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Metal typology contamination of surface waters of Za River, Lower Moulouya, Eastern Morocco

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ABSTRACT

The region Taourirt endures a big problem of pollution of surface waters. This pollution has diverse origins, domestic, agricultural and industrial. Evaluation of the concentration of the metals studied (Al, As, Se, Mn, Ni, Fe, Zn, Cu, Cr, Pb and Cd) in surface water has revealed the presence of a large metal contamination, mainly in the river downstream of releases. Heavy metals soluble in water after filtration is determined by atomic emission spectroscopy with inductive coupled plasma (ICP-AES) using a JY-type spectrometer. To better assess the impact of wastewater on water quality of the Za River and its tributary oued Tizeghrane, and analyze between the different variables through their structuring and guidance correlations and to identify the main factors responsible for the water quality of the surveyed environment, we treated statistically all data by Principal Component Analysis (PCA). The typological structure of the plan analysis F1 x F2 shows the identification of four areas, depending on the nature of metal pollutants, their degree of contamination and the "season", this factor seems to be a determining factor in the type of flow studied.

Keyword: heavy metals, industrial pollution, surface waters, Za River, PCA, ICP-AES.

INTRODUCTION

Industrial applications of heavy metals in various sectors of economic activity are numerous. They are increasingly encountered in natural waters and sediments at abnormally high concentrations[1] The industry has often favored sites close to rivers for three reasons: transport of raw materials, water supply (cooling facilities) and possibilities of industrial effluent. Heavy metals are micropolluants of nature to cause nuisances even when they are released in very small quantities, their toxicity develop by bioaccumulation [2];[3];[4].The absence of heavy metals degradation’s phenomena makes significant persistence in streams receptacles discharges upstream industries. Therefore, they finish with starting between the different compartments of the aquatic ecosystem (Water, suspended matter, algae, Fish, Sediments…) sometimes provoking the rupture of certain biological balance.

Higher awareness of the ecological effects of toxic metals and their accumulation through food chains has prompted a demand for purification of industrial wastewaters prior to their discharge into the natural water bodies and increasing interest has been shown in the removal of heavy metals [5]. Heavy metals are introduced in aqueous media in different forms: particulate, colloidal and or in solution [6]. Most of the metals are generally associated with the fine particle size fraction smaller than 63µm [7];[8]. Every metal possesses a certain affinity for organic matter and/or the mineral phase: clays, carbonates, iron oxides and manganese.

In Morocco, pollution of water resources by industrial effluents is increasingly important; three types of industries pose serious problems for producers of drinking water, namely: oil mills, sugar mills and tanneries; all of the results proved that area waters are showing signs of deterioration Moulouya, since the majority of values recorded revealed that they exceed the Moroccan standards [9].

In the peri-urbain zone of North East of Morocco, and at the level of the province of Taourirt, the watercourse of water of ZaRiver, largest affluent of the lower Moulouya, was naturally alimented with sources of brackish water. It played an important role at the irrigation of cultures, livestock watering and ecotourism animation of the cascade area. However, since few years, the watercourse receives at open air; the releases of Taourirt used water, where the ecologic and sanitary impacts are multiple. The population of the province has about 233,188 inhabitants, including 150,190 urban and rural 82998, this population is 43,676 households. 29944 divided into urban and rural 13 732, according to the last national census of 2014[10]. While it was estimated at 206,762 inhabitants in 2004.The consummation of drinkable water goes up 2.8 Mm^3/year in 2011, whereas in industrial water, it is 107 970 m^3/year. These releases are of 2.25 Mm^3/year, where almost 1.46 Mm^3/year are treated in a sewage treatment plant. In 2005, this plant of natural lagooning type is commissioned, serving 130.000 EH. The good functioning is challenged by the absorption of discharges of untreated olive crushing units (modern and traditional), and canning (anchovies, olives, apricot ...) that exist within the city.However, the industrial fabric of the city occupies an area of 70 hectares and contains 75 industrial units of which 67 are olive canneries, and only 21 of these units are operational. They generate more pollution with a rejected debit 2321 m3 / year. These industrial wastes are dumped untreated into Al Kariyane Wadiwho joined Tizehgrane. Za river aroused the interest of many researches on the study of the quality of its waters [11]; [12], and the longitudinal distribution of macroinvertebrates [13]; [14]; [15]; [16]; [17]. The work carried out on a stretch of the ouedTizehgrane is original, since no Eco toxicological research has been carried out before. This interest lies primarily in the fact that it receives domestic effluents of the city from Wadi-Et tyuor and industrial waste including vegetable water during the crushing of olive wastewater and cannery (anchovies, olives, apricot ...) from wadikariyane[11]. OuedTizehgrane is the only outlet for discharges of the city, which became thus a real sewer carting all wastewater categories. The facts on the ground findings are alarming. Foul odors emanating from the wadi, and blackish releases, suggesting the existence of a high degree of pollution of these waters. This work is a draft that outlines pollution of the river, which aims to alert and sensitize communities to address this pollution. Our study focuses on changes in the quality of theTizehgranewadi and its impact on the Za River, realizing a space-time monitoring of metals parameters of waters sampled in order to clarify the current situation of the pollution.

