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RELATIONSHIP BETWEEN TOTAL EXTRACTABLE ORGANIC CARBON AND SOME PARAMETERS OF SOILS FROM WESTERN SPAIN

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Abstract

Different units of soils from Western Spain were selected and some physico-chemical parameters analyzed. Samples of their soil horizons were submitted to humus fractionation and the total extraction of the humic substances of these horizons was calculated. A significant, inverse relationship between total extractable organic carbon (TEOC) and soil pH ($R = -0.57$, $p < 0.001$, 53 soil horizons) was found, which points to the importance of the exchangeable Ca^{2+} on the insolubilization of humic substances. This relationship improved ($R = -0.76$, $p < 0.001$, 38 soil horizons) when saline, sodic soils were excluded. Evidently, saline, sodic soils (soil pH > 8.5) undergo an auto-extraction of humic substances that hampers this relationship. TEOC had also a significant, inverse relationship with the degree of base saturation and the clay content of soils. It is concluded that TEOC is strongly dependent, at least, on the soil pH; this fact indicates that the former is not a valid key parameter for soil quality. TEOC is also dependent on the clay content of the soil epipedons. The results also rejected the general idea that low humus extraction means a low degree of humification, at least in the Mediterranean region.

Key words: humic substances, extractable organic carbon, Mediterranean soils, soil pH, clay.

INTRODUCTION

Recently, key parameters or indicators for finding out the quality of soils (Parr *et al.* 1992, Seybold *et al.* 1998), soil biodiversity (Kennedy and Papendick 1995), and the biodiversity of the ecosystems (Kennedy and Smith 1995, Whitford 1996) were sought and then tested. A clear indicator of the quality of a soil is the content of soil organic carbon (SOC; Herrick and Wander 1998); in this way the degree of disturbance or degradation of a soil can be estimated comparing the SOC content of the tested soil in relation to the SOC content of a virgin or scarcely disturbed soil. But this parameter refers mostly to the quantity rather than to the quality of the soil organic matter (SOM; Herrick and Wander 1998).

Thus, humic substances (HS) of soils can refer to the quality of SOM; for example, Zalba and Quiroga (1999) recently proposed the soil content of fulvic acids as a parameter of quality of soil and for assessing the impact of agricultural activities. Some authors have traditionally stated that the level extraction of HS is an index of intensity of humificaction (as example, see Ping *et al.* 1998). An additional problem is that the quantity of the extracted organic substances depends on the method of extraction (or fractionation; Kononova 1966, Vaughan and Ord 1985). One way to avoid this problem is to extract the HS to successive extractions (using 0.025M $Na_4P_2O_7$ and, subsequently, 0.1M NaOH; Moyano *et al.* 1991) and consider only the value of the total extractable organic carbon (TEOC; Gallardo-Lancho 1974).

The initial hypothesis is that the total extractable organic carbon (TEOC) could be an index of soil quality (because it is a result of the stability of the humus-mineral complex; Stevenson 1982, Duchaufour 1983) only if total extraction does not depend on another soil parameter.

The objective of this paper is to find out whether this hypothetical parameter of soil quality (TEOC) has any relation with the quantity of SOM or another soil parameter.

