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Statistical study of the accumulation of metallic trace elements in cereals and agricultural soils irrigated via the waters of the Sebou water basin (North-West of Morocco)

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Abstract: The analysis of metallic elements (As, Cd, Co, Zn, Ni, Pb, Cu and Cr) in the surface waters for irrigation of Sebou and Beht, agricultural soils and cereals collected near the Kenitra city (North-West of Morocco) was realized by Inductively Coupled Plasma Mass Spectrometry (ICP) in the National Center for Scientific and Technical Research (Rabat, Morocco). The results obtained were evaluated using statistical analysis methods (descriptive and global) which revealed high metal contents in agricultural soils due to their silty-clay textures. Also, the accumulation of heavy metals in cereals and soils irrigated by water pumping stations from Sebou exceeds that induced by water pumping stations from Beht.

Keywords: Heavy metals; Principal component analysis; Cereals; Agricultural soils; Oued Sebou; Oued Beht; Kenitra.

1. Introduction

Moroccan agriculture has made remarkable progress which has affected practically all production, both animal and crop. Overall production has almost tripled in constant value. Despite intense urbanisation, agriculture still accounts for 15% of the national wealth produced each year [1]. It is, therefore, essential to study the mobility of heavy metals (trace elements) in the samples taken for this study. Because the alimentations are the leading cause of the intoxication of the human by the trace elements [2]. The Sebou hydraulic basin (Sebou, Ouergha, Beht, Bas Sebou) intended for irrigation which receives a load of 142 t/year of metal elements [3] from, in particular, the craft industries estimated at 2000 units [4], can generate metal pollution drained along these rivers that will be transferred to the soil through irrigation waters and subsequently to crops intended for human and animal consumption (livestock). This study is based on statistical analysis that assesses the environmental impact of irrigation from a water pumping station in Sebou and Beht at the level of the various environmental media, namely: Irrigation water, agricultural soils and cereals.

2. Experimental

The choice of study sites in Kénitra was made based on the location of the pumping stations for irrigation water from the Sebou and Beht rivers (Fig.1).

Irrigated agricultural areas from four surface water pumping stations emanate from Oued Sebou, and Oued Beht are located at 27 Km (rural municipality of MOGRANE) and 44 Km (rural municipality of SIDI ALLAL TAZI) of the province of Kenitra (Table 1).

The two selected areas of each rural community were ranked in the following order:

Area 1: Agricultural area irrigated by the Sebou the surface water pumping station at SIDI ALLAL TAZI.

Area 2: Agricultural area irrigated by a pumping station developed on a channel to divert the flow of water from the Oued Beht to meet farmers' needs for irrigation of their crops at SIDI ALLAL TAZI.

Area 3: Agricultural area irrigated by the Beht surface water pumping station at MOGRANE.

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Area 4: Agricultural area located at MOGRANE and irrigated by guard dam waters which have the function to limit losses to the sea of the waters of OUED SEBOU and the maintenance of the water body that will serve as hydraulic source irrigation.