MATERIALS AND METHODS

2.1. Study area and sampling stations:

Za River, located in Morocco Oriental, is a permanent tributary of the right bank of the Moulouya (Figure 1). Its watershed has an area of 18 000 km^2, has its source in the "HautsPlateaux Oriental", It drains the southern and western part of the chain of Horsts formed of dolomite and limestone marl most to least. The general direction is South-East North-West. He joined the Moulouya to Melga El Ouidane, downstream of the city of Taourirt. It crosses from upstream to downstream the arid Mediterranean bioclimatic floor in the Highlands, semi-arid in the chain of Horsts and aride in the region of Taourirt [14].According to statistics for years (2010, 2011), provided by the hydrological basin agency of Moulouya, the annual average flow of about 1,42m^3/s. The scheme of this river is characterized by high water April 7,46m^3/s in October and 7.12 m^3/ s and low water in summer 1,8m^3/s in July[14], the summer low flow is accentuated by uncontrolled water diversions for irrigation. Tizeghrane wadi, a tributary of the left bank of the Za River, its length is estimated at 10 km, SSE-NNW orientation. It drains recent Quaternary formations formed talus and cones and not encrusted and equipment, based on the average Quaternary. In its southwest part, it drains conglomerates and Plio-Villafranchian based on marl calcareous clay and dolomite Jurassic[11].Tizeghrane river, receives the domestic waste led by Et-tyour river and industrial discharges led through Kariyane river. These discharges, olives washing water highly basic and high in salt, bleach water, water from brines coring step olives laden with salt, vegetable water from oil mills and releases of dairy.

Given the general objective of the study, the choice of sampling stations was carried out based on the implantation of human and industrial activities. Four stations were selected (Figure 1), three on the lower reaches of the Za river, and one on its tributary Tizeghrane river.

