

State-space estimation of soil organic carbon stock

Joshua O. Ogunwole^{1*}, *Luis C. Timm*², *Evelyn O. Obidike-Ugwu*³, and *Donald M. Gabriels*⁴

¹Department of Crop Production and Protection, Federal University, PMB 5001, Dutsin-Ma, Nigeria

²Department of Rural Engineering, Federal University of Pelotas, CP 354, 96001-970 Pelotas, RS, Brazil

³Federal College of Forestry, PMB 2019, Jos, Nigeria

⁴Department of Soil Management and UNESCO Chair on Eremology, Ghent University, Coupure Links 653, B 9000 Ghent, Belgium

Received March 25, 2013; accepted January 20, 2014

A b s t r a c t. Understanding soil spatial variability and identifying soil parameters most determinant to soil organic carbon stock is pivotal to precision in ecological modelling, prediction, estimation and management of soil within a landscape. This study investigates and describes field soil variability and its structural pattern for agricultural management decisions. The main aim was to relate variation in soil organic carbon stock to soil properties and to estimate soil organic carbon stock from the soil properties. A transect sampling of 100 points at 3 m intervals was carried out. Soils were sampled and analyzed for soil organic carbon and other selected soil properties along with determination of dry aggregate and water-stable aggregate fractions. Principal component analysis, geostatistics, and state-space analysis were conducted on the analyzed soil properties. The first three principal components explained 53.2% of the total variation; Principal Component 1 was dominated by soil exchange complex and dry sieved macroaggregates clusters. Exponential semivariogram model described the structure of soil organic carbon stock with a strong dependence indicating that soil organic carbon values were correlated up to 10.8 m. Neighbouring values of soil organic carbon stock, all water-stable aggregate fractions, and dithionite and pyrophosphate iron gave reliable estimate of soil organic carbon stock by state-space.

K e y w o r d s: aggregate-associated carbon, principal component analysis, semivariogram, soil spatial variability

INTRODUCTION

Quantitative information on soil organic carbon (SOC) variability within landscape is needed to improve our understanding of soil organic matter dynamics to support agricultural management decisions. Knowledge of the structure and pattern of variability of a soil property is valuable information for the modelling and prediction of the soil property. Spatial analysis of SOC and its estimation within

a landscape will, therefore, provide information needed to understand the structure and distribution pattern of SOC and to identify soil determinants for its prediction for informed decisions on soil management. Forests represent one of the largest carbon pools on earth (van de Walle *et al.*, 2001), and their soils an essential carbon sink. Factors like management and texture (Sleulet *et al.*, 2006), aggregate turnover (Oades, 1988) and oxides (Carter, 1996), in oxide-rich soils, play an active role in SOC stabilization. A considerable positive association of clay and SOC contents has been reported on the Broadbalk wheat field at Rothamsted (Watt *et al.*, 2006). Beare *et al.* (1994) indicated that macroaggregate structure provides some physical protection for SOC. Other workers like Jastrow *et al.* (1996) and Six *et al.* (1998) have maintained that physical protection of SOC is mostly in soil microaggregate fraction and microaggregates within macroaggregates. Although several of these studies confirmed the positive relationship between SOC and selected soil properties, the fact that these soil properties change significantly over short distances makes knowledge about soil variability dispersed, requiring further synthesis.

Soil mapping has revealed extensive variability of forest soils over small areas and short distances (Boruvka *et al.*, 2007; Bruckman *et al.*, 2011; Phillips and Marion, 2005). Such mappings usually show greater variability in forest – than in similar non-forest soils (Phillips and Marion, 2005). As a key variable for a number of climatic, ecological, hydrological and nutrient-based processes operating in different intensities and, at different spatio-temporal scale, SOC is highly variable in time and space (Nielsen and Wendroth, 2003) across landscapes. Spatial variability in

*Corresponding author e-mail: ogunwolejo@hotmail.com

forest SOC stock is caused principally by soil properties, forest management and resulting vegetation cover as well as environmental factors such as mean annual temperature and precipitation (Bruckman *et al.*, 2011). By deduction, soil properties may become a principal determining factor in forest SOC variability under similar climate, forest management and vegetation cover.

The Nimbia Forest Reserve in the moist Nigerian Savanna is a planted teak (*Tectonia grandis*) plantation traditionally managed as coppice with high forest management systems primarily for high quality timber production. In recent years, management goals shifted to fuel wood supply as indiscriminate poaching by nearby settlements has become rampant, and this may have far-reaching negative effects on the capacity of that forest ecosystem to sequester atmospheric carbon to balance the anthropogenic CO₂ emissions. The increasing demand for high resolution spatial soil information for planning and modelling has made accurate prediction method vital for producing high-quality digital soil maps. Understanding spatial distribution and pattern of SOC stock could assist in accurate prediction and planning to mitigate losses and maximise sequestration and, consequently, reconstruct effective site-specific carbon management policies.

This paper shows results obtained from classical and geospatial analyses of soil properties along transect at a block within the Nimbia Forest Reserve. The study examines frequency distributions, principal component, semivariance and autoregressive state-space analyses to:

- establish level of variability in measured soil parameters along transect,
- identify parameters or clusters of parameters defining variability,
- analyze structure of variability of SOC pools and
- estimate SOC stock.

MATERIALS AND METHODS

The Nimbia Forest Reserve is located in the north central Nigeria, on coordinates 08° 30'–35'E and 09° 29'–31'N, with an area of about 2 000 ha planted with teak (*Tectonia grandis*), divided into 220 compartments. Altitude of the sampling sites ranged from 620 to 641 m. All soils were formed on newer basalts and classified as Ultisols (Plinthustults). The prevailing natural vegetation ranged from Southern Guinea Savanna woodlands to Derived Savanna with vegetation cover such as *Daniella Oliveri*, *Khaya senegalensis*, *Khaya grandifolia*, *Parkia clappertonia*, *Millettia thonningii* *etc.* Mean annual rainfall is 1 260 mm and annual mean temperature is 22°C.

