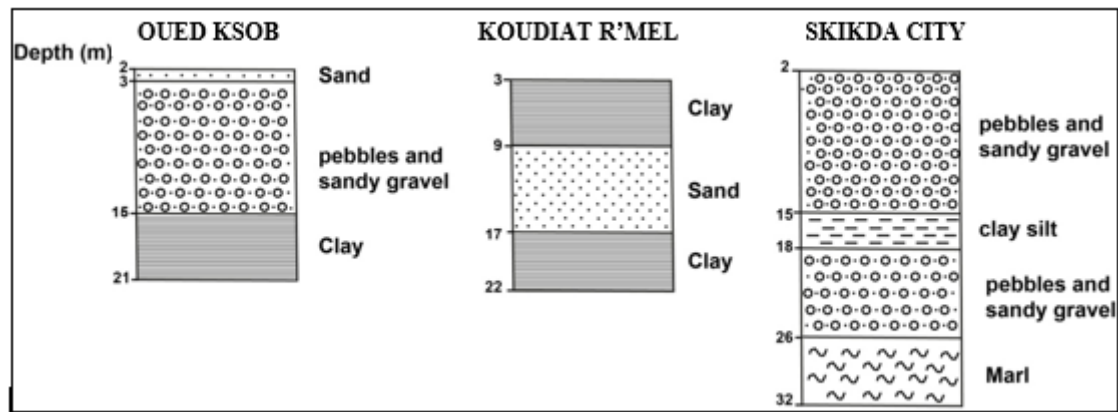


Figure 2. Characteristics of the stratigraphic formations around the city of Skikda.

which overlays impermeable layers as black clay from the Tertiary or metamorphic formations from the Paleozoic. The second type of terrain is Jurassic and is based on the metamorphic terrain of the Paleozoic (Vila 1980), (Figure 3).

The hydrogeological investigation conducted has revealed the presence of two superposed aquifers (Vila 1978). The first aquifer consists of Quaternary sandy formations, which sometimes overlays impermeable formations like marl or semi-permeable formations like sandy clay. The second aquifer is

composed of Quaternary gravelly formations, which rests on impermeable formations like marl and is occasionally confined by covers of sandy clay. These aquifers receive water infiltration from precipitation and also receive water supply from nearby basins (Vila 1980). In our research area, the sandy soil formations exhibit high permeability. Groundwater from the industrial area's aquifer primarily flows at shallow depths (<1m) in a southwest to northeast direction within the Mio-Pliocene alluvial aquifer composed mainly of sand and gravel.

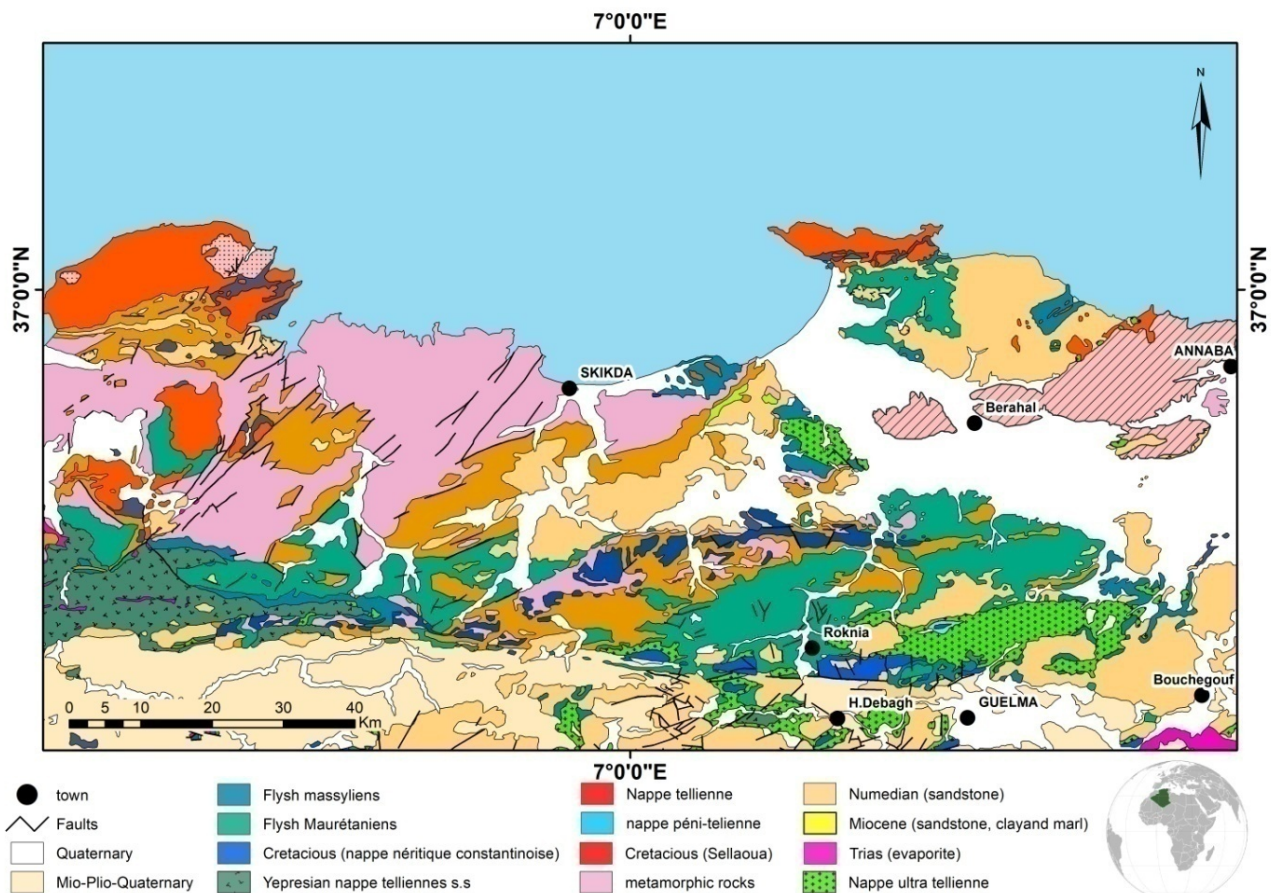


Figure 3. Geological map of Skikda area (Vila 1978)



## 2. MATERIALS AND METHODS

### 2.1. Sampling and analysis

A sampling campaign was conducted between July 2021 and March 2022 to gather diverse water and soil samples. The collected samples consisted of 8 surface water samples, 11 groundwater samples, and 10 soil samples. Before collecting groundwater samples, a 10-minute drawdown was performed to confirm the source as groundwater and not suspended water. Each sample, with a volume of 1 liter, was filtered through a membrane with a pore size of 0.45mm and acidified with a few drops of Nitric acid to achieve a final concentration of approximately 1. The acidified samples were then stored in a refrigerator at 4°C. The remaining non-acidified samples were analyzed on-site using a WTW 350i Multi-parameter instrument, measuring parameters such as pH ( $\pm 0.01$  unit), temperature ( $\pm 0.1^\circ\text{C}$ ), and electrical conductivity ( $\pm 1\text{ms/cm}$ ), (Rodier, 2009).

For chemical analysis, specific components including Sulfate, Nitrate, Nitrite, Ammonium, Calcium, Magnesium, Sodium, and Potassium were determined using spectrophotometry and atomic absorption spectrometry were analysed at Hydrogeology Laboratory of Constantine 1 University, Algeria. The concentration of heavy metals such as Arsenic, Cadmium, Cobalt, Chromium, Copper, Manganese, Nickel, and Lead was undertaken by Atomic absorption spectroscopy at Hydrogeology Laboratory of Constantine 1 University and at the LISTA/FSDM (University of Fes, Morocco) using ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry).

To study the origin and movement of water samples; twenty surface water and groundwater samples, as well as two rainwater samples from Skikda and Jijel, were collected for stable isotope analyses ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ). These samples were analyzed using a laser absorption spectrometer (Picarro L2110-i) at the Dating and Isotope Tracing Department of the Nuclear Research Centre (Algiers) and the chemical and isotopic analysis of geothermal and volcanic fluids laboratory in Florence, Italy. The results were reported as relative deviations ( $\delta$  in per mille ‰) from the Vienna Standard Mean Ocean Water (V-SMOW).

It is crucial to distinguish between natural background levels of heavy metals and those influenced by human activities to comprehend the impact of pollutants on soil. Soil geochemical tracking offers valuable information regarding the composition of heavy metals and potential enrichment resulting from human activities. Furthermore, we gathered sediment samples from three different river locations, specifically

targeting the uppermost 0-2 cm layer, and obtained soil samples from seven distinct locations, focusing on the 20 cm depth. These samples were obtained from both inside and around an industrial area, and their GPS coordinates were accurately recorded. All soil samples were naturally dried in the Laboratory (LGG) at the University of Jijel. Soil pH and conductivity were measured using specific procedures, while heavy metal concentrations were determined by extracting the metals from the soil using aqua regia, followed by analysis with atomic absorption spectrometry, were analyzed at Hydrogeology Laboratory of Constantine 1 University, Algeria. Plant debris and stones were eliminated from the samples, which were subsequently processed by grinding in a mortar and sieving through a 0.15 mm mesh size. The pH levels of the soil specimens were ascertained employing a multi-parameter instrument. To do this, 10 grams of soil were combined with 25 ml of distilled water in a 100 ml beaker, and the mixture was vigorously shaken for 1 minute using a glass rod. The mixture was then allowed to stand for 2 hours, and the pH measurement was taken using the multi-parameter device. The conductivity of the soil samples was determined using a multiparameter instrument. Ten grams of sieved soil (2mm) were placed in a 100 ml beaker, and 50 ml of distilled water were added. The solution was stirred with a magnetic stirrer for 2 hours, followed by a resting period of 30 minutes. The soil solution's conductivity was then measured using an electronic conductivity meter.

