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Modeling and optimization of relocation of some heavy metals and micro-nutrients in the Argan trees

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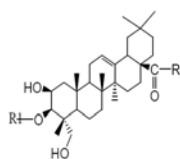
Abstract: This work constitutes a contribution to the study of the physical-chemical performance of some heavy metals and micro-nutrients in the Argan trees. The samples are harvested from small Argan trees, three samples (soil, wood, leaves) per tree. The content of various heavy metals and micro-nutrient in aerial parts (leaves, wood and soil) were analyzed in the Argan tree by the method of ICP-ES. The results of analysis of data for the chemical variables were measured for several trees at different measurement times. do not affect the dispersion of the data. The use of chemometrics has allowed us to interpret the results obtained especially those related to the characterization of heavy metals and micro-nutrient after calibration by variable regression of these results in order to get an overall estimate of the optimal content, and to follow changes in the methods of treatment. The results of the characteristics of Argan trees have been treated using the statistical method of Principal Component Analysis (MFA). The MFA was used to analyze the three groups simultaneously. These groups are fairly similar.

Keywords: Heavy metals, micro-nutrients, Argan trees, Principal component analysis MFA, (ICP-AES).

1. Introduction

The primary functions performed by the Argan trees in Morocco are particularly strongly linked to the economic, social and environmental aspects. In recent decades, the argan trees have been a significant deterioration especially; after the First World War, the production of carbon has reached 100,000 quintals. Argan oil is also capable to provide support and stabilize some two millions rural people. Similarly, the argan tree is considered as a green belt in the south Moroccan regions. The destruction of this tree would certainly causes desertification and exposes the rural population to rural migration [1]. Also, its phyto-chemical study revealed the presence of new triterpene saponins as shown in scheme 1, which constitutes Arganines glycosides of bayogenin [2, 3, 4]. The Argan oil extracted from the kernel is used in cooking and is incorporated in cosmetics and pharmaceutical products. The oleaginous almond represents only 3% of the fresh weight [5]. Usually, the oil is extracted by utilizing the classical technique, resulting in one hand a loss of 45% oil in cake, corresponding to 1.530 ton [6]. In the domestic economy, Argan oil is an important part of income [7]. The oil is an oleic-linoleic acid [8]. Several studies have focused on the Moroccan Argan to characterize the physical chemical or to determine the byproducts and study the

chemical composition of Argan oil in terms of its extraction and production mode [1-5, 12]. The objective of this study is to determine the levels of heavy metals and trace element in different parts of the Argan trees (soil, wood and leaves) to can be determine an approach and to develop a model of this distribution by determining correlations between various parameters and different concentrations of these compounds in order to optimize the relocation of heavy metals and micro-nutrients in the Argan trees.



Arganine G: R₁: glucose4-lapiose, R₂: glucose
 Arganine H: R₁: glucose4-lapiose, R₂: arabinose
 Arganine J: R₁: glucose 4-lapiose, R₂: arabinose2-1rhamnose4-1xylose3-lapiose

Scheme. 1 Triterpene of argan oil.

2. Materials and methods

2.1. Sites and samples

The samples needed for this study were made in three main parts (soil, wood, leaves), spreading over the argan tree and at different spans of time (April 2008, October 2008, June 2009). The samples of argan are harvested every six months, with three samples per tree.

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2.2. Analysis

The content of various heavy metals and micronutrients in parts (soil, leaves and wood) were determined by ICP-ES and in the next step carefully washed with distilled water, dried in an oven and then crushed, incinerated and mineralized.[9]. The physical-chemistry and soil particle size results are presented in Table 1. The analysis results are gathered in Tables 2, 3 and 4. The data table has 15 rows (individuals), each corresponding trees (S₀, A, B, C, D) with the measurement date (1 (after one month), 2 (after six month), 3(after 14 month) and 3x11 same variables that are the results of analysis of heavy metals and micronutrients (33 columns) naturally structured into 3 groups: leaves, wood and soil. The treatment results of the characteristics of argan was done using a statistical method MFA (Multiple factorial analysis) [10] which is a factorial method adapted to the treatment of tables in which a set of individuals is described by several groups of variables. This method allows a joint analysis of tables with individual groups of variables. It deals with finding the common factors assigned to groups and individuals by comparing each of these groups. The data is inevitably normalized in such kind of analysis. The

regression coefficient of variables RV is tested by some correlation [11].