Geo-referenced soil samples were collected from compartment NF 80 of the Reserve. Surface soil (0–0.15 m) was sampled along a 300 m transect, at 3 m intervals to give 100 samples. The soil samples were divided into two parts: one part was crushed and sieved through a 2 mm sieve after

air drying, for soil pH (1:2.5, soil water suspension) and particle size analyses. Prior to particle size determination, sodium hexametaphosphate was used for soil dispersion and the hydrometer method was used for particle size determination. The procedures of Page *et al.* (1982) were adopted for analysis of available phosphorus (Bray 1 method), exchangeable cations and cation exchange capacity (neutral normal ammonium acetate method) for these soil samples. The pyrophosphate (Fe_p), oxalate (Fe_o) and dithionite (Fe_d) forms of iron were analyzed, respectively, using the procedure of McKeague (1967), Schwertmann (1964) and; Mehra and Jackson (1960). Physical fractionation procedure was employed to determine the quantity and stability of soil aggregate fractions (modified from Cambardella and Elliott, 1994). Briefly, a sub-sample of air dry soil was dry sieved through five sieves of varying mesh sizes (5.0–2.0 mm *ie*, d₅₋₂, very large macroaggregates, 2.0–1.0 mm is d₂₋₁, large macroaggregates, 1.0–0.25 mm referred to d_{1-0.25}, macroaggregates, 0.25–0.0053 mm is d_{0.25-0.0053} or microaggregates and; < 0.0053 mm called d_{<0.0053}, silt plus clay sized particles) on a mechanical sieve shaker (Eijelkamp Agri-search Equip.) set at level 6 for 3 min. Aggregate fractions retained on each sieve were weighed and recorded. For water stable aggregate fractions, the second subsample of air dried soil was wet sieved (slaking pre-treatment) through a series of five sieves to obtain five aggregate fractions:

- 5.0–2.0 mm (WVLM, very large macroaggregates),
- 2.0–1.0 mm (WLM, large macroaggregates),
- 1.0–0.25 mm (WM, macroaggregates),
- 0.25–0.0053 mm (WMC, microaggregates) and
- < 0.0053 mm (WSC, silt plus clay-sized particles).

Aggregate fractions obtained through wet sieving were oven dried (60°C) and corrected for sand (Six *et al.*, 2000a). Surface soil bulk density (ρ_b , 0–5 cm) was determined by the core method (Blake and Hartge, 1986) and used to convert SOC concentrations to mass estimates by depth. The SOC content was determined by digestion in chromic acid and the excess was titrated against ferrous ammonium sulphate after the addition of concentrated phosphoric acid (Nelson and Sommers, 1982).

Descriptive statistics of central tendency and dispersion were calculated for each soil parameter using PASW 18 (SPSS, 2010). The shape of the frequency distribution was described by the coefficient of skewness. A varimax rotation with Kaiser Normalization (Kaiser, 1958) was performed in the Principal Component Analysis (PCA). The essence of the latter was to redistribute the variance in each parameter in such a way that each contributes strongly to one of the components and little to the others (Boruvka *et al.*, 2007). The PCA allows for the identification of clusters of parameters that are interrelated by identifying latent principal components (PCs) and the eigenvalue of a PC explains the extent to which a particular PC explains multiple correlations of the analyzed parameters (Burstyn, 2004).

Semivariogram was calculated to determine spatial dependence levels for the parameters, using the software GS⁺, Geostatistics for the Environmental Sciences, version 9.0 (Robertson, 2008). The experimental semivariogram was fitted to theoretical models and the shape parameters such as nugget effect (C_o), range (A_o) and the sill ($C_o + C$) were obtained and used to describe the spatial dependence for each soil parameter. The 'nugget effect' is defined as the variation at scale finer than the field sampling while the 'sill' is the maximum semivariance value where there is spatial dependence between sampled soil parameter values, and 'range' is the maximum distance where sampled soil parameter values are spatially correlated.

The semivariance value for each variable is defined as follows (Nielsen and Wendroth, 2003):

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [z(x_i) - z(x_i + h)]^2, \quad (1)$$

where: $\gamma(h)$ is the experimental semivariance value at lag distance h ; $z(x_i)$ and $z(x_i + h)$ are observed values of z at x_i and $x_i + h$, respectively. $N(h)$ is the number of pairs of observations at the distance h . Usually, semivariance values increase with sampling distance, approaching a plateau (constant value) referred to as 'sill'.

For numerical reasons, data for autoregressive state-space analysis are usually scaled or normalized (Wendroth *et al.*, 2003) as:

$$Xi, sc = \frac{Xi - (\bar{X} - 2\sigma)}{4\sigma}, \quad (2)$$

where: Xi, sc is the normalized value of the original value Xi and it is calculated based on the mean, \bar{X} , and the standard deviation, σ , of the original data set.

