# RESEARCH ARTICLE

## ASSESSMENT OF HEAVY METAL IN SPRING WATER, OF RABAT-SALE-ZEMOUR–ZAER AREA (MOROCCO)

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**ABSTRACT**

The quality of groundwater has in recent years undergone some deterioration because of uncontrolled liquid or solid urban waste, intensive use of chemical fertilizers in agriculture and its disorderly exploitation groundwater. It is, with this objective in mind, that the present study is to conduct a sampling campaign for a quantitative assessment of trace metals (Pb, Cu, Cd and Cr). The samples were collected between March and June 2010, 51 springs distributed over the study area sources. The results reveal the presence of a very low metal contamination compared to WHO recommended in all water sources values, except that of the source S51. For the entire study area, the Lead is the most dominant over the other heavy metals with a maximum of 15.9 μg L-1, Chrome is 10 μgL-1while the maximum copper is 6 μgL-1. However all sources show a concentration below the detection limit for cadmium. Moreover, if the concentrations recorded are not conducive to immediate concerns and cannot cause acute toxicity, the cumulative risk of lead and chromium in the various compartments of the ecosystem (water, flora and fauna) that is transmitted throughout the food chain should be noted.

## INTRODUCTION

Potential sources of groundwater pollution have increased in the last century (Danielpol and al., 2003). They can migrate into groundwater and represent a major health problem. In northern Russia, half a million people in the Kola Peninsula drink water contaminated with heavy metals, which explains the high infant mortality and endemic diarrheal and intestinal diseases that reported in this region (Edwards, 1997). They can also accumulate in the food chain and pose risks to human health (Jourdan and al., 2005). The presence of heavy metals in water takes place by means of natural and human sources. Indeed, intensive human activities generate high concentrations of heavy metals that come from several sources such as domestic and industrial wastewater, agricultural production, air pollutants, old uncontrolled landfills, and liquid and solid waste. But it can also be of natural origin via volcanoes, hot springs activity, mining, erosion. In addition, several factors seem to be decisive in the mode of contamination of groundwater by these metals, including: metal concentrations in soil type, rainfall, litho logy, and permeability of the aquifer used and the depth of the water (Kholtei and al., 2003). Generally, the majority of metal contaminants are likely to reach the groundwater passing through the soil. In this way, they can undergo bio-physico-chemical transformations, which have the effect of either to stop, delay, or promote. Solubilization and transport by seepage. In Morocco, the specific work revealed that the contaminated water by heavy metal is due to different sources of pollution. Indeed, some studies show the metal pollution in groundwater (Serghini and al., 2003); estuaries (Tahiri, 2005; Moghit, 2009); watercourses (Fekhaoui and al, 1996). All these studies conclude that these types of pollutants come from industrial, domestic well developed in these areas of study activities. Finally, other studies have found a natural metal contamination of surface water and feel that this pollution comes from mine drainage (El hachimi and al., 2005; M. El Adnani and al., 2005; El hachimiet al., 2007). Our study is based on the assessment of heavy metals, especially Lead, chromium, cadmium and copper in the rural area of the region of Rabat-Salé-Zemour-Zaer. The latter presents no potential sources of industrial pollution, without any time to exclude that of agricultural origin. The objective of this work is to contribute to a better understanding of the assessment and distribution of these elements in the different sources of RSZZ region, to identify similarities and distortions between the different parameters on the quality of these waters and to identify factors in the contamination by heavy metals through a coherent spatiotemporal structure. To do this we subjected the data quality of these water points to a principal component analysis (PCA).

