METAL TRACE ELEMENTS IN SOILS OF THE AREA M'POURIÉ – MAURITANIA

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Abstract: The development of the right side of the Senegal River can lead to the degradation of the soils around the neighboring countries. That's the reasons why this study was conducted on the soils of the plain of M'Pourié. A sampling of the soil was done by zig zag method, and carried out on three depths (20, 40 and 60 cm) in the South East area of the plain of M'Pourié. This sample has hydromorphic soils (type pseudo-gley), red brownish color with a granular structure. The study done on this sample is about some physico-chemical parameters (pH, organic matter and texture), major elements and metal traces elements (MTE). The results show that these soils have a silty clay texture and a low average of organic content (1.14%). PH has an acid tendency and this acidity increases with depth (6.74 6.15 and 5.7 respectively for 20, 40 and 60 cm). The major elements have an abundance of aluminum and iron with low concentration of carbonates. The highest MTE are Cr V and Ni while the lowest are Cd, Pb and As. The vertical dynamics of the majority of elements shows a low variability, yet the Cd, Pb and As are more concentrated near the surface (20 cm) the principal component analysis (PCA) shows that most of the MTE is controlled by the aluminum, iron, phosphorus, and calcium, which induces a lithogenic origin. Whereas Cd, Pb and As show a correlation with the organic material assuming, at least in part, a anthropogenic origin (fertilizers). The comparison of the values of ETM soils plain M'Pourié with environmental quality standards TEC and PEC shows contamination by Cd and Ni accompanied by Cr pollution.

Keywords: MTE, soils, M'Pourié, Senegal River, PCA,

1. INTRODUCTION

The Senegal River Basin is located in the western part of Africa between latitudes 10°30' and 17°30' North and longitudes 7°30 and 16°30 West. It is drained by a river 1800 km long, the three main tributaries (Bafing Bakoye and Falémé) have their source in the Fouta Djallon (Guinea). Its area is about 300 000 km^2; it extends over the highlands in northern Guinea, West part of Mali, the southern regions of Mauritania and northern Senegal's.

With the drought that started in the 70s, the three neighboring countries (Mali, Mauritania and Senegal), decided in 1972 to join their efforts within the framework of the organization for the development of the Senegal River (OMVS) for an integrated and coordinated development of the river basin they share together. OMVS can be seen as the culmination of a long process of attempts to control and rationalize the exploitation of the Senegal River valley and its resources.

Irrigated agriculture started in the sixties around the Senegal River delta and developed. Today with the building of dams along the river Senegal at Diama in 1985 and Manantali in 1988, fresh water and irrigated agriculture were made

available, and this is becoming the main activity of the populations, which led to their development.

In these areas, we are noted a considerable growth of the populations which resulted in an increase the requirement of foods. The use of irrigation leads to increased agricultural production, especially in the rice production, there by meeting those needs. In this context that the plain M'Pourié was established, the rice fields were installed and an experimental breeding center was created, the cattle are kept in large pens and fed with byproducts of rice.

Irrigation can resolve the main constraint to production, but it also generates a risk of soil degradation. The massive use of fertilizers, the systematic use of pesticides has led to a considerable increase in agricultural yields. Unfortunately they are accompanied by increased pollution of the farmland and inland waters by various inorganic or organic contaminants. Fertilizer materials, used in agriculture, often contain more or less amounts of metallic trace elements (MTE), which can accumulate in the soils, over the long term (Rattan et al., 2005). In fact, the heavy metals are usually associated with micro-elements, they tend to accumulate in the soil, causing serious environmental and health problems (Mihali et al., 2013).

To establish a sustainable management of arable lands vis-a-vis the contamination MTE, it is necessary to make a diagnosis of the state of contamination of agricultural soils, identify and quantify the total content of metal pollutants in soils. For that we need to study the contents of the soil geochemical background of soil MTE their vertical dynamics and origin. This approach is based on a better understanding of the processes occurring in such environments by integrating all compartments.

2. MATERIALS AND METHODS

2.1. Site of Study and sampling

The study area is located in the delta of the Senegal River, it is part of the plain M'Pourié 204km south of Nouakchott. It extend to the north-east of south-west axis of 16°30' to 16°32' north latitude and 15°48'50" 15°52'30" west longitude. The study concerns an irrigated area on the right bank of the Senegal River, west of the city of Rosso, and spread over an area of about 600ha. Irrigated plots made from the Senegal River via a pumping station located in the study area.

Soil sampling was carried out between March and December 2011, after the growing season and before the winter rains. Three criteria were taken into account in the selection of sampling points: The

slope, the spatial distribution of samples and the type of crops rice (Fig. 1). Samples were collected following a zigzag path with a manual auger at depths 20, 40 and 60 cm. Five samples were collected per plot and mix to make a composite sample, thereby we obtained 60 soil samples collected from each 1 kg on cloth bags.