The analyzed of soil properties were selected with SOC for the prediction of SOC using the state-space approach. These seven properties (the five water stable aggregate fractions, Fe_p and Fe_d) were selected because they correlated with SOC stock from the result of cross-correlation analysis (not shown here) performed. For estimation of SOC, a first-order autoregressive process with the aid of a state-space model approach was employed on the scaled parameters described by the state equation:

$$Z_j(x_i) = \varnothing_{jj} Z_j(x_{i-1}) + u_{z_j}(x_i), \quad (3)$$

with state vector $Z_j(x_i)$ at position i is related to the same vector at previous position $i-1$ through the state coefficient matrix \varnothing_{jj} (transition matrix) and an error associated to the state $u_{z_j}(x_i)$. The state-equation is embedded in an observation equation with observation vector $Y_j(x_i)$ related to the state vector $Z_j(x_i)$ through the observation matrix $M_{jj}(x_i)$ and by the observation error, $v_{y_j}(x_i)$ as given below:

$$Y_j(x_i) = M_{jj}(x_i) Z_j(x_i) + v_{y_j}(x_i). \quad (4)$$

The observation vector, $Y_j(x_i)$ of the process is generated as a function of the state vector $Z_j(x_i)$. The assumptions were that $v_j(x_i)$ and $u_j(x_i)$ are normally distributed and independent as well as being non-correlated among themselves for both lags. The SOC at location i was modelled as a function of soil parameters at location $i-1$.

RESULTS

Few of the parameters analyzed, such as soil pH, ρb coarse sand and dry-sieved macro- ($d_{1-0.25}$) and micro- ($d_{0.25-0.0053}$) aggregate fractions, tended to be more homogeneous in distribution, with coefficients of variation (CV) < 15% (Table 1) and only slightly skewed (< 1). The mean and median values of these soil properties were the same but for coarse sand whose median value was close to the mean. From their mean values, soil pH was slightly acidic in reaction and within the range classified as optimal for most plant growth (Roy *et al.*, 2006); ρb was low for a clay loam soil and may not pose a constraint to water infiltration if there is no abrupt increase in value. The $d_{1-0.25}$ and $d_{0.25-0.0053}$ aggregate fractions constituted 18% of the total dry sieved fractions, with larger aggregate fractions accounting for higher proportion of the total dry aggregates in bulk soil, an indication of the resilience of the soil structure to withstand wind erosion menace.

Coefficients of variation for a substantial number of analyzed soil properties were within 15 to 50% range, an indication of a considerable level of heterogeneity in the distribution of the parameters (Table 1). Most of these soil parameters still recorded skewness ≤ 1 . Considerable skewed (≥ 1) distributions were, however, recorded for available phosphorus (AP), wet sieved very large macroaggregate *ie* 5-2 mm (WVLM) and dry sieved silt plus clay fraction ($d_{<0.0053}$). For SOC stock, an indication of variability in its spatial distribution was evident with a CV of 16.1%, slightly skewed (< 1), with similar mean and median values.

The Fe_o , K^+ and Na^+ distributions were highly variable with large CV values exceeding 50% and highly skewed (> 1) except for K^+ with coefficient of skewness equalling 0.81. In conclusion, the soil parameters analyzed revealed a moderate fertility status with a high variability. The results of the first and second moments of probability distribution clearly showed that the arithmetic means of these analyzed soil properties cannot appropriately characterize the sampled soil parameters (Nielsen and Wendroth, 2003).

The PCA was aimed at identifying clusters of analyzed soil properties that would explain significant proportion the total variation (Duffera *et al.*, 2007). There were five PCs with significant loadings that collectively explained 66.4% of the total variance (Table 2). The PC 1 scores increased with very large macroaggregate (d_{5-2}) and large macroaggregate (d_{2-1}) of dry sieved aggregate fractions, soil pH, CEC and exchangeable K^+ , Na^+ , Ca^{2+} , Mg^{2+} ; explaining 26.1% of the total variation. Negative loadings were

Table 1. Mean, median, standard deviation, coefficient of variation and skewness of the parameters sampled along a transect (n = 100)

Parameters	Units	Mean	Median	Standard deviation	Skewness	CV (%)
Soil pH		6.06	6.05	0.57	0.02	9.4
CEC		13.4	13.8	3.25	-0.63	24.3
K ⁺	c mol _c kg ⁻¹	0.18	0.14	0.11	0.81	58.3
Na ⁺		0.46	0.36	0.42	1.25	91.3
Ca ²⁺		4.71	4.40	2.09	0.68	44.4
Mg ²⁺		3.02	2.90	1.37	0.26	45.4
Fe _p		0.01	0.01	0.004	0.44	40.0
Fe _o	%	0.18	0.17	0.15	9.90	83.3
Fe _d		0.05	0.04	0.02	0.78	40.0
SOC		t ha ⁻¹	41.1	41.5	6.59	0.25
ρ_b	Mg m ⁻³	1.03	1.03	0.10	0.17	9.3
Clay	%	30.66	31.0	8.28	0.09	27.0
Silt		25.94	22.0	9.18	0.83	35.4
Sand		43.4	43.0	8.91	0.31	20.5
AP	mg kg ⁻¹	0.27	0.23	0.10	1.90	39.0
d ₅₋₂	g g ⁻¹	0.85	0.81	0.22	0.68	25.9
d ₂₋₁		0.26	0.26	0.05	0.18	19.2
d _{1-0.25}		0.22	0.22	0.02	-0.66	9.1
d _{0.25-0.0053}		0.03	0.03	0.01	-0.07	3.0
d _{<0.0053}		6 10 ⁻⁴	5 10 ⁻⁴	3 10 ⁻⁴	1.04	50.0
Coarse sand	%	67.3	66.5	7.22	0.46	10.7
Medium sand		7.2	7.0	1.82	-0.13	25.3
Fine sand		25.6	27.0	6.13	-0.34	24.0
WVLM	g g ⁻¹	0.19	0.17	0.09	1.08	45.8
WLM		0.11	0.11	0.04	0.47	33.6
WM		0.14	0.14	0.03	-0.006	18.6
WM _c		0.03	0.03	0.01	0.28	24.1
WSC		0.002	0.002	0.006	0.84	30.0

ρ_b – soil bulk density, AP – available phosphorus, Fe_o – oxalate extractable iron, Fe_d – dithionite extractable iron, Fe_p – pyrophosphate extractable iron, K⁺ – exchangeable potassium, Na⁺ – exchangeable sodium, Ca²⁺ – exchangeable calcium, Mg²⁺ – exchangeable magnesium, CEC – cation exchange capacity, SOC – soil organic carbon stock, WVLM, WLM, WM, WM_c, WSC – water stable aggregate fractions retained on 5-2, 2-1, 1-0.25, 0.25-0.0053 mm, <0.0053 mm sieves, respectively, d₅₋₂, d₂₋₁, d_{1-0.25}, d_{0.25-0.05}, d_{<0.05} – dry sieved aggregate fractions retained on 5-2, 2-1, 1-0.25, 0.25-0.0053 mm, <0.0053 mm sieves, respectively, CV – coefficient of variation.