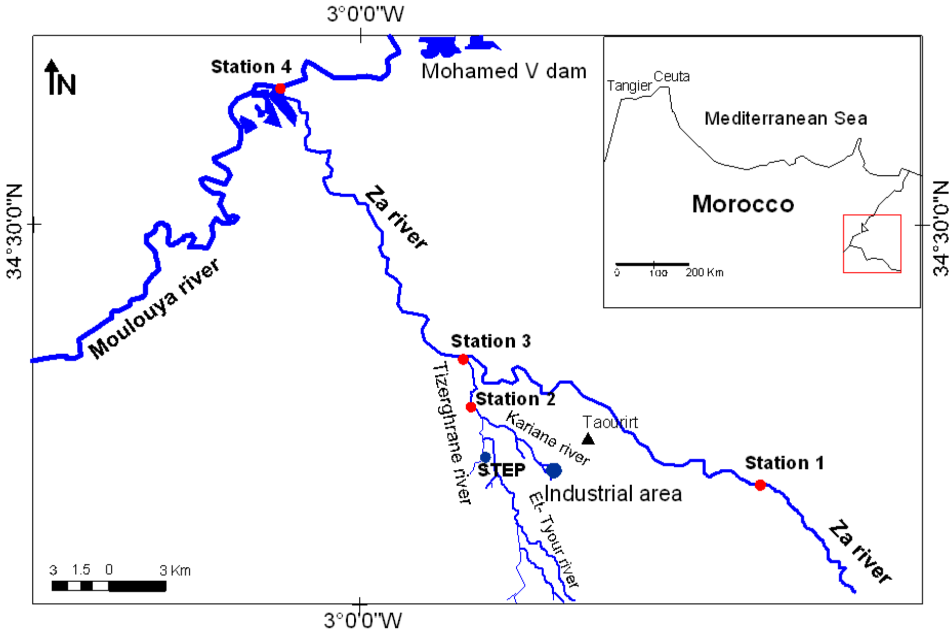

Figure1: Localization map of the study area and location of sampling stations area

• **Station 1**: The choice of this resort is critical, since it is considered as reference station. It is located at the Taourirt bridge downstream of the dam Za river and upstream of settlements and the release of the city. The maximum depth of 30 cm and width of 8 m. The substrate is heterogeneous, composed of pebbles, gravel, sand and silt. The valley on both sides of the river is very extended. The river is very clear with an average flow.

• **Station 2** is located at TizeghraneRiver; it was chosen to estimate the impact of the contributions of mixed waste (industrial and domestic) Za River. Its distance from the industrial area is 5 km, and STEP is 3 km. The river is very dark, cloudy, with a bad smell, and the presence of foam. The flow is average; the vegetation is different with filamentous algae in the middle and a large vegetation on the banks.

• **Station 3**: is located near the confluence of the river with the river Tizeghrane Za, downstream of the city of Taourirt, this resort is close to the station 2 of 3 km, while it moves away from station 1 of 18km. The flow rate is important in this resort; there is the mixture of clear waters of Za River with very dark waters and contaminated water of TizeghraneRiver.

• **Station 4**: is located downstream of the confluence of the Za river with Moulouya river at Melga el Ouidane. It is located 19km from the resort 3. It has been studied with the aim of assessing the impact of contributions of Za River on the Moulouya River. The river flow is very important compared to previous stations.

2.2. Analytical methods

The field sampling was carried out during a dry period (July) and during floods (February) during industrial activity period year (2010 and 2011). The main objective of this study is to assess the potential contamination of water examined during industrial activity.

The water samples are placed in polyethylene bottles, and then fixed with 2% HNO_3 and transported at low temperature (4°C) to the laboratory CNRST in Rabat, the polyethylene bottles were previously well washed, followed by acid baths (10% HCI) and finally rinsed several times with distilled water.

The heavy metals soluble in water after filtration is determined by Atomic Emission Inductively Coupled Plasma spectrometry (ICP-AES) using a type JY spectrometer.

ICP is a method of analysis by atomic emission spectrometry, the source is a plasma generated by inductive coupling. Plasma is an electrically neutral ionized gas. After passing in the heart of the plasma, the atoms and ions emit excited, turning to states of lower energy level, light radiation. The optical device scans the portion emitted in the UV-visible area

2.2. Statistical analysis:
In order to achieve a comprehensive overview of different metal parameters and to set up a space-time structure for identifying critical phenomena the operation of the water system, we performed a multivariate analysis (PCA), which is in descriptive statistics. Multivariate statistical analysis is an inevitable tool to study data from many observations made on several variables. It aims to summarize the information in the data on a small number of dimensions that best reflects the similarities between observations and variables [18].

We submitted all the data collected metal to a Principal Component Analysis (PCA), which can generate an overall summary of the information given [19] ;[20]; [21].

Multivariate statistical treatment is widely used to characterize and evaluate the quality of surface water and Freshwater, it is useful to testify spatiotemporal variations caused by seasonal natural and human factors [22][23];[24];[25].It is a widely used methodology for interpreting hydro chemical data [1];[26]; [27] ;[28];[29];[30];[31]; [32];[12].