2.2. Physicochemical and geochemical analysis of soils

The samples thus obtained are dried in the open air and then crushed and sieved to 2 mm. The samples thus prepared were analyzed in the laboratory of ALS minerals OMAC Limited (Ireland).

2.3. Physicochemical Parameters

pH: The pH_{H20} and pH_{KCl} were measured with a soil / solution 1/2.5 according to the protocols of NF U 44-117. The pH was measured in the supernatant after agitation for 1 hour and decantation.

The organic material is metered by calcination in an oven for 1 hour at 1000°C. The micro-size analysis was determined using a Malvern 2000 laser particle size, which allows the determination of the different size fractions (between 0.02 and 2000 microns) component soil.

2.4. Pedogeochemical soil

The quantification of the total metal concentration of the soil by two analytical methods: X-ray fluorescence (XRF), using the technique of lithium borate fusion XRF associated and inductively coupled plasma mass spectrometry (ICP-Ms) with the edta and citric acid.

2.5. Statistical Analysis

The data were processed statistically using the software XLSAT 2012, which allows principal component analysis (PCA) to establish correlations between variables and grouping of individuals of populations and to identify general trends.

3. RESULTS AND DISCUSSION

3.1. Physicochemical characterization of soils

It must be remembered that the sampling made before has allowed to evaluate the variability of the chemical composition of soils on three depths 20 cm, 40 cm and 60 cm.

Figure 1. Soil sampling in the study area.

The particle size, organic matter, carbonates and pH were performed on all samples of soil. The results are summarized in table 1. The pH average of soil M'pourié shows a trend acid. At 20cm deep it is close to neutral and it varies between 7.86 to 5.07 with an average of 6.74. At 40cm, it decreases slightly of 7.71 to 5 with an average of 6.15, and becomes more acidic by going to the depth (60cm) and varies from 7.22 to 4.70 with an average of 5.70. The samples B1P1 presented the highest pH and B9P10 the lowest pH for all depths combined. The pH_{KCl} is changing on the same way likethe pH_{H2O}.

The organic matter (OM), of all of soil is low and varies of 1.15, 1.31 and 1.10 % respectively for 20, 40 and 60cm of depths. It is noted that the rate of OM does not vary up to 60 cm deep.

The average concentration of carbonate ($CaCO_3$) is very low in all the samples in general, it is of 0.54, 0.57 and 0.62% respectively for the three depths 20, 40 and 60 cm. It is observed that the carbonate presented a diminution going in depth.

Soil texture is silt clay (SC) types and does not present a great diversity in the soil. A range comparable to that observed for the soil to the depth 20 cm, a lower frequency of sand samples was observed over the 60 cm depth. This indicates that the sandy character must be more frequently inherited from the nature of the rock as a soil changes from a balanced soil texture.

Table 1. physicochemical characterization of soils M'pourié

Depths		Average 20	Average 40	Average 60
pH_{H20}		6.74	6.15	5.70
pH_{KCL}		5.46	5.05	4.93
Clays	%	33.17	33.74	34.21
Fine silt	%	15.32	15.17	15.01
Coarse silt	%	23.87	23.26	23.74
Fine sand	%	23.36	22.83	23.37
Coarse sand	%	3.48	4.23	2.82
OM	%	1.15	1.17	1.10
CaCO3	%	0.60	0.57	0.62

3.2. The major components of soil

The analysis shows that the major components iron and aluminum are the two elements apart silica, which dominate in soils M'Pourié while the calcium

present in low concentration. Essentially we note that the concentration of these elements remain constant in all three sample depths (Table 2). However, we note the following order of abundance Al> Fe> K> Mg> Na> Ca> Mn> P.

Table 2. Major elements of soil M'Pourié

Major elements %	Averag_20	Averag_40	Averag_60
Al	7.93	7.88	7.83
Fe	4.53	4.55	4.58
K	1.10	1.13	1.16
Mg	0.47	0.46	0.45
Mn	0.04	0.05	0.04
Na	0.31	0.33	0.36
Ca	0.24	0.23	0.25
P	0.03	0.02	0.02

The major elements of the soil show a positive correlation ($r^2 > 0.5$) between them, except the manganese showed no significant correlation with other major elements. Table 3; the aluminum and iron have strong correlations with all major components (except the potassium and manganese) whereas the potassium has a good correlation with the sodium (Na/K, $r^2 = 0.61$) and magnesium (Mg/K, $r^2 = 0.50$).

