



## The Metallic pollution in the groundwater of Triffa Plain (Eastern Morocco)

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### Abstract

To determine the statue of the metallic trace elements contamination in the groundwater of Triffa's Plain (Eastern Morocco), the water of 34 wells were studied out through two sampling campaigns (June and November 2013 respectively). The results of the analyzes showed that the groundwater in the Triffa's Plain is heavily contaminated with metallic trace elements and that cadmium has alarming levels in excess of 7 to 83 times the WHO recommended limit for Human consumption. The intensive agricultural practices and the irrational use of fertilizers and pesticides are the main cause of this metallic pollution.

### 1. Introduction

Water resources in eastern Morocco and the Moulouya watershed are experiencing severe degradation, which continues to accelerate and become more and more worrying due to the increasing of the sources of pollution from domestic, industrial and agricultural backgrounds [1-9].

The plain of Triffa (Eastern Morocco) has great socio-economic importance in the region, the local economy is based specially on agriculture, which consumes the total water use. Indeed, the plain is characterized by two aquifers: a free one of secondary and quaternary formations; and a confined aquifer of Liassic formation [10]. The implanted wells number in the whole of its surface area is not officially known, but it is estimated to be about 700 wells, their exploitation has been very varied according to households, but source and well's water are often used for the consumption, irrigation and supply of the livestock. Currently, water resources in this part of the country are under serious pressure and agricultural practices often have negative impacts on groundwater quality [11-12].

Pollution caused by the presence of heavy metals in groundwater is generally due to industrial activities by their effluent discharge, the leaching of the stored products and the geological nature of the soil [13]. Some of these metallic elements are considered as undesirable and may present organoleptic disadvantages to the consumer, as is the case of copper, zinc, iron, manganese, aluminum. Other elements such as cadmium, Chromium, mercury and lead, may be toxic and pose risks to human health and environment [14-18]. As a result, the ground waters must be continuously diagnosed and thoroughly monitored to assess its quality and its possible impact on the environment and the human health.

Various work has been carried out on the Triffa Plain's aquifer since the 1980s [10, 19-22], most of which are interested in the physico-chemical parameters of the groundwater, but few are conducted on the metallic pollution.

#### 1.1. The study area

The plain of Triffa is located at the eastern end of Morocco. It is bounded to the east by Oued Kiss (Algeria), to the north by the Mediterranean Sea, to the west by Oued Moulouya and to the south by the Beni-Snassen ranges (Figure 1). It is an area of 61,000 ha and is one of the most fertile and productive areas in eastern Morocco [23].

Rainfall is irregular during the year and the bioclimatic stage prevailing in the plain is of the semi-arid Mediterranean type [2].

The groundwater of the Triffa plain occupies 3/4 of its surface area. It consists of two areas separated by the HassiSmia flexure in the south. The reservoir is formed by the superposition of lacustrine marlylimestones and red silts [10]. Formerly considered poor in water, the plain has developed irrigated perimeters from the wells collecting the water table. Frequent pumping, particularly during non-rainy periods, results in decreases in the piezometric level [23].

