

Study of granulometric and pedogenic allotment of limestone of cultivated soils under rainfall regime in the North-West of Tunisia

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Abstract – For studying assessment of carbonates of surface horizons in terms of soils types cultivated in cereals under rainfall conditions in the North-West of Tunisia, and to search at witch granulometric fraction the fine particles of limestone appertain, twenty points covering the most pedogenic types of these zones, have been sampled at the 0-20 cm and 20-40 cm levels. The forty samples collected have served to determine the limestone contents of soils and to specify their particle size compositions. The results have confirmed the domination of fine particle size and the generalized presence of limestone with less or more important proportions.

The comparison of the averages and variances of the obtained results has showed that differences between the values of the two horizons are not significant. This has permitted the use of the averages of the two horizons for the study of this limestone assessment according to soils types. The principal component analysis has especially put in evidence the limestone migration from the surface horizons of the cambisols.

The use of method of simple linear regression has showed that the limestone particles are more joined to the fine silts fraction. This dependency can be explained by the fact that the fine limestone fraction would be the most sensible to the attack of the dissolution product (very diluted ammonium oxalate).

Even this limestone is more abundant in the fine silts and it is not correlated to the clay and the fine sands, its assessment is generalized on the all particle size dimensions but with variable proportions. Its presence in the clayey fraction doesn't make any doubt like the particles reactivity theory suppose, but it's probably the extraction with diluted ammonium oxalate witch would be active preferably on the silts particles much more than the clayey fraction of this limestone.

Keywords: total limestone, active limestone, particle size, fine silts, cereal soils, Tunisia.

1. Introduction

The cereal soils of North-West Tunisia are confined to the North of the Dorsal (mountain range crossing the country in the West - North-East direction) and occupy alluvial plains or inter-mountainous valleys filled by quaternary deposits. These deposits originate from carbonate sedimentary rocks flush with the reliefs and mainly dating from the secondary and tertiaryeras (particularly Cretaceous) (Ben Hadj et al, 1985).

The alteration debris of these rocks of marly or calcareous nature are thus the constituents of the current soils used in agriculture to produce cereals. These soils are known for their fine texture (Belkhodja et al, 1973; Ben Hassine, 2002) and their richness in calcium carbonates whose contents can reach or exceed 30% often (Ben Hassine, 2005). These carbonates are responsible for the increase of the pH in these soils (> 8) and for the blocking of certain elements such as phosphorus (Ben Hassine, 2004), highly requested by semi-intensive cereal crops. This constituent is distributed almost in all the alluvial deposits of soils of North-West Tunisia, both along the pedological profile (vertically) and horizontally. The only exception in northwestern Tunisia is the Kroumirie-Mogods soils derived from siliceous sandstones and Oligocene little carbonated clays. These soils are in fact non-carbonated and often with acidic pH (Belkhodja et al, 1973).

With the dual objective of listing the particle size compositions and the carbonate contents of these soils firstly, and attempting to establish links between the two sets of variables secondly, a sampling campaign was carried out on 20 points spread over all of these soils that extend under two bioclimatic stages: the semi-arid (Zaghouan, Siliana, Le Kef, Jendouba) and the subhumid (Beja). The main purpose of the operation is to statistically analyze the spatial variation of these parameters and to establish a correlation



between the so-called active limestone and the fine particle size fraction. It is assumed that active limestone is the fine part of the total limestone that is susceptible to attack and solubilized by hydrolysis in soils (Sanaâ, 1983; Hannaoui, 1993). Would this active part of the limestone belong to the clay or silty fraction, or would it be distributed over all the fractions and the clays very abundant in these soils, would they consist mainly of carbonate particles or would they be silicate?

The present study thus proposes to approach these questions by carrying out the particle size analysis and that of the total and active limestone; the results will be subjected to different treatments to compare means and variances, to interpret the distribution and grouping by soil type of the samples using the principal components analysis and finally to seek to see in the light of the correlations to which fraction belongs to the active and total calcium carbonates. Such a result can lead to better placing the active limestone fraction in a given granulometric group and specify the estimates in limestone soils of the quantities of silicate mineral clay: phyllosilicates and quartz.

2. Materials and methods

2.1. Sampling soils

In order to cover the maximum of soil types and to make the study exhaustive, soil samples were distributed over the majority of cereal-producing geographical areas in North-West Tunisia. The sampling method took into account the pedogenic characteristics of the soils and was carried out on the two upper slices of 20 cm each, ie 0-20 and 20-40 cm. The samples thus taken represent the following types of soils (CPCS, 1967): fine-textured fluvisols (typic xerorthents), vertisols (typic chromoxererts), calcisols (calcixerollic or vertic xerochrepts) and cambisols (typic calcixerolls).

The number of points taken is 20; the samples are symbolized by the initials of the sampling sites preceded by those of the soil type; they are divided according to the types of soils as follows:

- Fluvisols: PE-Za1, PE-Za4, PE-Si4, PE-Ke1, PE-Ke2, PE-Je1, PE-Je2, PE-Bj4.
- Vertisols: VE-Si2, VE-Si5, VE-Bj1, VE-Bj2.
- Calcisols: CM-Za2, CM-Za3, CM-Si1, CM-Si3, CM-Ke5, CM-Bj3.
- Cambisols: IH-Ke3, IH-Ke4.

All these soils generally occupy flat surfaces corresponding to plains extending in the inter-mountainous valleys of the Tell (series of mountains north of the Dorsal). What they present in common is their geological origin since they are derived from sedimentary rocks of marly or calcareous nature, and their mode of cultivation intended for the production of cereals under rainfed conditions.