Table 3. Relationship between the major components of soil

	Al	Fe	K	Mg	Mn	Na	Ca	P
Al	1	**0.97**	0.40	**0.88**	0.23	**0.64**	**0.50**	**0.81**
Fe		1	0.37	**0.87**	0.26	**0.61**	**0.53**	**0.79**
K			1	**0.50**	0.18	**0.61**	0.33	0.11
Mg				1	0.42	**0.55**	**0.62**	**0.60**
Mn					1	-0.10	0.11	0.00
Na						1	0.39	**0.54**
Ca							1	0.29
P								1

3.3. The trace metal soil

Total concentrations were measured for 9 MTE (Fig. 2), in the three depths (20, 40 and 60 cm) plain M'Pourié vary slightly around the mean and the order of abundance these elements is as follows: Cr> V> Ni> Zn> Cu> Co> Pb> As> Cd.

The most abundant MTE are Cr, V, Ni and Zn, respectively, with average concentrations (145.24, 122, 47.67 and 41.33 mg/g). For other MTE concentrations ranged from 19.67 mg/g (Cu), 16.67 mg/g (Co), 11.13 mg/g (Pb); 8.23 g/g (As), and 1.5 mg/g (Cd). Overall the mean values are very close to the median. There has, across the plain, little

dispersion in concentrations measured MTE.

A variation of concentrations can be observed between the different plots and between the depths of the same plot (Fig. 3 and Fig. 4). The majority of MTE have a higher concentration near the surface (20 cm) deep. Certain depths show a tendency for higher values to 20cm for the majority of ETM (B3P3, B7P7 and B9P9). Other profiles seem rather enriched depth (B2P2, B4P4 and B9P10). Finally accumulation levels at mid-depth can be observed (B6P6 and B5P5). Generally ETM have a vertical variation, except in the case of Zn (B1P1, B5P5, B8P8 and B9P10) and V (B1P1 and B5P5), which remain constant.

In the soils of M'Pourié (Table 4), the average concentration of ETM does not have high variability, however, for some elements (As, Cd and Pb), there is a larger average 20 cm deep.While the average Cr concentration slightly increases in depth up to 60 cm.

Table 4. The average concentration of ETM (µg/g) depending on the depth

MTE	20 cm	40 cm	60 cm
As	9.8	8.8	6.1
Pb	11.9	11.5	10
Cd	1.726	1.208	0.52
Co	18	15	17
Zn	43	40	41
Cu	20	18	21
Ni	49	50	44
V	122	120	124
Cr	143.00	145.06	147.66

Acidic pH (<6) promote the availability of As and Cd mobility, but the lead is less movable due to its affinity with the organic matter, (Rodier et al., 1996, Baize, 1997; Tremel-Schaub & Feix, 2005; Van der Perk, 2006). This could explain the slightly higher mean concentrations of 20 cm for As and Pb. Despite the mobility of Cd there is more concentrated near the surface (20 cm), this is probably due to inputs of manure and phosphate fertilizers (100 kg/ha), rich on Cd.

3.4. Relations between the ETM and the major components of soil

The principal component analysis (PCA) was performed on the contents of ETM, major elements (Al, Fe, Mn, P, Ca) and organic matter (OM), respectively retained as active and passive variables to distinguish the groups of elements which have a concentration profile in the soil near. The principal axes of inertia was expressed as % of variance. The

PCA results are shown in table 5. Based on these results, four major components (1, 2, 3 and 4) have eigenvalues greater than 1 and combine them to four 78.51% of the total variance. Factors loading PCs (known as eigenvectors or as weight) are also shown in this table, where values greater than 0.5 are considered significant and therefore highlighted in bold. The set of variables was reduced and studied in four main dimensions (Fig. 5).

The first main component (PC1) largely dominates over the other two and represents approximately 50.72% of the total variance. It shows a high loading of Al, Fe, Ca, P, Zn, Cu, Cr, Ni, Co and V (loading factors > 0.60). Among these ETM, two subgroups can be distinguished: the first comprises Co, Cu and Zn, V, and the second is composed of Cr and Ni.

The strong association of Al and Fe with PC1 translated this component expresses the action of clay minerals and iron oxides in the ETM control. Indeed aluminum and iron are typically associated with phyllosilicates, especially the feldspars (found in clay and silty fine size fractions), as well as oxides and hydroxides of iron.