This analysis allows, from a matrix with n samples and p variables, the description of the cloud in a space (np) dimensions. Statistical analysis was used to establish significant correlations between variables and their possible mode of distribution. Indeed, the CPA is among the more conventional techniques of multivariate statistics [33]. PCAis applied to identify potential pollution and its characteristic features. It has been used in several studies [34];[35] ;[36];[37];[38].

RESULTS AND DISCUSSION

3.1. Description of data matrix:
PCA was performed on a data matrix consisting of four samples (4 stations x 1 wet season) and 4 samples (4 stations x 1 dry season). These results of this analysis are shown in Table 1, 2, 3, 4 and Figure 2 and 3.

This analysis was performed on a data table of four individuals (stations) and eleven variables: aluminum (Al), chromium (Cr), copper (Cu), cadmium (Cd), Nickel (Ni), Iron (Fe), arsenic (As), zinc (Zn), selenium (Se), manganese (Mn) and lead (Pb).

The codes of the four Stations during two periods of studies (July and february) are illustrated in Table 1

Table 1: ***Dates and codes of samples taken.***

Sampling Dates	July 2010	February 2011
Station 1	J1	F1
Station 2	J2	F2
Station 3	J3	F3
Station 4	J4	F4

Table 2: Matrix data grouping estimated 11 metals variables studied in eight Samples

Record number	As	Cd	Cu	Cr	Se	Ni	Mn	Fe	Al	Pb	Zn
J1	12	12	2	2	30	15	21	340	3	39	8
J2	11	12	2	2	36	98	70	1540	2	79	8
J3	13	12	2	2	33	15	32	510	2	66	6
J4	12	12	2	2	31	16	8	1380	12	65	5
F1	4	23	2	11	64	24	326	1516	285	16	14
F2	7	12	10	11	62	11	611	4260	210	15	162
F3	6	12	5	10	58	8	627	545	182	13	58
F4	4	12	4	8	63	5	797	2730	309	10	74

For the eleven metals parameters evaluated, all the results are illustrated in Table 2. The same table also contains the matrix data statistically processed by the PCA. It is a matrix of data consisting of a double entry table"1 variable time 11 samples. ‘The codes of eleven metals parameters and the numbers of samples taken during one year used in PCA are reported in Table 2.

3.2. Choice of Eigenvalues (selectable number of factors):

The Eigen value analysis is used to choose the number of factors, and therefore the number of axis to be considered in the analysis in order to minimize the loss of information. Table 3 shows the variances of the different factors.

Table 3. ***Eigen values (contributions and percentage)***

	F1	F2
Eigenvalues	7.15	1.97
Variance (%)	65.06	17.90
Cumulative (%)	65.06	82.97

The analysis of results shows that the first two factorial axes explain the majority of information (Tables 3,4and Figures 2, 3). The contributions of different parameters in the expression of the first two factorial axes F1 andF2 are respectively **65.06%** and **17.90 %** or **82.97 %** of the information explained. The maximum of thetotal inertia is accumulated by the plan formed by the factorial axis F1 × F2.Thus, the significance of metals factor axis F1 and F2 is necessary.