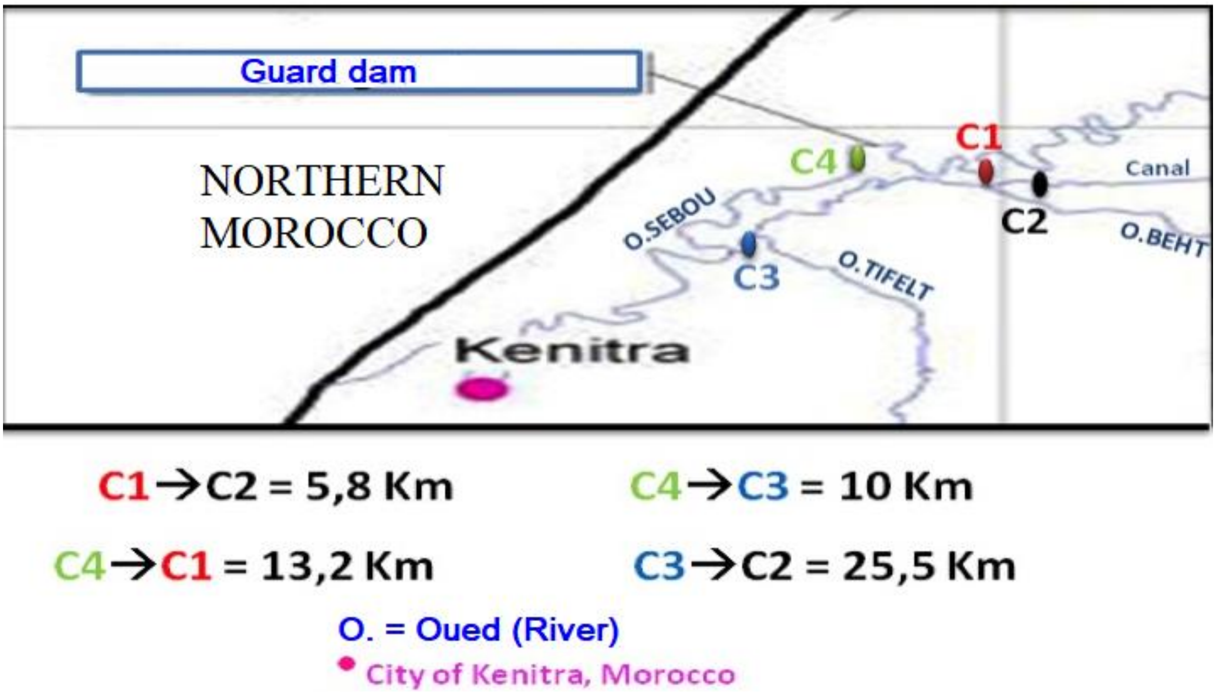

Figure 1. Location of study areas on Oued Beht and Oued Sebou

Table 1. Topographical coordinates of sampling sites.

Area	Latitude (N)	Longitude (W)
Area 1	34° 30 minutes 22 seconds	6° 17 minutes 13 seconds
Areas 2	34° 29 minutes 37 seconds	6° 14 minutes 04 seconds
Area 3	34° 24 minutes 36 seconds	6° 25 minutes 48 seconds
Areas 4	34° 28 minutes 59 seconds	6° 24 minutes 08 seconds

2.1. Materials Used

Samples of the water taken from the pumping stations were filled in sterile 500 ml polyethylene bottles before being transported to the laboratory and stored at 4°C.

The ground was zigzagged from an average of five points at each site using a helical auger. The soils (layer: 0-15 cm) of the same zoned are gathered, placed in a plastic bag and labelled to be forwarded to the laboratory.

Cereals (soft wheat and barley) collected from five points in each sampling area on 20/04/2014 were placed in a clean plastic bag and labelled for transport to the laboratory or washed with tap water followed by rinsing with distilled water to remove dirt and dust. Plants have been subdivided into several substrates such that stems and seeds are sorted and mixed.

2.2. Sample processing and analytical methods

A 10 ml water sample was taken by 10 ml of 50% hydrofluoric acid and dried in a Teflon beaker on a sand bath. The resulting residue is dissolved by adding 7,5 ml of hydrochloric acid and 2,5 ml of nitric acid. The beaker is covered with a watch glass and then placed on a heating plate until the red vapours disappear, synonymous with complete mineralization. The solution obtained after filtration is supplemented to 50 ml by distilled water [5].

One gram of soil of the same depth sifted through a 1mm sieve and dried at 70°C for 48 hours was burned in a 450°C muffler oven for 2 hours. The sample was then taken up in 10 ml of 50% hydrofluoric acid and dried again in a Teflon beaker on a sand bath. The residue is dissolved by a mixture of hydrochloric and nitric acid (7,5 and 2,5 ml). The suspension of the solution obtained after filtration was supplemented at 50 ml by distilled water [6].

A sample of 1 to 2 g of a dried plant at 70°C for 48 hours and ground, was burned in a 450°C muffler oven for 4 hours. The ash obtained is mineralized by the regal water (25% HNO_3 and 75% HCL), then dried over a sand bath until the solution discolours. The residue obtained in 10 ml of HCL (5%) is resolved and filtered to 0,45 µm, then diluted with HCL (5%) to the final volume of 20 ml [5].