The origin of the discrimination of the two groups of ETM associated with this component is difficult to establish. Indeed when looking at their distribution in the plane (PC1-PC2), we note that the group consisting of Cr and Ni is more influenced by phosphate, while the second group (Co, Co, V and Zn) orients much more towards oxides of iron, aluminum and calcium. However, if placed in the plane (PC1-PC3) we see that P stands calcium and just gather around Al and Fe.
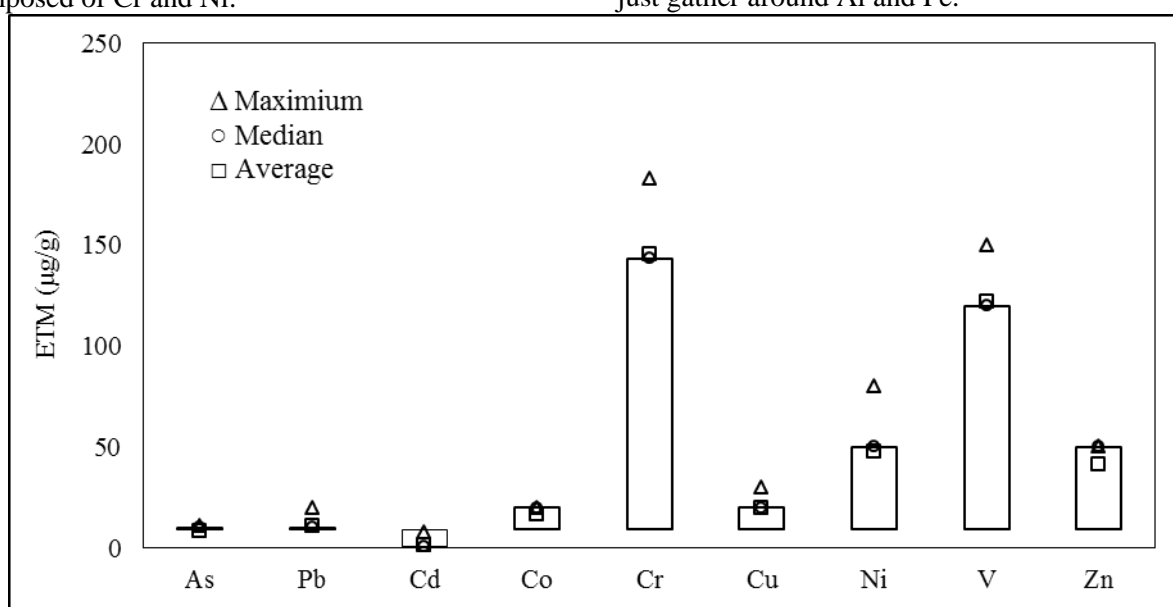

Figure 2. The total concentration of MET of soil M'Pourié

Table 5. Results CPA: percentage of variance for each component and correlation coefficient of each variable with 4 components