2.2. Physico-chemical analyses

The 40 samples taken were air dried, crushed and screened to 2 mm. On the fine earth, the following analyzes were carried out: granulometry, total limestone and active limestone.

- The particle size analysis: 20 grams of fine earth are attacked with oxygenated water (110 volumes) under hot temperature to destroy the organic matter, then are shaken for 4 hours in the presence of water and dispersant (sodium hexametaphosphate). The soil suspension is then transferred to a test tube and then filled with water to 1 liter. The determination of the weight of each granulometric fraction is obtained by pipette Robinson method: 10 ml of suspension are sucked after the necessary fall time calculated according to the Stokes law.
- Total limestone: 0.5 g of finely ground soil is attacked with 25% HCl in an Erlenmeyer flask connected to Bernard's calcimeter and the volume of CO₂ released is measured. This volume is compared to that of 0.3 g of pure limestone. The result gives the total amount of limestone in the soil expressed in%.
- Active limestone: 2.5 of soil were attacked with 0.2 N ammonium oxalate solution and stirred for 2 hours. A solution of 0.1 N potassium permanganate is used to determine the excess of unreacted oxalate with the limestone. The difference between the amount of oxalate added and the amount of permanganate is equivalent to the amount of active limestone in the soil. The result is expressed in% of the total mineral matter.

2.3. Statistical analyses

In order to analyze and compare the vertical and spatial distributions of the values of the studied parameters firstly and to identify the particle size fraction to which the percentages of total and active limestone are related, secondly, following statistics analyzes were used:

- Comparison of the variances between the values of the parameters relative to horizons 0-20 and 20-40 cm.
- Application of the pairing method (or couples method) to compare parameter values in the 0-20 and 20-40 cm horizons. This makes it possible to see if the results differ or not in the same sampling site.
- Principal component analysis of the spatial distribution of parameters according to sampling points and soil types.
- Study of the correlation between the two forms of limestone and the different particle size fractions. This operation aims to specify the membership of the limestone particles of these types of soils to one or the other of the particle size fractions. It has been shown that the type of parent material of a soil influences the granulometry of its limestone: the highest proportions of active limestone belong to fine silt in the case of laminated marly rock and chalky limestone, and with coarse sands in the case of an oolitic limestone. Limestone size of clays ($< 2 * 10^{-6}m$) is not absent since 11.5% is found in chalky limestone soil and 10.4% in flaky marl soil (Baize, 1988).

3. Results

3.1. Distribution of two soil layers according to parameter values

The results in Table 1 provide the following findings:

- All the soils collected are carbonated and the carbonate contents are variable from one point to another. The highest total limestone value appears at point CM-Bj3 with 58 and 59% respectively in the 0-20 and 20-40 cm soil slices. Other high values are observed at CM-Si3, PE-Ke2 and VE-Si2. The lowest values are observed at the points IH-Ke3 (horizons 0-20 and 20-40 cm) and IH-Ke4 (horizon 0-20 cm). These two points represent partially decarbonated soils on the surface, the limestone having migrated in depth by leaching, a process favored by a flat and stable geomorphological form and a Mediterranean climate with contrasting seasons allowing carbonates to be solubilized in winter and reprecipitated in the dry season. .
- The contents of active limestone are generally proportional to those of the total limestone, but values higher than 20% are frequent: CM-Si1, VE-Si2, CM-Si3, PE-Ke2, CM-Bj3. Such values must have a negative effect on phosphate fertilizer inputs, some of which must be downgraded to insoluble forms in these soils (Ben Hassine, 2004). The lowest levels do not fall below 5% and are observed in the IH-Ke3 points, IH-Ke4 (0-20 cm), CM-Ke5 and PE-Je2 (20-40 cm). Even if these values are lower, this does not prevent that they can raise the pH of the soil solution and be responsible for the precipitation of several elements, other than phosphorus, useful for vegetable nutrition (Fe, Cu, Zn, etc.).
- For particle size, the samples richest in clay and having a percentage of this fraction greater than 30% are: PE-Za1, VE-Si2 (20-40 cm), CM-Si3, PE-Si4, VE-Si5 (0-20 cm), IH-Ke3 (20-40 cm), CM-Ke5, PE-Je1 (0-20 cm), VE-Bj1, VE-Bj2 and CM-Bj3 (20-40 cm). Thus, more than half of the points taken have a fine texture. Values less than 20% are relatively few and appear only in the CM-Si1 (0-20 cm), VE-Si2 (0-20 cm) and PE-Ke1 points. All other values are between 20 and 30%, six of which are greater than 25%. The fine silt ($2-20 * 10^{-6} m$) constitutes a significant fraction in the granulometric composition of these soils. Indeed, several points have a value greater than 40% of this fraction: CM-Za2 (0-20 cm), CM-Si1, CM-Si2, PE-Ke1 (20-40 cm) and PE-Je2 (20-40 cm). The lowest value is in the point IH-Ke3 (0-20 cm) where the fractions of coarse silt and fine sand are the most important. The sandy fraction often has values below 20%; we note, however, exceptions with 40.7% and 34.3% of fine sand at points VE-Si5 (0-20 cm) and IH-Ke4 (0-20 cm). Coarse sands are practically the weakest fraction with two exceptions: CM-Za2 (0-20 cm), IH-Ke4 (20-40 cm) and CM-Ke5 (0-20 cm) where values exceed slightly 20%.