Table 1: Soil characteristics

Profile N° (Province)	Site *Soil unit*	*Horizon*	pH (KCl)	pH (H_2O)	SOC (mg/g)	CEC (cmol+/kg)	SB (cmol+/kg)	V (% of CEC)	TEOC (% of SOC)
I (Cáceres)	El Piornal *Humic Cambisol*	*Ah1*	4.1	5.0	65.5	16.7	1.6	16	26
		Ah2	4.2	5.0	51.8	12.8	2.4	19	31
		ABw	4.3	5.1	22.6	8.1	1.8	22	37
		BC	4.3	5.2	7.4	7.7	2.0	26	41
		C	4.3	5.3	5.1	7.2	3.3	46	55
II (Avila)	Navacepeda *H. Cambisol*	*Ah1*	5.0	6.0	48.4	13.4	3.4	25	22
		Ah2	4.2	5.5	14.6	10.3	4.3	42	33
III (Avila)	Hoyos del Espino *H. Cambisol*	*Ah*	4.3	5.5	40.2	14.6	5.5	38	23
IV (Avila)	Candeleda *Dystric Cambisol*	*Ah*	3.8	5.0	34.5	12.6	7.2	57	25
V (Avila)	Candeleda *D. Cambisol*	*Ah*	4.2	5.4	31.4	11.1	6.8	61	33
VI (Salamanca)	Peñaparda *H. Cambisol*	*Ah*	4.0	4.5	45.7	16.4	1.3	8	39
		Bw	4.2	5.2	11.5	8.7	1.0	11	35
VII (Salamanca)	Peñaparda *H. Cambisol*	*Ah*	4.2	5.1	35.1	17.7	2.5	10	51
		Bw	4.3	5.1	14.6	8.5	1.2	14	58
VIII (Avila)	Navacepeda *H. Cambisol*	*Ah1*	4.5	5.2	38.8	15.0	3.8	25	34
		Ah2	4.6	5.3	13.6	10.6	3.2	30	53
IX (Avila)	Montalbán *Gleyic Cambisol*	*Ah*	4.1	5.3	12.9	7.2	4.5	63	39
X (Salamanca)	Villasrubias *H. Cambisol*	*Ah*	3.8	4.6	31.6	13.5	8.4	62	38
		Bw	3.7	4.7	6.4	6.8	2.9	43	51
XI (Salamanca)	El Payo *H. Cambisol*	*Ah*	3.9	4.8	73.3	23.0	5.7	25	37
		Bw	4.0	5.0	10.5	8.1	5.3	65	55
XII (Cáceres)	Gata *D. Cambisol*	*Ah*	4.0	5.0	58.9	19.1	0.4	2	37
		Bw	4.2	5.2	11.3	6.0	0.7	12	50
XIII (Cáceres)	Perales del Puerto *D. Cambisol*	*Ah*	3.9	5.0	26.5	9.4	1.6	17	34
		Bw	4.2	5.4	8.2	5.9	1.7	29	62
		BC	4.3	5.3	10.3	5.7	2.2	39	66
XIV (Cáceres)	Garrovillas *Chromic Luvisol*	*Ap*	5.9	7.0	24.8	35.5	30.2	85	18
		Bt	5.3	6.6	7.8	48.6	29.4	60	29
XV (Palencia)	Astudillo *Calcaric Cambisol*	*Ah*	6.8	7.6	41.1	30.8	30.8	100	12
		ABw	6.8	7.6	36.5	30.5	30.5	100	13
		Bk	6.6	7.6	33.4	N.d.	N.d.	N.d.	12
XVI (Palencia)	Villagimena *Rendsic Leptosol*	*Ah*	6.8	7.6	23.0	N.d.	N.d.	N.d.	11
		AC	6.8	7.7	15.5	N.d.	N.d.	N.d.	24
		C	6.8	7.7	11.1	N.d.	N.d.	N.d.	25
XVII (León)	La Vid *Haplic Luvisol*	*Ah*	6.1	7.1	69.0	30.9	30.4	95	15
		Bt	6.1	7.1	33.4	33.9	29.1	86	16
		BC	6.4	7.4	17.8	35.0	32.8	94	12
XVIII (León)	Valporquero *Chromic Luvisol*	*Ah*	6.5	7.3	46.5	26.8	24.6	92	16
		Bt1	6.4	7.2	14.6	26.2	23.9	91	13
		Bt2	6.4	7.4	11.3	29.7	27.9	94	12
XIX (Salamanca)	Pedraza de Alba *Gleyic Cambisol*	*Ah*	7.4	7.6	31.6	19.7	19.7	100	15
		Bg	6.9	7.4	5.4	16.1	16.1	98	19
XX (Salamanca)	La Orbada *Mollic Solonchack*	*Ah*	7.2	7.4	38.4	37.1	36.5	98	16
		B	8.0	8.3	15.4	36.7	36.4	99	22
XXI (Avila)	El Oso *Calcic Solonetz*	*Ah*	6.4	6.9	29.4	20.5	19.8	97	31
		Bt	8.0	8.5	6.8	23.8	23.8	100	46
XXII (Palencia)	Palacio de Campos *Gleyic Solonchack*	*A*	7.0	7.7	50.6	20.3	19.4	96	13
		Bt	7.1	7.8	9.0	14.7	14.7	100	28
		Bz	6.9	7.7	8.3	13.8	13.8	100	44
XXIII (Salamanca)	El Salobral *Calcic Solonetz*	*Ah*	5.4	6.4	23.1	8.2	6.5	79	38
		Bt	6.7	7.5	13.3	16.3	14.0	86	33
XXIV (Avila)	Fontiveros *Gleyic Solonetz*	*Ah*	6.7	7.5	47.0	32.4	32.4	100	21
		Eg	6.8	7.7	8.9	33.9	33.9	100	39
		Bt	6.6	7.3	18.7	38.0	38.0	100	29
		Bz	6.9	7.4	6.3	42.1	42.1	100	30
XXV (Valladolid)	Medina del Campo *Calcic Solonetz*	*Ah*	6.1	7.1	8.3	4.5	4.0	89	39
XXVI (Salamanca)	Pajares de la Laguna *Calcic Solonetz*	*Ah*	4.2	5.4	17.2	6.8	4.0	59	32