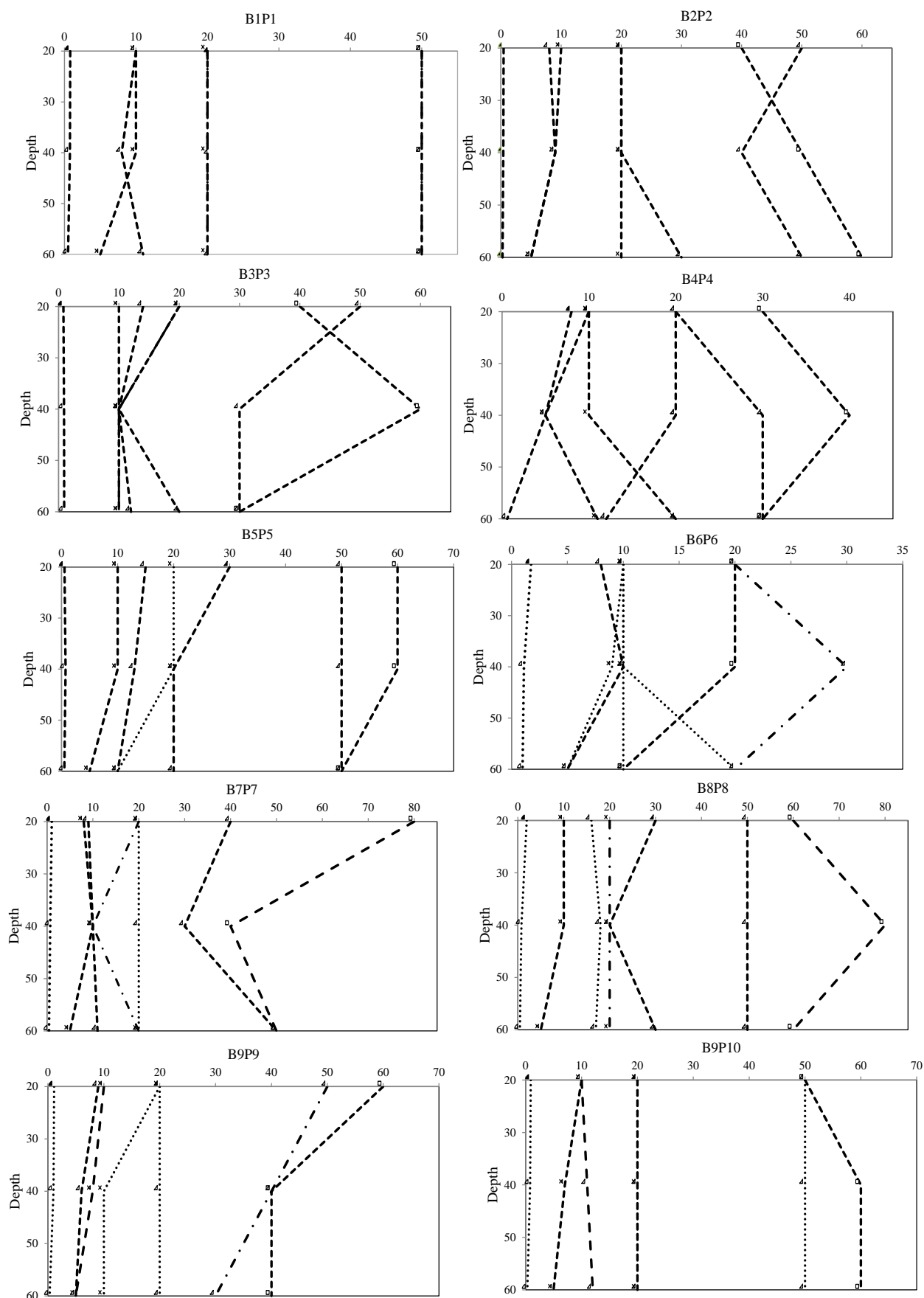| Components	Eigenvalues			Matrix components				
	Variance	% variance	% cumulé de variance	Elements	PC1	PC 2	PC 3	PC 4
1	**7.60**	**50.72**	**50.72**	Al	**0.97**	0.01	0.01	-0.11
2	**1.80**	**12.02**	**62.74**	Fe	**0.96**	-0.06	0.04	-0.11
3	**1.29**	**7.970**	**70.72**	Mn	0.31	-0.26	0.34	**0.77**
4	**1.16**	**7.780**	**78.51**	Ca	**0.60**	-0.11	0.47	0.07
5	0.81	5.42	82.82	P	**0.82**	0.18	0.01	-0.29
6	0.74	4.96	87.78	MO	0.17	**0.67**	0.18	-0.19
7	0.56	3.71	91.49	As	-0.05	0.38	**0.78**	-0.22
8	0.50	3.31	94.79	Pb	0.01	**0.84**	-0.16	0.28
9	0.25	1.68	96.47	Cd	-0.58	**0.62**	-0.14	0.31
10	0.19	1.24	97.71	Co	**0.63**	-0.05	0.07	0.18
11	0.15	1.01	98.72	Cr	**0.94**	0.15	-0.05	-0.20
12	0.09	0.60	99.32	Cu	**0.77**	0.05	-0.27	0.16
13	0.07	0.50	99.82	Ni	**0.77**	0.25	-0.08	0.23
14	0.02	0.12	99.94	V	**0.95**	0.00	-0.14	-0.14
15	0.01	0.06	100.00	Zn	**0.92**	-0.01	0.08	0.16