Analyses of soil and irrigation water physico-chemical parameters were carried out in the ORMVAG laboratory and determination of metal fractions (Chromium, Cobalt, Copper, Zinc, Arsenic, Lead, Cadmium and Nickel) at the level of the media developed, were read at the ICP-AES (Ultima 2) at the National Center for Scientific and Technical Research (Rabat). The analysis laboratory uses standards (accurate to 1000 ppm of Jobin Yvon) certified by ISO 9001 quality assurance system.

The formula for converting metal concentrations from mg/l to mg/kg for solid media is presented in Equation 1.

$$\mathbf{Cech}_{(mg/kg)} = \mathbf{Cech}_{(mg/l)} * \mathbf{V}_{\mathbf{Mineralisation\ (l)}} / \textbf{dry mass tested}_{\textbf{sample taken (kg)}}$$

Where $C_{ech\ (mg/kg)}$ the final metal concentration in mg/kg, $\mathbf{C}_{\mathbf{ech\ (mg/l)}}$ the final metal concentration in mg/l, $V_{Minéralisation}$ the volume of the sample after mineralization in L and dry mass tested $_{sample\ taken(kg)}$ the mass of the dried sample before calcination.

Statistical analysis of average heavy metal contents of irrigation water, agricultural soils and cereals were carried out by descriptive analysis (ANOVA 1) and principal component analysis (PCA) according to the procedure published by several authors [7,8]. The calculations and graphic representations were made by the IBM SPSS STATISTICS software.

3. Results and Discussion

The results of trace element contents in the different samples taken show significant differences depending on the nature of the medium. This variation was the subject of a statistical study to establish the relationship between the metal values shown in Table 2. This part involves studying the homogeneity of the separated metal contents and the effect of the nominal variables (stations and compartments) on trace element concentrations by calculating the coefficients of variation (CV%) and variance analysis (ANOVA 1).

3.1. Separate analysis of heavy metals

This part involves studying the homogeneity of the separated metal contents and the effect of the nominal variables (stations and compartments) on trace element concentrations by calculating the coefficients of variation (CV%) and variance analysis (ANOVA 1).

Table 3 shows the breakdown of concentrations expressed in ppm of the metals analysed. The results obtained show that most metals show differences that exceed the average levels. The analysis of the coefficient of variation expressed as a % (CV%) shows a high degree of heterogeneity in trace elements exceeding 100%, between the various compartments, namely, the irrigation waters, agricultural soils, seeds and stems of cereals. However, the trace element as shows a considerable variation resulting in a minimum value of 0 ppm and a maximum value of 40.2 ppm; this expresses the stability of the values measured on the four compartments.

The variance analysis of the effect of irrigation water pumping stations from OUED BEHT and OUED SEBOU on the fluctuation of metal concentrations shows no significant difference. However, ANOVA 1 shows a very significant difference between the compartment differences (Table 4) for all trace elements analysed.

Table 2. Results of ppm metal concentrations in irrigation waters, agricultural soils and cereals.

	Sample	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Area 1	Waters 1	0,24	0,04	0,03	0,21	0,11	0,13	0,29	0,55
Area 1	Soil 1	34,4	9,5	21,75	499	43,4	41,65	14,4	122,7
Area 1	Seeds 1	<LQ	0,71	0,23	0,48	5,51	4,24	1,55	23,68
Area 1	Rods 1	<LQ	0,89	0,23	0,88	2,97	1,66	2,62	23,2
Area 2	Waters 2	0,26	0,03	0,03	0,23	0,08	0,08	0,17	0,11
Area 2	Soil 2	25,45	5,65	15	239,7	22,35	27,6	19,65	74,55
Area 2	Seeds 2	<LQ	0,56	0,23	0,56	4,24	3,24	4,3	18,44
Area 2	Rods 2	<LQ	0,64	0,21	0,82	4,82	2,47	3,46	12,34
Area 3	Waters 3	0,71	0,04	0,07	0,69	0,18	0,32	0,38	0,41
Area 3	Soil 3	<LQ	7,2	13,5	391,7	48,5	38,05	36,55	91,7
Area 3	Seeds 3	<LQ	1	0,2	0,78	6,68	4,24	4,2	20,87
Area 3	Rods 3	<LQ	0,6	0,19	0,7	4,48	5,17	1,86	13,23

Area 4	Waters 4	0,28	0,05	0,06	0,41	0,21	0,21	0,43	0,31
Area 4	Soil 4	40,2	8,9	27,2	366,85	42,25	46,65	36,25	133,3
Area 4	Seeds 4	<LQ	0,5	0,25	0,45	3,89	2,6	2,8	16,38
Area 4	Rods 4	<LQ	1,25	0,23	0,88	9,39	4,06	8,99	11,15

Table 3. Descriptive studies of metal content.