Table 2. Principal component loadings and estimated communalities of the parameters along a transect

Parameters	Units	Principal components					Communality
		PC 1	PC 2	PC 3	PC 4	PC 5	
Eigenvalue		7.8	4.7	3.4	2.0	1.9	
Variance		26.1	15.8	11.3	6.7	6.5	
Cumulative variance	%	26.1	41.9	53.2	59.9	66.4	
		Rotated loadings of retained eigenvectors					Communality
Soil pH		0.765a	0.347	0.014	0.101	-0.139	0.742
CEC		0.556a	-0.335	0.378	-0.371	-0.161	0.815
K ⁺		0.784a	-0.015	-0.115	0.023	-0.180	0.741
Na ⁺	c mol _c kg ⁻¹	0.517a	-0.545a	-0.074	-0.423	-0.078	0.793
Ca ²⁺		0.810a	0.102	0.176	-0.148	-0.234	0.876
Mg ²⁺		0.793a	0.022	0.130	-0.201	-0.234	0.876
Fe _p		-0.017	-0.641a	0.368	0.052	-0.032	0.560
Fe _o	%	-0.076	0.189	0.138	-0.247	-0.020	0.516
Fe _d		-0.534a	-0.309	0.106	0.198	0.233	0.383
SOC	t ha ⁻¹	0.404	0.182	0.068	0.053	0.651a	0.723
ρb	Mg m ⁻³	-0.096	0.144	-0.677a	0.157	0.418	0.818
Clay		0.175	-0.302	-0.544a	0.536a	-0.443	0.906
Silt	%	-0.502a	0.433	-0.245	-0.585a	0.102	0.902
Sand		0.354	-0.165	0.758a	0.106	0.307	0.861
AP	mg kg ⁻¹	0.391	0.453	-0.198	0.200	-0.484	0.497
d ₅₋₂		0.755a	-0.193	-0.404	-0.111	0.242	0.903
d ₂₋₁		0.756a	0.487	-0.029	0.020	-0.047	0.860
d _{1-0.25}	g g ⁻¹	-0.336	0.433	0.424	0.048	-0.333	0.802
d _{0.25-0.0053}		-0.871a	-0.216	0.192	0.028	-0.051	0.904
d _{<0.0053}		-0.734a	-0.291	0.034	0.390	-0.006	0.860
Coarse sand		0.354	-0.165	0.758a	0.106	0.307	0.909
Medium sand	%	-0.498	0.396	0.207	0.026	-0.009	0.580
Fine sand		-0.405	0.796a	0.120	-0.089	-0.086	0.859
WVLM		0.408	0.698a	0.213	0.200	0.209	0.787
WLM		0.298	0.814a	0.178	0.133	0.116	0.832
WM	g g ⁻¹	-0.565a	0.544a	-0.098	-0.161	-0.026	0.691
WM _c		-0.793a	-0.274	0.073	0.019	0.117	0.762
WSC		-0.679a	-0.002	-0.098	0.247	-0.052	0.724

a – rotated standardized data with loadings $\geq \pm 0.5$. Explanations as in Table 1.

recorded for dry sieved silt plus clay and $d_{0.25-0.0053}$ fractions, silt mineral particle, Fe_d and macro- and micro-aggregate fractions of wet sieved soil samples and the silt and clay fractions, which only showed that they are lacking latent variable associated with PC 1 (Burstyn, 2004). Six soil properties were clustered in PC 2 which explained 15.8% of the total variation. There was a sharp drop in eigenvalue from PC 1 to PC 2 (*ie* 7.8 to 4.7). Here, all the wet sieved macroaggregate fractions and fine sand displayed latent variable associated with the PC. Sand and clay mineral particles and ρb clustered at PC 3, which accounted for 11.3% of total variation (Table 2). In this PC, only sand mineral particle recorded a positive loading (0.758). For PCs 4 and 5 which, respectively, explained 6.7 and 6.5% of the total variance, had clay and SOC stock as sampled parameters, respectively. Communalities values are indicative of the proportion of each parameter explained by PCA. In this analysis, communality values generally ranged from medium (0.516 for Fe_p) to high (0.909 for coarse sand), except for Fe_d and AP which recorded low communality values (Table 2). In conclusion, spatial variability in the top soil (15 cm) of this forest field was dominated by three principal clusters which accounted for 53.2%. The first factor was the exchange complex cluster and the second was the water stable soil structure cluster, dominated by the wet sieved macro-aggregate fractions, and the third cluster, which described less variability in the field, was the sand mineral particle size (sand and fine sand). A high proportion of most of the analyzed parameters were effectively explained by the PCA and this can be confirmed from their communality values.