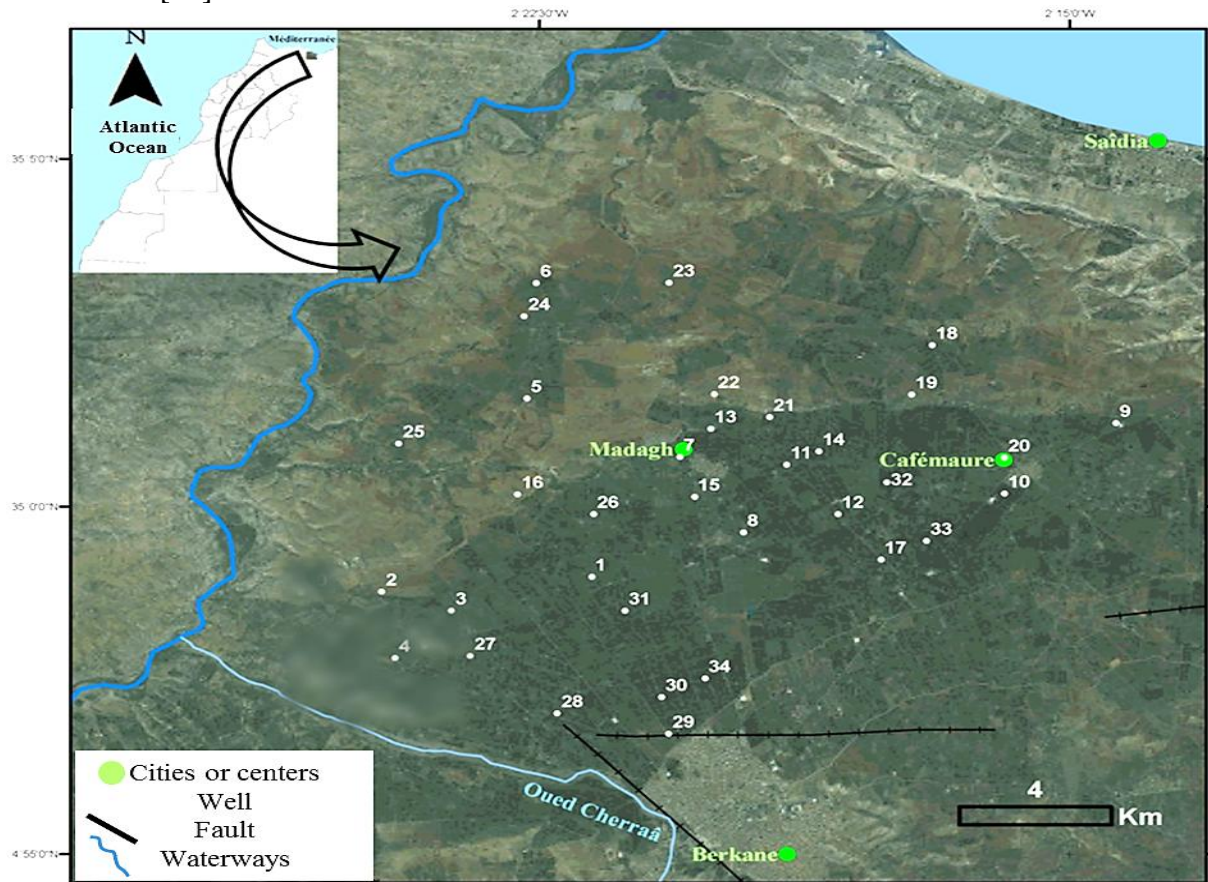


Figure 1 : Location of study area and sampled wells

## 2. Materiel and methods

### 2.1. Sampling and analysis

In order to diagnose the pollution by the metallic trace elements in the groundwater of Triffa, 34 wells distributed throughout the plain were surveyed for water sampling during two sampling campaigns, respectively in June and November 2013.

The heavy metals dosing (ETM) was performed by Atomic Emission Spectrometry Coupled to the Induced Plasma (ICP-AES = Inductively Coupled Plasma - Atomic Emission Spectroscopy). The Analytical emission spectrometry is a very sensitive method for measuring the contents of almost all elements present in aqueous, organic or solid solutions by the Ultima 2 Jobin Yvon device with a detection limit of 0.1917 ppb.

All previously prepared samples were subjected to analyze of the following heavy metals: iron (Fe), Zinc (Zn), Cadmium (Cd) and Lead (Pb) by the ICP-AES method in the laboratory of the UATRS (Technical Support for Scientific Research Unit) at CNRST in Rabat.

### 1.2. Statistical analysis

The statistical analyzes were carried out using R software in 3.3.1 version.

A matrix of six abiotic parameters representing the average of the two campaigns of March and November 2014 (Table 1) was subjected to a standardized principal component analysis in order to realize a typology of the prospected wells according to their mesological affinities. This method of analysis has already shown its effectiveness in hydrology and particularly in eastern Morocco [1-5].

**Table 1 :** Results of the analyzed parameters of the 34 wells and their geographic coordinates (June and November 2013)

Wells	GPS		pH	CE μS/cm	AL (mg/l)	Cd (mg/l)	Cu (mg/l)	Fe (mg/l)	Zn (mg/l)
	X	Y							
P1	777310.44	490694.57	7.395	3925	0.22	0.026	0.038	0.251	0.303
P2	772802	490168.44	7.32	4150	0.0455	0.0235	0.08	0.045	0.044
P3	774319.65	489707.03	7.34	3300	0.06	0.021	0.034	0.0395	0.11
P4	773147.73	488413.58	7.69	2940	0.1595	0.0215	0.08	0.1075	0.142
P5	775783.99	495398.99	6.885	3520	0.006	0.0205	0.0355	0.063	0.035
P6	775899.07	498462.19	7.085	4105	0.25	0.02	0.0325	0.1105	0.4095
P7	779115.7	493931.07	7.325	3190	0.083	0.025	0.039	0.1095	0.07
P8	780545.07	491964.05	7.39	2855	0.041	0.022	0.08	0.098	0.117
P9	788472.94	495111.06	7.26	2415	0.006	0.03	0.145	0.0715	0.05
P10	786129.63	493169.96	7.36	2910	0.006	0.0555	0.0425	0.229	0.121
P11	781419.7	493791.72	7.295	3075	0.07	0.025	0.032	0.046	0.045
P12	782565.62	492517.75	6.86	2960	0.053	0.0215	0.0805	0.2915	0.0985
P13	779762.56	494708.55	7.29	1200	0.172	0.027	0.122	0.045	0.077
P14	782100.97	494172.64	7.41	2760	0.07	0.0205	0.0275	0.093	0.02
P15	779463.12	492881.24	7.13	2645	0.02	0.02	0.03	0.03	0.07
P16	775660.25	492840.64	6.87	4260	0.186	0.049	0.076	0.036	0.065
P17	783524.92	491334.56	7.355	3105	0.2765	0.038	0.0775	0.211	0.2935
P18	784458.98	497064.08	9.26	4095	0.439	0.037	0.0845	2.06	0.2655
P19	784054.18	495740.33	7.265	2565	0.0595	0.032	0.076	0.1395	0.069
P20	786104	494123.79	7.25	2030	0.111	0.023	0.076	0.146	0.059
P21	781015.8	495047.02	7.35	2415	0.061	0.0225	0.0755	0.072	0.053
P22	779803.98	495629.2	7.225	2270	0.2665	0.0295	0.075	0.083	0.0315
P23	778745.72	498558.13	7.095	4710	0.0865	0.0365	0.0765	0.1155	0.0335
P24	775658.45	497578.32	7.305	3530	0.093	0.0295	0.075	0.104	0.0405
P25	773060.25	494116.14	6.995	4400	0.087	0.25	0.0935	0.0445	0.1095
P26	777299.85	492364.74	7.31	3645	0.1555	0.0465	0.081	0.2615	0.1795
P27	774760.54	488517.32	7.47	2445	0.17	0.02	0.03	0.25	0.09
P28	776679.75	487037.5	7.165	1622.5	0.18	0.05	0.03	0.19	0.15
P29	779086.63	486560.16	7.055	1895	0.02	0.06	0.01	0.006	0.02
P30	778907.27	487535.34	7.23	3295	0.11	0.14	0.026	0.006	0.0125
P31	778057.98	489809.92	7.02	3650	0.15	0.1	0.025	0.053	0.0225
P32	783588.36	493395.45	7.2	2330	0.13	0.11	0.022	0.068	0.0125
P33	784488.31	491856.62	7.11	3940	0.5	0.05	0.023	0.006	0.0175
P34	779829.97	488063.73	7.405	3860	0.06	0.09	0.021	0.006	0.02

### 3. Results and Discussions

#### 3.1. Typological study

A first analysis of the mesological parameters of the various wells surveyed in standardized principal components shows that the first three axes F1, F2 and F3 (figure 4a, 4b, et 4c) hold the bulk of the information since they represent 70.54% of the total inertia. The test of the correlations between the axes and the various mesological components studied explains the significance of each axis in the structured distribution of the well cloud and the relationship between the typological structure and the environmental variables.