The extraction procedure outlined in the study conducted by Hoenig (2001) involves the addition of aqua regia to 1 gram of dried and sieved soil particles (2mm). Aqua regia is composed of 3 ml of concentrated hydrochloric acid (HCl) and 1 ml of concentrated nitric acid ( $\text{HNO}_3$ ). The mixture is placed in a 250 ml ground Erlenmeyer flask, which is then fixed under a refrigerator and heated to boiling for 15 minutes. After cooling, the condenser is rinsed with a small amount of demineralized water. The contents of the Erlenmeyer flask are filtered using filter paper or a Millipore-type membrane, with the filtration rate adjusted to medium. A calibrated flask ranging from 50 to 100 ml is used as necessary. The extracted soil samples are then subjected to analysis using a specific analytical technique, such as the SAA, to determine the concentrations of heavy metals, including arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), and lead (Pb).

### 2.2. Multivariate Statistical analysis

The application of linear correlation and multivariate statistical analysis has been utilized in scientific research to categorize and analyze

groundwater, surface water, and soil samples, aiming to identify the key factors that influence their chemical composition. This approach allows for the grouping and correlation of samples, as well as establishing relationships between their chemical parameters. Other researchers, (Barkat et al., 2021; Barkat et al., 2022; Belkhiri et al., 2017; Bouaicha et al., 2019; Bouteraa et al., 2019; Foued et al., 2017) have also utilized this tool to investigate various environmental problems and gain insights into both natural and human-induced processes.

Two widely used methods in the analysis of water quality data are Correlation Analysis (CA) and Principal Component Analysis (PCA). These unbiased techniques provide valuable information by revealing meaningful relationships among variables. In particular, PCA is considered an effective multivariate statistical technique for extracting linear relationships between a set of variables, as reported in (Barkat et al., 2021).

In the specific context of identifying the relationship between heavy metals and physical-chemical parameters in the study area, multivariate statistical analyses are employed. These techniques assist in interpreting complex data matrices, enabling a better understanding of various environmental factors. Notable studies by Belkhiri et al., (2017) and Barkat et al., (2022) emphasize the usefulness of multivariate statistical techniques in this regard.

### 2.3. Environmental risk assessment methodology

For the purpose of scientific analysis, the environmental risk assessment involved the utilization of various indices to determine the extent and potential sources of heavy metal contamination. This assessment focused on evaluating pollution levels, health risks, and ecological impacts resulting from the ingestion of heavy metals present in the phreatic groundwater aquifer, whether introduced by human activities or occurring naturally. Several indices were employed to assess groundwater contamination by heavy metals.

#### 2.3.1. The degree of contamination ( $C_{deg}$ )

The degree of pollution ( $C_{deg}$ ) is a cumulative reflection of several water quality parameters that are considered harmful for domestic drinking water use (Backman et al., 1998). The value of the degree of pollution is described by the following equation (1):

$$C_{deg} = \sum_{i=1}^n C_{fi}$$

Where:

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}}$$

where  $C_{fi}$  is contamination factor for the  $i$ -th component,  $C_{Ai}$  is analytical value for the  $i$ -th component and  $C_{Ni}$  is upper permissible concentration of the  $i$ -th component ( $N$  denotes the 'normative value'), The resultant  $C_d$  value which are grouped into three categories as follows:  $C_d < 1$  (low),  $C_d = 1-3$  (medium) and  $C_d > 3$  (high).

Furthermore,  $C_{fi}$ ,  $C_{Ai}$  and  $C_{Ni}$  are the contamination factor, the analytical value and the maximum allowable concentration of the  $i^{th}$  component, respectively, and  $N$  is the 'normative value'. In this case,  $C_{Ni}$  is considered the maximum permissible concentration (MAC). Based on (Backman et al., 1998), the contamination degree was classified as low when  $C_{deg} < 1$ , medium when  $1 < C_{deg} < 3$  and high when  $C_{deg} > 3$ .

#### 2.3.2. Heavy metal pollution index (HPI)

The methodology of the Heavy Metal Pollution Index (HPI) is innovative: each selected pollution parameter is assigned a score or weighting factor ( $W_i$ ) on which the index is built. The score is a random value between 0 and 1 indicating the relative importance of certain quality aspects. For each parameter, it can be defined as inversely proportional to the proposed norm ( $S_i$ ) (Horton 1965). In the case of this study, the maximum allowable concentration ( $S_i$ ) represents the maximum allowable concentration in drinking water in the absence of alternative sources, while the maximum allowable concentration ( $S_i$ ) represents the maximum allowable concentration in drinking water in the absence of alternative sources, and the maximum desirable one ( $I_i$ ) reflects the standard limits for the same parameters in drinking water of each selected parameter based on (WHO 2011). Index method use for determining the level of heavy metals present in water samples; the HPI is calculated according to the formula of Mohan et al., (1996):

$$HPI = \frac{\sum_{i=1}^n W_i \cdot Q_i}{\sum_{i=1}^n W_i}$$

Where;  $Q_i$  is the sub-index of the  $i^{th}$  parameter,  $W_i$  is the unit weight of the  $i^{th}$  parameter, and  $n$  is the number of parameters used in the calculation.  $Q_i$  was determined using the following equation (2):

$$Q_i = \sum_{i=1}^n \frac{|M_i - I_i|}{S_i - I_i} * 100$$

Where;  $M_i$  denotes the monitored heavy metal and  $I_i$  and  $S_i$  denote the ideal and standard values for the  $i^{th}$  parameter, respectively. The negative algebraic sign was ignored in the difference between  $M_i$  and  $I_i$ . The  $I_i$  values came from the metals' MAC values, and the  $S_i$  values were derived from the WHO standard

values.

Where  $M_i$ ,  $I_i$ , and  $S_i$  are the monitored heavy metal, ideal, and standard values of the  $i^{\text{th}}$  parameter, respectively. The sign (-) denotes a numeric difference between the two values, regardless of the algebraic sign. The classification of Mohan et al., (1996) was used to classify the results as (safe water for drinking and free from heavy metals when  $HPI < 100$ , and water is contaminated or polluted with heavy metals when  $HPI > 100$ ).

### 2.3.3. Geo-accumulation index ( $I_{geo}$ )

As it was introduced by Muller (1969), the Geo-accumulation index ( $I_{geo}$ ) is used for the quantification of the degree of the pollution load that may accumulate due to anthropogenic or geogenic origins. The importance of this index is that it can provide information through a quantitative assessment on the level of the dissolved (HM) in porous media (soil/sediments/water) (Egbueri & Unigwe 2020). The  $I_{geo}$  model is expressed by the following equation (3):

$$I_{geo} = \log_2 \left[ \frac{C_n}{1.5 \cdot B_n} \right]$$

Where  $C_n$  is the observed total concentration of metals in samples (Ug/L),  $B_n$  is the geochemical background values of metals (Ug/L), and 1.5 is the lithogenic effects background matrix adjustment factor.

The constant 1.5 enables the analysis of natural fluctuations in the concentration of a specific substance found in the environment (Adimalla & Wang 2018; Bhutiani et al., 2017; Muller 1969). The  $I_{geo}$  indices were classified to uncontaminated ( $I_{geo} \leq 0$ ), uncontaminated to moderately contaminated ( $0 < I_{geo} < 1$ ), moderately contaminated (from 1 to 2), moderately to strongly contaminated (from 2 to 3), strongly contaminated (3 to 4), strongly to extremely contaminated (4 to 5) and extremely contaminated when  $I_{geo} > 6$  (Adimalla & Wang 2018; Bhutiani et al., 2017; Muller 1969).

### 2.3.4. Enrichment factor (EF)

The enrichment factor is used to examine the sources of dissolved metals in water/soil/sediment, as well as the degree of the contribution of anthropogenic sources of HM to water system pollution. The reference metal in this investigation was Fe. The equation was used to compute the EF is equation (4):

$$EF = \frac{\left(\frac{M}{Fe}\right)_{sample}}{\left(\frac{M}{Fe}\right)_{background}}$$

Where EF is the enrichment factor, (M/Fe)

sample is the ratio between the metal and Fe concentration of the sample and (M/Fe) background is the ratio between the metal and Fe concentration of a background. Background metal concentrations were taken from soils in an undisturbed area.

According to Bhutiani et al., (2017) classification, EF1 denotes background concentration, EF (1-2) minor enrichment, EF (3-5) moderate enrichment, EF (5-10) moderate severe enrichment, EF (10-25) severe enrichment, EF (25-50) very severe enrichment, and EF > 50 indicates extremely severe enrichment. To establish the origins of pollutants based on EF values, EF values ranging from 0.5 to 1.5 indicate lithogenic sources, whereas EF values more than 1.5 indicate anthropogenic origin (Hakima et al., 2017).

## 3. RESULTS AND DISCUSSION

### 3.1. Physical-chemical characterization of surface water and groundwater

#### 3.1.1. Physical-chemical parameters

Physical-chemical parameters of both analyzed water surface and groundwater were summarized in Table 1.

Table 1. The minimums, maximums, mean, standard deviation of the analyzed hydrochemical parameters and heavy metal in groundwater.