Based on the results obtained from semivariance analysis, it is evident that different pattern of spatial structure and level of spatial dependence was exhibited by the analyzed soil properties. The exchange complex cluster (*ie* exchangeable bases and CEC) that was modelled was best fitted by a spherical model except for CEC (Table 3). From the soil particle size cluster, silt, sand and medium sand particle fractions fitted the spherical model while medium sand fraction had a good fit with coefficient of determination, R^2 of 0.97, and a residual sums of squares, RSS of 0.261 (Table 3). The sand and silt mineral particle fractions weakly fitted with RSS of 4.247 and 1.073, respectively. The lower the RSS, the better the model fit, and RSS is a more robust indicator of model fit than the R^2 (Robertson, 2008) as it provides exact measure of model fitness. The soil structure cluster (dry and water-stable aggregate fractions) was diffuse in model type and fit, while the dry sieved large macroaggregate (d_{2-1}), water stable micro-aggregate (WMC) and their respective silt plus clay fractions were well fitted to the spherical model, depicting spatial structures whose boundaries are not clearly defined, while the remaining water stable macroaggregate fractions (WVLM, WLM and WM) exhibited structures with smoother spatial pattern (Gaussian) than the spherical model (Table 3). Experimental semivariogram models for coarse and fine

sand, Fe_d , Fe_o and soil pH displayed a continuous gradual variation which fit the Gaussian model, and RSS for coarse and fine sand were large. For Fe_p , its pure nugget and exponential model for ρb (Table 3), semivariogram was pure nugget effect indicating no observed spatially structured variation between adjacent observations at the sampling scale (Nielsen and Wendroth, 2003), inferring large point-to-point variations mainly controlled by random factors with no spatial dependence at the scale of investigation. The variation in CEC, AP, clay and dry sieved macroaggregate fraction fitted the rather abrupt changes at all distances and was best depicted by the exponential model; only the RSS for clay and CEC were large suggesting a weak fit (Table 3). The SOC stock fits an exponential model (Fig. 1) with a strong spatial dependence at 10.8 m (Table 3). As mentioned earlier, the maximum distance over which adjacent observations of a parameter are correlated is referred to as effective range (A_o) and it ranges from 10.8 m for SOC stock to 932.7 m for available phosphorus. Spatial dependence has been classified as strongly, moderately and weakly spatially dependent if the nugget-to-sill ratio falls within <25, 25-75 and >75%, respectively (Duffera *et al.*, 2007). Apart from Fe_p and ρb , all other parameter were between moderately to strongly spatially dependent.

Autoregressive SOC stock estimation is presented for the soil based state vector. Using all 100 observations of each of eight selected soil parameters, values of SOC with space analysis were estimated (Fig. 2) with sum of transition coefficients being 1.1774 ($= -0.0215 + 0.554 + 0.0085 + 0.2373 - 0.2921 + 0.054 - 0.244 + 0.8811$). The contribution of neighbouring values of organic carbon stock, large macro-aggregates and silt plus clay fractions were much lower than those of the remaining five soil parameters. The lowest contribution to the SOC estimation was wet sieved large macro-aggregate (*ie* 2.0-1.0 mm) while the pyrophosphate iron made the highest contribution to SOC estimation. A linear regression between estimated and measured values of SOC (Fig. 3) showed a reliable estimation as it yielded a coefficient of determination R^2 of 0.955.

DISCUSSION

Complex interactions between SOC stock and aggregate stability exist in soils (Lawal *et al.*, 2009). Aggregation is one of the pedospheric processes that facilitate SOC storage. On the other hand, SOC maintains the stability of soil structure. The mechanisms promoting these complex interactions may probably have been responsible for the correlation of aggregate fractions with SOC stock. For PCA, magnitude of the eigenvalue was used as criterion for interpreting the relationship between soil properties. The aggregate-SOC stock interaction theory could have accounted for the various results under PCA. In the process of aggregation, formation of soil organo-mineral complexes

Table 3. Parameters of the fitted semivariogram models for the measured soil properties

Parameters	Units	Model	Nugget (C _o)	Sill (C + C _o)	C _o /(C+C _o)	Range (A _o , m)	R ²	Spatial dependence	RSS
Soil pH		Gaussian	0.074	0.058	0.13	101.9	0.99	strong	1.05 10 ⁻³
CEC		Exponential	3.3	16.36	0.20	162.6	0.92	strong	13.6
K ⁺	c mol _c kg ⁻¹	Spherical	0.00254	0.01768	0.14	177.1	0.98	strong	1.23 10 ⁻⁶
Na ⁺		Spherical	0.027	0.201	0.134	110.1	0.98	strong	9.3 10 ⁻⁴
Ca ²⁺		Spherical	1.63	8.07	0.202	149.4	0.97	strong	0.33
Mg ²⁺		Spherical	0.742	2.735	0.271	144.7	0.72	moderate	0.034
Fe _p		Pure nugget	0.000	0.00002	–	–	–	random	–
Fe _o	%	Gaussian	0.0238	0.0606	39.3	283.7	0.99	moderate	3.22 10 ⁻⁶
Fe _d		Gaussian	0.00009	0.00034	0.265	87.9	0.94	moderate	7.95 10 ⁻⁹
SOC	t ha ⁻¹	Exponential	7.10	44.66	0.159	10.8	0.30	strong	93.9
ρ _b	Mg m ⁻³	Exponential	0.00036	0.00862	0.042	21.0	0.38	strong	1.51 10 ⁻⁵
Clay		Exponential	17.1	109.4	0.156	173.7	0.92	strong	404
Silt	%	Spherical	0.1	134.9	0.0007	101.0	0.96	weak	1073
Sand		Spherical	15.4	84.5	0.182	33.7	0.38	weak	4247
AP	mg kg ⁻¹	exponential	0.0056	0.02	0.28	932.7	0.72	moderate	1.4 10 ⁻⁵
d ₅₋₂		Gaussian	0.019	0.0736	0.258	134.9	0.99	moderate	6.9 10 ⁻⁵
d ₂₋₁		Spherical	0.0005	0.0038	0.132	232.8	0.99	strong	1.2 10 ⁻⁷
d _{1-0.25}	g g ⁻¹	Exponential	0.00026	0.00058	0.448	398.7	0.74	moderate	2 10 ⁻⁸
d _{0.25-0.0053}		Gaussian	0.00003	0.00015	0.200	140.1	0.99	strong	2.4 10 ⁻¹⁰
d _{<0.0053}		Spherical	0.00019	0.00125	0.152	105.3	0.99	strong	1.38 10 ⁻⁸
Coarse sand		Gaussian	16.4	110.16	0.149	209.5	0.99	strong	105
Medium sand	%	Spherical	2.0	5.704	0.351	270.6	0.97	moderate	0.261
Fine sand		Gaussian	11.8	82.98	0.142	223.3	0.99	strong	37.3
WVLM		Gaussian	0.00426	0.03022	0.141	537.9	0.80	strong	9.6 10 ⁻⁶
WLM		Gaussian	0.00063	0.00655	0.096	537.9	0.87	strong	2.9 10 ⁻⁷
WM	g g ⁻¹	Gaussian	0.00032	0.0012	0.267	146.2	0.99	moderate	1.6 10 ⁻⁸
WM _c		Spherical	0.00003	0.0001	0.300	230.5	0.97	moderate	1.4 10 ⁻¹⁰
WSC		Spherical	0.00181	0.0043	0.424	103.5	0.87	moderate	1.3 10 ⁻⁶