The F1 axis (37.67% of total inertia) is negatively correlated with iron, pH, aluminum and zinc. The F2 axis (19.07% of the total inertia) is mainly due to conductivity and cadmium.

The F3 axis (13.78% of total inertia) expresses a gradient directly related to copper. Thus, the planes F1-F2, and F1-F3 isolate four wells P18, P25 and (P9, P13) rich respectively in iron, cadmium and copper.

The F4 axis (not included in the study) represents a weak correlation with zinc.

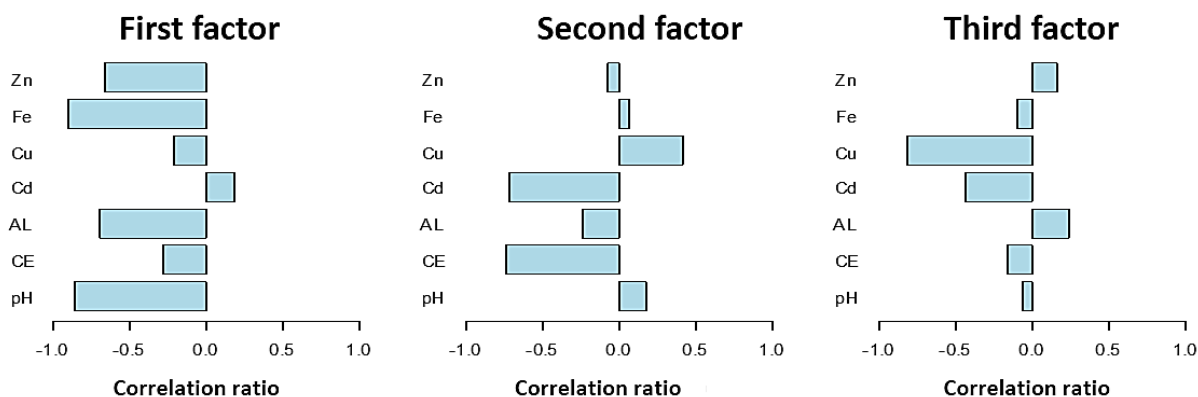


Figure 2 : Correlation ratio between the mesological parameters and the first three factors of the CPA.

	pH	CE	AL	Cd	Cu	Fe	Zn
F1	-0,857	-0,289	-0,694	0,182	-0,213	-0,904	-0,664
F2	0,178	-0,742	-0,241	-0,716	0,414	0,070	-0,078
F3	-0,064	-0,154	0,238	-0,433	-0,809	-0,096	0,171

Figure 3 : Values of the correlation between the mesological parameters and the first three factors of the CPA.