3. Results and discussion

The results of analysis of metal content in different parts of Argan at different periods are shown in Tables 2, 3 and 4. In this variation, a preliminary study has shown that potassium is the most abundant element in soil, wood and leaves of argan. Among other tested metals, magnesium attains the second position in the wood and leaves into the soil while the iron is in second position. Moreover, the wealth of potassium in leaves and wood argan analyzed perfectly reflects the rich soil of this element as shown in Figures 1, 2 and 3. 2. In fact, the comparison between the mineral composition of leaves, wood and soil spreads the minerals into two groups:

-Group 1 consists of Al, Ca, Fe, Mg and Cu. In this group the soil has the highest concentrations in most trees, they are followed by the leaves and wood which the sort order is: soil> leaves> wood.

- Group 2 consists of potassium and zinc. For these elements, the wood takes the second position after the soil (soil> wood> leaves).

However, the distribution of most metals in different parts of sampling shows that the soil is the one which accumulates more metals analyzed in the argan tree..

Table 1 Physico-chemical and particle size analysis results of the soil.

Semples	Region	pH		N%	C%	MO%	P ₂ O ₅ mg/100g	Argil%	Fine silt %	Coarse silt %	Sandy %	Coarse sand %
		Eau	KCl									
Sol	Rabat	8,2	7,3	0,07	1,7	2,98	6,71	16,34	3,52	9,20	34,32	36,62
		7	7	8	3							

Table 2 Results obtained by the analysis of various heavy metals and micronutrientS in three parts of the argan (24/04/2008 (after one month of watering)).

Trees	Cd (ppm)	Cr (ppm)	P (ppm)	Al (ppm)	Ca (ppm)	Fe (ppm)	K (ppm)	Mg (ppm)	Cu (ppm)	Mn (ppm)	Zn (ppm)	
S ₀	Leaves	24,39					5374,356			28,356	15,741	
	Wood	0,105	2	671,869	166,1691	166,1691	223,686	1	3532	11,282	3	9
	Soil	0,757	6	596,617	123,8286	123,8286	136,5922	4	2	7,7495	9	4
		0,218	9,211	581,335	24888,88	24888,88	32981,97	47347,99	9803,75		686,98	
A	Leaves	32,22		1372,74						2217,92	330,04	17,266
	Wood	0,275	9	7	183,0591	183,0591	271,7823	6930,869	6	3,051	4	2
	Soil	0,306	6	525,794	122,2987	122,2987	108,2372	5	4	2,142	224,94	19,74
		0,215	6	1266,92	24010,79	24010,79	30701,05	49533,64	9425,98		520,64	101,03
B	Leaves	0,284	35,24	1702,94	238,1569	238,1569	275,6356	18852,09	1752,09	7,2521	33,968	10,857

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		2					2	7		3	5
	Wood	16,24	1214,26					1253,65			14,972
	0,346	2	5	246,2383	246,2383	218,676	11190,24	8	11,318	5,0254	7
	Soil	14,01	2105,45	18757,26	18757,26	22322,76	44331,76	5529,60		520,64	
	0,298	1	8	2	2	2	8	4	22,861	3	111,04
C	Leaves	33,09	10611,6				7502,605	2258,92			
	0,981	2	8	275,9484	275,9484	988,11	1	1	9,0827	1,0168	22,06
	Wood	16,04	1537,39				8664,860	1477,09		17,164	
	0,488	6	3	172,2476	172,2476	888,6777	3	2	7,6879	3	26,07
	Soil	18,54	8899,63	24570,88	24570,88	27933,33	50144,66	8040,85		557,00	143,08
0,836	1	9	7	7	5	1	4	21,787	6	9	
D	Leaves	37,35	14835,0				8436,082	3024,00		43,978	
	0,994	4	4	158,8782	158,8782	618,4068	3	7	7,957	1	10,759
	Wood	14,34	2531,34				8851,859				
	0,57	4	7	189,6049	189,6049	108,2315	5	783,231	5,7804	7,7269	28,949
	Soil	35,63	13449,7	22848,04	22848,04	27198,14	51659,96	7344,95		436,42	141,18
0,923	8	3	7	7	9	9	9	23,705	4	5	