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## MATERIALS AND METHODS

### Study sites and sampling

RSZZ theregionis characterized by a geographical diversity defined by a limited to a narrow coastal strip (area of Rabat-Salé) oceanic domain, a semi-continental area (areas Tiflet, Rommani and Khémiss) and a mid-mountain area (Oulmèsarea).This prospective study was conducted during a single campaign between March and June2010.It is based on the evaluation of trace metals (Pb, Cu, Cd and Cr) 51sources of RSZZ region. The criterion for selection of sources is based on anon-exhaustive enumeration but rather on the sustainability of the water flow in all seasons and the frequency of use by households. The coordinates of each selected source were recorded using a GPS Explorist 400. For the analysis of trace metals (SEM), all samples are performed in polyethylene tubescontaining50mlof nitric acid (Merck, 65%) high purity fix. The study area was divided in to sub-regions: the sub-region Zaer, the sub-region Sehoul, sub-region Tiflet and sub-region Oulmès (Figure 1 and Table 1).

**Table 1.Distribution of analyzed by sub-region sources**

| Sub-region | Number of Sources analyzed |
|---|---|
| Zaer | 25 (from S1 to S25) |
| Sehoul | 13 (from S26 to S38) |
| Tiflet | 6 (from S39 to S44) |
| Oulmès | 7 (from S45 to S51) |

For each source as signed a unique code, one is composed of the letters followed by a number indicating the source was. In the sub-region Zaer is the largest and fill in the continent which has been operational since 2007, deals with household garbage and industrial waste from the municipalities of Rabat, Saléand Temaraarea. To better assess the impact of the land fill each at eon water sources, we divided the sub-region in to two sub regions Zaer: Oum Azzawheresitudis charge and Nkhila-Merchouch-Zhiliga (Table 1) & (Figure 1).

### Methods of analysis

**Physical Variables:** The temperature of the water sources was made using a mercury thermometer graduated to 1/10 of a degree Celsius, pH measurements were made using a pH meter ORION Research, Ionalyser model ORION model 607 91-05 with specific electrode, the conductivity measurements (expressed as S / cm) were made using a YSI conductivity type (model 33); S-C-T Meter.

**Determination of Heavy Metals:** Concentrations of lead, copper, chromium and cadmium were determined by Atomic Absorption Spectrophotometer electro thermal (GF-AAS) VARIAN.240.Zeeman kind.

**Statistical Analysis:** The spatio-temporal variability of metal concentrations was investigated by the principal component analysis performed using statistical software SAS (Statistical Analysis System) and STA-FITC on a data matrix consisting of 51 samples corresponding to the seven variables (water temperature, pH, conductivity, Pb, Cu, Cd and Cu).

## RESULTS AND DISCUSSION

### Physical Parameters

The analysis of physical parameters (Table II) shows water temperatures ranging from 19 sources to 25°C except the source S50 which recorded a temperature of 42°C. The measured pH is generally in the range of standard for potability and near neutrality with values varying between 6.4 (S24) and 7.79 (S18) with the exception of sources (S46, S22, S50, S23), which respectively show pH of 5.38; 5.5; 5.87 and 6.06. The values of electrical conductivity measured ranged from 91.7 µs/cm recorded at the source and S46 2380 µs/cm found at the source S51. All other values in the range of the required standard by WHO potability and not exceeding 2700 µs/cm except the source S18 which records a conductivity of 3690 µs/cm.
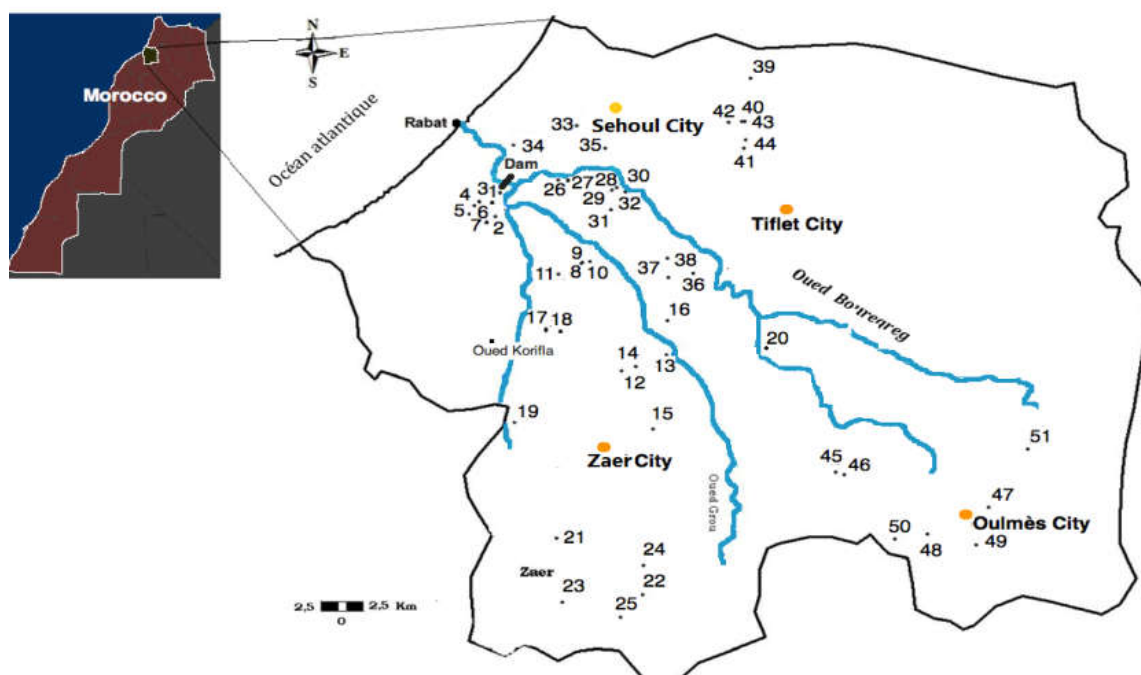