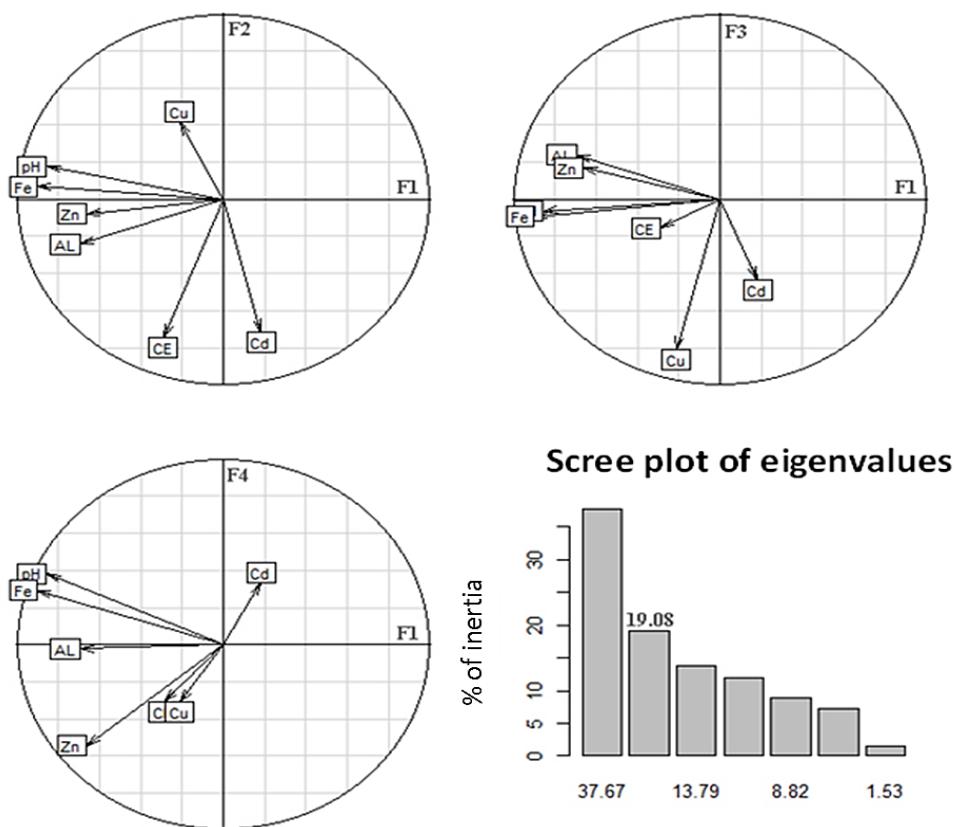
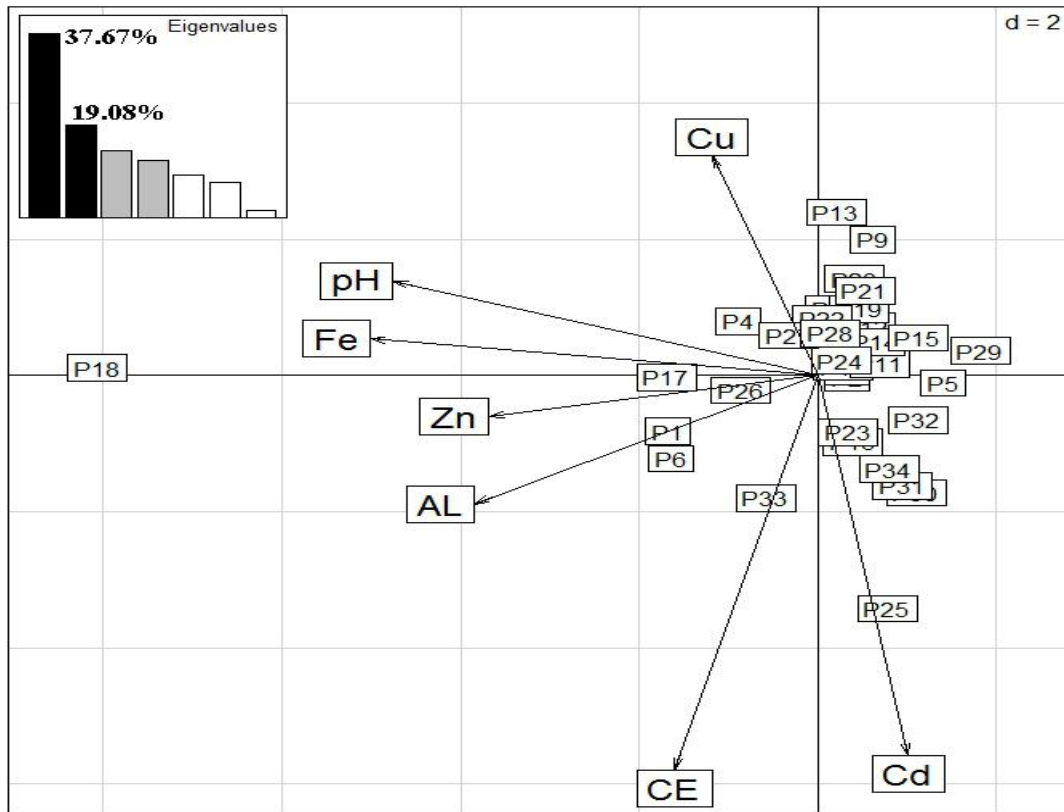
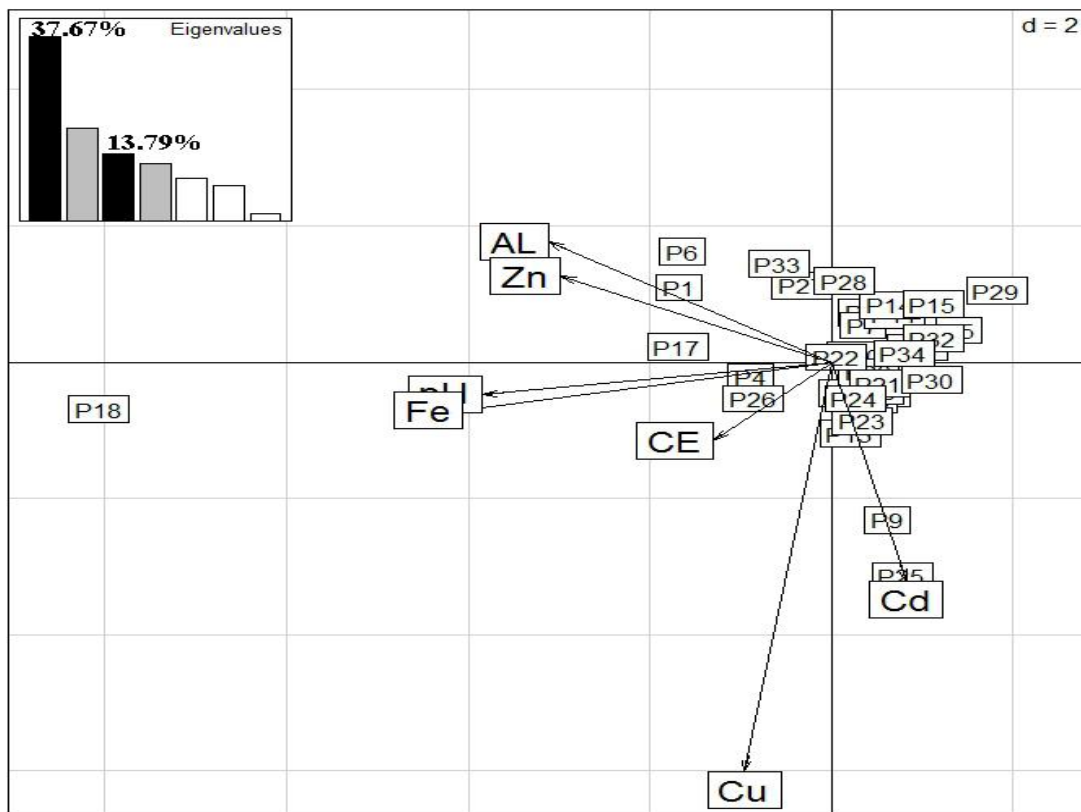


Figure 4a : Circles of correlations between variables, plans F1-F2, F1-F3 and F1-F4. Histogram of the eigenvalues of the normed CPA.