(SOC: Soil organic carbon; CEC: Cation exchange capacity; SB: Sum of bases; V: Percentage of base saturation; TEOC: Total extractable organic C

MATERIAL AND METHODS

A total of 26 typical soil profiles from Western Spain, belonging to different soil units, was selected, sampled, and analyzed. The selected soil units were (FAO/UNESCO 1990): *Rendsic Leptosol, Cambisols* (*Dystric, Humic, Calcaric,* and *Gleyic*), *Luvisols* (*Haplic* and *Chromic*), *Solonchaks* (*Mollic* and *Gleyic*), and *Solonetzs* (*Calcic* and *Gleyic*). The general characteristics of the 26 soils are given in Table 1 (Gallardo and Bacas 1973, Gallardo and Garcia-Rodriguez 1973, Garcia-Rodriguez *et al.* 1973). In addition, 12 soil epipedons (*Ap* horizons) belonging to cultivated soils of the semiarid area of the Duero Basin were also sampled and analyzed; the units of these soils were *Luvisols* (*Haplic, Calcic, Mollic,* and *Vertic*), excepting one *Dystric Cambisol*. The general characteristics of the 12 soil epipedons are shown in Table 2 (Moyano *et al.* 1991).

The methods for chemical analysis were: soil pH (in water and KCl solution), cation exchange capacity (CEC) using 0.1 M ammonium acetate solution (pH 7.0) as eluent, sum of bases (SB) determining exchange cations by flame emission (Na, K) and atomic absorption (Mg, Ca) spectrometry; SOC by wet method (sodium dichromate), and TEOC extracting successively with 0.025M $Na_4P_2O_7$ and Na_2SO_4 (pH 7.0), 0.025M $Na_4P_2O_7$, and finally with 0.1M NaOH (Gallardo-Lancho 1974). All fractions were joined and the extracted-C contents were determined by a Carmhograph Wösthoff (Gallardo *et al.* 1987).

Correlation and regression analyses were performed using the Statview for Macintosh statistical package.

RESULTS AND DISCUSSION

Table 3 shows the correlation matrix obtained with the more important soil parameters (including all their analyzed horizons) of all the 26 (53 horizons) selected soils.

The most important thing is that TEOC is significantly, inversely correlationed with all the parameters ($p < 0.001$). The lower correlation is established with SOC ($p < 0.01$).

Table 4 shows the resulting correlation matrix if saline, sodic soils are deleted from the former soils and only 19 soils (38 horizons) are included. The correlation of TEOC with the other soil parameters has increased, with the exception with SOC which has diminished (only $p < 0.05$).