Parameters	Unit	Min	Max	Std. deviation	Mean
As	Mg/l	0.01	2.21	0.67	0.41
Cd	Mg/l	0.01	2.50	0.73	0.48
Co	Mg/l	0.004	0.76	0.28	0.26
Cr	Mg/l	0.08	1.65	0.54	0.55
Cu	Mg/l	0.02	0.46	0.18	0.24
Mn	Mg/l	0.04	1.31	0.53	0.67
Ni	Mg/l	0.09	2.71	0.80	0.56
Pb	Mg/l	0.16	2.98	0.54	0.62
Fe	Mg/l	0.12	10.93	3.39	2.32
Zn	Mg/l	0.14	2.44	0.85	0.63
EC	Mg/l	214	5560.0	1900	1874.7
pH	Mg/l	7.12	9.00	0.72	8.24
DO	Mg/l	2.06	30.40	28.46	38.96
$Mg^{+2}$	Mg/l	18.32	980.06	291.82	167.58
Na <sup>+</sup>	Mg/l	44.5	5039.0	1559.20	978.90
$Ca^{+2}$	Mg/l	22.00	359.09	114.63	166.43
$Cl^-$	Mg/l	25.00	357.00	125.50	203.51
$K^+$	Mg/l	5.12	210.23	115.63	84.41
$NO_2$	Mg/l	0.15	12.62	3.56	2.98
$NO_3^-$	Mg/l	6.58	46.15	77.19	30.98
$NH_4^+$	Mg/l	1.50	26.03	7.78	7.08
$SO_4^{2-}$	Mg/l	13.96	325.98	94.27	195.35

Results during the high water period illustrate that Temperature values were ranged from 17 to 21°C of surface water and not exceeded FAO guidelines for irrigation (25°C). Indeed, groundwater samples in

high water period vary from 15 to 17.6°C. All samples show that temperature were lower than the values fixed by WHO 25°C (WHO 2011) and, as the water surface is very sensitive to air. Surface and groundwater temperatures did not change much during the low water period. pH of surface water varies between 6.90 and 8.08, where the water has an alkaline pH in adequacy with FAO guidelines for irrigation (6.5-9). Therefore, the groundwater pH was ranged between 7.28 to 9.23, in adequacy with guidelines of the World Health Organization (WHO 2011). On the other hand and during the low water period, pH of surface water is conforms to FAO for irrigation, it varies from 7.87 to 8.9. groundwater pH varies from 7 to 8.95; all water samples show neutral to slightly alkaline. Dissolved oxygen values of groundwater vary from 7.54 to 89.03 mg/l and from 13 to 52.25 mg/ of surface water. Results during the high water period illustrate that dissolved oxygen of groundwater was ranged between 3.5 to 12.05 mg/l. dissolved oxygen in surface water did not change much during the wet season.

During the high water period, conductivity values in Surface water were comprised between 1663 and 10620  $\mu\text{S}/\text{cm}$  largely exceeding FAO guidelines for water irrigation (2500  $\mu\text{S}/\text{cm}$ ). Moreover, conductivity of groundwater oscillates from 214 to 5560  $\mu\text{S}/\text{cm}$  with high conductivities measured at P1, P3, P4, P5, P6, P8 and P9, situated in the downstream of the study area, which exceed WHO guidelines fixed at 2500  $\mu\text{S}/\text{cm}$ . During the dry period, the surface water conductivity varies between 134 to 24000  $\mu\text{S}/\text{cm}$  which are exceeded than the FAO standards for water irrigation (2800  $\mu\text{S}/\text{cm}$ ), and varies between 112  $\mu\text{S}/\text{cm}$  to 33 000  $\mu\text{S}/\text{cm}$  in groundwater, which are higher than WHO standards (2500  $\mu\text{S}/\text{cm}$ ). on the other hand the average value of conductivity groundwater (2030  $\mu\text{S}/\text{cm}$ ) is higher than that of surface water (1650  $\mu\text{S}/\text{cm}$ ), reflecting the infiltration of surface water into the aquifer, which contaminates groundwater. Only one sample was classified as good for irrigation ( $\text{EC} = 250\text{--}750$ ), five samples were classified as acceptable for irrigation ( $\text{EC} = 750\text{--}2000$ ), eight samples were classified as doubtful for irrigation ( $\text{EC} = 2000\text{--}3000$ ) and the remaining seven samples were classified as unsuitable for irrigation ( $\text{EC} > 3000 \mu\text{S}/\text{cm}$ ).

$\text{Na}^+$  was the most dominant cation mean with 1494.32 mg/l, followed by  $\text{Ca}^{2+}$  mean 153.12 mg/l,  $\text{Mg}^{2+}$  mean 111.23 mg/l, and  $\text{K}^+$  mean 78.21 mg/l. The average values of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were higher than the WHO (2011) standard values for water 20 mg/l, 100 mg/l, 50 mg/l respectively. Which can be attributed to ion exchange. Ammonium concentration measured between 0.2 and 13.5 mg/l, sulfate 6.32 and 792.23 mg/l, nitrite 0.02 and 12.69 mg/l, nitrate 1.7 and 299.36

were observed in different samples of Oued Safsaf: O0 (5.03 mg/l-102.3 mg/l-0.95 mg/l-125.02 mg/l respectively); O1 (3.65 mg/l-225.3 mg/l-0.95 mg/l-128 mg/l); O2 (1.03 mg/l-103.03 mg/l-13.5 mg/l-300 mg/l). High concentrations-contents of ammonium groundwater samples p2, p4, and p6 situated in the up stream are due to both the unauthorized dump and the untreated sewage of Skikda city. Chloride ( $\text{Cl}^-$ ) was predominant with an average in groundwater of 777.2 mg/l providing from the evaporate deposit, anthropogenic pollution (salting of roads, spraying, wastewater), proximity of sea.  $\text{SO}_4^{2-}$  in groundwater with an average 735.12 mg/l,  $\text{NO}_3^-$  with an average of 299.03 mg/l the mean concentration of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in groundwater were exceeded the international standard (WHO 2011) fixed at 250 mg/l, 500 mg/l, 50 mg/l respectively.

Proposed natural and anthropogenic sources, such as rock erosion, leaching of dissolved salts and agricultural activities. High concentrations of ammonium, sulfates, nitrate and nitrite depend on nutrient inputs from agricultural soils (application of manure, animal waste and fertilizers) and untreated wastewater. Nitrate content of groundwater is low. The main anthropic contributions are essentially linked to agricultural activities; increase the yield of agricultural soil, farmers use high doses of chemical fertilizers (ammonium nitrate, superphosphate). However, the nitrates and phosphates in the soil are transported by surface water, which infiltrates through the soil and subsequently contaminates the aquifer. Furthermore, unconfined aquifers near the surface facilitate the vertical transport of all pollutants into groundwater.

### 3.1.2. Heavy metal concentrations

Table 2 shows the minimum, maximum, standard deviation and mean of 10 heavy metals in surface water. Overall, the highest average concentrations recorded per element were Fe, Cd, As, Cr, Pb, Cu, Ni, Mn, Co, Zn the measured concentrations were 3.28, 1.62, 1.33, 0.51, 0.93, 1.83, 0.05, 0.34, 1.72 and 1.83 mg/L, respectively.

The majority of average concentrations of these metals exceeded the standards set by the WHO in 2011. The WHO guidelines recommend concentrations of 0.3, 0.001, 0.05, 0.1, 2, 0.4, 0.07, (no guideline value for Co), and 3 mg/l respectively.

It has been observed that heavy metal pollution in surface water is concentrated in open-air effluents inside the SONATRACH industrial zone and decreases with distance from the zone (samples from the river).

The average concentrations of these heavy metals in groundwater, ranked in descending order,



Table 2. The minimums, maximums, mean, standard deviation of the analyzed hydrochemical parameters and heavy metal in surface water.

Parameter s	Unit	Min	Max	Std. deviation	Mean
As	Mg/l	0.23	2.26	0.66	1.33
Cd	Mg/l	0.56	2.45	0.63	1.62
Co	Mg/l	0.04	1.02	0.41	0.34
Cr	Mg/l	0.11	1.20	0.33	0.51
Cu	Mg/l	0.01	0.10	0.03	0.05
Mn	Mg/l	0.41	1.38	0.40	0.85
Ni	Mg/l	0.99	3.50	0.88	1.83
Pb	Mg/l	0.14	2.21	0.69	0.93
Fe	Mg/l	0.25	8.87	3.04	3.28
Zn	Mg/l	0.54	3.04	0.97	1.72
EC	Mg/l	1062	24000	10500.41	8836.63
pH	Mg/l	7.26	8.87	0.48	7.92
DO	Mg/l	7	90.00	35.54	50.35
Mg <sup>+2</sup>	Mg/l	15.98	280.95	88.72	87.69
Na <sup>+</sup>	Mg/l	23.56	5032.30	1885.80	1438.64
Ca <sup>+2</sup>	Mg/l	37.06	350.00	96.02	183.96
Cl <sup>-</sup>	Mg/l	37	706	216.67	239.64
K <sup>+</sup>	Mg/l	10	260.32	91.82	87.26
NO <sub>2</sub>	Mg/l	0.26	6.02	2.09	2.69
NO <sub>3</sub>	Mg/l	2.61	90.50	114.39	97.25
NH <sup>+</sup>	Mg/l	0.85	12.5	3.86	4.96
SO <sub>4</sub> <sup>2-</sup>	Mg/l	11.62	294.32	88.51	201.78