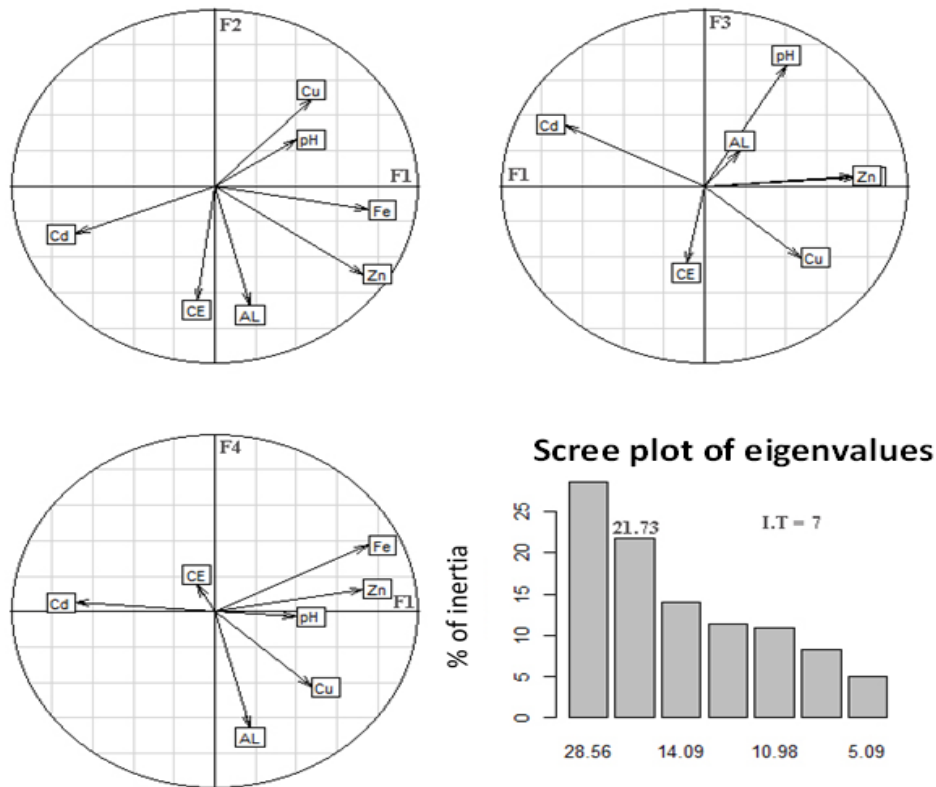
**Figure 4b :** Biplot variables and wells, plans F1-F2 of the standardized CPA.



**Figure 4c :** Biplot variables and wells, plans F1-F3 of the standardized CPA.

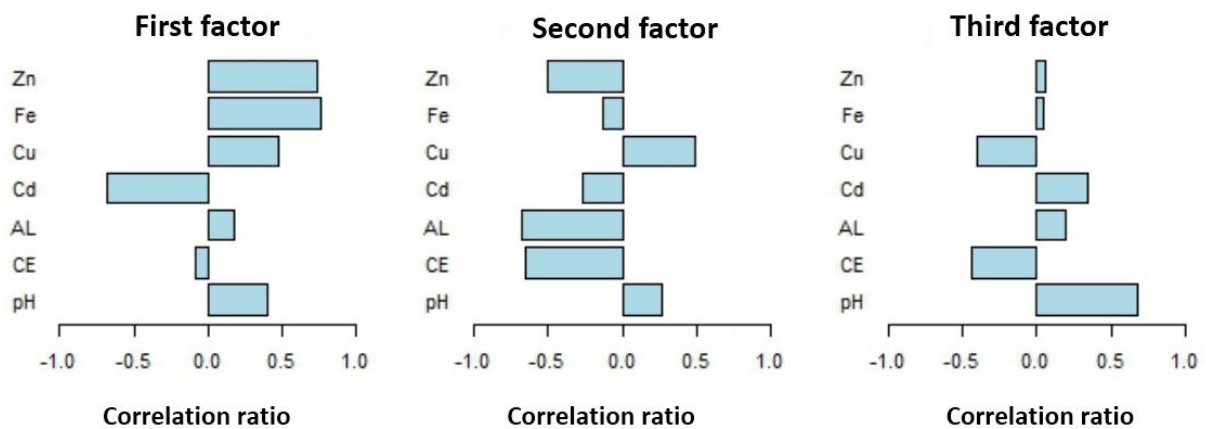
The other wells are concentrated at the centers of the CPA axes. For a better typology of the wells, a second standardized CPA was carried out by eliminating the wells that contributed the most in the formation of the first three axes, P18 and P25.





**Figure 5 :** Circles of correlations between variables, plans F1-F2, F1-F3 and F1-F4. Histogram of the eigenvalues of the second standardized CPA.

The second analysis of the mesological parameters of the various surveyed wells in standardized principal components, shows that the first three axes F1, F2 and F3 (Figure 5) hold the bulk of the information since they represent 64.37% of the total inertia. The test of correlations between the axes and the various mesological components studied (Figure 6 and 7) makes it possible to explain the significance of each axis.