Metals	Average	Standard error of the average	Minimum	Maximum	CV %
As	6,35	3,42	0,00	40,2	215%
Cd	2,35	,84	,03	9,5	144%
Co	4,96	2,26	,03	27,2	182%
Cr	94,02	43,45	,21	499,	185%
Cu	12,44	4,23	,08	48,5	136%
Ni	11,39	4,16	,08	46,65	146%
Pb	8,61	3,03	,17	36,55	141%
Zn	35,18	11,1	,11	133,3	126%

Table 4. Analysis of variance with a single classification criterion "compartment effect".

Metals	The Sum of squares	ddl	Average of squares	F	Signification
As	1858,65	3	619,55	7,87	,004
Cd	160,75	3	53,58	67,69	,000
Co	1105,9	3	368,63	36,7	,000
Cr	419004,03	3	139668,01	49,26	,000
Cu	3867,1	3	1289,03	36,38	,000
Ni	3942,49	3	1314,16	77,008	,000
Pb	1779,04	3	593,01	16,71	,000
Zn	27241,81	3	9080,6	46,58	,000

Nevertheless, for each metal, the multiple analysis of the comparison of the mean concentrations by the Tukey test allowed the latter to be subdivided into two groups, not overlapping:
The first group consists mainly of the average trace element content in the soil.

The second group consists mainly of the average metal contents in the other compartments (water, stems and seeds).

Moreover, the quantities of trace elements determined in the soil remain higher than that determined in irrigation water, stalks and seeds.

Agricultural soils are a stable and constant environment with time; This increases their capacity to retain heavy metals, mainly preventing irrigation through the surface waters of Sebou and Beht for several years. Thus for the agricultural soils studied characterized by a clay texture, the maintenance of the elements of metal traces is done by adsorption according to two modes [9]:

Adsorption by the formation of a covalent bond between metal and groups –Terminal OH of the surface of the solid according to the following mechanism:

$$\mathbf{X\text{-}O\text{-}H + M^{n+} \rightarrow XO\text{-}M^{n-1} + H^{+}}$$

Adsorption by ion-exchange based on ion substitution at the lamellar space of clays. This mechanism depends on the load and relative size of the metal elements exchanged.

Plant supports (stems and seeds of cereals) and irrigation water vary from one agricultural season to the next. However, only a small fraction of the total metal trace element content in the soil is available for plant roots [10] (Lowest from 1 to 3 orders of magnitude).

3.2. Overall Analysis

3.2.1. Principal component analysis of the metal contents in the different compartments

The overall analysis by the MCA method (principal component analysis) aims to group different trace elements into a limited number of factors, to facilitate the detection of independent relationships between different metal concentrations.

The correlations on the axis of factors 1 and 2 (component 1 and component 2) are visualized on the factorial map after rotation (Fig. 3). However, we note that all the metal elements are positively correlated on both axes. Thus we have:

The high correlation of variables: Zn, Pb, Cu, Ni, Cr and Cd on axis 1 (correlations>0.7)

Fig. 2 illustrates the degree of information (Proper value %) represented by each factor (Component Number). The first factor represents 92% of the total information of the variables (As, Cr, Cd, Co, Cu, Ni, Pb and Zn), while the second factor represents 5.4% of the variables. So factor 1 and factor 2, which represents 97% of the variables, will be adopted to explain the correlation between the different metal contents.

The high correlation of the variables as and Co on axis 2 (correlations>0.7).

Hence factor 1 is the most important grouping of variables (Zn, Cr, Cu, Ni, Pb, Cd) which are highly accumulated in agricultural soils, cereal stalks and cereal seeds, while factor 2 is the trace elements (Co, As) which are less assimilated by cereals.