Explanations as in Table 1.

takes place and some organic matter, on the other hand, gets encapsulated within stable soil aggregates. This process ensures the protection of the encapsulated soil organic matter against microbial processes and enzymatic reaction (Holeplass *et al.*, 2004), consequently increasing the organic carbon capacity due to soil structure. It is also widely known that the clay size fraction provides protection for organic

carbon against microbial and enzymatic processes (Trujillo *et al.*, 1997). Six *et al.* (2004) suggested three mechanisms for SOC protection. First, is physical stabilisation through microaggregation and, secondly, intimate association with silt and clay particles as earlier suggested with clay size fraction. Finally, formations of recalcitrant SOC can biochemically stabilize the organic carbon in soils.

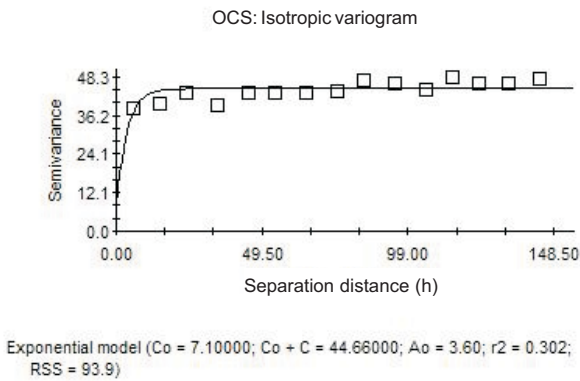


Fig. 1. Measured and fitted semivariogram of soil organic carbon stock sampled along a transect.

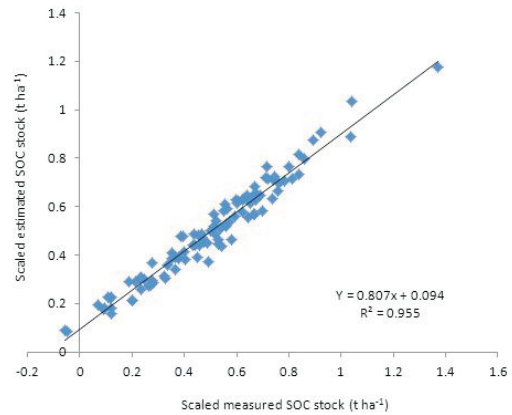


Fig. 3. Classical regression of state-space estimated and measured soil organic carbon stock.

Exchangeable cations have been generally accepted as critical for stabilisation of SOC and aggregates. This is made possible through their roles in the formation of clay-polyvalent cation-organic matter complexes (Muneeer and Oades, 1989), consequently increasing the capacity of the soil to exchange cations (CEC). For instance, calcium and potassium additions to soils have been reported to increase aggregation levels in soils (Imbufe *et al.*, 2005; Six *et al.*, 2000b) leading to increased SOC protection. Further, the amount of organic carbon in particle fractions may have been influenced by mineralogy, specifically iron oxides. In an earlier work, Ogunwole and Ogunleye (2004) reported a strong positive correlation between total elemental iron (Fe) and macroaggregation, suggesting a contributory role of Fe to aggregation of soil particles at the level of macroaggregation. The high transition coefficients of the Fe_p and Fe_d in the state-space equation here portray the contributory

roles of these iron fractions in SOC storage. Oxides of iron are dominant binding agents in oxide-rich tropical soils through the adsorption of organic matter on oxide surfaces (Oades *et al.*, 1989) and/or electrostatic binding may occur between these oxides and negatively charged clay mineral particles (El-Swaify and Emerson, 1975). A coat of iron oxides on the surface of minerals may form bridges between primary and secondary particles (Muggler *et al.*, 1999) facilitating macroaggregation and stabilization of SOC (Shang and Tiessen, 1997, 1998).

It is noteworthy from this study that SOC stock was significantly influenced by aggregate stability mechanisms, suggesting that most organic carbon stock in this soil was that protected or sequestered in soil aggregates. Any management practice or intervention that adversely affects stability of these aggregates will lead to the release of sequestered organic carbon, leading to reduction in SOC stock.

