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## Characterization of clay bound organic matter using activation energy calculated by weight loss on ignition method

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Soil organic matter (SOM) through intimate associations with clay particles forms clay bound organic matter (CBO), which contributes mainly to long-term stability of SOM in most soils. The CBO fraction contributes mainly to more meaningful carbon sequestration due to their long-term stability and hence storage. The formation and stabilization of CBO is a complex process and studies on determination of the exact composition of this fraction are meagre. In this study, an attempt was made to characterize the CBO of a soil in terms of the other SOM fractions such as fulvic fraction (FF), humic fraction (HF) and fine soil litter. The weight loss on ignition (LOI) data of extracted SOM fractions and fine soil litter were used to characterize CBO. Rate constants ( $k$ ) of the oxidation reactions during the LOI were calculated using percentage weight losses at different temperatures of the FF, HF and fine soil litter. Calculated activation energies ( $E_a$ ) of the other SOM fractions at different temperatures were used in a multiple regression analysis to predict the  $E_a$  of the CBO fraction. The results showed that the activation energy of the CBO [ $E_a$  (CBO)] was positively related to that of the fine soil litter [ $E_a$  (fine soil litter)] and the FF [ $E_a$  (FF)]. The relationship indicates that the CBO of the soil is composed of a mixture of fine soil litter and the FF, as also proposed in the literature.

**Keywords:** Activation energy, clay bound organic matter, fine soil litter, fulvic fraction, humic fraction.

THE soil organic matter (SOM) is a physically and chemically heterogeneous mixture of organic compounds of plant, animal and microbial origin, and has components at different stages of decomposition. The type of land use and soil are important factors controlling SOM storage in the soils. Their storage reflects the relative importance of different mechanisms of SOM stabilization<sup>1</sup>. Several mechanisms have been proposed to contribute to the SOM stabilization in soils<sup>2</sup>. The SOM can be (i) biochemically stabilized through the formation of recalcitrant SOM compounds, (ii) protected by intimate association with silt and clay particles, and (iii) physically stabilized through aggregate formation.

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The SOM protection through intimate association with clay particles is resulted by organomineral complexation and contributes mainly to more meaningful carbon sequestration due to their long-term stability<sup>3</sup>. This clay-bound fraction is better protected against decomposition compared to the silt fraction<sup>4</sup>.

The SOM stabilization by clay particles depends on the relationship between clay types, contents and organic matter accumulation. The fulvic and humic substances and their polymers are tightly adsorbed onto clay mineral surfaces by chemical bonds<sup>5</sup>. In addition, soil litter particles are also closely associated with clay fraction during the formation of clay bound organic matter (CBO)<sup>6</sup>.

Wershaw<sup>7</sup> explained that all living organisms are made of molecules that form non-covalently bonded molecular aggregates (supramolecular aggregates). Humification is a three-step process of degradation, aggregation of the degraded products, and degradation of the aggregated products<sup>7</sup>. Therefore, he proposed that CBO is composed of molecular aggregates of the degraded products of plant tissues. Stabilization of organic matter is essential for tropical soils. Since the climatic conditions of the tropics favour decomposition of organic matter, tropical soils would be very poor in organic matter without this stabilization process<sup>8</sup>. There are studies that describe clay mineralogy of organo-mineral complexes in soils<sup>2,5,8,9</sup>. However, information on organic matter constituents of these complexes in tropical soils is meagre. The studies reported so far on the determination of the composition of CBO involve advance technologies which are not easily available in many laboratories<sup>8,10</sup>, especially in developing countries. Therefore, the present study aims at characterizing organic matter in clay mineral complexes of a tropical forest soil in terms of activation energies of the other SOM fractions (i.e. fulvic fraction (FF), humic fraction (HF) and fine soil litter) by the simple loss of ignition (LOI) method.

Cambisols (FAO, 1993) from an undisturbed forest at 700 m asl in Sri Lanka (5°54'N–9°52'N lat. and 79°39'E–81°53'E long.) with pH of 6.13, organic matter content of 4.1% and clay content of 9.9% were selected for the study. After removing soil surface litter layer from random locations, 20 composited soil samples were taken from 0 to 20 cm depth. Each composite sample comprised three soil cores. These samples were then extracted for FF and HF using the International Humic Substances Society (IHSS) method<sup>11</sup>. The HF and FF were separated by centrifugation. Several purification steps were carried out with 0.1 M HCl and 0.3 M hydrofluoric acid to reduce the inorganic impurities of the HF precipitate. The supernatant was dialysed against spectrapor membrane (1000 Dalton) to remove salts and finally freeze dried to obtain the FF. However, the isolates were not purified up to pure humic and fulvic acids. The soil was also extracted to obtain the fine soil litter<sup>12</sup> for the analysis using the method described by Smucker<sup>13</sup>. The soil sample was agitated in water to separate soil and fine soil litter particles.