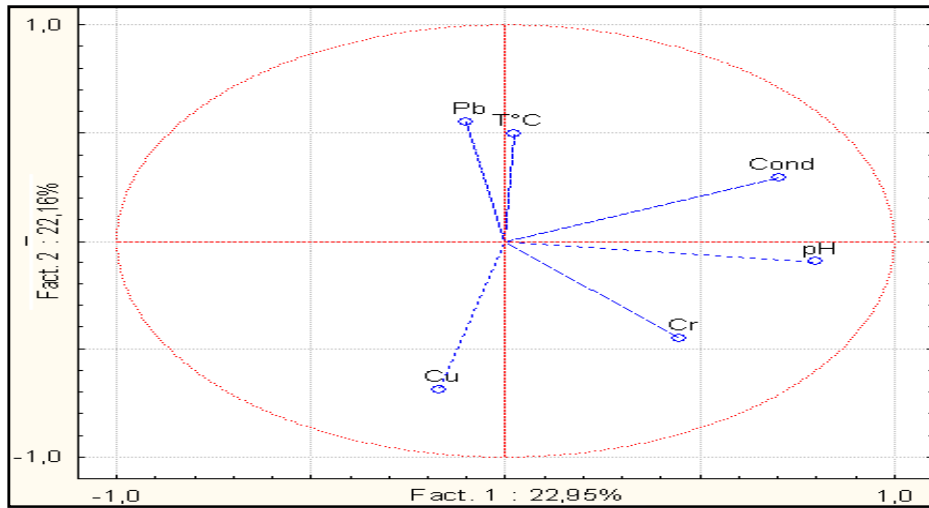**Figure1.Geographic location of the sources studied**