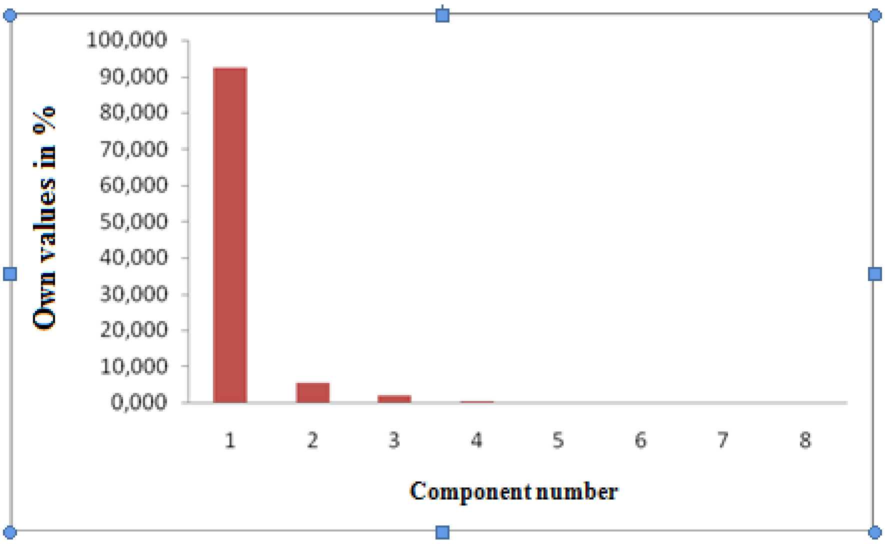

Figure 2. Diagram of the values of each component

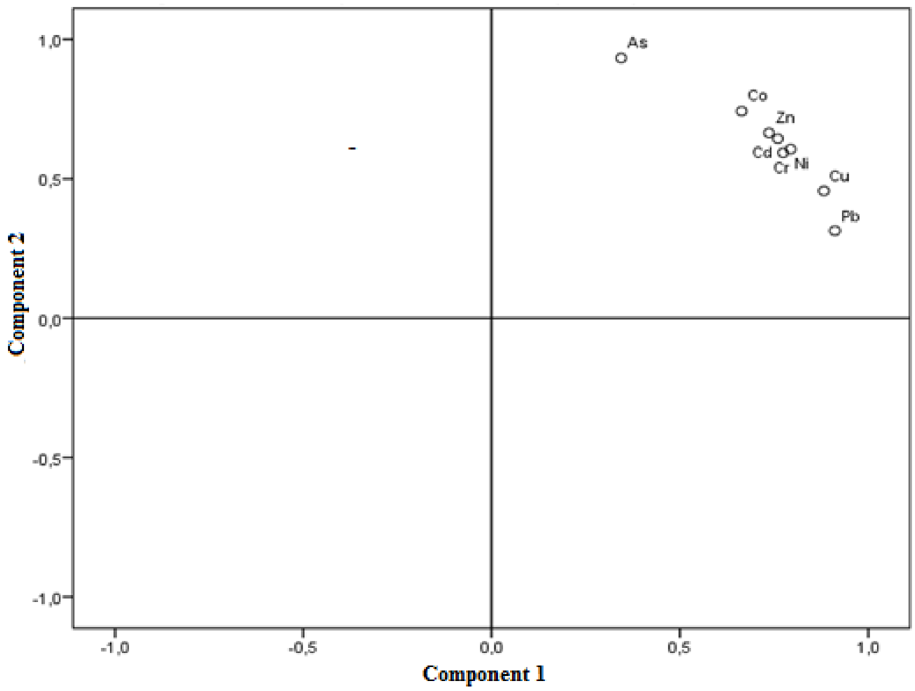

Figure 3. Correlation of metal trace elements on the axes of component 1 and component 2

3.2.2. Principal component analysis of average concentrations for each station

The proper values shown in Figure 4 show that factors 1 and 2 (Component 1 and Component 2 represent 84% of the variables. So axis 1 and axis 2 will be constituted respectively by factor 1 and factor 2.