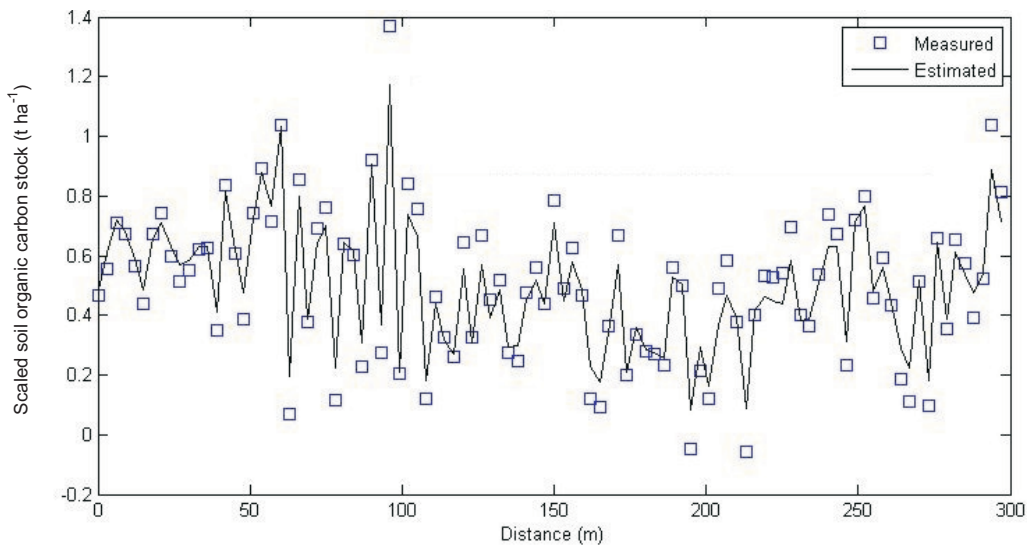


Fig. 2. State-space estimation of soil organic carbon stock based on values of the soil properties.

CONCLUSIONS

1. Distributions of soil properties such as water stable aggregate fractions and various forms of iron in forest Ultisols (Plinthustults) were very diverse and variable.

2. A combination of 16 parameters explained 53.2 to 66.4% of the variation in soil properties with the cumulative eigenvalues indicating the high level of variability in soil properties.

3. Soil exchange complex and soil structure factors were principal determinants of variation in soils.

4. The mechanisms that facilitated aggregate stability and soil organic matter protection were the link for the soil organic carbon stock in soils.

5. The state-space analysis reliably estimated the soil organic carbon which is generated and created by aggregate stability, oxalate and pyrophosphate forms of iron of neighbouring locations, with the largest contribution from the pyrophosphate.

6. Results obtained can assist as a basis in soil management for the soil organic carbon in these soils.

ACKNOWLEDGEMENT

The first two authors acknowledged with thanks the Regular Associate fellowship of the Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste-Italy that provided the platform for putting this article together.

REFERENCES

- Beare M.H., Hendrix P.F., and Coleman D.C., 1994.** Water-stable aggregate and organic matter fractions in conventional- and no-tillage soils. *Soil Sci. Soc. Amer. J.*, 58, 777-786.
- Blake G.R. and Hartge K.H., 1986.** Bulk density. In: *Methods of soil analysis*. Agronomy Monograph (Ed. A. Klute). Am. Soc. Agronomy Press, Madison, WI, USA.
- Boruvka L., Mládková L., Penížek V., Drábek O., and Vašát R., 2007.** Forest soil acidification assessment using principal component analysis and geostatistics. *Geoderma*, 140, 374-382.
- Bruckman V.J., Yan S.S., Hochbichler E., and Glatzel G., 2011.** Carbon pools and temporal dynamics along a rotation period of *Quercus* dominated high forest and coppice with standard stands. *For. Ecol. Manag.*, 262, 1853-1862.
- Burstyn I., 2004.** Principal component analysis is a powerful instrument in occupational hygiene inquiries. *Ann. Occup. Hyg.*, 48, 655-661.
- Cambardella C.A. and Elliott E.T., 1994.** Carbon and nitrogen dynamics of soil organic matter fractions from cultivated grassland soils. *Soil Sci. Soc. Amer. J.*, 58, 123-130.
- Carter M.R., 1996.** Analysis of soil organic matter storage in agroecosystems. In: *Structure and organic matter storage in agricultural soils* (Eds M.R. Carter, B.A. Stewart). CRC and Lewis Press, Boca Raton, FL, USA.
- Duffera M., White J.G., and Weisz R., 2007.** Spatial variability of Southeastern U.S. coastal plain soil physical properties: implications for site-specific management. *Geoderma*, 137, 327-339.
- El-Swaify S.A. and Emerson W.W., 1975.** Changes in the physical properties of soil clays due to precipitated aluminium and iron hydroxides. 1. Swelling and aggregate stability after drying. *Soil Sci. Soc. Amer. Proc.*, 30, 1056-1063.
- Holeplass H., Singh B.R., and Lal R., 2004.** Carbon sequestration in soil aggregate under different rotations and nitrogen fertilization in an Inceptisol in southeastern Norway. *Nutrient Cycl. Agroecosys.*, 70, 167-177.
- Imbufe A.V., Patti A.F., Barrow D., Surapaneni A., Jackson W.J., and Milner A.D., 2005.** Effects of potassium humate on aggregate stability of two soils from Victoria, Australia. *Geoderma*, 125, 321-350.
- Jastrow J.D., Boutton T.W., and Miller R.M., 1996.** Carbon dynamics of aggregate-associated organic matter estimated by carbon-13 natural abundance. *Soil Sci. Soc. Amer. J.*, 60, 801-807.
- Kaiser H.F., 1958.** The varimax criterion in analytic rotation in factor analysis. *Psychometrika*, 23, 187-200.
- Lawal H.M., Ogunwole J.O., and Uyovbisere E.O., 2009.** Changes in soil aggregate stability and carbon sequestration mediated by land use practices in a degraded dry savanna Alfisol. *Tropical Subtropical Agroecosys.*, 10, 423-429.
- McKeeque J.A., 1967.** An evaluation of 0.1 M pyrophosphate – dithionite in comparison with oxalate as extractants of the accumulation products in podzols and other soils. *Can. J. Soil Sci.*, 41, 95-99.
- Mehra O.P. and Jackson M.L., 1960.** Iron oxide removal from soils and clays by a dithionite-citrate system buffered with Na bicarbonate. *Clays Min.*, 5, 317-327.
- Muggler C.C., van Griethuysen C., Buurman P., and Pape T., 1999.** Aggregation, organic matter and iron oxide morphology in oxides from Minas Gerais, Brazil. *Soil Sci.*, 164, 759-770.
- Muneer M. and Oades J.M., 1989.** The role of Ca-organic interactions in soil aggregate stability. II. Field studies with ¹⁴C-labelled straw, CaCO₃ and CaSO₄.2H₂O. *Aust. J. Soil Sci.*, 27, 401-409.
- Nelson D.W. and Sommers L.E., 1982.** Total Carbon, organic carbon, and organic matter. In: *Methods of Soil Analysis* (Ed. A.L. Page). Agronomy Soc. America Madison, WI, USA.
- Nielsen D.R. and Wendroth O., 2003.** Spatial and temporal statistics-sampling field soils and their vegetation. *Catena Press*, Reiskirchen, Germany.
- Oades J.M., 1988.** The retention of organic matter in soils. *Bio-geochemistry*, 5, 35-70.
- Oades J.M., Gillman G.P., and Uehara G., 1989.** Interactions of soil organic matter and variable charge clays. In: *Dynamics of soil organic matter in Tropical Ecosystems* (Eds D.C. Coleman, J.M. Oades, G. Uehara). Hawaii Press, Honolulu, HI, USA.
- Ogunwole J.O. and Ogunleye P.O., 2004.** Surface soil aggregation, trace and heavy metal enrichment under long term application of farm yard manure and mineral fertilizers. *Communications in Soil Sci. Plant Anal.*, 35, 1505-1516.
- Page A.L., Miller R.H., and Keeney D.R., 1982.** Methods of soil analysis. American Soc. Agronomy, Madison, WI, USA.