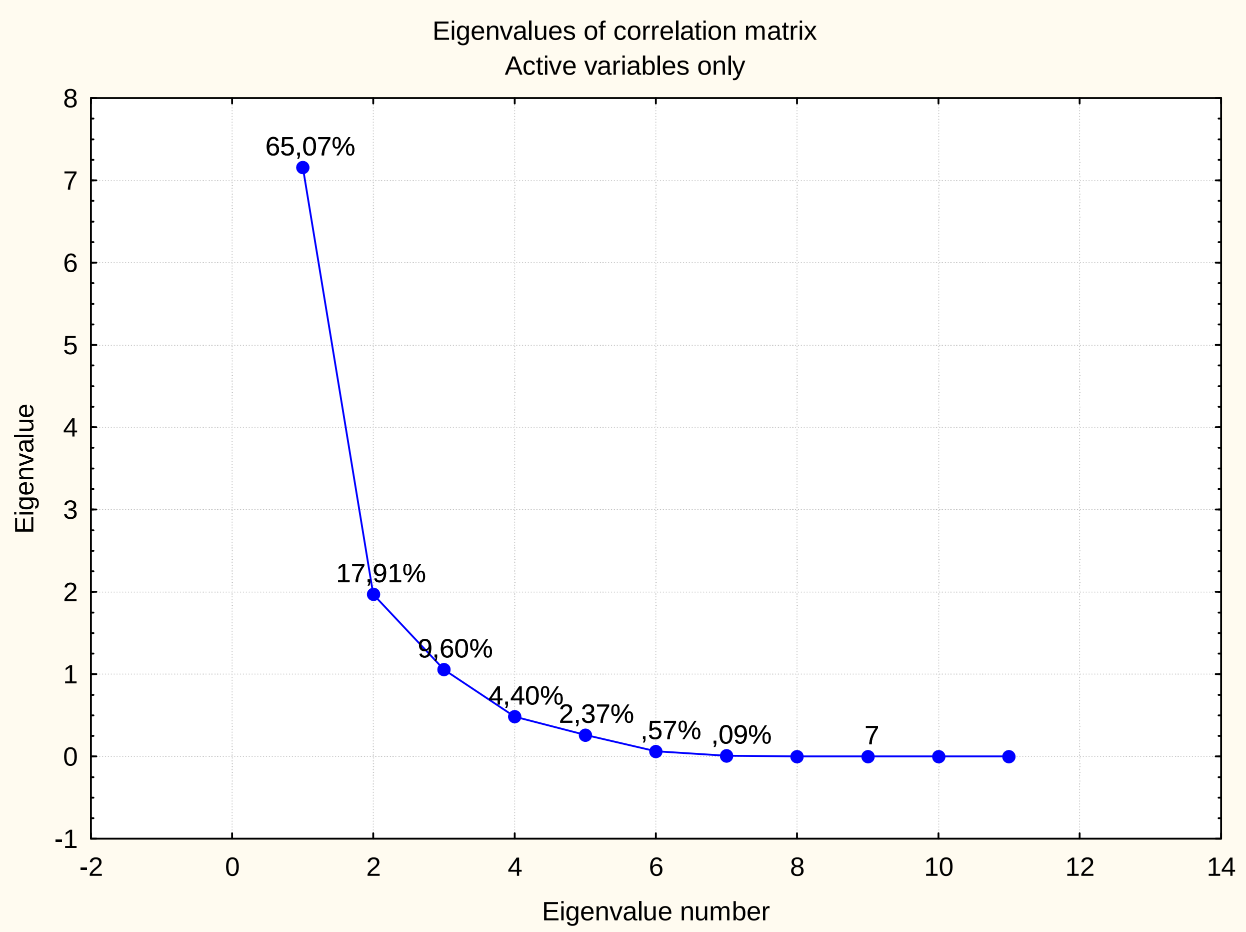

Figure 2: Eigen values of correlation matrix

3.3. Analysis of the distribution metals parameters in the plan F1xF2:

The examination of the correlation matrix between variables (Table 4) reveals the presence:

A first set of variables consisting of weakly or strongly correlated water descriptors, it is about significant correlations between:

As/Pb(r=0,866) ; As/Ni (r=0,285)
Cd/Cr (r=0,461) ; Cd /Se (r=0,430)
Cu/Cr (r=0,647) ; Cu/ Mn(r=0,671) ; Cu/Fe (r=0,775) ; Cu/Zn(r=0,984)
Cr/Se(r=0,965) ; Cr/Al (r=0,904) ; Cr/Mn (r=0,830);
Fe/Zn (r=0,840), Fe/Al (r=0,875)