Table 3 Results obtained by the analysis of various heavy metals and micronutrients in three parts of the argan (23/10/08 (six months)).

Trees	Cd (ppm)	Cr (ppm)	P (ppm)	Al (ppm)	Ca (ppm)	Fe (ppm)	K (ppm)	Mg (ppm)	Cu (ppm)	Mn (ppm)	Zn (ppm)
S0	Leaves	24,39		166,169		223,686	5374,356				15,741
	0,11	2	671,869	1	166,1691	8	1	3532	11,28	28,36	9
	Wood	15,19		123,828		136,592	8342,991	1665,77			
	0,76	6	596,617	6	123,8286	2	4	2	7,76	10,48	22,09
Soil	581,335	24878,3	24888,88	32990,0	47347,99				686,9		
0,21	9,211	9	7	3	1	6	9808,6	24,66	1	127,2	
A	Leaves	34,01	1390,65	190	193,92	290,09	6930,869	2223,1	3,76	341	17,63
	Wood						18374,48			232,0	
	0,32	20,12	597,65	122,01	128	113,35	5	705,99	2,17	3	19,71
	Soil	9,526	1286,2	24632	24015,69	1	6	9495,71	18,09	531,3	101,31
0,27	6										
B	Leaves	35,24					18852,09				
	0,28	2	1710	253,51	272,07	291,01	2	1787,87	7,84	34,07	10,88
	Wood	16,24									
	0,37	2	1223,43	274,07	253,37	237	11190,24	1283,53	11,97	5,06	14,98
Soil	19005,1	3	18790,37	22400		44331,76	5545,09	21,41	3	113,2	
0,298	14,36	2203,11									
C	Leaves	10687,1					7502,605				
	0,98	34,12	7	279,44	276,5	991	1	2283	9,93	1,02	22,06
	Wood						8664,860				
	0,5	16,91	1590,91	175,47	181,04	901,76	3	1500,1	7,69	17,21	26,07
Soil	24670,5	6	24681,63	5	1	50144,66	8087,57	23,71	7	143,08	
0,88	19,11	8899,87									
D	Leaves	8436,082									
	0,99	37,51	14983	159,5	167,67	634,08	3	3064	8,19	44,37	10,77
	Wood						8851,859				
	0,61	14,48	2620,13	188,99	191,05	120,08	5	786,19	5,96	7,81	28,98
Soil	13674,0	22896,1				51659,96			467,1		
0,92	35,4	9	7	22980,1	27234	9	7376,51	24,19	3	141,53	

Table 4 Results obtained by the analysis of various heavy metals and micronutrients in three parts of the argan (18/06/2009 (after fourteen months)).

Tree s	Cd (ppm)	Cr (ppm)	P (ppm)	Al (ppm)	Ca (ppm)	Fe (ppm)	K (ppm)	Mg (ppm)	Cu (ppm)	Mn (ppm)	Zn (ppm)	
S0	Leaves	24,39					5374,356		11,28	28,356	15,741	
	0,105	2	671,869	166,1691	166,1691	223,6868	1	3532	2	3	9	
	Wood	15,19					8342,991	1665,77	7,749	10,409	22,098	
	0,757	6	596,617	123,8286	123,8286	136,5922	4	2	5	9	4	
Soil	581,335	24888,88	24888,88	32981,97	47347,99	9803,75		24,68	686,98			
0,218	9,211	9	3	3	2	6	5	1	6	127		
A	Leaves	42,22	1412	196,91	203,03	327,78	6893,87	2387,13	3,9	339,87	17,8	
	Wood	23,79	609,79	122,17	141,28	137,72	19000,61	765,12	4,67	391	19,76	
	Soil				24010,79							
	0,67	15,54	1681,09	24564,99	8	30830,93	49567,54	9567,85	18,53	543,43	101,05	
B	Leaves	0,284	38,46	1702,94	238,1569	238,1569	275,6356	18852,09	1752,09	7,252	33,968	10,857