are as follows: Zn > Fe > Cd > Ni > Mn > Pb > Cr > As > Cu > Co. Specifically, the average concentration of Zn was found to be 2.68 mg/L, slightly below the WHO guideline recommendation of 3 mg/L. However, for other heavy metals such as Cd, Ni, Fe, Cu, As, Cr, Pb, Co, and Mn, the measured concentrations were 1.05, 1.12, 2.1, 0.88, 0.44, 0.5, 0.69, 0.27, and 0.75 mg/L, respectively. It is noteworthy that the mean concentrations of these metals exceeded the standards set by WHO in 2011. Specifically, the WHO guidelines recommend concentrations of 3 mg/L, 0.003 mg/L, 0.07 mg/L (no guideline value for Ni), 2 mg/L, 0.01 mg/L, 0.05 mg/L, 0.01 mg/L, 0.4 mg/L, and 0.2 mg/L for Zn, Cd, Ni, Fe, Cu, As, Cr, Pb, and Mn, respectively. The spatial distribution of heavy metals in groundwater was established in Figure 4. The area is heavily polluted by Cr, Pb and As, measured respectively at 0.5, 0.69 and 0.44 mg/l exceeding the WHO fixed respectively 0.05, 0.01, 0.01 mg/l. Of all the elements analyzed, the spatial distribution of As, Cr, Cd, Pb, Cu, Zn, Ni and Fe follows a similar trend, and their concentration generally increases inside the industrial zone. The surroundings of the study area were less polluted, while the southern periphery was identified as having the lowest concentration. Revealed that the studied area was considerably polluted with Ni as its measured concentration was more than the OMS standards. There was believed that the burning of oil was the major source of Ni concentration. Inside the industrial area has a higher concentration of heavy metals. In addition, there is another trend in the distribution of Co in wells P7, P1

and P11 with concentrations of 0.75, 0.76 and 0.85 mg/l respectively and Mn in wells P6 and P9 with concentrations of 1.31 and 1.40 mg/l respectively, which extends to the south and west of the industrial area with high concentrations. Note that there are no major sources of pollution in the western part of the area except for a public landfill in the north or inside SONATRACH industrial complexes shown in Figure 4. As a result 3 pollution persists for a fairly long period of time and spreads uniformly from the sources into downstream. The presence of high traffic density on the main roads as well as agricultural practices could make the southern part of the mapping area more polluted by vehicle emissions and pesticides in the case of Mn and Co, according to the discussion of the multivariate analysis.

Anthropogenic sources include wastewater containing heavy metals and harmful compounds from many industrial effluents from which its flow is estimated at 379397m<sup>3</sup>/year in 2022 (National Sanitation Office, Jijel), such as: smelting, refining, manufacturing processes, steel and textile industry, electroplating, nickel-cadmium battery production, welding, production of PVC products and paint pigments, are all potential sources of metal pollution. These wastewaters may leach into the unsaturated zone of the soil, thus contaminate the soil, and groundwater. Therefore, emissions from the industrial area, cars and vehicles were a major source for these elements, not to mention the uncontrolled use of pesticides.

### 3.1.3. Cluster analysis (CA) and Principal component analysis (PCA)

The spatial similarities and well classification was detected using HCA (Q-mod method). Samples in the same group contain the similar characteristics respect to the analyzed parameters. to carry out the cluster analysis concentrations for 10 heavy metals (Fe, Cr, Cd, Co, Cu, As, Ni, Mn, Zn, Pb) were used as variables. Main groups can be distinguished in the dendrogram shown in Figure 5 and 6. The first group was composed of the wells P2, P3, P4, P5, P6, P8, P9, P10, O2, and M1 and presents 48.13% the water samples of Group 1 included samples with the highest concentrations of Mn and Cd. The mean concentrations of Mn and Cd are 0.79 and 0.35 mg/l, respectively. The second group including P7 occupies 17% of the water samples; this group does not present high concentrations in heavy metals. The third group was represented by the wells O0, O1, E1, E4, M2 and E0 and concerns 11.15% of water samples of Group 3 included samples with the highest concentrations of Mn, Cd, Zn and Ni. The mean concentrations of Mn, Cd, Zn and Ni are, 0.59, 1.95, 4.25 and 3.05 mg/l,

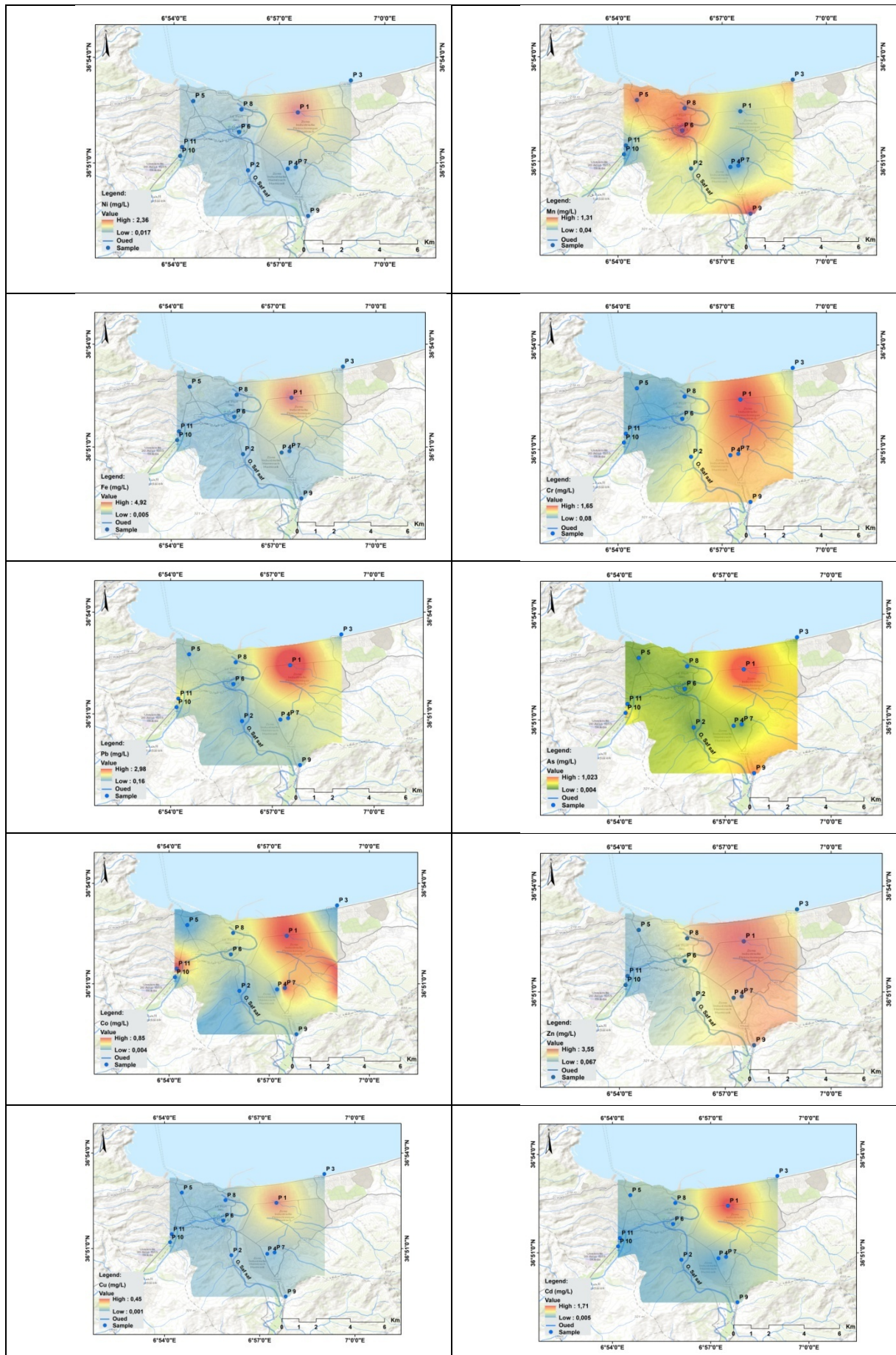


Figure 4. Spatial distribution of major heavy metals in groundwater of the study area

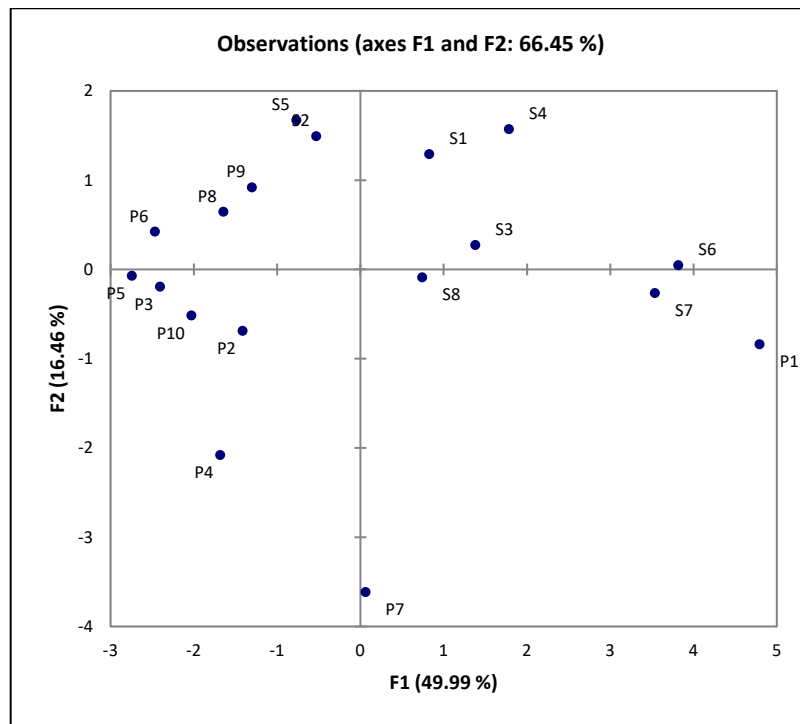


Figure 5. Projection of the wells on the factor-plane (1x2).