Figure 3. Variation of concentrations (mg / g) in different ETM with depth for les10 horizons M'pourie: As:∗; Pb: Δ; Cd :●; Co:×; Ni:□; Zn:◊; Cu: ▲;
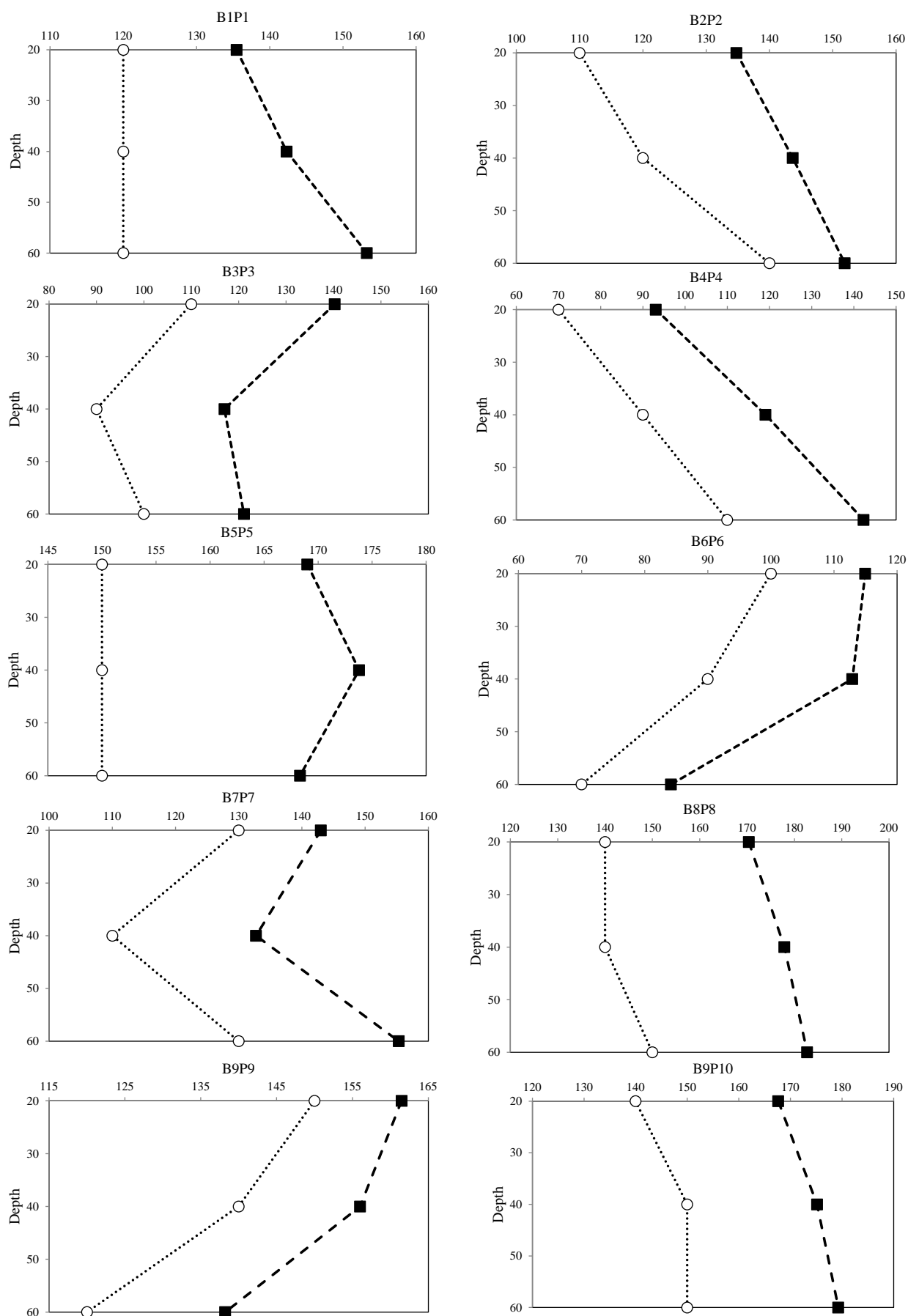
Figure 4. Change in concentrations (mg/g) in different ETM with depth for les10 horizons M'Pourié Cr:■; V:○
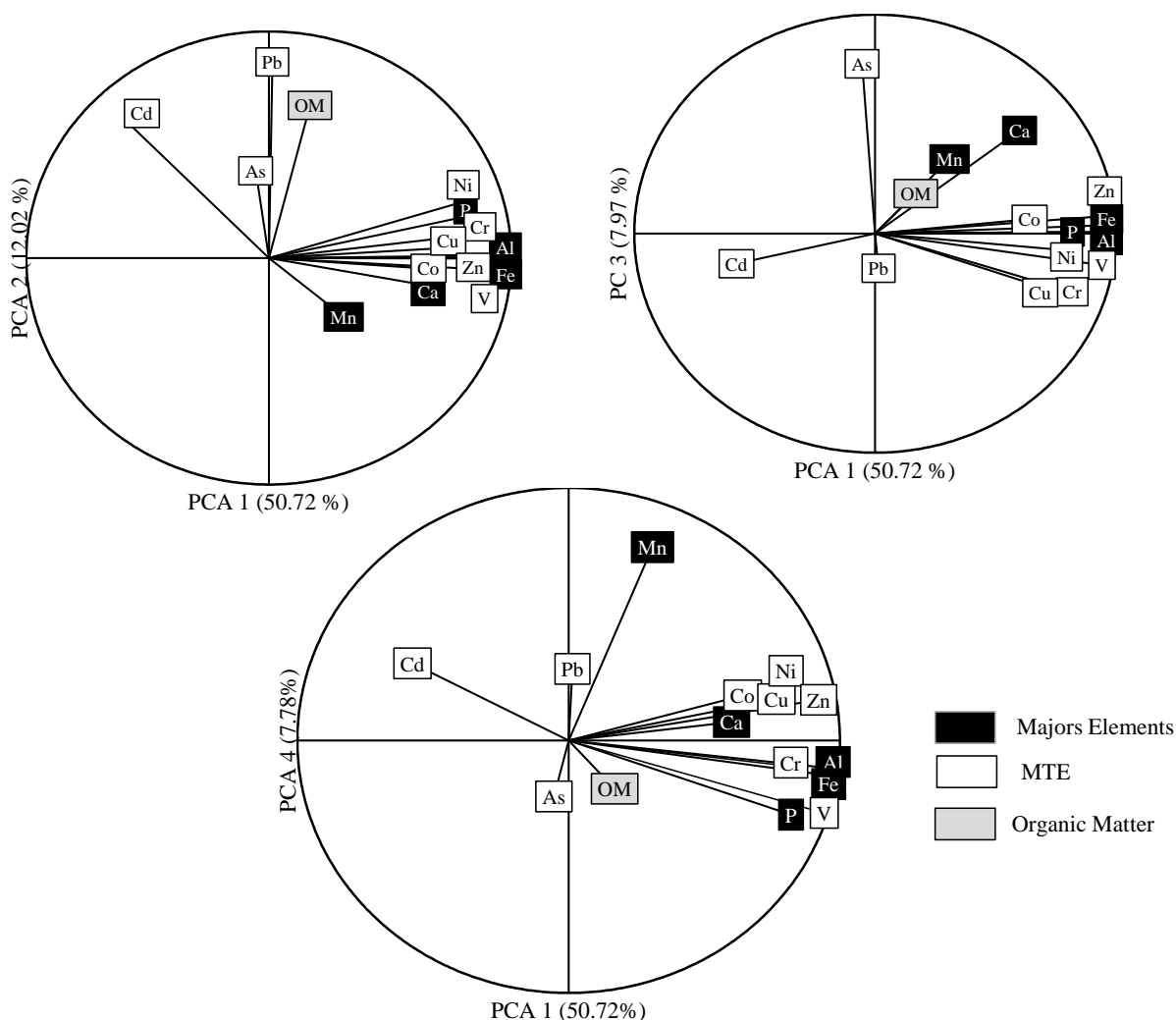
Figure 5. Representation concentrations MTE, major elements and OM in three dimensions according to the components 1, 2, 3 and 4 in PCA.