**Figure 6 :** Correlation ratio between the mesological parameters and the first three factors of the second CPA.

	pH	CE	AL	Cd	Cu	Fe	Zn
<b>F1</b>	0,401	-0,089	0,171	<b>-0,685</b>	0,475	<b>0,754</b>	<b>0,731</b>
<b>F2</b>	0,262	<b>-0,646</b>	<b>-0,671</b>	-0,270	0,492	-0,134	-0,499
<b>F3</b>	<b>0,683</b>	-0,437	<b>0,198</b>	0,346	-0,402	0,052	0,058

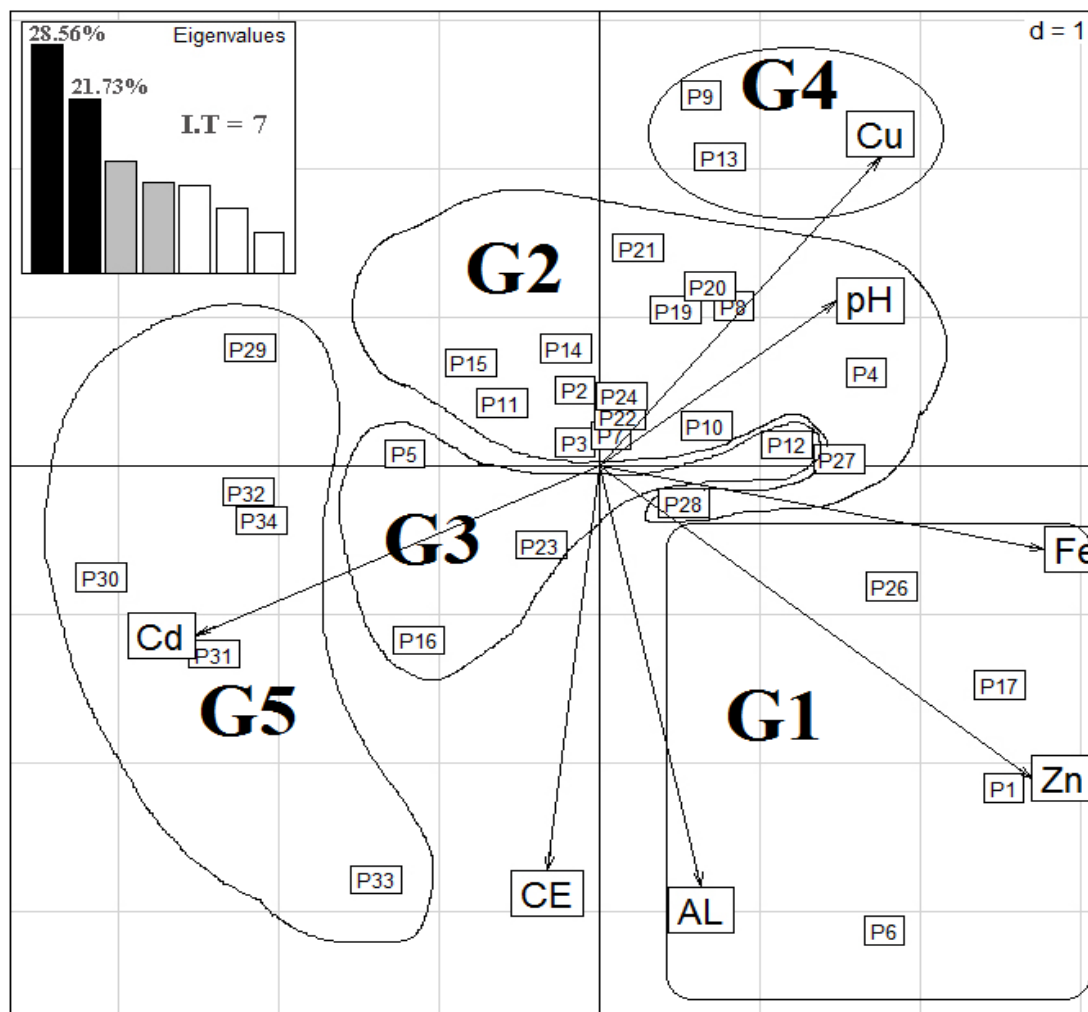
**Figure 7 :** Correlation values between the mesological parameters and the first three factors of the second CPA.

The F1 axis (28.56% of total inertia) is positively correlated with iron and zinc, and negatively with cadmium; The axis F1 thus separates in its ends two groups of wells, one group rich in iron and zinc to the right of the axis and another group to the left of the axis regroups the wells whose water has high values in cadmium.

The F2 axis (21.73% of total inertia) expresses a negative correlation with aluminum and conductivity, and a low positive correlation with copper. The F2 axis isolates at the bottom a group of wells whose water has high aluminum values such as wells P6 and P33 which record 0.25 mg / l and 0.5 mg / l respectively, and at the top the wells representing High copper values, such as wells P9 and P13 which record respectively 0.145 mg / l and 0.122 mg / l of this element.

The F3 axis (14.09% of total inertia) expresses a gradient directly related to pH.

Thereby, the F1-F2 and F1-F3 plans of the two ACPs used make it possible to discriminate five groups of wells (Figure. 8, 9 and 10).