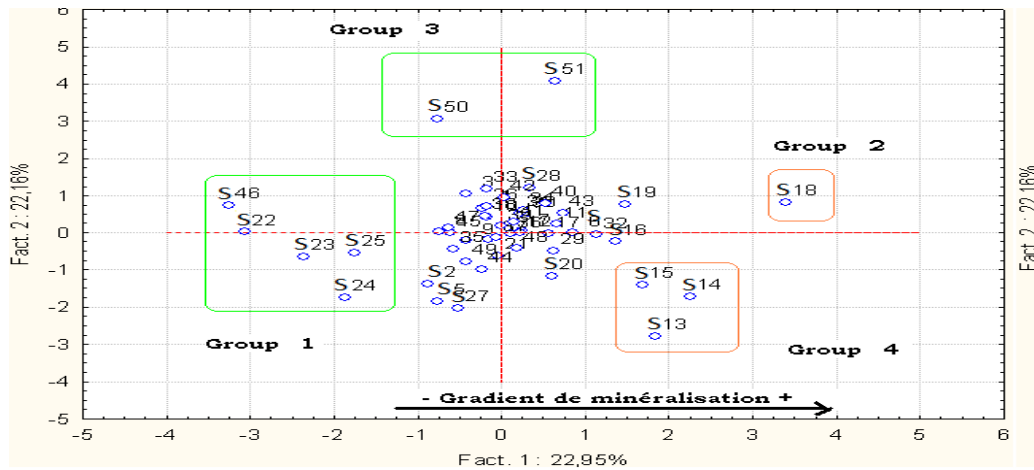**Figure 2. Graphical representation of PCA-based analysis in F1XF2 plane Factorial map variabls**



**Figure 3.Graphical representation of PCA-based analysis inF1XF2plane Factorial mapsources**

## Chemical Parameters: Metallic Trace Elements (MTE)

The concentrations of trace metals vary from one station to another and from one element to another. In general, they show a very low metal contamination compared to what WHO suggested except the source S51 which has a high lead concentration values. The presence of these elements is most often dominated by Pb with a maximum of 15.9 µgL-1 (S51), the Cr is 10.55 µgL-1 (S13) while the Cu is 6 µgL-1 (S5). However all sources show a cadmium concentration of less than the detection limit (see results in Table 2).

**Table2. Average chemical composition insometrace elements (ppm) invarious rocksfromVinogradov,1956 and Turekian and Wedepohl, 1961**

| Heavy metals | Vinogradov,1956 | | Turekian et wedepohl, 1961 | |
|---|---|---|---|---|
| | Basalts | Clays and shales | Sandstone | Carbonate rock |
| Pb | 8 | 20 | 7 | 9 |
| Cu | 100 | 57 | .. | 4 |
| Cr | 200 | 100 | 35 | 11 |
| Cd | 0,19 | 0,3 | 0 | 0,035 |

**Table 3.Concentrations of trace elements (ppm) in rocks of Watershed Bouregreg (Bounouira, 2007)**

| Rocks | Lead | Chrome |
|---|---|---|
| Ordovician shales | 13,4 | 148,65 |
| Devonian shales | 22,39 | 127,5 |
| Ment granites | 27 | 20,5 |
| Granites Oulmès | 23,93 | 19,2 |
| Triassic basalts | 2,29 | 309,45 |
| Quaternary basalts | 21,52 | 7,49 |
| Ordovician quartzites Superior | 3,98 | 16,21 |
| Visean limestones | 8,88 | 27,23 |
| The shales of the Triassic | 28,5 | 108,96 |

**Table 4.Percentage of element concentrations detectable traces in the water source are a RSZZ**

| Heavy metals | Percentage of the lower detection levels | Percentage of detectable levels |
|---|---|---|
| Lead | 1,9% | 98,03% |
| Chromium | 27,45% | 72,54% |
| Copper | 24,49% | 74,5% |
| Cadmium | 100% | 0% |

**Table 5. Distribution of inertia between the two axes (F1XF2)**

|  | F1 | F2 |
|---|---|---|
| Proper value | 1,377047 | 1,329381 |
| Inertia (%) | 22,95078 | 22,15635 |
| Cumulative inertia % | 22,9508 | 45,1071 |

**Table 6. Codes of variables and correlations with the variousaxes of the PCA**

| Variabls | code | F1 | F2 |
|---|---|---|---|
| T°C | T°C | 0,02 | 0,499 |
| pH | pH | 0,80 | -0,098 |
| conductivity | cond | 0,702 | 0,293 |
| lead | Pb | -0,100 | 0,551 |
| copper | Cu | -0,17 | -0,69 |
| chromium | Cr | 0,449 | -0,450 |