Several unknowns such as the anthropogenic influence of one group over another, and labile and residual proportions of each element could be the cause of this discrimination.

The second component (PC2) is 12.02% of the total variance. She strongly associated Pb, Cd and MO. These elements may have a source of phosphate fertilizers that are used in this region or phosphogypsum for desalination of soils. However phosphogypsum contains heavy metals concentration. For example, the cadmium content of about 16ppm, or 16g/t and 5.3ppm lead (Loyer, 1989).

Massive and repeated applications of phosphogypsum could therefore lead to an accumulation of these elements in the soil and possibly cultures. These elements can be of natural or anthropogenic, this component appears to reflect the mixture of anthropogenic inputs and natural inputs. In fact, due to its link with the MO we can assume that cadmium has an anthropogenic origin in soils M'Pourié

because phosphate fertilizers are often identified as important sources of Cd pollution in rural areas (Avril 1992, Nicholson et al., 2003. Mico et al., 2007). However, the relationship between Cd, Pb and OM in our samples, certainly reflects an anthropogenic origin.

The third component (PC3) represents approximately 7.97% of the total variance. Is strongly linked with As, with a load factor of about (r^2 = 0.78).

Finally, the fourth component (PC4) represents approximately 7.78% of the total variance. It is strongly associated with the Mn, with a loading factor of about (r^2 = 0.77)

Particle size, pH, organic matter, carbonates, phosphates and oxides of Fe and Al are commonly considered as the main soil parameters (Sumner, 2000; Sparks, 2003; Shtangeeva, 2005). They influence the behavior of MTE, imposing a maximum capacity of fixing or controlling their distribution between particulate and dissolved phases.

Indeed, direct comparison of total concentrations (PC2) is not sufficient to discriminate a anthropogenic influence considering that soil processes have influenced the distribution of MTE.

To take into account the influence of soil formation on the distribution of MTE in order to distinguish the influence of pollution, several indicators are available. We compare in table 6 concentrations MTE soils M'Pourié.

Table 6. Levels in the soils of the MTE M'Pourié compared to quality standards values: PEC and TEC (MacDonald et al., 2000).