Table 1. Analysis results of limestone and particle size fractions (%) of the studied soils

Bioclimatic zone	Soils types	Sampling points	Depts cm	Total CaCO ₃ %	Active CaCO ₃ %	Clay %	Fine silt %	Coarse silt %	Fine sand %	Coarse sand %
Semi-arid	Fluvisols	PE-Za1	0-20	29.2	11.5	30.1	16.3	16.9	20.3	14.5
			20-40	28.8	12.5	30.6	18.6	16.5	17.8	15.4
		PE-Za4	0-20	24.9	11.5	24.6	28.4	21.6	14.9	7.9
			20-40	24	14.5	25.9	15.5	34.5	12.2	10.5
		PE-Si4	0-20	34.5	15.5	30.1	18.3	21.6	25.3	4.6
			20-40	31	15	34.3	19.7	11.6	29.5	4.2
		PE-Ke1	0-20	47	22	15.9	27.6	42.3	9.8	4.3
			20-40	36	19.5	17.3	67.9	4.3	6.2	3.4
		PE-Ke2	0-20	45.1	24.5	22.4	34.6	28.4	11.8	2.1
			20-40	46	21.5	21.2	36.2	22.4	12.9	5
	PE-Je1	0-20	15.8	11	30.6	35.1	17.2	9.4	5.9	
		20-40	16.5	12.5	26.1	21.6	41.9	6	2	
		0-20	38.8	17.5	22.7	39.6	15.8	13.3	5.7	
		20-40	19.4	5	20.1	44.1	21.6	7.5	4.1	
	PE-Bj4	0-20	22.4	11.5	21.8	35.3	28.4	6	6	
		20-40	24.2	14.5	30	24.7	17.2	20.3	5.5	
	Vertisols	VE-Si2	0-20	41.7	20.5	11.1	56.1	22.2	6.7	3
			20-40	41.2	20	31.9	45.2	12.5	0.2	9.4
		VE-Si5	0-20	36	17	32.4	14.8	4.3	40.7	5.7
			20-40	36.6	19	24.6	19.4	42.7	7	3.7
CM-Za2		0-20	38.8	17.5	20.3	40.6	10	12.7	14.3	
	20-40	36	24	23.7	31.9	6.1	13.5	23.7		
CM-Za3	0-20	16.6	8.5	24.6	24	15.1	25.1	9.6		
	20-40	19.4	11.5	23.1	24.6	17.2	24.6	9.1		
Calcisols	CM-Si1	0-20	33.7	22.5	18.2	50.7	12.9	11.9	3.5	
		20-40	31.2	21	25.6	44.3	13.8	9.8	4.3	
	CM-Si3	0-20	45.6	20.5	34.5	20.9	5.4	14.7	21.6	
		20-40	44.4	25.5	40.9	8.6	40.3	6.9	1.8	
	CM-Ke5	0-20	19.6	6	35.8	3.2	16.4	18.4	24.1	
CM-Bj3	20-40	18.2	6	39.5	13.2	20.7	11.9	11.9		
	0-20	58	23	26.4	34.1	12.9	12.4	12.9		

Subhumid	Cambisols	IH-Ke3	20-40	59	24	25.8	29.1	17.2	14.8	10.8	
			0-20	8.1	6.5	23.7	7	30.1	27.1	9.7	
		IH-Ke4	20-40	9.1	7	38.4	20	4.3	27.3	9.5	
			0-20	8.6	6.5	29.1	5.7	12.1	34.3	18.7	
	Vertisols	VE-Bj1	20-40	21.4	17.5	21.1	4.7	31.1	20.1	20.1	
			0-20	25.4	11.5	32.8	29	25.9	9	5.4	
		VE-Bj2	20-40	26.4	14.5	32.8	36.9	13.7	9.7	5.9	
			0-20	19.6	10.5	35.6	3.7	23.7	21.2	13.9	
			VE-Bj2	20-40	21.1	12.5	32.4	3.8	50	9.4	2.1

The granulometric composition of these soils is therefore dominated by the fine fractions: silts and clays. Although the sandy fraction is present, its particles are much more in the fraction of fine sand than in that of coarse sand.

The mineralogical composition of these granulometric fractions is largely composed of carbonates whose values are only weak in the two points IH-Ke3 and IH-Ke4 representing cambisols. In what fraction are these carbonates or how are their particles distributed over the different textural classes observed?

3.2. Analysis of the variance of parameters values of the two horizons : 0-20 and 20-40 cm

In order to compare the values of the two horizons of the set of sampling points, the mean and variance for each parameter and for the two 0-20 and 20-40 cm soil slices were calculated (table 2). The averages and standard deviations of the two horizons are at fairly similar values almost for all parameters. The fraction of fine sands (SF) seems to be the exception since the averages are quite different. The average total limestone is around 30%, that of active limestone around 15%. The values of clay fractions (A) (26 to 28%) and fine silts (LF) (26.5% approximately) are close to each other with a slight advantage for the clay. For the other fractions, their averages are in the following order: LG, SF, SG.

The ratio F of the variances is calculated for the 7 parameters. Its values fall within the acceptance range defined by the interval ($F_{0.95} - F_{0.05}$) at 19 degrees of freedom (dof). The ratio F of the coarse fraction is outside the range of acceptance, so the variances of the two sets of values of each horizon are therefore different from each other; the difference between the two variances is indeed the most important among all the other parameters (83.14 for the 0-20 cm horizon and 184.09 for the 20-40 cm horizon). It should be noted, however, that the value of $F = 0.45$ is only slightly outside the range ($F_{0.95} - F_{0.05}$).