Table 4: Correlation matrix of ETM studied in water

	As	Cd	Cu	Cr	Se	Ni	Mn	Fe	Al	Pb	Zn
As	1,000000										
Cd	-0,494743	1,000000									
Cu	-0,403264	-0,232402	1,000000								
Cr	-0,907629	0,461757	0,647183	1,000000							
Se	-0,967050	0,430888	0,585944	0,965646	1,000000						
Ni	0,285722	-0,000000	-0,315565	-0,385023	-0,320846	1,000000					
Mn	-0,865194	0,018043	0,671679	0,830856	0,899136	-0,411538	1,000000				
Fe	-0,464971	-0,026405	0,775897	0,528100	0,584356	-0,073275	0,585161	1,000000			
Al	-0,980107	0,476526	0,453065	0,904836	0,970136	-0,399521	0,875431	0,542647	1,000000		
Pb	0,866000	-0,312030	-0,559382	-0,886393	-0,871276	0,627491	-0,852663	-0,398613	-0,884870	1,000000	
Zn	-0,493812	-0,201645	0,984119	0,679034	0,657353	-0,336953	0,750788	0,840390	0,554587	-0,621552	1,000000

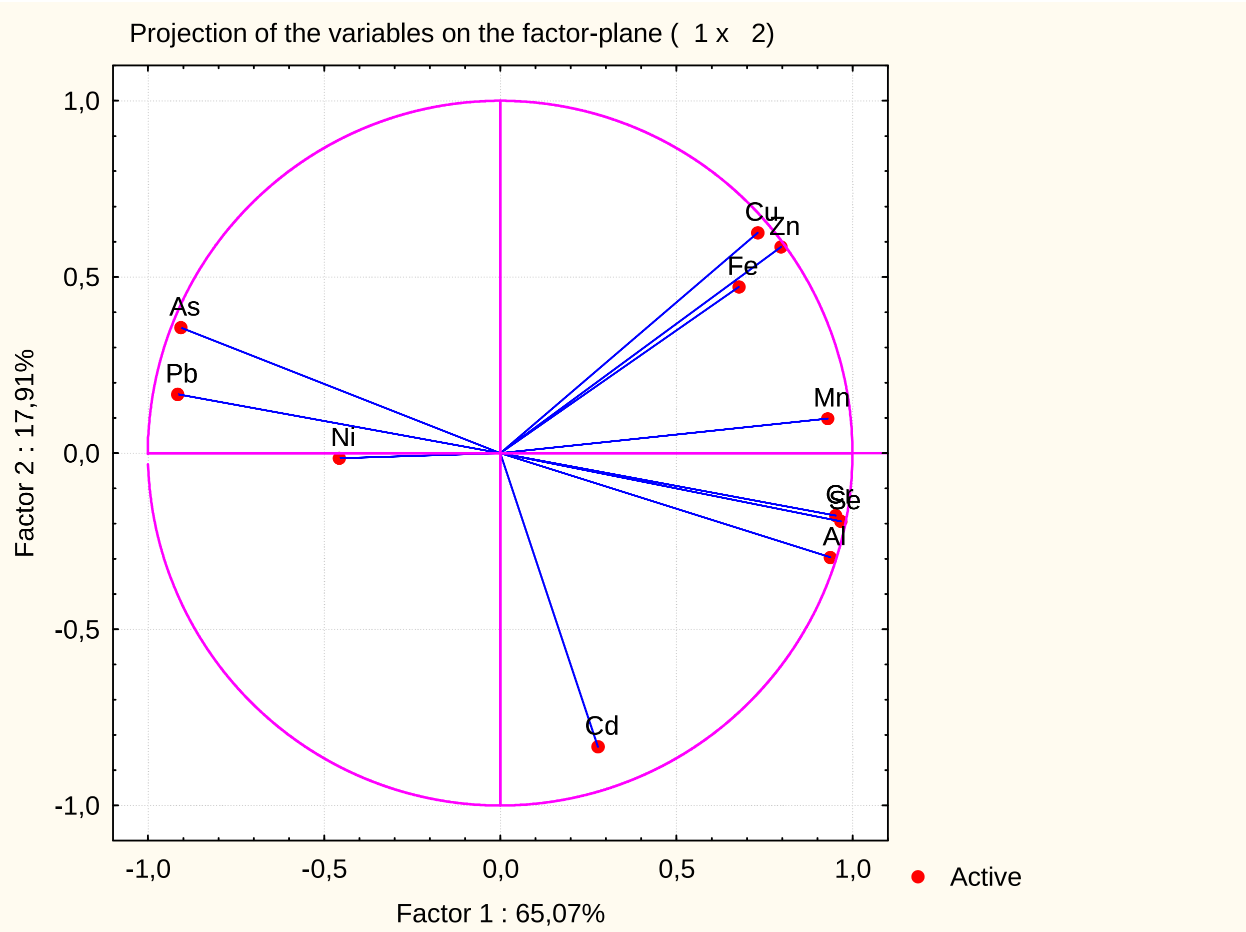

Figure 3: Projection of metals parameters in the factorial F1xF2

Principal component analysis (PCA) was conducted to identify trends, correlations and phenomena that may influence the distribution of metallic elements in surface waters of the Oued Za.

The correlation circle formed by the axis F1 and F2 (Fig. 3) shows 82.97% of the total information. In the factorial design (F1 x F2), the first component (F1 axis) which describes 65.06**%** inertia, translates in contamination of the water by Ni, Pb and As. The second component (F2 Axis) is with an inertia 17.90**%** describes the enrichment of water Cu, Zn, Fe, Mn, Cr, Se, Al, Cd.

From right to left (Figure 3), the axis F1 reflects a water enrichment gradient Ni, Pb and As. From the top down, the axis F2 translates the general evolution of the degree of water contamination by Cu, Zn, Fe, Mn, Cr, Se, Al, Cd.