Recent studies indicated that weight LOI is an accurate method for estimating the SOM. Weight LOI measures weight loss of the SOM fractions due to oxidation upon heating<sup>14,15</sup>. Therefore, the LOI data (105–600°C) of the extracted SOM fractions and fine soil litter above were used for the characterization of CBO. A particular range of temperatures oxidizes a certain group of organic compounds depending on their activation energies of oxidation. Therefore, materials composed of comparable structures oxidize at a certain range of temperatures<sup>16</sup>. The LOI is more accurate for the SOM fractionation than the chemical extraction methods<sup>16,17</sup>.

Mass loss percentages at different temperatures ( $T$ ) of the FF, HF and fine soil litter were used as rate constants ( $k$ ) of their oxidation reactions during combustion. For each fraction, graphs were plotted for  $\ln k$  vs  $1/T$  (Figure 1). The best models were fitted for these graphs by using curve expert<sup>18</sup> (Figure 1). Derivatives of  $\ln k$  with respect to  $T$  of different fractions were calculated using these models.

The nonlinear nature of these relationships implies non-Arrhenius behaviour of the reactions, the activation energies ( $E_a$ ) of which are described from the following relationship<sup>19</sup>

$$E_a = RT^2 \left[ \frac{d \ln k}{dT} \right],$$

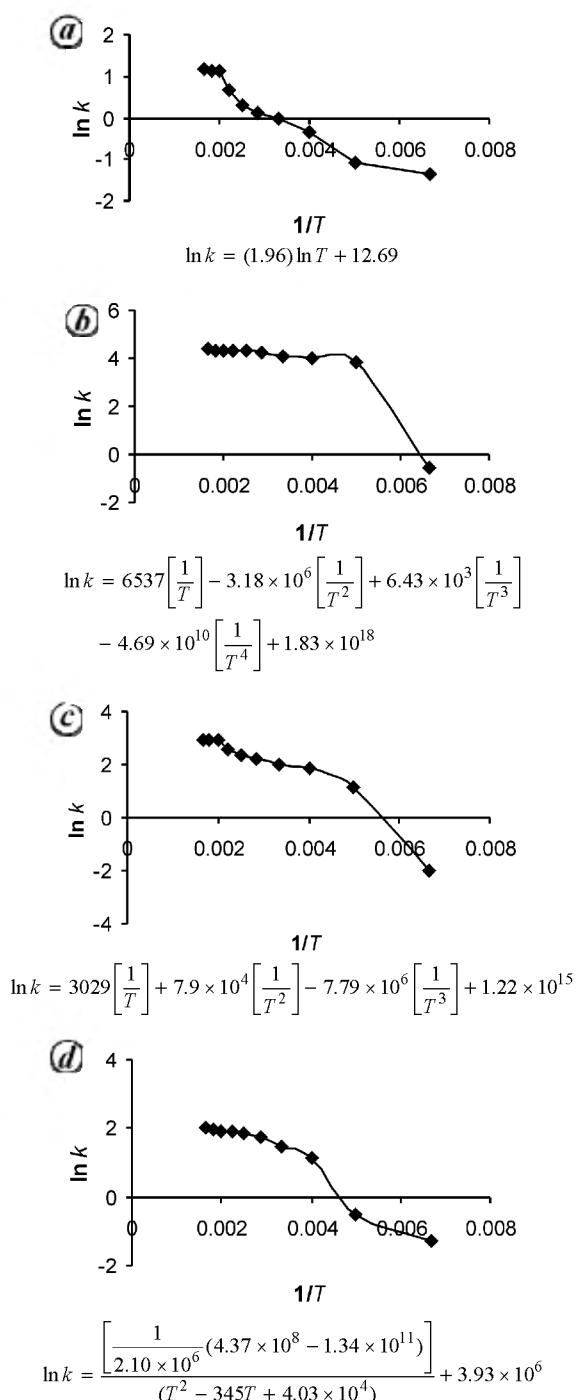
where  $R$  is the ideal gas constant.

Those derivatives were substituted to the above equation and the activation energies were calculated at different temperatures (Table 1). The  $E_a$  of the other SOM fractions at different temperatures was used in a multiple regression analysis to predict  $E_a$  of the CBO fraction. The results showed that the activation energy of the CBO [ $E_a$  (CBO)] was positively related to that of the fine soil litter [ $E_a$  (fine soil litter)] and the FF [ $E_a$  (FF)] in the following form

$$\begin{aligned} E_a(\text{CBO}) &= 0.065 E_a(\text{fine soil litter}) \\ &\quad + 4.59 \times 10^{-9} E_a(\text{FF}) + 7518 \\ r^2 &= 0.99; P < 0.01. \end{aligned}$$

The relationship indicates that the CBO is composed of a mixture of fine soil litter and the FF. Having fine particles soil litter contributes mostly to the CBO<sup>20,21</sup>. Kerek *et al.*<sup>21</sup> reported that humus accumulates as CBO and makes it resistant to further degradation. This further proves what was obtained from the regression equation of the present study. The CBO is composed of soil litter transferred into soil aggregates and the FF, a component of humus. Several studies<sup>20,22,23</sup> have confirmed this, that shoot or root-derived litter fragments in the soil are transformed to humus layer and encapsulated within clay and sand in the formed aggregates, which are then known as

the CBO. Using scanning electron microscopy, Wattel-Koekkock *et al.*<sup>8</sup> observed that the CBO fraction contains free plant remains. Using Py-GC/MS and NMR technique they reported that the CBO separated from four soil types in the tropics is enriched with polysaccharide products<sup>24</sup>, which are mostly found in the FF.