We can conclude, therefore, that for each parameter, the differences between the means and the variances of the two horizons are not important. This seems ordinary because the two horizons follow one another and are placed both on the surface of the soil. The physico-chemical constitutions of the two soil slices can be considered as similar and any measure of amendment or fertilization can concern the two layers without any difference.

Table 2. Comparison of variances of parameters values in the 0-20 and 20-40 cm layers

Parametrs	Depths cm	Mean	Variance*	SD	$F = \frac{s^2/s^{*2}}{n-1}$	dof	$F_{0.05}^{**}$	$F_{0.95} = 1/F_{0.05}$	(AA) Area of acceptance	Comments
Total	0-20	30.47	186.44	13.65						
CaCO ₃ %	20-40	29.50	145.42	12.06	1.28	19	2.174	0.460	(0.460 – 2.174)	F ∈ AA
Active CaCO ₃ %	0-20	14.78	36.25	6.02	1.01	19	2.174	0.460	(0.460 – 2.174)	F ∈ AA
	20-40	15.88	35.76	5.98						
Clay %	0-20	26.14	46.31	6.81	1	19	2.174	0.460	(0.460 – 2.174)	F ∈ AA
	20-40	28.03	46.40	6.81						
Fine silt %	0-20	26.25	228.33	15.11	0.91	19	2.174	0.460	(0.460 – 2.174)	F ∈ AA
	20-40	26.5	251.02	15.84						
Coarse silt %	0-20	19.16	83.14	9.12	0.45	19	2.174	0.460	(0.460 – 2.174)	F ∉ AA
	20-40	21.98	184.09	13.57						

Fine sand %	0-20	17.25	86.50	9.30	1.45	19	2.174	0.460	(0.460 – 2.174)	F € AA
	20-40	13.86	59.85	7.74						
Coarse sand %	0-20	9.67	41.06	6.41	1.12	19	2.174	0.460	(0.460 – 2.174)	F € AA
	20-40	8.12	36.53	6.04						

* s² : Values variance of 0-20 cm layer
 s² : Values variance of 20-40 cm layer
 ** F_{0,05} : value read on the distributions table F (p = 0,05) with 19 liberty degrees

3.3. Comparison by pairing test the average of each parameter of the horizons 0-20 and 20-40 cm

This method completes the previous one and makes it possible to compare the averages of each parameter in the two horizons. It results in the determination of a value $t' = x/(s/\sqrt{k})$ which must be less than a theoretical value t on the Student's table at $(k-1)$ degrees of freedom and at $p = 0.05$.

The theoretical value read on the table of Student distributions at 19 degrees of freedom (dof) is 2.093; it is greater than t' calculated for the 7 parameters (Table 3). As a result, the differences between the averages at the 20 representative points of the cereal soils of North-West Tunisia are not significant. Using an average of the two values of each sampling point seems reasonable.

Table 3. Comparison with pairing test of the averages of each parameter for the horizons 0-20 and 20-40 cm

Parameters	Average differences \bar{x} *	$\Sigma(xi-x)^2$	s **	$t' = x/(s/\sqrt{k})$	t at 19 dof, p = 0,05	Comments
Total CaCO ₃	0.975	691.14	6.03	0.224	2.093	$t' < t$
Active CaCO ₃	-1.1	386.8	4.51	-0.252	2.093	$t' < t$
Clay	-2.13	933.88	7.01	-0.489	2.093	$t' < t$
Fine silt	-0.25	2879.61	12.33	-0.057	2.093	$t' < t$
Coarse silt	-2.82	7067.93	19.29	-0.647	2.093	$t' < t$
Fine sand	3.87	1629.0	9.26	0.888	2.093	$t' < t$
Coarse sand	1.55	807.91	6.52	0.356	2.093	$t' < t$

* \bar{x} = differences average x_i between the values of each couple of variables.
 ** $s = \sqrt{\Sigma(xi-x)^2/(k-1)}$

3.4. Principal component analysis (ACP) of parameters distribution based on soil types

This analysis is carried out with a matrix of data comprising as columns the means of the values of the parameters of the two depth levels of each sampling point and as lines the sampling sites or sites also expressing the types of soils. This approach aims at distributing the different parameters at the points where they are best represented, which can reveal the specificities of each sampling point or soil type.

To carry out this analysis, the parameters or variables were symbolized as follows: Cat for total limestone, Caa for active limestone, A for clay, LF for fine silt, LG for coarse silt, SF for fine sand and SG for coarse sand. For sampling sites, they kept the same symbols listed in Table 1.

The contribution of the 3 axes of this ACP to the total variation is 82.9% with 47.3% for axis 1, 20.6% for axis 2 and 15% for axis 3. The circle of correlations opposes two sets of parameters related to axis 1 (Figure 1).