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							2	7	1	3	5
	Wood		1214,26					1253,65	11,31		14,972
	Soil	0,41	18,98	5	246,2383	246,2383	218,676	11190,24	8	8	5,0254
				2105,45	18757,26	18757,26	22322,76	44331,76	5529,60	22,86	520,64
		0,91	15,23	8	2	2	2	8	4	1	3
	Leaves	1,83	56,1	10731,8	297,63	282,91	1071,41	7892,03	2341,91	9,9	1,16
	Wood	0,69	21,03	1621,93	179,76	182,76	915,33	8876,4	1765,87	8,08	17,16
	Soil	0,91	20,61	9087,91	2553,87	24870,66	28501,4	51167,45	8203,54	29,76	559,16
C	Leaves	1,05	43,76	17540	162,87	198,88	638,41	8436,78	3274,07	9,14	50,83
	Wood	0,96	11,35	2731,47	189,6	197,32	131,45	8893,76	779,98	6,78	8,26
	Soil		35,63	13749,7							
D		1,67	8	5	23345,43	22846,41	27498	51659,04	7384,87	29,91	491,27
											144,83

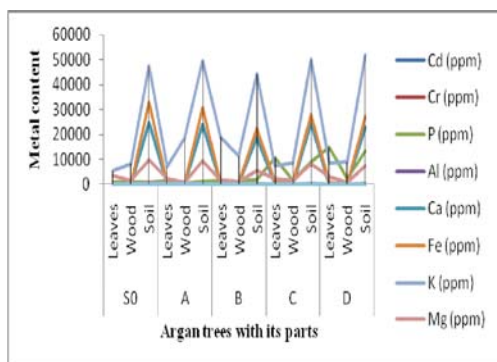


Fig. 1 Representation of different levels of heavy metals and micronutrients in wood, leaves and soil of the argan tree (24/04/2008).

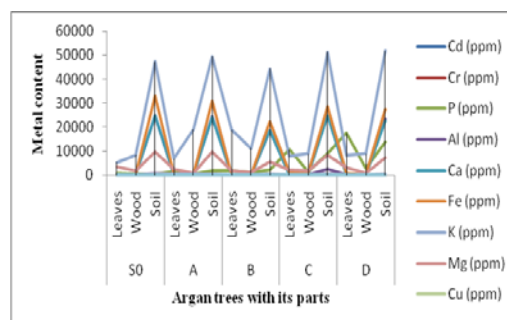


Fig. 3 Representation of different levels of heavy metals and micronutrients in wood, leaves and soil of the argan tree (18/06/2009).

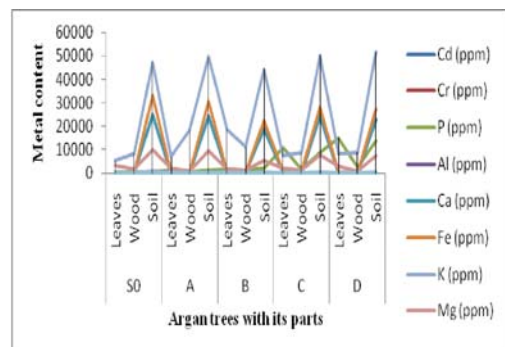


Fig. 2 Representation of different levels of heavy metals and micronutrients in wood, leaves and soil of the argan tree (23/10/08)

In case of classes of argan, the coefficient RV was calculated which is being presented in table 7 that shows that the coefficients of Sol RV and Leaf are relatively higher. The Wood Group is less correlated with the other two groups. Such type of behavior is somewhat bizarre. The principal component analysis was conducted using eleven variables (heavy metals and trace elements). For principal components, we selected four components that explain 85% of total inertia as shown in table5.