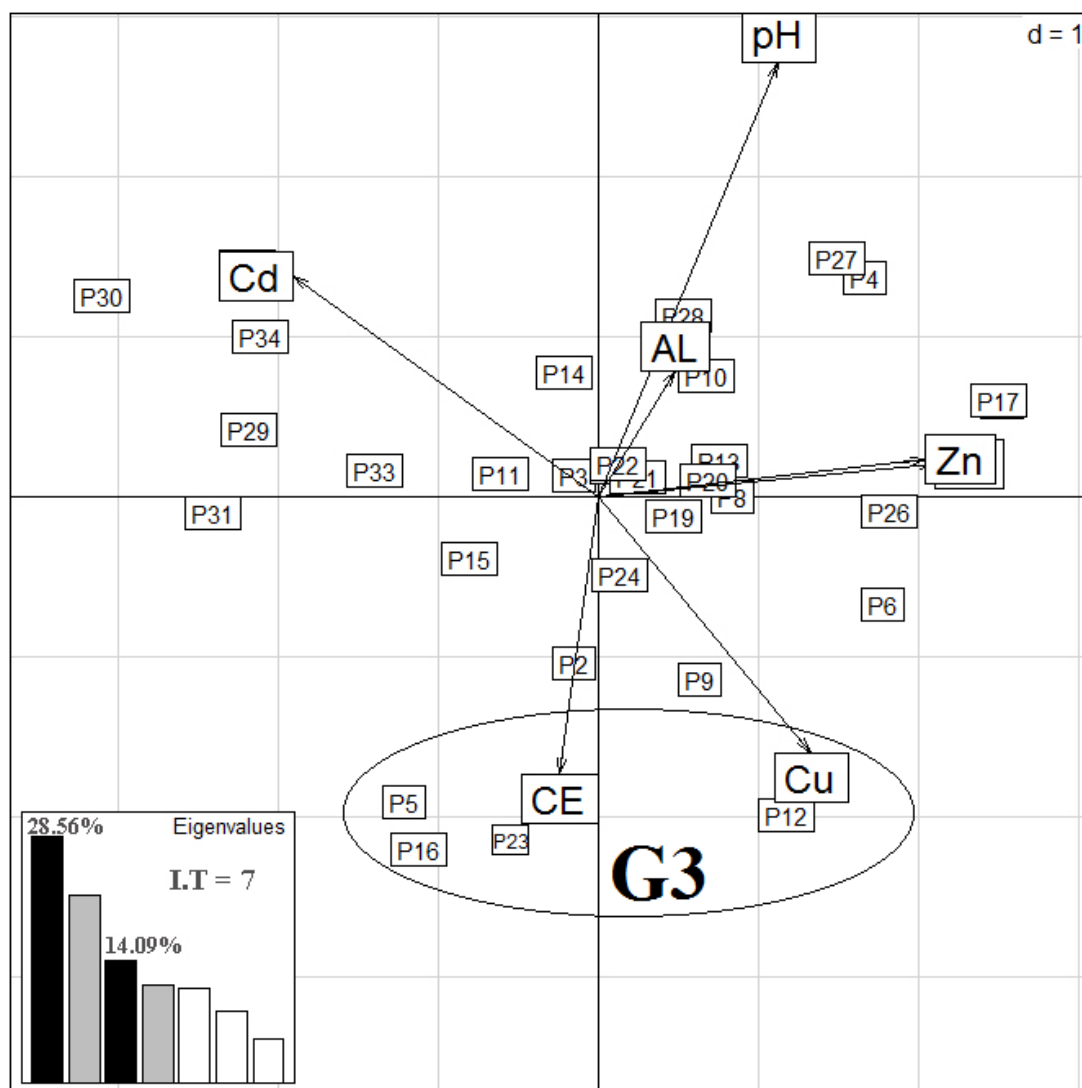


**Figure 8 :** Simultaneous representation of variables and wells on the factorial plane F1-F2 of the second standardized CPA.

**Group1 :**It regroups four wells whose particularity of the waters is the richness of iron and / or zinc; the water in this group of wells P1, P6, P17, and P26 has the highest iron values ranging from 0.11 to 0.26 mg/l and zinc with levels of 0.179 to 0.4 mg/l. The P18 well with the highest iron value 2.06 mg/l belongs to this group. Wells in this group are also distinguished by moderately high aluminum values (P6 = 0.25 mg / l, P18 = 0.439 mg / l).

Trace element concentrations in drinking water should be less than 0.3 mg/l for iron and zinc and 0.2 mg / l for aluminum according to WHO (2006) and NM 2006).All the wells in this group exceed these standards either in aluminum or / and zinc except the well P26 which exceed these standards only in conductivity (norm = 2700  $\mu$ scm-1, P26 = 3645  $\mu$ scm-1).

The trace element concentrations of this group are explained by the leaching and infiltration of phosphate fertilizers rich in aluminum salt used in intensive agriculture to increase crop growth and yield.



**Figure 9 :** Simultaneous representation of variables and sinks on the factorial plane F1-F3 of the second standardized CPA.

**Group 2 :** Contains the following three subgroups (P10, P4, P27, P28, P22), (P8, P19, P20, P21) and (P2, P24, P11, P15, P14, P3, P7). The waters of this group generally record average values of the seven mesological descriptors compared to all the wells. The wells of the different subgroups have affinities and similarities between the values of the different measured elements. The waters of this group of wells do not exceed the limits recommended by the WHO as a metallic element, contrary to the conductivity which is between 1622 and 4150  $\mu\text{scm}^{-1}$ ; and exceeds the recommended limit in 9 wells. The high conductivity is probably due to the geological nature of the soil.

**Group 3 :** This group which records values generally close to group 2 is isolated at the bottom of the axis F3 and groups together the wells P12, P16 and P5, all of which have a low pH close to neutrality (of the order of 6.8) and The well P23 with a value of 7.09. The high conductivity of this group of wells (between 2960 and 4710  $\mu\text{scm}^{-1}$ ) renders the water unsafe according to WHO standards. The geological nature and richness of the limestone soil may explain the high conductivity and low pH of this group.