## Lead

For the entire study area, lead concentrations ranged from below the detection limit of minima and maxima of 15.9 µgL-1 (S51) raised to OULMES. However, different regions show low spatial variability. Indeed, the region of Sehoul has values between 0µgL-1 and 7.2 µgL-1(S33). Zaer region subdivided into region of Oum Azza which shows a variation between 0.2 µgL-1 (S5) and 5.5 µgL-1 (S3), while the sub-region Nkhila Merchouch-Zhiliga has values between 0,2 µgL-1 (S9) and 4.5 µgL-1 (S22). Around Tiflet, these values are between 0.1µgL-1 (S41) and 4.5µgL-1(S42). Only the source (S51) located Oulmès which has a value that exceeds the lead recommended by WHO (10 µgL-1) value.

## Chromium

The concentration of chromium varies between less than the detection limit value (DLV) and a maximum of 10.55 µgL-1 (S13) raised to Nkhila-Merchouch-Zhiliga, the sub-region of Oum Azza shows a variation between DLV and 7.1 µgL-1 (S6). However, different regions show low values. Indeed Sehoul region has a value between DLV and 3.9 µgL-1 (S32). Around Tiflet, these values are 0.42 µgL-1 (S42) and 1.92 µgL-1 (S44). While OULMES region has a value between DLV and 1.91 µgL-1 (S48). However, chromium concentrations remain very low compared to the maximum permissible concentration determined by WHO (50 µgL-1).

## Copper

Around Zaer (sub region Oum Azza and sub region Nkhila Merchouch-Zhiliga), the concentration of copper varies between DLV and 6 µgL-1 (S5) and 5 µgL-1 (S5, S20) respectively in Oum Azza and in Nkhila-Merchouch-Zhiliga. The region of Sehoul has a copper value not more than µgL-1 (S27). In Tiflet the values are between DLV and 3 µgL-1 (S44). While OULMES region value does not exceed 2 µgL-1 (S 49,S50). However, copper concentrations are very low compared to the maximum permissible concentration determined by WHO (2000 µgL-1).

## Cadmium

It is noted that cadmium content was undetectable in all samples studied.

## Metal contamination

The conductivity, temperature and pH are used to define the basic characteristics of water.

Research contrasts these physicochemical parameters between different measurement points facilitate the detection of polluted areas or different geology. In our study, the conductivity values measured at the 51 sources of RS2Z region oscillate between 91.7 and 2380 µs/cm not exceeding 2700 µs/cm value corresponding to the required standard for drinking water by the WHO. Spatial variations are very important and indicate a large diversity of litho logical facies of the region. Source (S18) which records a conductivity of 3690 µs/cm and a pH of 7.79 is an exception that could be due to the heavy pollution to the emergence of this source. Moreover, the sources (S46), (S22), (S50) and (S23) which show respectively pH 5.38; 5.5; 5.87 and 6.06 are of water crossing granitic rocks. Resented their influences on the pH drop. Despite the presence in the environment close to the emergence of certain sources of waste containing heavy metals such as batteries (Pb, Cd), plastics (Cd), paper cartons (Pb) (De Miquel, 2001) we found minimal values of these metal elements. This suggests that the soil of the region, characterized mainly by shales, sandstones and quartzites (Combe M., and al, 1975), probably not only facilitates the transition metal elements by infiltration of water to the water groundwater. In addition, these metal contaminants, which are usually very low dose, does not influence directly on the quality of the water flowing in the soil in depth.

Outside source Kharouba located Oulmès and has a value of 15 µgL-1 of lead exceeding the WHO recommended value, detailed analysis of the levels of SEM shows a low metal contamination. Indeed, the majority of water sources known low value, these results are in agreement with the work of (Serghini and al., 2003) who studied the pollution of groundwater in Mohammedia, as the results obtained during the study on groundwater in most provinces of the Kingdom and which shows concentrations of lead and cadmium which are well below the drinking water standards Moroccan and reveals values not exceeding 6 µgL-1 for lead and 0.5 µgL-1 for cadmium (Rapport, 2005).