**Figure 1.** Mass loss percentages at different temperatures ( $T$ ) of the SOM fractions and their rate constants ( $k$ ) of their oxidation reactions during combustion, plotted as  $\ln k$  vs  $1/T$ . Their predicted models are also shown. **a**, Clay bound organic matter (CBO); **b**, Fine soil litter; **c**, Humic fraction (HF); **d**, Fulvic fraction (FF).

**Table 1.** Calculated activation energies at different temperatures of different soil organic matter fractions

Temperature (K)	Activation energy (kJ mol <sup>-1</sup> )			
	CBO	Fine soil litter	HF	FF ( $\times 10^7$ )
423	6.89	-16.86	32.94	8.1
473	7.7	-4.55	31.09	12
523	8.52	4.85	29.77	17.1
573	9.33	12.18	28.81	23.6
623	10.15	18	28.52	31.7
673	10.97	22.69	27.52	41.6
723	11.78	26.52	27.08	53.6
773	12.6	29.69	26.74	67.9
823	13.41	32.35	26.46	84.8
873	14.22	34.59	26.23	105

CBO, Clay bound organic matter; HF, humic fraction; FF, fulvic fraction.

According to the molecular aggregate model, the SOM is composed of molecular aggregates of partially degraded products of plant polymers, held together by non-covalent bonds<sup>7</sup>. The preponderance of evidence favours this model. The regression model in the present study also supports the molecular aggregate model. In the regression model, oxidation energy of the CBO balances with that of its constituent fine soil litter dominated by lignified materials and the FF, agreeing with the law of conservation of energy. During the formation of CBO, strong non-covalent bonds are formed with a variety of different types of compounds<sup>7</sup> and, in particular, with carbohydrates and proteins. The energies of these non-covalent bonds, which bind the lignins and polysaccharides of the FF<sup>24</sup> forming the CBO are negligible when compared to that of covalent bonds that are broken during the oxidation reactions.

The available literature showed that the regression model reported in the present study was accurate. Therefore, this method can be used to characterize CBO in terms of other SOM fractions. The limited studies reported on the determination of the composition of clay-bound organic matter in soils describe lengthy procedure which involves technique like <sup>13</sup>C NMR spectroscopy, Py-GC/MS, etc<sup>8</sup>. However, our method describes a rapid and simple technique that can be applied easily. Further, the quantification of CBO, being a very stable SOM fraction, is important in studies on carbon sequestration potential of soils.

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## On the mathematical significance of the dimensions of the Delhi Iron Pillar

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**The dimensions of the 1600-year-old Delhi Iron Pillar have been re-analysed in light of new scholarship on the traditional Indian unit of measurement. The dimensions of the pillar can be well reconciled considering the basic unit of measurement as 17.63 mm. The low percentage errors between the theoretical and actual measurements provide further support to this analysis. The significant mathematical ratios embedded in the relative dimensions of the pillar have also been set forth. The close association of the basic unit of measurement and the mathematical ratios with those of the Harappan civilization offers evidence for continuity of scientific ideas and traditions from the Harappan civilization to the Ganga civilization. Analysis of dimensions of the characters of the Gupta–Brahmi inscription revealed the possible use of the decimal system.**

**Keywords:** Delhi Iron Pillar, dimensional analysis, mathematical significance, Harappan civilization.

THE dimensions of the Delhi Iron Pillar have been measured in great detail by Beglar<sup>1</sup> and Ghosh<sup>2</sup>. These available dimensions have been analysed earlier by Balasubramaniam<sup>3</sup> to show the inherent symmetry in the design of the pillar, by considering the rough bottom portion to be buried underground during its original erection at Udayagiri. The relative proportion of the various parts of the pillar was understood. The decorative bell capital is one-third of the cylindrical portion of the pillar above the ground and one-fourth of the total height of the pillar above the ground. The height of the decorative bell capital was also equal to the depth of burial below the ground. When the overall dimensions of the pillar were analysed<sup>3</sup>, it was pointed out that one could relate the dimensions of the pillar to the unit of modern inch, which was called *U* (see figure 3 in Balasubramaniam<sup>3</sup>). This is equal to 25.40 mm.

A detailed statistical analysis of available length measurements of several Harappan civilization cites by Danino<sup>4,5</sup> has revealed recently that the basic Harappan unit of measurement (traditionally referred in India as ‘angulam’) measured 17.63 mm. The angulam that was in use in the Harappan civilization continued all the way to later periods in Indian history, certainly up to the classical period<sup>4,5</sup>. Danino has further shown by a simple procedure and without any a priori assumptions<sup>4,5</sup>, that the largest possible unit to measure Harappan town plans, such that the dimensions could be expressed as integral multiples,

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