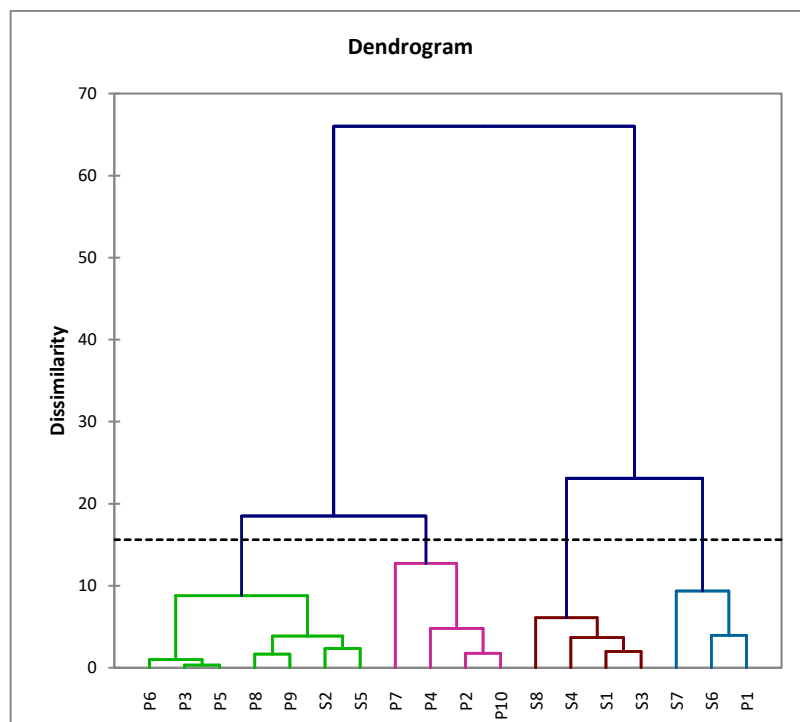


Figure 6. Hierarchical cluster results or dendrogram obtained by CA of the groundwater samples.

respectively. The last group was presented by the wells P1, E2 and E3 and concerns 8.26% of water samples, this group included samples with the highest concentrations of Fe, Cr, Co and Pb the mean concentrations of Fe, Cr, Co and Pb are 4.95, 1.65, 0.76 and 2.98 mg/l.

The PCA results show that there are two values greater than one and that these two factors explain 65.38% of the total variance (Figure 5). The first factor

explains 48.13% of the total variance and is heavily loaded on Pb, Zn, As, Cr, Fe, Ni, Cd and Co, which are supported by cluster 1. This result can be supported by the existence of two industrial companies, SONATRACH and Coca Cola, in the study area, in addition tonatural and agricultural activities. Factor 2 showed higher Cu and Mn loads, accounts for 17.25% of the total variance and is adequately supported by cluster 2, (Figure 6 and 7). PCA confirmed and

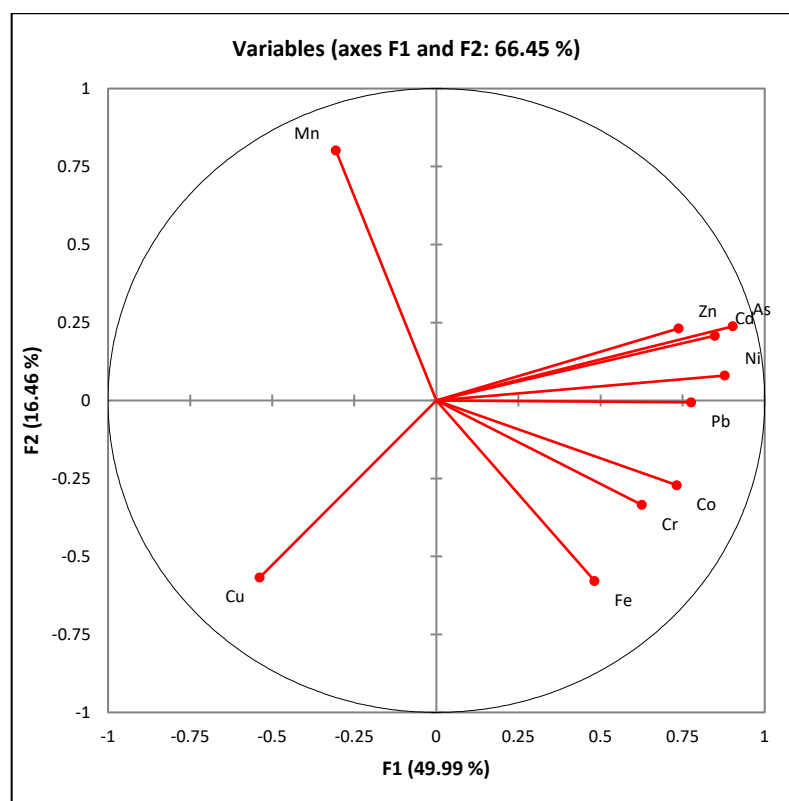


Figure 7. Projection of the variables on the factor-plane (1×2).

complemented the overall CA results; PCA and CA indicated significant natural sources. The high concentrations of heavy metals are marked in the interior well and the effluents of the industrial zone. Whereas the other wells have moderate concentrations of heavy metals. Only exception the wells downstream of the public uncontrolled landfill, which show anomalies in Mn and Cu, as this garbage, dump is located on a high slope at 140m from sea level. Which accelerates the leaching and runoff of different elements from the waste rejected in this area, which explains the presence of these elements in the lowest areas near the coast.

### 3.1.4. Soil monitoring

pH values were alkaline at the majority of sampling sites and ranged from 7.20 to 8.05 with an average value of 7.62. These values don't exceed Afnor standards (1999) ranged between (4-12). However, EC concentration was ranged from 112  $\mu\text{S}/\text{cm}$  to 390  $\mu\text{S}/\text{cm}$  exceeded Afnor standards (1999). Results of heavy metal show that the mean contents of Zn, Cd, Ni, Fe, Cu, As, Co, Cr, and Mn were analyzed respectively at 249.3, 66.4, 64.7, 522, 26.2, 33.5, 12.1, 7.2 and 1.9 ppm. Mean concentration of selected heavy metals in soils were classified as followed  $\text{Zn} > \text{Fe} > \text{Cd} > \text{Ni} > \text{As} > \text{Cu} > \text{Co} > \text{Cr} > \text{Mn}$ . It was indicated that minimum and maximum of Cd is ranged between 35.32 to 95.12 ppm, for Fe oscillates from 145.1 to 702 ppm, As values variate from 1.03 to 81.85 ppm, and Zn between 50 and 520.32

ppm. These contents were considered as dominant metals in the studied soils. However, concentration of Mn, Co and Cr were considered lower respectively 1.97, 12.11 and 7.25 ppm compared to Fe and As respectively 522, 33.54 ppm, while the lowest average Mn concentration was recorded around the study area 0.26 ppm, (Table 3).

Table 3. Descriptive statistics of heavy metal and physico-chemical concentrations (mg/kg) in soil. *std. deviation*: standard deviation. *Min.*: Minimum, *Max.*: Maximum.

parameters	Unit	Min	Max	Std. deviation	Mean
As	Mg/kg	1.25	60.50	22.95	24.55
Cd	Mg/kg	35.80	86.05	17.65	52.78
Co	Mg/kg	47.50	149.00	32.72	97.91
Cr	Mg/kg	10.50	59.13	18.47	32.07
Cu	Mg/kg	6.42	38.11	11.00	19.56
Mn	Mg/kg	32.70	120.33	34.62	82.47
Ni	Mg/kg	11.61	92.12	31.16	53.87
Pb	Mg/kg	10.11	50.34	16.63	27.77
Fe	Mg/kg	128.20	128.20	205.47	488.60
Zn	Mg/kg	25.80	461.50	167.47	157.13
EC	Mg/kg	112.00	390.00	95.35	215.29
pH	Mg/kg	7.00	8.36	7.74	7.69

It was shown that the distribution of the highest concentrations of heavy metals in the soil is mainly found in industrial zones. The concentrations of heavy metals in the soil within the industrial zone varied between Zn, Cd, Fe and As, corresponding to 520.32, 95.12, 702 and 81.85 ppm respectively. However, the lowest concentrations were measured in the residential area above the industrial zone. The lowest concentrations



of Zn, Cd, Fe and As were found in the industrial area, corresponding to 25.80, 35.8, 128.2 and 1.25 ppm respectively. The Concentrations of Cd and As in soil were mainly dependent on anthropogenic factors, with the explanatory power of industry category and distance to it being significantly higher. Our results indicate that Cd and As contamination of soils in nearby areas by local industry is particularly high. Wastewater, exhaust, waste and coal combustion products emitted by many enterprises in the study area (Skikda industrial zone) may be important sources of Cd and As in soil. The high concentration of cadmium (0.99 mg/L) corresponds to a neutral pH value (7.6). Iron is the most influential substance controlling the mobility of As. Different soil types are the result of erosion of different parent materials, resulting in differences in clay mineral and organic matter content as shown by Mahmoodi et al., (2016). Migration and accumulation of heavy metals are closely related to soil pH and organic matter as reported by Zeng et al., (2008).

Numerous studies confirm that the presence of chromium (Cr) in soils is mainly due to the parent material, as reported by Facchinelli et al., (2001) and Xu et al., (2021). It should be noted that Cr content is generally higher in siltstone and shale soils, while enrichment is observed in ironstone soils, as reported by Wang et al., (2022) and Zinn et al., (2020).

The grain size composition of different soil types also significantly influences the distribution of heavy metals, due to differences in surface areapermeability and related factors. In addition, emissions from large highways contain many detectable pollutants, such as cadmium (Cd), chromium (Cr) and other heavy metals, as confirmed by Werkenthin et al., (2014). Although the proximity to highways partly clarifies the spatial distribution of heavy metals in soil, their overall influence remains limited. In our study area, the movement of heavy metals along rivers and the zone of influence of irrigation wastewater can be relatively large.