- Phillips J.D. and Marion D.A., 2005.** Biomechanical effects, lithological variations and local pedodiversity in some forest soils of Arkansas. *Geoderma*, 124, 73-89.
- Robertson G.P., 2008.** *GS⁺: Geostatistics for the environmental sciences*. Gamma Design Press, Plainwell, MI, USA.
- Roy R.N., Finck A., Blair G.J., and Tandon H.L.S., 2006.** Plant nutrition for food security: a guide for integrated nutrient management. *FAO Fertilizer and Plant Nutrition Bulletin*, Food and Agriculture Organization, Rome, Italy.
- Schwertmann U., 1964.** The differentiation of Iron oxide in soils by a photochemical extraction with acid ammonium oxalate. *Z. Pflanzenernaehr Dueng. Bodenkd.*, 105, 194-202.
- Shang C. and Tiessen H., 1997.** Organic matter lability in a tropical Oxisol: evidence from shifting cultivation, chemical oxidation, particle size, density and magnetic fractionations. *Soil Sci.*, 162, 795-807.
- Shang C. and Tiessen H., 1998.** Organic matter stabilization in semi arid tropical soils: size, density and magnetic separations. *Soil Sci. Soc. Amer. J.*, 65, 1247-1257.
- Six J., Bossuyt H., DeGryze S., and Denef K., 2004.** A history of research on the link between (micro) aggregates, soil biota and soil organic matter dynamics. *Soil Till. Res.*, 79, 7-31.
- Six J., Elliott E.T., and Paustian K., 2000a.** Soil macroaggregate turnover and microaggregate formation: a mechanism for carbon sequestration under zero tillage agriculture. *Soil Biol. Biochem.*, 32, 2099-2103.
- Six J., Merckx R., Kimpe K., and Paustian K., 2000b.** A re-evaluation of the enriched labile soil organic matter fraction. *European J. Soil Sci.*, 51, 283-293.
- Six J., Elliott E.T., Paustian K., and Doran J.W., 1998.** Aggregation and soil organic matter storage in cultivated and native grassland soils. *Soil Sci. Soc. Amer. J.*, 62, 1367-1377.
- Sleulet S., DeNeve S., Beheydt D., Li C., and Hofman G., 2006.** Regional simulation of long term organic carbon stock changes in crop land soils using the DNDC model: 1. large scale model validation against a spatially explicit data set. *Soil Use Manag.*, 22, 342-351.
- SPSS, 2010.** *PASW Statistics, Release 18.0*, Westland Centre, Quarry Bay, Hong Kong.
- Trujillo W., Amezcua E., Fisher M.J., and Lal R., 1997.** Soil organic carbon dynamics and land use in the Colombian Savannas. 1. Aggregate size distribution. In: *Soil processes and the carbon cycle* (Eds R. Lal, J.M. Kimble, R.F. Follett, and B.A. Stewart). CRC Press, Boca Raton, FL, USA.
- van de Walle I., Mussche S., Samson R., Lust N., and Lemeur R., 2001.** The above and below ground carbon pools of two mixed deciduous forest stands located in East-flanders (Belgium). *Ann. For. Sci.*, 58, 507-517.
- Watt C.W., Clark L.J., Poulton P.R., Powlson D.S., and Whitmore A.P., 2006.** The role of clay, organic carbon and long term management on mouldboard plough draught measured on the Broadbalk wheat experiment at Rothamsted. *Soil Use Manag.*, 22, 334-341.
- Wendroth O., Reuter H.L., and Kersebaum K.C., 2003.** Predicting yield of barley across a landscape: a state-space modeling approach. *J. Hydrol.*, 272, 250-263.