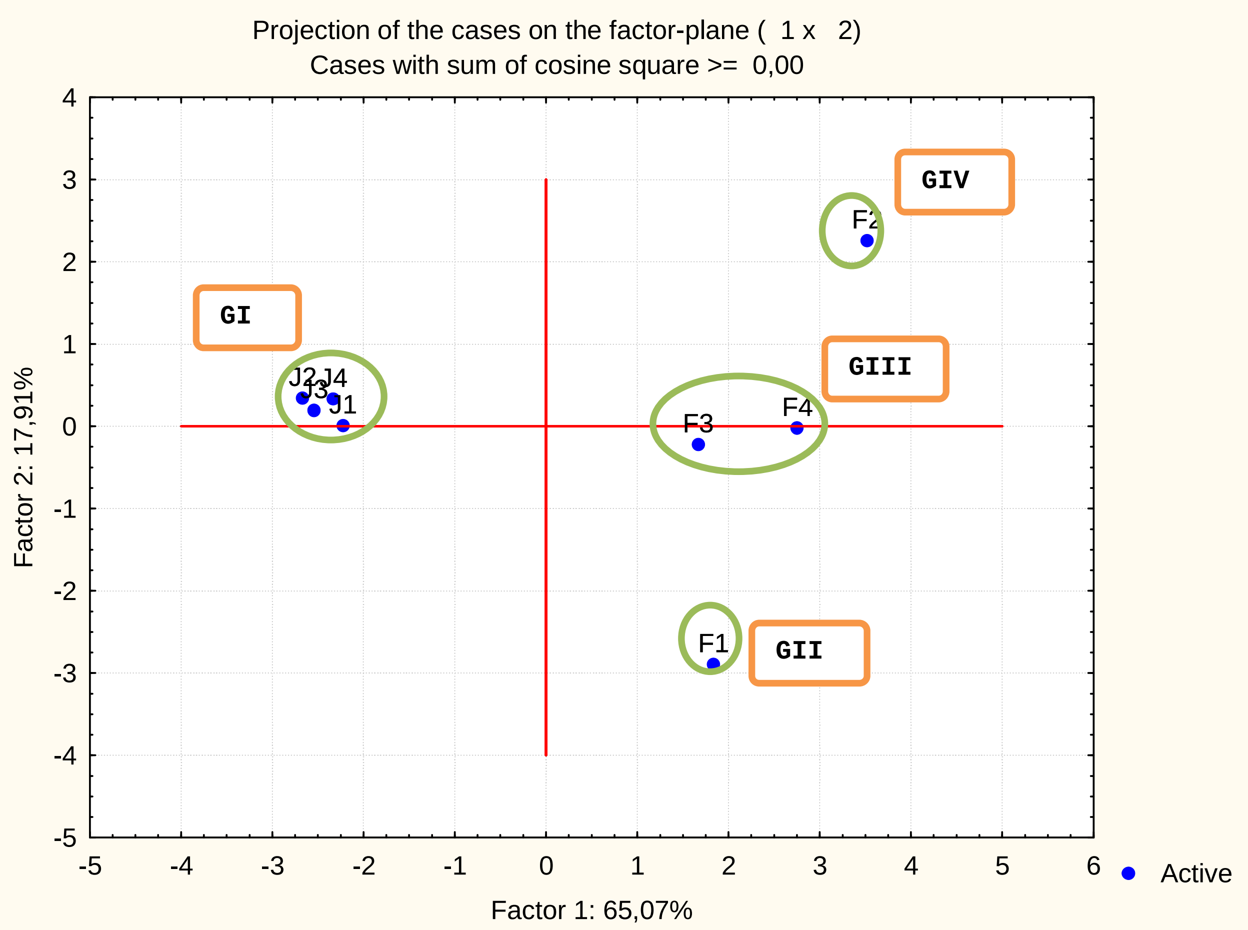

Figure 4: representation of stations of the map factor F1 × F2

The clear typological structure of the plan analysis F1 x F2 (Figure 4) shows the identification of four areas (GI, GII, GIII, and GIV), depending on the nature of metal pollutants and their degree of contamination:

- ✓ **Group I (GI):** The surface water in this area are characterized by pollution Ni, Pb and As. This area has a wide distribution of these metals at the stations J1, J3, J4 of the Za river, and J2 station of Tizeghrane, corresponding to the summer period in July (Figure 4). This could be due to domestic waste in the city of Taourirt and industrial discharges very high cannery in the summer period[11]. This heavy load on these metals Ni, Pb and As, occupies the negative part of the axis F1.

- ✓ **Group II (GII):** This area shows a high degree of contamination at the F1 station Oued Za by a high concentration of cadmium in February. This very high concentration of Cadmium 23µg / l has a positive correlation with the axis F1. These recorded high values could be attributed firstly to domestic and industrial waste from the city of Taourirt, and secondly to leaching of fertilized soil which can also be a source of cadmium intake. Indeed, analysis of metals in fertilizers revealed levels up to 6.3 mg / kg of cadmium. Contamination by this element in the waters Za river, worsens beyond the standard Moroccan 5µg /l [39], and the value for irrigation (10 µg / l). Therefore, these waters belong to the poor class (≥ 5µg / l).