Notably, cadmium (Cd) and arsenic (As) appear to be predominantly influenced by industrial activities, particularly those of polluting companies, whereas chromium (Cr) exhibits a stronger correlation with natural factors such as soil pH and type. Notably, the excessive use of pesticides by local farmers in our study area stands out as a significant source of copper (Cu) contamination, alongside other potential sources such as chemical waste.

### 3.2. Heavy metal pollution index (HPI)

Table 4 presents a summary of the methodology employed to calculate HPI (Heavy Metal Pollution Index) values for nine different samples denoted as P1

to P9. To compute these HPI values, we utilized the mean concentrations of ten heavy metals, specifically Cobalt (Co), Cadmium (Cd), Iron (Fe), Lead (Pb), Chromium (Cr), Nickel (Ni), Arsenic (As), Manganese (Mn), Copper (Cu), and Zinc (Zn). It's worth noting that the HPI index has a critical threshold of 100, as established by Prasad & Mondal in 2008, as well as Prasad & Sangita in 2008. Any HPI value exceeding this threshold (i.e., greater than 100) is indicative of pollution levels deemed unacceptable for consumption.

To comprehensively evaluate pollutant levels and assess water quality across all monitoring stations, we independently calculated the HPI index for each sampling station. Notably, station P1 exhibited a significant deviation from the average HPI value, recording the highest HPI value of 180.10. This is the only HPI value that was above the critical limit of the HPI value for drinking water. Station P1 is located in the Skikda industrial zone; stations with HPI values above the critical limit of the latter were also marked as P2, which is located near the public landfill site in the city of Skikda, which has a population of over 200,000. In addition, very high HPI values were observed at sampling stations (wastewater from the area) close to the industrial area (industrial wastewater, landfill leachate and domestic wastewater), including stations (O0, O1, E0 and E2), as shown in Figure 1; the other stations had a low HPI value (<100).

Table 4. The HPI and quality classification for groundwater samples of the study area.

Station	HPI(heavy metal pollution index)value	Statue
P1	180.10	Polluted
P2	129.10	polluted
P3	79.72	Not polluted
P4	86.25	Not polluted
P5	77.59	Not polluted
P6	78	Not polluted
P7	41.11	Not polluted
P8	77.54	Not polluted
P9	71.19	Not polluted
P10	86.96	Not polluted
O0	112.50	Polluted
O1	100.08	Polluted
O2	96.25	Not polluted
E0	120.45	Polluted
E1	78.14	Not polluted
E2	108.21	Polluted
E3	80	Not polluted
E4	98.20	Not polluted
<b>HPI's Average</b>	<b>94.52</b>	<b>Not polluted</b>

### 3.3. Geo-accumulation index ( $I_{geo}$ )

Pb, As and Cd, whose the average of geoaccumulation index are basically higher than those of Zn, Ni, Cr, Fe, Cu, Co, Mn are the three main



soil contamination elements in the study area. The ranking of the soil pollution levels of Cd, Pb and As, which are assessed by I<sub>Geo</sub>, is quite high as it is classified as extremely contaminated soil. The I<sub>Geo</sub> method checks for elements with high soil content or high toxic response factor values.

The contamination factor was used to assess the level of contamination of each element in the studied soils. The elemental concentrations could be classified as follows: Co, Cu, Ni and Zn in the low contamination category Zn in the Considerable degree of contamination category (Table 5). Mn, Cd, Pb, As, Fe and Cr in the category of very high contamination factor. These indices were used to assess the overall pollution level of the site resulting from the observed metals. The results of the contamination degree index indicate that the study area is classified as very high contamination degree category (average C<sub>deg</sub> = 117.04, which is greater than 4m (m = 6) based on the categories.

Table 5. The I<sub>Geo</sub> and quality classification soil samples of the study area.

Heavy metal	Average I <sub>Geo</sub>	I <sub>Geo</sub> class	Level of contamination classification
As	7.88	6	Extremely contaminated
Cr	4.81	5	Strongly to extremely contaminated
Cu	-1.36	0	uncontaminated
Mn	0.54	1	Uncontaminated to moderately contaminated
Ni	-0.65	0	uncontaminated
Zn	1.04	2	Moderately contaminated
Fe	2.88	3	Moderately to heavily contaminated
Cd	7.21	6	Extremely contaminated
Pb	6.45	6	Extremely contaminated
Co	-1.79	0	uncontaminated

### 3.4. Enrichment factor (EF)

The maximum EF of Cd, Co, Cr, Mn and Fe are above 40, which shows that Cd, Co, Cr, Mn and Fe in the study site soils are in class 5 (Extremely high enrichment) and mainly originate from an anthropogenic source in the industrial area of Skikda. The maximum EF value of As, Zn, and Pb is oscillate between 6.35 and 10.61 (Table 6), falling in the significant enrichment class 3, and those of Ni is 3, falling in class 2 (Moderate enrichment), it is concluded that the enrichments for these elements come mainly from anthropogenic activity. The order of the average EF values is almost similar to the order of I<sub>Geo</sub>, which can also be seen as the decreasing order of their overall soil contamination degrees in the industrial area passing through the center of the city of

Skikda.

Table 6. The EF for soil samples of the study area.

metals	EF	Value Soil dust quality
As	10.61	Significant enrichment
Cd	47.8	Extremely high enrichment
Co	50.64	Extremely high enrichment
Cr	150.97	Extremely high enrichment
Cu	1.58	Moderate enrichment
Mn	52.97	Extremely high enrichment
Ni	3	Moderate enrichment
Zn	6.35	Significant enrichment
Fe	52.11	Extremely high enrichment
Pb	7.85	Significant enrichment

## 4. ISOTOPIC WATER ANALYSIS

In Table 7 all the samples were aligned along an evaporation line with a slope of 6.1, which, for an O18 value of -5.6 to -5.7 per thousand, originates from the Western Mediterranean line with a slope of  $y=8x+14$ . Our groundwater would be greatly influenced by rainfall originating from the air masses coming from the Western Mediterranean.

The evaporation rate of the P1, situated inside the industrial area, seems very high which indicates that the portion of the studied aquifer has similar behaviour to surface water (river). It was due to several factors; the first one is the water depth measured from the inside of the industrial area not exceeding 60 cm. The unsaturated zone oscillates between 9.30 cm in March 2022 and 10 cm in July 2022 and piezometric levels were measured at 0.65 m in march 2022 and 0.75 m in July 2022. The second factor is the type of soil which is a sandy soil; it is linked with a high permeability  $K= 2.75$  (National Agency for Land Intermediation and Regulation), which facilitates the hydrological process, rainwater infiltration, and groundwater evaporation. Subsequently, they would have undergone an evaporative process that can be explained by the excess deuterium obtained, which for most points is less than 10 (see table,  $d= 8H_2O-18$ ). Also, the regression line obtained with a slope of less than 8 is indicative of evaporation. Only four points. In this evaporative process, they all have a  $d>10.818O$  and  $\delta^2H$  values for groundwater are ranged from 2.45 to -5.33‰ and 19.82 to -1.67‰ vs. V-SMOW standard, respectively. All points are distributed along the Meteoric Water Line for the western Mediterranean region, (Figure 8).

The isotopic makeup of meteoric replenishment is affected by high evaporation before or during infiltration. The stable isotope in groundwater is between the GMWL and the LMWL, suggesting a clear hydrological connection between recharge and

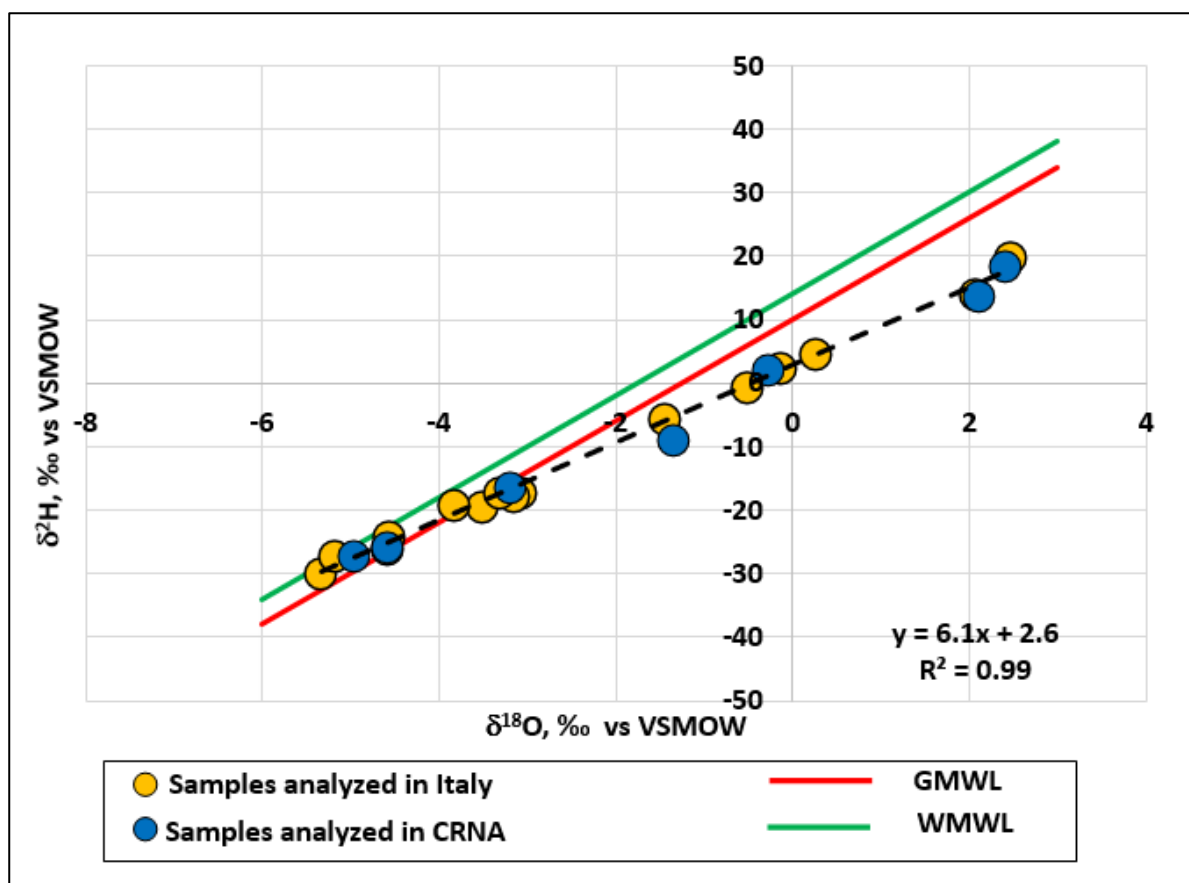


Figure 8. Plot of  $\delta^2\text{H} = f(\delta^{18}\text{O})$  (GMWL: Global Meteoric World Line, WMWL: Western Mediterranean World Line, V-SMOW : Standard Mean Ocean Water, CRNA: Centre de Recherche Nucléaire d'Alger).