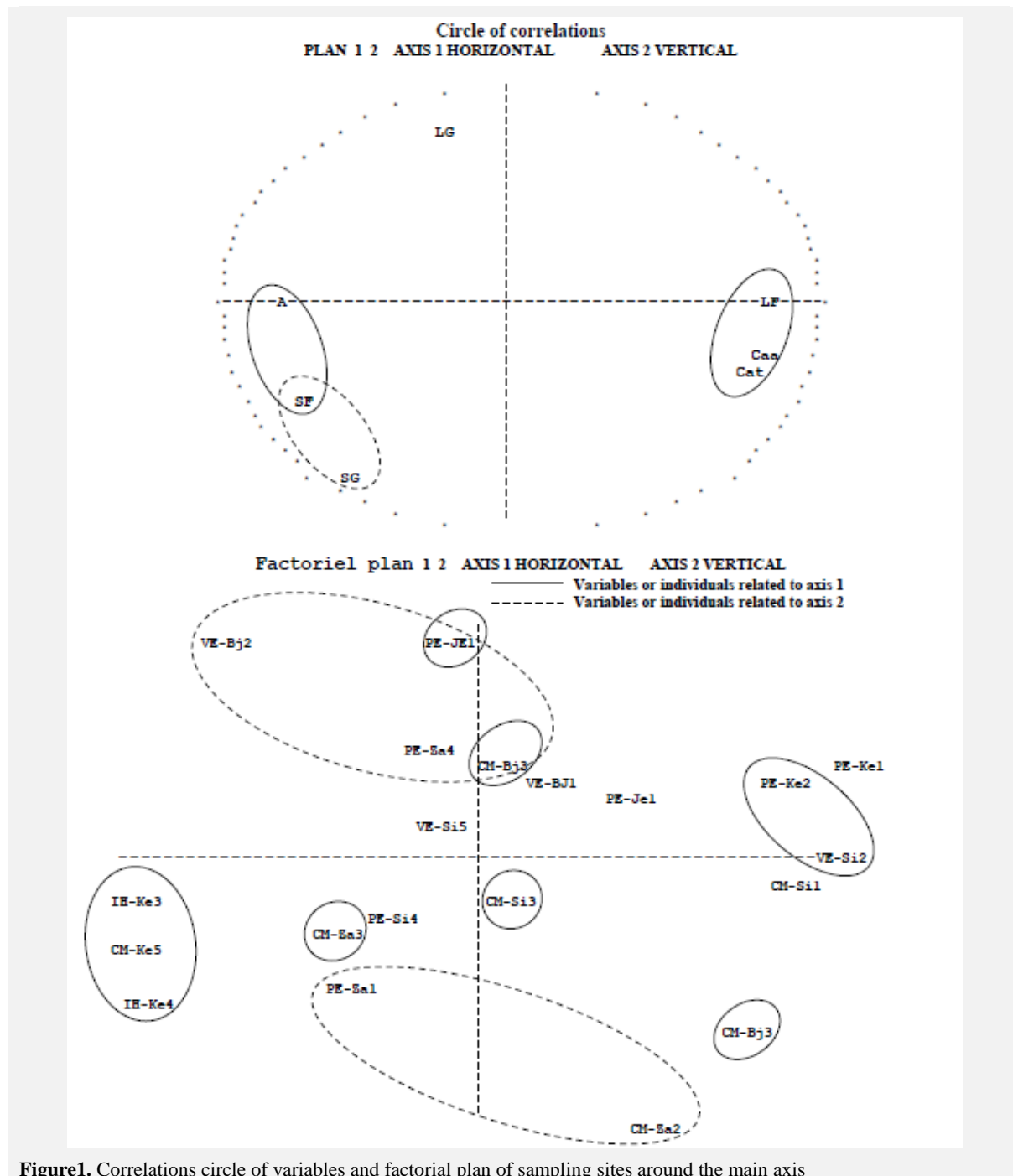


Figure1. Correlations circle of variables and factorial plan of sampling sites around the main axis

- LF, Caa and Cat on the extreme right side of the axis, corresponding on the factorial plan of the individuals to the sampling sites PE-Ke2 and VE-Si2. These two types of soils are the richest in total limestone (> 40%) and active limestone (> 20%); at the same time, fine silt may exceed 50% of the total mineral fraction (Table 1).

- A and SF on the left side of the axis to which the observations correspond to the factorial plan, the sampling sites IH-Ke3, IH-Ke4 and CM-Ke5 which must be characterized by low limestone contents (active and total) and fine silts, with a sharper abundance of clay and fine sand (Table 1).

Axis 2 makes it possible to isolate the SF and SG parameters that do not correspond to precise sampling sites, which shows that the soils of the regions studied do not include large fractions of fine and coarse sands.

Such results show that the more limestone is abundant, the more fine silts there are and the less clay and fine sand. The abundance of limestone would increase the percentage of fine silt and vice versa. Its low rate would be observed in soils with higher clay and fine sand content.

We can arrive at the consequence that there is already an opposition between clay and fine sands on one side and limestone total and active on the other. In addition, an affinity exists between limestone and fine silt.

Such results also explain pedogenic trends that are not the same in these different regions: limestone depletion of surface horizons by deep migration in a plain with stable geomorphology, abundance of this limestone on the surface in a fluvisol (PE -Ke2) and a vertisol (VE-Si2) reflecting a weak evolution firstly and an unstable state by the reversal movements in a vertisol secondly.

3.5. Correlations between limestone content and granulometric fractions

This method seeks to discern links between the limestone reserves in the 20 sampling points representative of all the cereal soils of northwestern Tunisia, and especially the active fraction and the particle size fractions. The results will make it possible to specify to which particle size group each of the two limestone forms belongs and to draw conclusions as to the possible mineralogical nature of the clay fraction in particular.