MTE (µg/g)	Min	Average	Max	TEC	PEC
As	5	8.23	11		
Pb	5	11.13	20	35.8	128
Cd	0.26	1.15	8	0.99	4.98
Co	10	16.67	20	0.99	4.98
Cr	84.16	148.74	182.69	43.4	111
Cu	10	19.67	30	31.6	149
Ni	10	47.67	80		
V	70	122	150		
Zn	20	41.33	50	121	459

Total concentrations of trace metals in soil are commonly used for determining the maximum contents permitted in the legislation of many countries (Zogaj et al., 2014)

In the present work, the environmental quality of soils M'Pourié was evaluated by comparing the concentrations measured MTE with the environmental quality standards (Table 6): PEC and TEC (MacDonald et al., 2000). The TEC (threshold effect concentration) is the concentration below which a contaminant is not normally toxic. The PEC (probable effect concentration) is the concentration above which a contaminant is probably toxic. At a concentration between the TEC and PEC, a contaminant may be toxic.

Mean concentrations of most parts of MTE in soils M'Pourié are all below PEC and TEC (except Cr, Cd and Ni), these concentrations exceed the values above which they will be toxic (Mac Donald et al., 2000).

Chromium (Cr), shows an enrichment towards most of the plots (B1P1 , B2P2 , B4P4 , B8P8 and B9P10) north east of the plain, but the highest concentrations are found in the surface plot (B7P7) to South West plain M'Pourié. Chromium concentrations ranging between 84.16 and 182.69 mg / g (average = 145.24). These values exceed the levels above which the chromium is toxic

Cadmium (Cd), is characterized by a surface enrichment of all parcels (except B3P3) (Fig. 4). The enrichment of soil by Cd is favored by the use of fertilizers, application of mud, manure and phosphate fertilizer containing Cd trace (Cakmak et al., 2004). While some contributions in Cd is probably due to the exploitation of triphosphates in plain M'Pourié (Trarza region). Cd contents vary between 0.26 and 8 mg/g (average = 1.15), according to the toxicity thresholds (Mac Donald et al., 2000), cadmium shows widespread a pollution on the plain without exceeding the toxic values (except B4P4_20 and B4P4_40).

Nickel (Ni), it is more enriched in mid-depth for most of the plots , and varies from 10 to 80 mg/g (average = 47.67); it shows a heterogeneous and particular relative the chromium and cadmimium, which are clearly enriched or depleted, while nickel can remain constant (B1P1), or even have an opposite trend (B7P7 and B9P10). According toxicity thresholds, nickel shows pollution but does not exceed the toxic values (except B6P6).

The differences of the levels of metal concentration compared with bibliographic data show areas contaminations higher or lower. Plain M'Pourié being an area or activity of man there is very developed, the origin of these concentrations higher or lower still to be determined more accurately: Anthropogenic contamination and/or natural origin Geological? Where are located the sources of contamination? How to quantify the contamination? These are the questions we try to answer the following hand.

The principal component analysis (PCA), which is a statistical tool commonly used in geochemical studies to simplify the number of variables and to facilitate interpretation of the data (Facchinelli et al., 2001. Liu et al., 2002). In addition, this multivariate analysis identifies the parameters that influence the distribution of concentrations of ETM in environments such as sediments (Einax & Soldt, 1999; Mico et al., 2007) and water (Cave & Reeder, 1995).

In this statistical study, we can say that as Cd, Pb and As reveal unusual behavior compared to other ETM studied. While the distribution of Cu, Co, Cr, Ni, V and Zn is controlled by aluminosilicates (clay minerals feldspar, mica) and/or the oxy hydroxides of Al, Fe, carbonate minerals, phosphorus. Mn and (to a lesser degree) the positive correlations Cr - Al and Ni- Al; Cr Fe, Ni-Fe; V -Al; Zn -Al and Co -Al, leash assume that these elements have the same origin (Nolting et al., 1999). The concentrations of Cd, Pb and As in soils are rather governed by organic matter. The action of organic matter does not seem insignificant in the distribution

of ETM, especially for Cd, Pb and As, despite these low levels of MO (<2%) in the soils of the region.

4. CONCLUSIONS

The soil parameters M'Pourié, show little variability between the three depths (20, 40 and 60 cm). The acidity of these soils, probably due of the significant presence of aluminum, may explain the low concentrations of carbonates. These soils are low in organic matter.

The major elements in the soil are strongly associated and have very low spatial variability, except Mn. Among the MTE soil analyzed, Cd is less concentrated, while Cr, V, Ni and Zn have by far the highest concentrations.

The majority of MTE show no contamination in soils M'Pourie, according to quality standards (TEC and PEC). However Cd and Ni are contaminated in some plots. While most plots show a pollution Cr

Among these MTE, cadmium, lead and arsenic, show unusual behavior characterized by good association with organic matter, suggesting a lithogenic origin and probably anthropogenic through fertilizers. This is also the only elements that correlate with the organic material. While other MTE are correlated. The distribution of concentrations of other MTE is controlled by aluminum, iron, phosphorus, and calcium. Against by the Mn and MTE show no significant correlation.

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