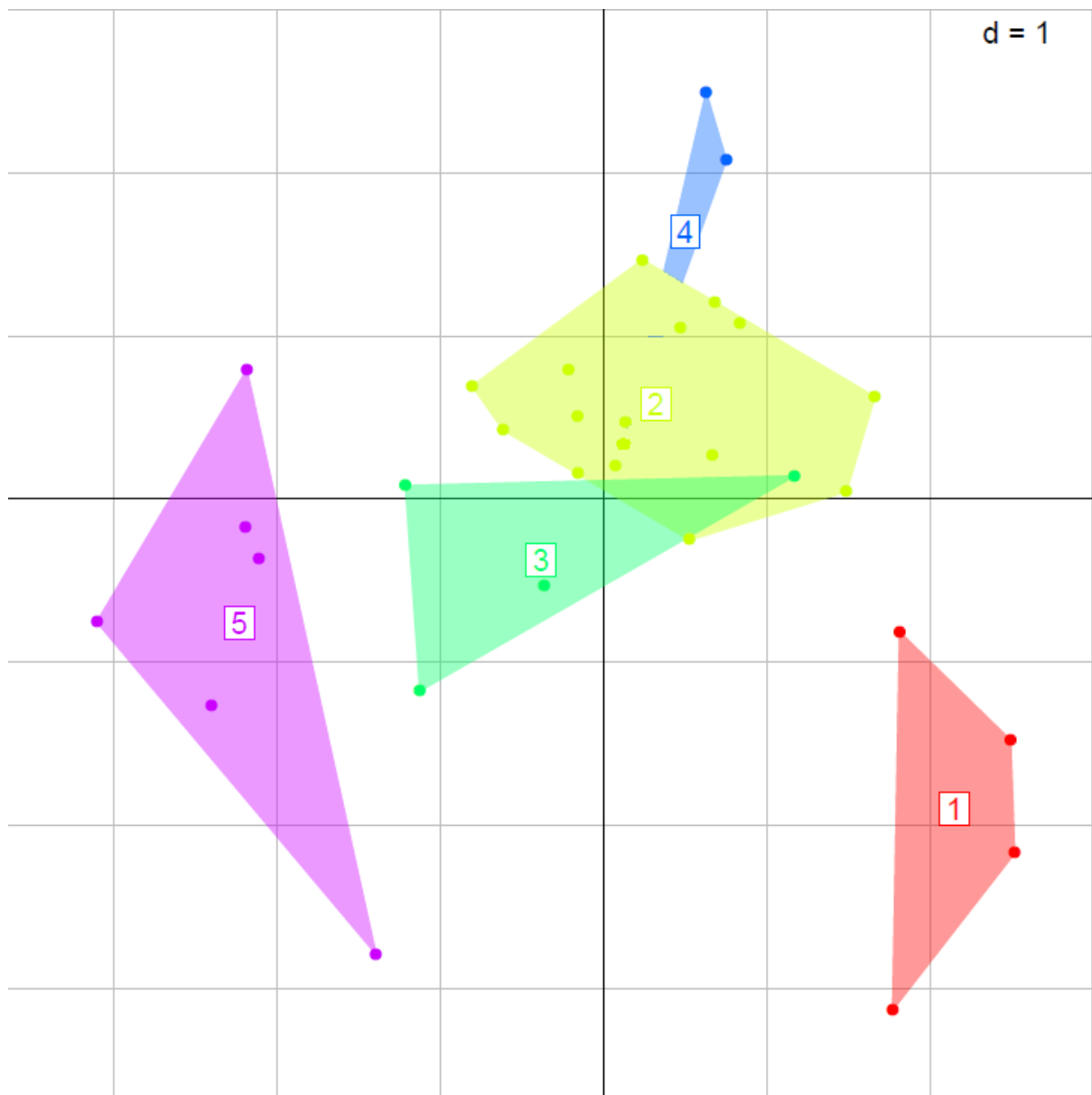
**Group 4 :** This group represented by P9 and P13 has the specificity of having the waters richest in copper; these two wells record respectively 0.14  $\text{mg l}^{-1}$  and 0.12  $\text{mg l}^{-1}$ , these values remain below the WHO standard for drinking water. Copper sulfate used as fertilizer and fungicide for fruit trees in orchards near P9 and P13 may explain the values recorded for copper.



**Group 5 :** Contains the following six wells P33, P31, P29, P30, P32 and P34, This group gathers the wells with the richer cadmium waters (rates vary between 0.06 and 0.14 mg<sup>l</sup>-1), P25 joins this group and has the highest value of cadmium which is of the order of 0.25 mg- 1.

The origin of cadmium in soils is both natural and anthropogenic, but in agricultural areas, the first vectors of this trace metal element are phosphate fertilizers, calcium amendments and pesticides.

For water intended for human consumption, WHO recommends a limit value of 3 µg -1; Directives of the Council of European Communities and the French regulations set a limit value of 5 µg<sup>l</sup>-1. The lowest dose of cadmium in this group is 20 times the value recommended by WHO, and the P25 is 83 times higher.



**Figure 10 :**Representation of the five well groups on the factorial plane F1-F2 of the second standardized CPA.

## Conclusion

The results of the statistical analyzes made it possible to discriminate five types of wells, three of which represent different concentrations of trace metallic elements; These are groups 1, 4 and 5 which record high values of iron-zinc, copper and cadmium, respectively. The other two groups are distinguished by high conductivity and low pH.

The lowest recorded value of the trace metallic element cadmium in the 34 surveyed wells is of the order of 0.02 mg / l, which is 7 times higher than the limit value recommended by WHO for Water intended for human consumption. All prospected wells contain water that is unsuitable for human consumption due to high contamination of cadmium.

Intensive agricultural activity and the irresponsible use of fertilizers and pesticides remain the main cause of the metallic pollution of the groundwater of the Triffa Plain groundwater.

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