- ✓ **Group III (GIII):** This group is represented by the stations F3 and F4. It is characterized by a large load in metals (Al, Cr, Se, Mn), occupying the positive part of the axis F1. The presence of these elements in the surface waters of the Oued Za could be related to the concentration of industrial human activity. Chromium can also have such other origin, agricultural pollution (Go[40] since the study area is agriculture-based. Overall the concentrations found at the Za river remain significantly lower than the value set by the Moroccan standard of surface water (≤50µg / l) .From this, on this element, these waters are classified good medium quality. However this water is of poor quality by the presence of high contamination due to the very high concentration of Selenium (64µg/ l), far exceeding the normal content of surface waters (10µg / l), specified in the standard Moroccan[39].

- ✓ **Group IV (IV)**: Occupies the positive parts of the two axes F1 and F2. It is represented by a single station F2 Tizeghrane river, a major source of pollution of this site because it receives wastewater and industrial waste from the city of Taourirt [11]. This zone is the most polluted in the studied metal elements (Fe, Cu, Zn) during flood periods.

CONCLUSION

The presence of point discharges and localized related to an important industrial activity may explain the spatial presence of heavy metals in our study area, and translated, despite their rarity in nature and their high toxicity, wide application in l industry contributing to a dangerous contamination of surface waters. Despite considerable efforts to reduce the load of metals in wastewater, they continue to carry large quantities of heavy metals into the environment.

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