The results show significant correlations between fine silts firstly and total and active limestone secondly (Table 4). The two correlations are significant at the 0.01 threshold at 38 degrees of freedom (n-2 dof) with correlation coefficients r of 0.406 for total limestone and 0.415 for active limestone (Figures 2 and 3). Limestone particles are therefore mainly among fine silts. The correlation of the two forms of limestone with the fine sands is also significant but at the 0.05 threshold and with a correlation coefficient r negative (Figures 4 and 5). There is therefore a certain antagonism illustrated by these two correlations between limestone and fine sands: if the content of one increases, that of the other decreases, which means that the fine sands consist mostly of non-carbonated particles in these soils. Their nature would probably be quartzous in the absence of other minerals that can be classified in this fraction.

Table 4. Linear correlations results between limestone and particle size fractions

Correlated parameters	Number n of pairs of values	Coefficient of determination R ²	of Coefficient correlation r	of Meaning at n-2 dof	threshold	Equation
Clay – Cat*	40	0.0326	- 0.181	NS		-
LF - Cat	40	0.1648	0.406	p = 0.01		LF = 0.488Cat + 11.76
LG - Cat	40	0.0055	- 0.074	NS		-
SF - Cat	40	0.1121	- 0.335	p = 0.05		SF = -0.228Cat + 22.15
SG - Cat	40	0.0141	- 0.119	NS		-
Clay – Caa**	40	0.0648	- 0.255	NS		-
LF – Caa	40	0.172	0.415	p = 0.01		LF = 1.065Caa + 10.05
LG - Caa	40	6 x 10 ⁻⁵	0.08	NS		-
SF - Caa	40	0.1304	- 0.361	p = 0.05		SF = -0.526Caa + 23.38
SG - Caa	40	0.0334	- 0.183	NS		-
Caa - Cat	40	0.7679	0.876	p = 0.001		Caa = 0.41Cat + 3.042

* Cat : total limestone

** Caa : active limestone

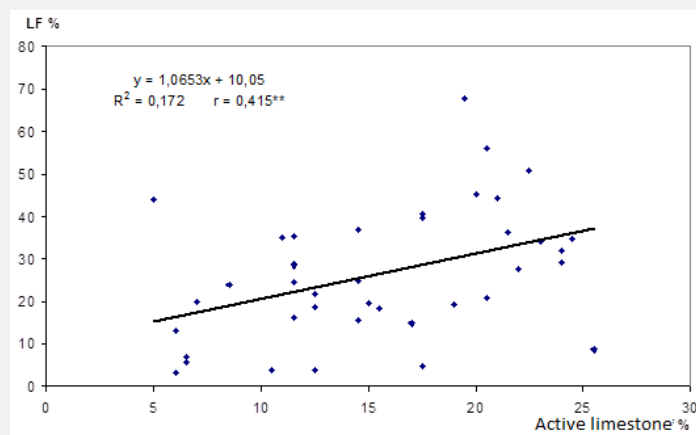


Figure 2. Correlation straight between active limestone and fine silts (n = 40, **: p = 0.01)

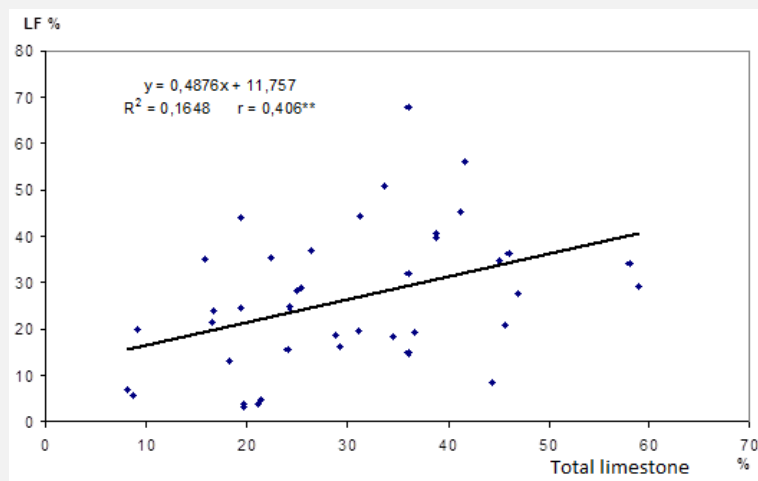


Figure 3. Correlation straight between total limestone and fine silts (n = 40, **: p = 0.01)

For both limestone forms, their correlation is highly significant with a threshold of 0.001 and a correlation coefficient of 0.876 (Figure 6). It is thus demonstrated that active limestone is a part directly proportional to total limestone and that the majority of their particles are the size of fine silts. Total limestone is not correlated with coarse silt or sand (Table 4). Its particles, like active limestone, are included in the dimensions of fine silt. The assumption that active limestone is the fine-scale limestone of clays providing more surface area for solutions for hydrolysis attack is not confirmed for these soil types sampled only in their surface horizons.