Otherwise, lead is present in the earth's crust and in all compartments of the biosphere. In air emissions of lead from conveyed in the soil after degradation and erosion volcanic dust. But generally, these natural processes only rarely lead to high concentrations of lead in the environment. The presence of lead to higher than normal concentrations in groundwater must be connected to urban, industrial and agricultural. It is not essential to living organisms and its presence at high levels is toxic. In fact, lead is responsible for many harmful diseases in humans (brain disorders, reproduction, metabolism, poisoning ...).Chromium is present in small amounts in nature and preferentially concentrates in the basic rocks, unlike siliceous rocks. Its solubility is low due to the phenomena of leaching. Chromium is an element foreign to water: its presence is due to emissions from plating shops. Chromium is required in small quantities to ensure the health of humans and animals. But when taken in too large quantities, metal accumulates in various organs in humans such as the kidneys, liver and spleen and cause renal, and pulmonary arterial lesions manifested by cancer, decreases male fertility, increased intrauterine mortality. In our study, the maximum chromium concentration remains low compared to the values suggested by the WHO, it must however take into account the bio accumulative risk of this metal during continuous use and for long periods of these water sources. Copper occurs in nature as mineral native copper ores or oxidized sulfur.

Copper salts (sulfate, acetate, organic derivatives) are used as fungicides or algicides in agriculture. Copper is an essential component of the diet and is necessary for many enzymatic reactions. But it is toxic at high concentrations. In our study area, copper shows very low values with a maximum of 6 µgL-1 and are far from the WHO recommended values. From these results it does not present a health risk. Cadmium is a natural element in the earth's crust average concentration of 0.2 ppm. This may be due to alteration and erosion of cadmium-bearing rocks. When very high levels of cadmium are found in the waters of groundwater, its origin must be sought in industrial effluents. In addition, the presence of cadmium as a contaminant in fertilizers used in agriculture can contribute to the pollution of the aquifer (Helcom 2002). Rural area RSZZ lies in an area far from urban pollution brought by sewage, garbage leachate except the OumAzza landfill, as well as outside of any industrial pollution represented by effluents, solid waste and atmospheric inputs, which explains the low levels of heavy metals. This low detection can also be explained by the lack of agricultural pollution is represented by the use of poor fertilizer these metals. Therefore, the influence of human activities such metal pollution appears to be low, reflecting the low content of these elements. Against all odds, we also noted that the sources (S1, S2, S3, S4, S5, S6, S7) located near the Oum Azza shock, do not exhibit significant values for heavy metals analyzed in this study. For against, the source has a maximum value Kharouba lead over other sources and is far from anthropogenic pollution, suggesting that the lead intake cannot be explained by its presence in the bedrock aquifer that consists Oulmes granites. In Table 2, we present the average chemical compositions of trace elements (Pb, Cu, Cr and Cd) in the rocks that form the bedrock geology of the study area. This table shows the extent to which these geological formations contribute to the enrichment of the aquifer by trace elements (Table 2). From Table 2, we see that these rocks contain high levels of chromium in copper means but relatively low lead.

While rates of cadmium in these rocks are very low, this explains the absence of cadmium in water sources in the region of study. Table 3 shows that the chemical analysis of lead and chromium performed on rocks collected along the watershed of Bouregreg (Bounouira H, 2007). From this table, we see that the chromium in these rocks has the highest rate, but when compared with those in the water sources we see the opposite case (Table 4). Indeed, chromium has the lowest rate compared to lead in water sources. This table shows that lead is detectable in almost the majority of spring water even at low levels, and that other metals (chromium and copper) are present in similar percentages (72.54%, 74.5%) but relatively low compared to those of lead. While the cadmium is un detectable. The concentrations of lead dissolved in the water source depend on several factors such as pH, alkalinity, water temperature, water hardness and nature of the rock aquifers. Indeed, lead carbonate rocks in the chemically etched by carbonic acid is easily dissolved in water, which explains its high content in the source water has an acidic pH S51 which, excess $CO_2$ and presence of this metal in the aquifer represented by granite rock Oulmes. Reverse against low chromium contents can be explained partly by the fact that these elements do not exhibit contact surfaces with water sufficiently large to be potential sources of chromium, on the other hand the characteristics of the metal and the physicochemical conditions of the aquifer has the effect of adsorbing. It is certain that some conclusions require to be confirmed by refining the arguments by extensive research on the behavior of heavy metals in their natural conditions studies. In general, the mobility of trace metals depends on the ion adsorption phenomena or exchanges, their involvement in acid-base equilibria and redox.