Table 5 Four components that explain 85% of total inertia as shown below.

	Eigenvalue	inertia	cumulative inertia
Comp1	2.23	30.64	30.64
Comp2	1.68	23.00	53.64
Comp3	1.37	18.75	72.39
Comp4	0.92	12.68	85.07

To determine correlations between metal content analyzed in one hand, and the spatial and temporal variation on the other hand; all kind of analytical data from studied metals was subjected to a principal components

analysis. In order to calculate the decomposition of the inertia of each main component according to each group, we used the statistical method that is normalized MAF as shown in Table 6 .

Table 6 Decomposition of total inertia group (%).

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	Dim.1	Dim.2	Dim.3	Dim.4
F	35.07630	36.17980	28.77679	62.98865
B	25.33440	27.64914	45.51514	19.80726
S	39.58930	36.17106	25.70807	17.20409

The results of this mathematical analysis showed that the four major components (P1, P2, P3, P4) are the 75% of the data with percentages of inertia by 23%, 30.64%, 18.75% and 12.68%. The other components contribute a little as compared to the total inertia and will not be considered for the analysis of metals. For the first 2 factors and the inertia due to leaves and soil groups are balanced. The total inertia is high enough for the group timber for the third factor and is completely dependent on the group for factor 4. For a better understanding of the acronyms used; factorial designs represent each tree with the measurement date, for example: D3: D tree, date 3 (June 2009). Only variables that correlated are greater than 0.7 appear in factorial designs. The figure 4 (plan (1.2)) shows significant differences between the trees. The times of measurements were fairly categorized for each tree. Trees C and D are closed while the trees A, B and S₀ are scattered on the plan. On the one common factor, there is a marked contrast between the tree A with tree

C and D. The position of the shaft A is explained by its greater abundance of manganese and potassium, mainly in the leaf and wood and whatever the date of action is. Trees C and D are much more characterized by several chemical components, such as phosphorus and cadmium. The difference is more pronounced at the time 3. The figure 4 opposes the trees S₀ which is rich in magnesium, especially at date 3, where the tree B is rich in potassium. The tree B at date 1 (April 2008) is richer in manganese than B2 and B3. Figure 5 (plan (1.4)) shows the difference between the tree C and the tree D. The tree C is much richer in Al and Ca at the leaves and Fe at the wood. The difference is more pronounced at the time 3. The figure 6 (plan (3.4)) is interesting, it allows separation of trees. The axis between three trees is on one side with high soil potassium in those with high copper timber. Trees S₀ and B are more spread out along this axis. Unlike trees C and D, the trees A, B, S₀ are not influenced by the factor 4.

Table 7 RV coefficient values in different parts of Argan.

F: leaves, B: Wood, S: soil.

	F	B	S
F	1.0000000	0.5164048	0.7145771
B	0.5164048	1.0000000	0.4881846
S	0.7145771	0.4881864	1.0000000

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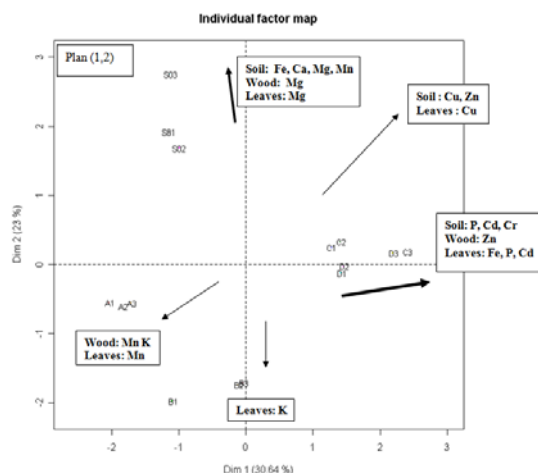


Fig. 4 Plot in the plane P1×P2 of multiple factorial analysis normalized heavy metals contents and micronutrients of the Argan trees at different dates.