Table 7. Statistical summary of isotopic analysis.

Name	Calibrated $\delta^2\text{H}$ Mean	Calibrated $\delta^{18}\text{O}$ Mean	Uncalibrated $\delta^{18}\text{O}$ precision	Uncalibrated $\delta^2\text{H}$ precision	Depth (m)
Meteoric water	-5,02	-31,98	0,15	0,55	
P15ALG	-5,33	-29,94	0,06	0,22	2.40
P8ALG	-0,31	0,01	0,35	1,51	5.20
P7ALG	0,25	3,91	0,48	2,06	3.90
P5ALG	-0,50	-1,67	0,05	0,27	4
P12	-3,08	-17,26	0,06	0,19	1.70
P4	2,45	19,82	0,19	0,91	8.40
P2	0,26	4,49	1,05	4,10	5.80
P3	2,06	14,02	0,49	2,08	2
P1	-3,17	-17,88	0,13	0,68	0.65
P13	-3,53	-19,51	0,43	1,81	9.30
P11	-3,85	-19,26	0,79	3,32	1.85
P9	-4,58	-26,01	0,22	1,22	1.65
P6	-5,19	-27,20	0,39	1,67	6.45
P14	-4,57	-24,20	0,27	1,05	3
P10	-3,31	-17,40	0,29	1,26	2.50

groundwater. The high potential of aquifer-river exchanges illustrates the high interplay between groundwater and surface water. Surface water has stable isotope values that are comparable to those found in groundwater and are discovered in the exact area. Therefore, wells situated near the study area were

feeding from the river during the low water period (April to September) characterized by both low rainfall and recharge. The fluctuation of stable isotope values in the groundwater is generated by the mixing of rainwater, surface water, and groundwater, as well as by the variation in stable isotope content of precipitation

and the effect of evaporation during the aquifer precipitation pathway. The groundwater isotope results showed that the samples between GMWL and LMWL indicate that groundwater recharge mainly resulted from rainfall and direct infiltration through the soil.

The latter hypothesis is supported by the isotopic similarities between the stable isotope values in river water and groundwater, and the high permeability of the geological formations. The formations in the foothills area (Quaternary river terraces and slope sediments) are mainly gravel and sand sediments. The site stable isotope values in groundwater with flow direction decreased downstream and upstream due to the main groundwater flow.

The groundwater in the downstream wells (p1, p13, p11, p12), definitely seems to be younger than that upstream (p2, p3, p4) because the aquifer is shallow (about 1m) and has been continuously regenerated by rainfall, which infiltrates quickly. There is a rapid recharge of the aquifer, and the infiltrated rainwater is recharged by the pollution generated by SONATRACH, which contaminates quickly the groundwater. The infiltration process of the company pollutants is faster due to the shallow wells in the area. Nevertheless, by linking these hydrological processes to the transport mechanisms of pollutants, the downstream part of the aquifer represented by P1 seems to be an extremely vulnerable zone to surface pollution. Indeed, any pollutant coming from the surface will quickly reach and contaminate the aquifer. The age of the groundwater is young because of the recharge and the rapid renewal of the stock because of the shallow depth of the aquifer and the type of soil.

## 5. CONCLUSION

The physico-chemical properties of most groundwater samples showed that the concentration of heavy metals in the water samples exceeded the WHO limits for drinking water. The same was also observed in soil samples, where heavy metal concentrations exceeded AFNOR limits, except in a few locations, which were within the guideline limits. According to the classification of the groundwater contamination assessment indices, the HPI indicates that most samples indicate medium to high levels of contamination in the study area. However, the values of this index are above the critical values. Nevertheless, stringent precautionary measures are recommended in this area, such as controlling the use of agricultural inputs, avoiding the use of wastewater and sewage sludge in agriculture, controlling the excessive use of industrial wastewater and organic fertilisers. After studying the integrated pollution indicators, it is estimated that 35% of water samples are unfit for consumption due to the

concentration of metal ions.

For the soil contamination indices, Igeo, Cdeg and EF show that most heavy metals have low and high loadings; the results of the CA and PCA analyses show that most of the variations can be explained by anthropogenic contaminants. Human activities such as wastewater from industrial sites, irrigation, fertilisation and groundwater abstraction have a significant impact on groundwater quality. Heavy metal contamination in these areas is high and continuous monitoring of water quality is important to avoid further deterioration of water resources. The data from this study will not only contribute to a better understanding of the factors affecting groundwater hydrochemistry and quality, but will also provide information on the potential uses of these water resources, thus contributing to resource management. This information is vital for groundwater management. It contributes to the efficient use of groundwater resources.

## REFERENCES

- Adimalla, N., & Wang, H.**, 2018. *Distribution, contamination, and health risk assessment of heavy metals in surface soils from northern Telangana, India*. Arab J Geosci 11:390. <https://doi.org/10.1007/s12517-018-4028-y>
- Afnor** 1999. *Norme française, microbiologie alimentaire, recherche des moisissures et levures, Méthode de routine*, Standard no.V 08-022.
- Backman, B., Bodiš, D., Lahermo, P., Rapant, S., & Tarvainen, T.**, 1998. *Application of a groundwater contamination index in Finland and Slovakia*. Environmental Geology 36:55–64. <https://doi.org/10.1007/s002540050320>.
- Barkat A., Bouaicha F., Bouteraa O., Mester T., Ata B., Balla D., Rahal Z, & Szabó G.**, 2021. *Assessment of Complex Terminal Groundwater Aquifer for Different Use of Oued Souf Valley (Algeria) Using Multivariate Statistical Methods, Geostatistical Modeling, and Water Quality Index*. Water 13:1609. <https://doi.org/10.3390/w13111609>
- Barkat A., Bouaicha F., Mester T., Debabeche M., & Szabó G.**, 2022. *Assessment of Spatial Distribution and Temporal Variations of the Phreatic Groundwater Level Using Geostatistical Modelling: The Case of Oued Souf Valley—Southern East of Algeria*. Water 14:1415. <https://doi.org/10.3390/w14091415>
- Belkhiri L., Mouni L., Sheikhy Narany T., & Tiri A.**, 2017. *Evaluation of potential health risk of heavy metals in groundwater using the integration of indicator kriging and multivariate statistical methods*. Groundwater for Sustainable Development 4:12–22. <https://doi.org/10.1016/j.gsd.2016.10.003>
- Bhutiani R., Kulkarni DB., Khanna DR., & Gautam A.**, 2017. *Geochemical distribution and environmental risk assessment of heavy metals in groundwater of an*