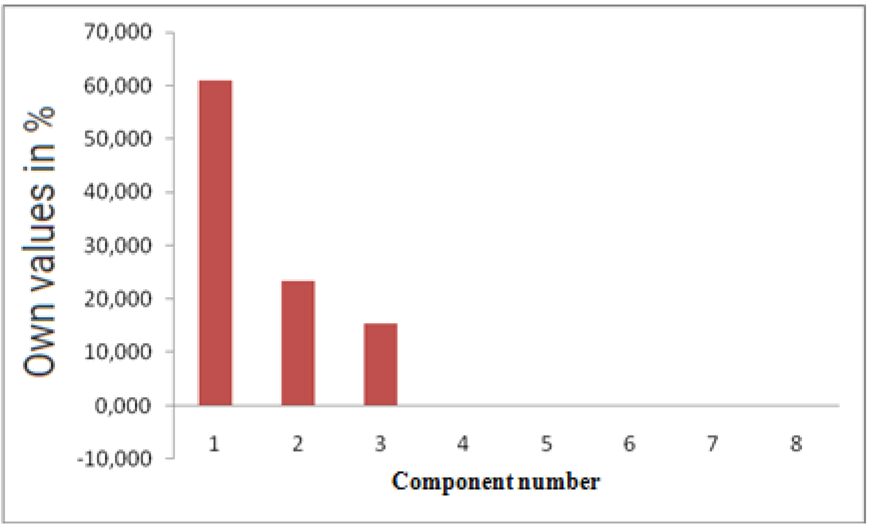

Figure 4. diagram of the specific values of each component

The correlations of the metal elements reported by the factorial map after rotation (Fig. 5) enabled the following observations to be made:

The variables Ni, Cr, Cd, Co and Zn are well represented and positively correlated on axis 1 (correlation>0.7). This is confirmed by reference to the correlation matrix.

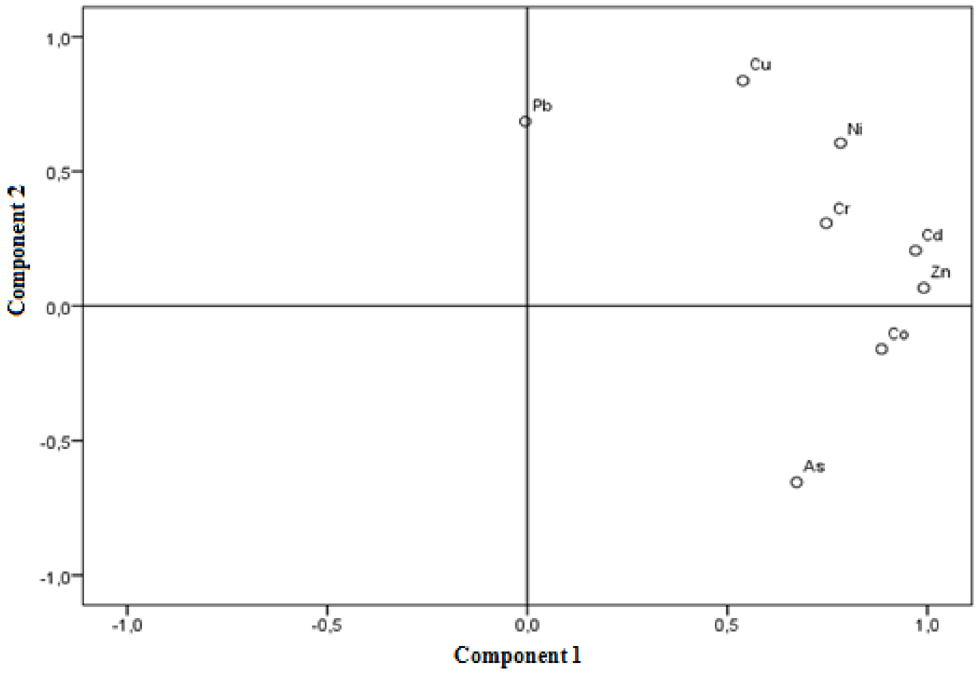

Figure 5. Correlation of metal trace elements on the axes of component 1 and component 2

Trace elements As Pb and Cu are well correlated on axis 2. However, the projection of As (-0.655) is negative while that of Pb (0.686) and Cu (0.837) is positive, so it can be deduced that the increase in the As content in a station leads to a decrease in Pb and Cu concentrations and vice versa.