Table 2: Characteristics of soil epipedons (Ap) of Central Western Spain (same symbols as in Table 1)

Site (Province)	*Soil units*	Ap horizons	pH (H_2O)	SOC (mg/g)	CEC (cmol+/kg)	V (% of CEC)	TEOC (% of SOC)	Clay (% soil)	Silt + Clay (% soil)
Pedraza A. (Salamanca)	*Haplic Luvisol*	XXVII	5.0	5.5	10.4	15	55	17	22
Macotera (Salamanca)	*Dystric Cambisol*	XXVIII	5.9	6.5	12.8	79	42	28	34
Peñaranda de B. (Salamanca)	*Haplic Luvisol*	XIX	6.3	6.8	12.8	70	27	18	24
Villasflores (Salamanca)	*Haplic Luvisol*	XXX	7.9	7.0	7.2	100	29	9	17
Cantalpino (Salamanca)	*Calcic Luvisol*	XXXI	5.3	6.6	10.0	48	40	16	21
P. de Negrilla (Salamanca)	*Mollic Luvisol*	XXXII	6.2	4.5	18.4	69	40	15	21
A. de Figueroa (Salamanca)	*Calcic Luvisol*	XXXIII	5.2	5.5	20.8	52	48	30	36
Alaejos (Valladolid)	*Haplic Luvisol*	XXXIV	6.1	4.0	19.2	61	39	30	36
La Seca (Valladolid)	*Haplic Luvisol*	XXXV	6.0	4.8	7.2	60	55	15	21
Cervillego de C. (Valladolid)	*Haplic Luvisol*	XXXVI	5.2	2.3	8.0	24	58	9	14
Fuentelapeña (Valladolid)	*Vertic Luvisol*	XXXVII	6.3	5.0	19.2	45	30	24	31
Villanueva del P. (Valladolid)	*Haplic Luvisol*	XXXVIII	5.7	1.8	17.6	28	32	11	16

Table 3: Correlation matrix between soil parameters (the all soils samples)

	pH (KCl)	pH (H_2O)	SOC	CEC	SB	V	TEOC
pH (KCl)	1.000	***	ns	***	***	***	***
pH (H_2O)	0.985	1.000	ns	***	***	***	***
SOC (mg/g)	-0.122	-0.149	1.000	ns	ns	ns	**
CEC (cmol(+)/kg)	0.644	0.652	0.174	1.000	***	***	***
SB (cmol(+)/kg)	0.821	0.732	-0.015	0.917	1.000	***	***
V (% of CEC)	0.874	0.896	-0.181	0.579	0.821	1.000	***
TEOC (% of SOC)	-0.551	-0.569	-0.405	-0.621	-0.631	-0.546	1.000

N = 53 observations were used in this computation (4 cases were omitted due to missing values).
Ns: no significant; ** significant $p < 0.01$; *** significant $p < 0.001$.

Table 4: Correlation matrix between soil parameters (without saline and sodic soils)

	pH (KCl)	pH (H_2O)	SOC	CEC	SB	V	TEOC
pH (KCl)	1.000	***	ns	***	***	***	***
pH (H_2O)	0.980	1.000	ns	***	***	***	***
SOC (mg/g)	0.011	-0.023	1.000	ns	ns	ns	*
CEC (cmol+/kg)	0.687	0.732	0.266	1.000	***	***	***
SB (cmol+/kg)	0.867	0.911	0.058	0.889	1.000	***	***
V (% of CEC)	0.835	0.861	-0.097	0.606	0.875	1.000	***
TEOC (% of SOC)	-0.740	-0.756	-0.372	-0.709	-0.754	-0.662	1.000

N = 38 observations were used in this computation (4 cases were omitted due to missing values).
Ns: no significant; * significant $p < 0.05$; *** significant $p < 0.001$.