- industrial area and its surroundings, Haridwar, India. *Energ. Ecol. Environ.* 2:155–167. <https://doi.org/10.1007/s40974-016-0019-6>
- Bouaicha F., Dib H., Bouteraa O., Manchar N., Boufaa K., Chabour N., & Demdoun A.,** 2019. *Geochemical assessment, mixing behavior and environmental impact of thermal waters in the Guelma geothermal system, Algeria.* *Acta Geochim* 38:683–702. <https://doi.org/10.1007/s11631-019-00324-2>
- Bouteraa O., Mebarki A., Bouaicha F., Nouaceur Z., & Laignel B.,** 2019. *Groundwater quality assessment using multivariate analysis, geostatistical modeling, and water quality index (WQI): a case of study in the Boumerzoug-El Khroub valley of Northeast Algeria.* *Acta Geochim* 38:796–814. <https://doi.org/10.1007/s11631-019-00329-x>
- Chaturvedi A., Bhattacharjee S., Singh AK., & Kumar V.,** 2018. *A new approach for indexing groundwater heavy metal pollution.* *Ecological Indicators* 87:323–331. <https://doi.org/10.1016/j.ecolind.2017.12.052>
- Dhaouadi, S., Ghannem, S., Kanzari, S., & Bilal E.,** 2023. *Ecological risk assessment of heavy metals accumulation in soil and Zygophyllum Album: A case study of industrial phosphate vicinity, Tunisia,* *Carpathian Journal of Earth and Environmental Sciences* August 2023, Vol. 18, No. 2, p. 447 – 459; DOI:10.26471/cjees/2023/018/272
- Dinesh Kumar M., Jagadeesan S., & Sivamohan MVK.,** 2014. *Positive externalities of irrigation from the Sardar Sarovar Project for farm production and domestic water supply.* *International Journal of Water Resources Development* 30:91–109. <https://doi.org/10.1080/07900627.2014.880228>
- Durand-Delga M.,** 1969. *Mise au point sur la structure du nord-est de la berbérie.* *Publi. Serv. Geol. Algérie.* Nle série, pp 89-131
- Egbueri JC., & Unigwe CO.,** 2020. *Understanding the Extent of Heavy Metal Pollution in Drinking Water Supplies from Umunya, Nigeria: An Indexical and Statistical Assessment.* *Analytical Letters* 53:2122–2144. <https://doi.org/10.1080/00032719.2020.1731521>
- Facchinelli A., Sacchi E., & Mallen L.,** 2001. *Multivariate statistical and GIS-based approach to identify heavy metal sources in soils.* *Environ Pollut* 114:313–324. [https://doi.org/10.1016/S0269-7491\(00\)00243-8](https://doi.org/10.1016/S0269-7491(00)00243-8)
- Foued B., Hénia D., Lazhar B., Nabil M., & Nabil C.,** 2017. *Hydrogeochemistry and geothermometry of thermal springs from the Guelma region, Algeria.* *J Geol Soc India* 90:226–232. <https://doi.org/10.1007/s12594-017-0703-y>
- Hakima Z., Mohamed M., Aziza M., Mehdi M., Meryem EB., Bendahhou Z., & Jean-Francois B.,** 2017. *Environmental and ecological risk of heavy metals in the marine sediment from Dakhla Bay, Morocco.* *Environ Sci Pollut Res Int* 24:7970–7981. <https://doi.org/10.1007/s11356-017-8367-0>
- Hoenig M.,** 2001. *Preparation steps in environmental trace element analysis - facts and traps.* *Talanta* 54:1021–1038. [https://doi.org/10.1016/S0039-9140\(01\)00329-0](https://doi.org/10.1016/S0039-9140(01)00329-0)
- Horton RK.,** 1965. *An Index Number System for Rating Water Quality.* *Journal of the Water Pollution Control Federation*, 37, 300-306.
- Kumar A., Cabral-Pinto M., Kumar M., & Dinis PA.,** 2020. *Estimation of Risk to the Eco-Environment and Human Health of Using Heavy Metals in the Uttarakhand Himalaya, India.* *Applied Sciences* 10:7078. <https://doi.org/10.3390/app10207078>
- Liu Z., Fei Y., Shi H., Mo L., & Qi J.,** 2022. *Prediction of high-risk areas of soil heavy metal pollution with multiple factors on a large scale in industrial agglomeration areas.* *Sci Total Environ* 808:151874. <https://doi.org/10.1016/j.scitotenv.2021.151874>
- Mahmoodi M., Khormali F., Amini A., & Ayoubi S.,** 2016. *Weathering and soils formation on different parent materials in Golestan Province, Northern Iran.* *J. Mt. Sci.* 13:870–881. <https://doi.org/10.1007/s11629-015-3567-x>
- Marre A.,** 1992. *Le Tell oriental algérien: de Collo à la frontière tunisienne. Etude géomorphologique.* *Travaux de l'Institut de Géographie de Reims. France*
- Mehdi MR., Kim M., Seong JC., & Arsalan MH.,** 2011. *Spatio-temporal patterns of road traffic noise pollution in Karachi, Pakistan.* *Environ Int* 37:97–104. <https://doi.org/10.1016/j.envint.2010.08.003>
- Mohamadi A., Demdoun A., Bouaicha F., & Menani MR.,** 2021. *Evaluation of the quality of groundwater for its appropriateness for irrigation purposes using Water Quality Index (WQI), Mchira-Telegma aquifer case study, northeastern Algeria.* *Sustain. Water Resour. Manag.* 7:155. <https://doi.org/10.1007/s40899-021-00571-3>
- Mohan SV., Nithila P., & Reddy SJ.,** 1996. *Estimation of heavy metals in drinking water and development of heavy metal pollution index.* *Journal of Environmental Science and Health. Part A: Environmental Science and Engineering and Toxicology* 31:283–289. <https://doi.org/10.1080/10934529609376357>
- Muller G.,** 1969. *Index of Geoaccumulation in Sediments of the Rhine River.* *GeoJournal*, 2, 108-118.
- Prasad B., & Mondal KK.,** 2008. *The Impact of Filling an Abandoned Open Cast Mine with Fly Ash on Ground Water Quality: A Case Study.* *Mine Water Environ* 27:40–45. <https://doi.org/10.1007/s10230-007-0021-5>
- Prasad B., & Sangita K.,** 2008. *Heavy Metal Pollution Index of Ground Water of an Abandoned Open Cast Mine Filled with Fly Ash: a Case Study.* *Mine Water Environ* 27:265–267. <https://doi.org/10.1007/s10230-008-0050-8>
- Rahman MATMT, Paul M., Bhounik N., Hassan M., Alam MK., & Aktar Z.,** 2020. *Heavy metal pollution assessment in the groundwater of the Meghna Ghat industrial area, Bangladesh, by using water pollution indices approach.* *Appl Water Sci* 10:283. <https://doi.org/10.1007/s13201-020-01266-4>
- Rajkumar H, Naik PK, & Rishi MS.,** 2019. *Evaluation of heavy metal contamination in soil using geochemical indexing approaches and chemometric techniques.* *Int. J. Environ. Sci. Technol.* 16:7467–7486. <https://doi.org/10.1007/s13762-018-2081-4>

- Raoult J F.**, 1974. *Géologie du centre de la chaîne numidique (Nord - Constantinois, Algérie)*. Mém. Soc. Géol. Fr., N.S., t. LIII, n 121, 164 p
- Rezaei A., Hassani H., Hassani S., Jabbari N., Fard Mousavi SB., & Rezaei S.**, 2019. *Evaluation of groundwater quality and heavy metal pollution indices in Bazman basin, southeastern Iran*. Groundwater for Sustainable Development 9:100245. <https://doi.org/10.1016/j.gsd.2019.100245>
- Rodier J.**, 2009. *L'Analyse de l'Eau: Eaux Naturelles, Eaux Résiduaire et Eaux de Mer*. 9th Edition, DUNOD, Paris, 1384.
- Saleem M., Iqbal J., & Shah MH.**, 2015. *Geochemical speciation, anthropogenic contamination, risk assessment and source identification of selected metals in freshwater sediments—A case study from Mangla Lake, Pakistan*. Environmental Nanotechnology, Monitoring & Management 4:27–36. <https://doi.org/10.1016/j.enmm.2015.02.002>
- Samia TB., Houria KB., Nacer K., & Marc C.**, 2013. *Assessment and management of water resources in Northeastern Algeria: case of watersheds Kebir West Safsaf and Guebli rivers, Skikda*. Appl Water Sci 3:351–357. <https://doi.org/10.1007/s13201-013-0085-2>
- Singh UK., & Kumar B.**, 2017. *Pathways of heavy metals contamination and associated human health risk in Ajay River basin, India*. Chemosphere 174:183–199. <https://doi.org/10.1016/j.chemosphere.2017.01.103>
- Suvarapu LN., & Baek S-O.**, 2017. *Determination of heavy metals in the ambient atmosphere*. Toxicol Ind Health 33:79–96. <https://doi.org/10.1177/0748233716654827>
- Uugwanga MN., & Kgabi NA.**, 2021. *Heavy metal pollution index of surface and groundwater from around an abandoned mine site, Klein Aub.* Physics and Chemistry of the Earth, Parts A/B/C 124:103067. <https://doi.org/10.1016/j.pce.2021.103067>
- Vila J. M.**, 1978. *Carte structurale au 1/500 000 de la chaîne alpine d'Algérie orientale et des confins Algéro-Tunisiens*. C.N.R.S & B.E.I.C.I.P. France.
- Vila J. M.**, 1980. *La chaîne alpine d'Algérie orientale et des confins algérotunisiens*.
- Wagh VM., Panaskar DB., Mukate SV., Gaikwad SK., Muley AA., & Varade AM.**, 2018. *Health risk assessment of heavy metal contamination in groundwater of Kadava River Basin, Nashik, India*. Model. Earth Syst. Environ. 4:969–980. <https://doi.org/10.1007/s40808-018-0496-z>
- Wang Z., Wei J., Peng W., Zhang R., & Zhang H.**, 2022. *Contents and spatial distribution patterns of heavy metals in the hinterland of the Tengger Desert, China*. J. Arid Land 14:1086–1098. <https://doi.org/10.1007/s40333-022-0027-7>
- Werkenthin M., Kluge B., & Wessolek G.**, 2014. *Metals in European roadside soils and soil solution—a review*. Environ Pollut 189:98–110. <https://doi.org/10.1016/j.envpol.2014.02.025>
- WHO.**, 2011. *Guidelines for drinking-water quality, 4th edn*. World Health Organization, Geneva
- Wildi W.**, 1983. *La chaîne tello-rifaine (Algérie-Maroc-Tunisie): structure, stratigraphie et évolution du Trias au Miocène*. Revue de Géologie Dynamique et Géographie Physique, pp 201–298.
- Xu L., Dai H., Skuza L., & Wei S.**, 2021. *Comprehensive exploration of heavy metal contamination and risk assessment at two common smelter sites*. Chemosphere 285:131350. <https://doi.org/10.1016/j.chemosphere.2021.131350>
- Zeng X-b., Li L-f., & Mei X-r.**, 2008. *Heavy Metal Content in Chinese Vegetable Plantation Land Soils and Related Source Analysis*. Agricultural Sciences in China 7:1115–1126. [https://doi.org/10.1016/S1671-2927\(08\)60154-6](https://doi.org/10.1016/S1671-2927(08)60154-6)
- Zinn YL., Faria JAd., Araujo MAd., & Skorupa ALA.**, 2020. *Soil parent material is the main control on heavy metal concentrations in tropical highlands of Brazil*. CATENA 185:104319. <https://doi.org/10.1016/j.catena.2019.104319>

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