The projection of the stations on the factors already developed (Factor 1 and Factor 2) is shown in Figure 6.

It can be seen that the pumping stations for irrigation water from Sebou are positively correlated on axis 1 (60% of the variables) while the irrigation water pumping stations from Beht are projected with negative correlations, which shows that the water from Sebou generates higher metal pollution than from the water from Beht, this is in good agreement with literature [4,11]. Thus, the quality of the waters of Sebou (6000 km2), from the Middle Atlas, deteriorates downstream of the city Fès [11], which generates by its population of one million inhabitants and its diversified industrial park, a significant pollution estimated at more than 105,000 m³/d of wastewater [4], whereas the waters of Beht (a perennial, relatively mighty river and also originated in the Middle Atlas) receive less pollution, mainly downstream of the cities of Meknes and Sidi Slimane [11].

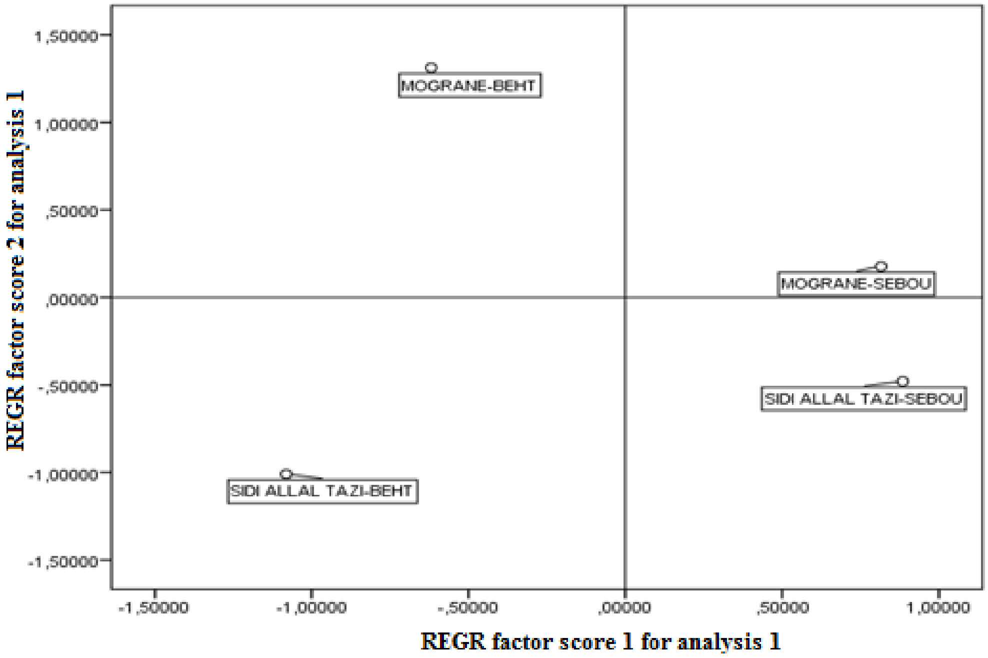

Figure 6. Graphical representation of individuals on axis 1 and axis 2

4. Conclusion

The present study carried out in northwestern Morocco confirmed that the areas located at the level of the rural communities of Sidi Allal Tazi and Mograne, show a degree of metal pollution. Metallic enrichment for cereals is respected at the level of the four sites in the following order: Zn>Cu> Ni~Pb >Cd> Cr>Co>As.

On the other hand, the descriptive analysis of trace element contents made it possible to subdivide the substrates characterised into two distinct groups (Group 1: Agricultural soils and Group 2: cereals and irrigation water) illustrating a very significant gap between them.

However, the principal component analysis (PCA) has stated that the metallic inflow of irrigation water from Oued Sebou exceeds the transfer of trace elements from the irrigation water of Oued Beht. As far as the correlation between the various metals is concerned, the increase in the average Cu and Pb contents in all media combined is accompanied by a decrease in As.

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