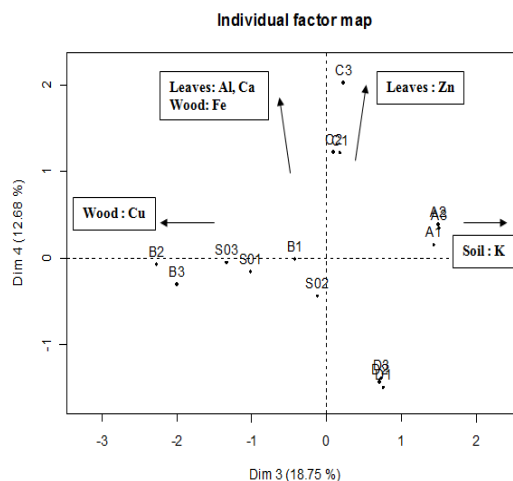


Fig. 6 Plot in the plane P3×P4 of multiple factorial analysis normalized heavy metals contents and micronutrients of the Argan trees at different dates.

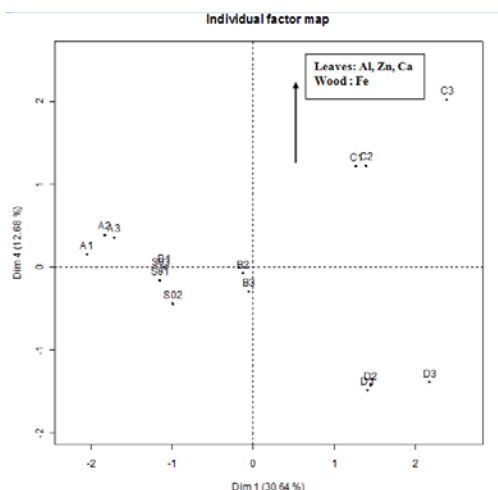


Fig. 5 Plot in the plane P1×P4 of multiple factorial analysis normalized heavy metals contents and micronutrients between the tree C and the tree D.

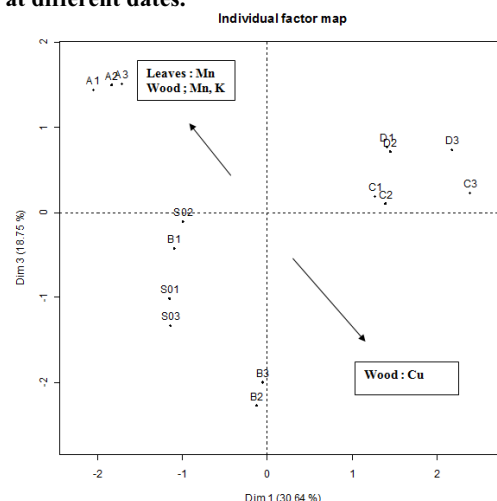


Fig. 7 Plot in the plane P1×P3 of multiple factorial analysis normalized heavy metals contents and micronutrients of the Argan trees at different dates.

4. Conclusions

Heavy metals and micronutrients were analyzed in the argan by atomic absorption. The samples of Argan trees are harvested from small trees, three samples (soil, wood, leaves) per tree. The results of analysis of data for the chemical variables were measured for several trees and at different times. A principal component analysis of analytical data collected shows that the behavior of these elements analyzed in different parts of Argan (soil, wood, leaves) correlates them. AFM was used to analyze the three groups simultaneously. These groups are fairly similar. Overall, the

measurement times do not affect the dispersion of data. The trees are not homogeneous with respect to measurements, there are significant differences. Trees C and D are quite close, but can be distinguished according to certain wealth level of the leaves.

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