## Typological Structure of The Metal Contamination of Water Sources

This principal component analysis (PCA) is performed on a matrix composed of 51 corresponding to the seven variables (water temperature, pH, and conductivity, Pb, Cu, Cd and Cu) data.In the factorial design F1XF2: Clean the two components F1 and F2 values and their contribution to the total inertia are shown in Table 5 and Figure 2 variable codes are shown in Table VI. Both axes to be considered to describe the correlations between the variables related to spatial structures, hold 45% of the total information with 22.9% and 22.15% respectively(Table 6)The principal axis (F1) is determined by the pH (r2 = 0.8) and the conductivity (r2 = 0.7) (Table 6). It defines a gradient mineralization leading to an increased mineralization represented by Conductivity.The principal axis (F2) is moderately correlated with T ° C (r2 = 0.49), Pb (r2 = 0.55), and negatively with the Cu (r2 = -0.69) and chromium (r2 = -0.45). It defines an increasing gradient of contamination by lead on the positive side and the copper and chromium on the negative side of the gradient (Figure 2).The organization identified by F1XF2 plane (Figure 3) can distinguish four groups of stations according to their degree of mineralization and the burden of trace metals: (Figure 3)

**Group 1** represented by S22, S23, S24, S25 and S46 are the sources of water with low mineralization and low metal loading.

**Group 2** is represented by the single source S18. It is the pole of the most significant mineralization.

**Group 3** represented by the sources S50 and S51 are that at high temperature and high load in Lead respectively.

**Group 4** defined by S13, S14 and S15 is one of sources where the content of copper and chromium are the most significant sources.

At the center of these groups include the rest of the sources whose quality is intermediate (average mineralization and average attendance Metal trace element).The interpretation of the results of analyzes of water sources can generate a very variable quality in a wide range of related processes and localized contamination (geological influences group 3 and 4, 2 and anthropogenic influence group specific influence space for monometallic other groups).

## Conclusion

Other than the source Kharouba having a lead concentration that exceeds the standard, the majority of sources recorded however heavy metal concentrations well below the maximum permissible concentrations recommended by the international standard (WHO) for drinking water. The rural area of Rabat-Salé-Zemour-Zaer, known by the absence of significant industrial pollution, reveals low concentrations heavy metals. Nonetheless, the comparison with the results of other work on the metal contamination of the estuary Bouregreg located in the same region showed a strong contamination of certain

heavy metals (Pb, Cr, Cd, Cu) and believe that this contamination is discharges of domestic and industrial wastewater from two cities Rabat and Salé (El Adnaniand et al., 2005). This shows the influence of human activity on the transfer of heavy metals in a natural environment. On the other hand, these results suggest a lack of intake of heavy metals by agricultural activity in water sources. Thus, the low heavy metals are due to the geological formation of the aquifer through which groundwater. But, the teneure cadmium is undetectable in all samples studied; indicate that the metal is not a natural constituent of the rocks.Unlike many organic pollutants, heavy metals are not removed by biological pathway, which promotes their cumulative effect in the various compartments of the ecosystem (water, sediment, flora and fauna). Indeed, if the recorded concentrations of lead and chromium lesser degrees, do not lead to immediate concerns and can cause acute toxicity, it should be stressed that the bio accumulative risk of lead and chromium can be transmitted throughout the food chain, posing a risk to health.

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**Conflict of interest**
The authors declare no conflicts of interest

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