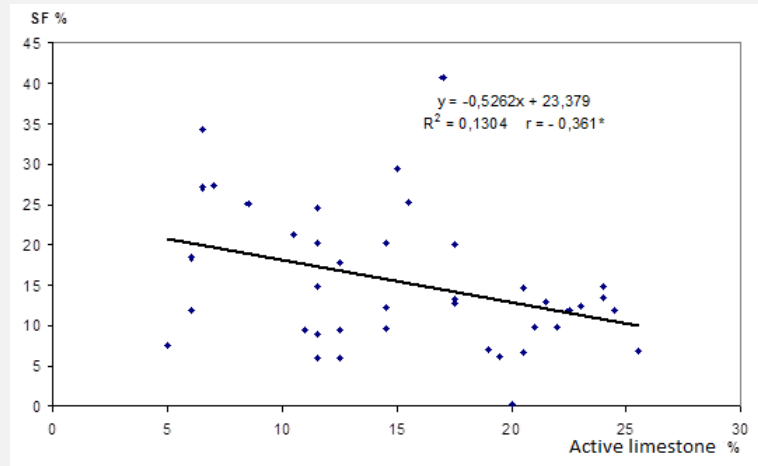


Figure 4. Correlation straight between active limestone and fine sands (n = 40, *: p = 0.05)

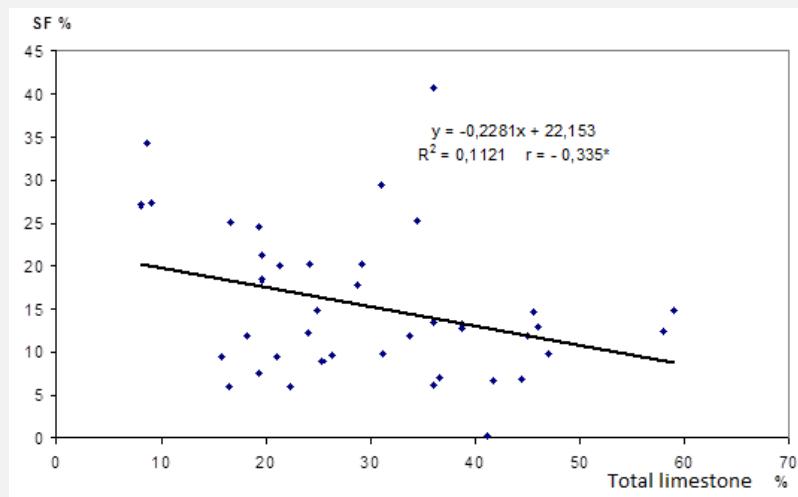


Figure 5. Correlation straight between total limestone and fine sands (n = 40, *: p = 0.05)

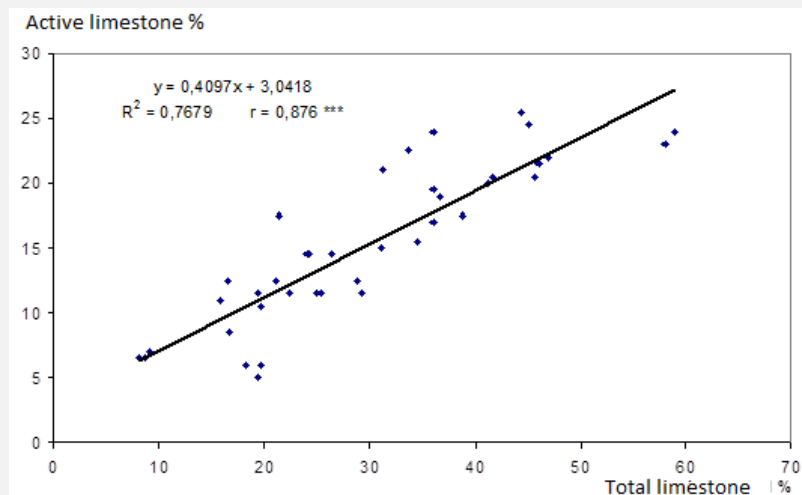


Figure 6. Correlation straight between active limestone and total limestone of the cereal soils in the North-West of Tunisia (n = 40, ***, p = 0,001)

3.6. DISCUSSION

Statistical tests comparing variances and averages have shown that limestone and particle size fractions are normally distributed and that the differences are, on average, almost non-existent between the two successive horizons of each sampling point. This could lead to the use of the means of each site to assess the distribution of the various parameters according to their sampling location. The data processing by the PCA method has demonstrated that active and total limestone combine on the factorial plan with fine silt, especially in the CM-Si1 and PE-Ke2 points, and oppose the fine sand (SF) and clay (A) more expressed in the sites IH-Ke3, IH-Ke4 and CM-Ke5. We already note with this result the affinity between fine silts and limestone contents; soils low in limestone would be more enriched in clay and fine sands. We feel thus, the beginnings of the contribution of limestone with its two active and total components to the increase of fine silt levels in these soils of North-West Tunisia.

If there are differences between these soils, their common point is the widespread presence of carbonates with more or less significant proportions, except for the sites IH-Ke3 and IH-Ke4. Although this presence of limestone is useful for stabilizing the structure by rapidly evolving organic matter into stable inherited forms (Duchaufour, 1991), it is nonetheless chemically binding since several elements are either immobilized (trace elements) or demoted to insoluble forms such as phosphorus (Ghazanshahi and Jaouich, 2001, Ben Hassine, 2004).

Soil limestone is considered to belong to all sizes of their mineral particles; as we find in the form of fine particles, we also see in the form of coarse elements of the size of gravel, pebbles, stones and even blocks. In fine earth, it is in the form of crystals of calcite, aragonite, vaterite or hydrates (Brooks et al., 1950 in Sanaã, 1983), whose diameters can be distributed over all the dimensions of the constituents of soils. Its fine fraction, called active limestone, is considered to be the most highly divided and therefore the most exposed to solubilization. Several authors agree that active limestone is finely divided (the size of silts and even clays) and is likely to exert a chemical activity, in particular by reacting with CO₂ and the organic acids of soil solutions (Duchaufour, 1977; Magny and Baur, 1990; Guigou et al, 1990). After isolation of the clay fraction for X-ray diffraction and after partial decarbonation with a highly diluted acetic acid solution, the diffractograms showed the presence of calcite in the disoriented powder sample (Ben Hassine, 2002). This confirms the particular nature of these soils, mainly of carbonate sedimentary rocks (limestone and marl), whose carbonates are distributed between the fractions of fine silts and clays. Baize (1988) reports that hard marl soils have the following granulometric distribution of their limestone particles: 32.2% fine silt, 10.4% clay, 5.2% coarse silt, 1.8% fine sands, and 3.5% coarse sands.