Table 5: Correlation matrix between soil parameters (only soil epipedons)

	pH (H_2O)	SOC	V	TEOC	Clay	Silt + Clay
pH (H_2O)	1.000	ns	***	***	***	*
SOC (mg/g)	0.006	1.000	ns	**	ns	***
V (% of CEC)	0.864	-0.082	1.000	***	**	ns
TEOC (% of SOC)	-0.653	-0.495	-0.563	1.000	***	***
Clay (% soil)	0.528	0.317	0.477	-0.524	1.000	***
Silt + Clay (% soil)	0.360	0.518	0.289	-0.557	0.858	1.000

N = 38 observations (see text) were used in this computation.
Ns: no significant; * significant $p < 0.05$; ** significant $p < 0.01$; *** significant $p < 0.001$.

Considering that there could be an interaction between horizons belonging to the same soil, only the superficial, *A* horizons (epipedons) were chosen in a second approximation. In order to have the same number of data, data from epipedons (*Ap*) of 12 ploughed soils of Western Spain were added to the 26 epipedons from Table 1 and results are shown in Table 5.

A high correlation between TEOC and pH (in water) or degree of base saturation (V; $p < 0.01$) remains. In addition, high correlations between clay (or silt plus clay) and TEOC were also found; it should take into account that the influence of the clay illuviation of the soils was deleted considering only the epipedons.

Relationships between the parameters studied (Tab. 6) showed an inverse, significant relationship between TEOC and SOC ($R^2 = 0.14$; $p < 0.01$; $n = 57$) and between TEOC and soil pH (in KCl solution; $R^2 = 0.38$ $p < 0.001$; $n = 57$).

The former relationship points out the increase of SOC is facilitated by a strong link between organic and inorganic substances (organic-clay complex; Duchaufour 1983, Cornejo and Hermosin 1996, Kay 1997).

When the pH in water was considered, the relationship with TEOC increased ($R^2 = 0.38$; $p < 0.001$; $n = 57$). Obviously, the soil acidity hinders the stability of the humus-mineral complex, by limiting microbiological activity (Dommergues and Mangenot 1970, Cheasire 1985, Ladd *et al.* 1996). This relationship is improved when saline, sodic soils are excluded ($R^2 = 0.58$; $p < 0.001$; $n = 42$) and the effect of exchangeable cation Na^+ deleted.

If a polynomial (degree two) curve is fitted ($R = 0.62$; $p < 0.001$; $n = 57$), it is possible to observe an increase of TEOC after pH > 8.0; this means that the exchangeable Na^+ has an extraction effect and then hinders the stability of humus-mineral complex (Duchaufour 1983). Obviously, this relationship is even better (R^2 = 0.77; p < 0.001; n = 42) if saline, sodic soils (soil pH > 8.0) are not considered.

Evidently, there was also an inverse relationship between TEOC and V (R^2 = 0.44; p < 0.001; n = 42), because the latter paramater indirectly indicates the content of exchangeable Ca^{2+} in relation of the total CEC, which favours the links between HS and inorganic colloids (Bruckert 1979, Zech and Guggenberger 1996).

Considering only epipedons (*Ah* and *Ap* horizons) the relationships found are similar (Tab. 6). In these Mediterranean soils a very acid soil (pH 4.0) theoretically only atteints a TEOC value of 50% (another 50% should be non-extractable humin). Concerning the degree of base saturation (V), a polynomial equation (R = 0.63; p < 0.001; n = 38) points out that TEOC is higher when there is a mid saturation (V = 50 %), decreasing faster when V approaches full saturation (Andreux 1996).

The presence of clay also favours the presence of humin (increasing SOC and decreasing TEOC; Andreux 1996, Ladd *et al.* 1996), as deduced from the equation (R^2 = 0.49; p < 0.001; n = 26). If silt plus clay is considered r^2 increases to 0.74. These data agree with the general idea that the presence of clay improves the stability of SOM (Wild 1992, Kay 1997).