Although in this study, it was not possible to confirm by the correlation method, the link between clay and limestone; which has been demonstrated internationally is valid for similar materials regardless of the geographical location. Under these conditions, the following remarks may be made:

- The clays of these soils must be essentially silicate in nature and not only composed of phyllosilicates of the illite type, smectite, kaolinite and illite-smectite interstratified (Ben Hassine, 2006) but also of

finely divided quartz. Indeed, this type of mineral was observed in the diffractogram of disoriented powder of carbonate soils of North-West Tunisia (Ben Hassine, 2006). The presence of these phyllosilicates would have an anti-chlorotic effect on plants by inhibiting the reactivity of active limestone (Hannaoui, 1993).

- The product used to dissolve the active limestone, in this case ammonium oxalate, would not attack the clay particles that would tend to agglomerate into pellets (Callot and Dupuis, 1980), but would act mainly on those fine silt in which is included most of the total limestone soil. It has been demonstrated in this study that total limestone is well correlated with fine silt. The method of analysis used, even if it is adopted in a universal way, would not be the one that would act on the carbonates of the size of the clays whose agglomeration in larger particles would protect them against the solubilizing action of the oxalate. The product would strongly attack particles having the dimensions of fine silts which are little fractured, sufficiently free and not agglomerated; they would thus offer maximum reactivity to ammonium oxalate (Callot and Dupuis, 1980); this is a peculiarity for this type of constituent since the theory assumes that the solubility of crystalline substances is related to the size of crystals whose specific surface area increases with the state of division (Stumm, 1970 in Sana, 1983). According to this theory, the finest particles (of clay size) would be the most exposed to solubilization and this is what Magny and Baur (1990) report by pointing out that the activity of limestone in soils depends mainly on the fineness of its particles. Sana (1983) supports this hypothesis by stating that all the carbonates in the clay fraction are active while only half of the silty fraction is of this form.

The activity of these carbonates results in the increase of the pH of the soil to the value of 8.4 in a solution of pure water and in open system. The calcium concentration under these conditions would be $10^{-4.8}$ mol/l. With the decomposition of organic matter and the saturation of the solution with CO_2 , the concentration of the calcium solution would increase to $10^{-3.85}$ mol/liter (Chamayou and Legros, 1989). Under these conditions of solubilization, the limestone of the cereal soils of northwestern Tunisia could act:

- First, favorably on the structure by releasing the calcium that saturates the exchange sites and participates in the transformation of clay minerals from the illite stage to the beidellite stage that has the smectite behavior (Ben Hassine, 2006). Its role as a stabilizer of the structure does not stop with the process of liberation of the divalent cation Ca^{2+} , but also affects the lignin of the organic matter that it coats of a protective film preventing it from any future evolution. This form of organic matter is the inherited humina (Duchaufour, 1977) that resists microbial biodegradation through this limestone coating.

- Then negatively on the phosphate ions of the solution by blocking them in the form of insoluble apatite. These soils would require the annual renewal of their phosphate reserves by inputs in the form of soluble fertilizers.

- Finally, favorably on plant nutrition since the Ca^{2+} cation becomes available in the solutions. Its excess can, however, lead to deficits of assimilation of Mg and trace elements such as Fe, Mn, Cu, Zn and B (Guigou et al, 1990).

4. Conclusion

The cereal soils of Northwest Tunisia which are derived from limestone and marly sedimentary rocks all have higher or lower levels of calcium carbonates in their surface horizons. The spatial distribution of this limestone reproduces mainly pedogenic characters highlighting the following processes: tendency to the migration of limestone in the plains succeeding the northern slopes of the Tellian mountains, vertisolization of lithomorphic origin on marly materials and recent deposits undisturbed in the valleys. The multiplication of sampling points to cover the majority of soil types in these regions has made it possible to demonstrate a diversity in limestone contents and a predominance of fine particles (A + LF) in the mineral constituents of these soils.

The limestone of these soils is divided according to the size of its particles in the fraction of fine silt essentially ($2 - 20 \times 10^{-6}$ m). This fraction would be the most vulnerable to the action of the extraction product (0.2 mol/l ammonium oxalate) despite its low concentration. This relationship has already been demonstrated previously and has been explained by the fact that the clay particles of limestone agglomerate into balls and resist in this way to dissolution. This is contrary to the theory that specifies that the reactivity of a constituent increases with its state of division and therefore with its specific surface. The carbonates of soils derived from marl thus have this particular behavior as regards their

reactivity in laboratory conditions regardless of the geographical situation or the ecological environment. Clay limestone is therefore not necessarily active in the cereal soils of northwestern Tunisia and any future estimate of the mineralogical composition of the clay fraction of these soils should take this feature into account. In addition, even if the clay fraction of these soils contains limestone particles, it is however dominated mainly by silicates which must be divided between phyllosilicates represented by clays and tectosilicates represented by quartz in particular.

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