To weight the joint influence of the pH (in water) and clay on TEOC, the following equation was obtained:

$$\text{TEOC}(\%) = 75.8 - 6.30 \cdot \text{pH} - 0.29 \cdot \text{Clay}(\%)$$
$$R = 0.687 \qquad (n = 38).$$

Note that the multiplying factor for soil acidity (6.3) is substancially higher than that for soil clay content (0.29), and the clay content of the soil epipedons considered is not too high (lower than 15%; this is usual in soils from Western Spain, because these have mostly sandy to loamy textures; Forteza *et al.* 1988).

Table 6: Relationships between soil parameters and resulting significances and equations

Dependent variable (Y)	Equation	Number of data	r	p <	r^2 (x 100)	Independent variable (X)
Forest and grassy soils (including salin, sodic soils)						
TEOC (% of SOC)	$Y = 39.1 - 0.30X$	57	- 0.38	0.01	14	SOC (mg/g)
TEOC (% of SOC)	$Y = 94.5e^{-0.22X}$	57	- 0.60	0.001	-	pH (KCl)
TEOC (% of SOC)	$Y = 65.3 - 6.2X$	57	- 0.58	0.001	33	pH (KCl)
TEOC (% of SOC)	$Y = 140e^{-0.25X}$	57	- 0.62	0.001	-	pH (H_2O)
TEOC (% of SOC)	$Y = 76.3 - 7.1X$	57	- 0.60	0.001	38	pH (H_2O)
TEOC (% of SOC)	$Y = 186 - 43.0X + 2.83X^2$	57	- 0.62	0.001	-	pH (H_2O)
Forest soils (no salin, sodic soils)						
TEOC (% of SOC)	$Y = 303e^{-0.40X}$	42	- 0.84	0.001	-	pH (H_2O)
TEOC (% of SOC)	$Y = 95.2 - 10.6X$	42	- 0.76	0.001	58	pH (H_2O)
TEOC (% of SOC)	$Y = 30.8 + 10.8X - 1.71X^2$	42	- 0.77	0.001	-	pH (H_2O)
TEOC (% of SOC)	$Y = 53.6e^{-0.012X}$	42	- 0.76	0.001	-	V (% of CEC)
TEOC (% of SOC)	$Y = 48.9 - 0.32X$	42	- 0.66	0.001	44	V (% of CEC)
TEOC (% of SOC)	$Y = 35.9 + 0.43X - 0.007X^2$	42	- 0.72	0.001	-	V (% of CEC)
Epipedons (A_h and A_p horizons)						
TEOC (% of SOC)	$Y = 183e^{-0.30X}$	38	- 0.71	0.001	-	pH (H_2O)
TEOC (% of SOC)	$Y = 79.6 - 7.9X$	38	- 0.65	0.001	43	pH (H_2O)
TEOC (% of SOC)	$Y = 47.7e^{-0.008X}$	38	- 0.60	0.001	-	V (% of CEC)
TEOC (% of SOC)	$Y = 44.9 - 0.22X$	38	- 0.56	0.001	32	V (% of CEC)
TEOC (% of SOC)	$Y = 35.7 - 0.27X + 0.004X^2$	38	- 0.63	0.001	-	V (% of CEC)
TEOC (% of SOC)	$Y = 44.2e^{-0.027X}$	26	- 0.72	0.001	-	Clay (%)
TEOC (% of SOC)	$Y = 41.0 - 0.64X$	26	- 0.70	0.001	49	Clay (%)
Silt + Clay (% soil)	$Y = 9.40 - 1.11X$	26	- 0.86	0.001	74	Clay (%)
SOC (mg/g)	$Y = 3.16 + 0.77X$	38	+ 0.52	0.001	27	Silt + Clay (%)

N.B.: Same symbols as in Table 1.

CONCLUSIONS

It is confirmed that TEOC is strongly dependent, at least, on the soil pH; this fact indicates that the former is not a valid key parameter of soil quality. TEOC is mainly dependent on the pH and, also, on the clay content of the soil horizons. Results reject the general idea that low extraction means low degree of humification (at least in the Mediterranean region) because usually a low extraction of HS (low value of TEOC) is related to a neutral soil reaction (giving as result a more intense bacteriological activity) and the presence of clays, i.e., a stable humus-mineral complex (abundance of humin).

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